METAL ANALYSIS WITH ION-BEAM METHODS

FÉMVIZSGÁLATOK IONNYALÁB ANALITIKAI MÓDSZEREKKEL

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Abstract

A review presents application of PIXE spectrometry using in-air proton beam on the metal archaeological objects from Slovenia. Among the copper-based alloys, the examples include analysis of prehistoric bronze, analysis of coloured metals used for the Roman military equipment, the introduction of brass, analysis of medieval bronze fiery weapons, and analysis of aluminum bronzes in modern coinage. The silver objects represent artefacts from the Late Iron Age including Celtic coins, and medieval silver coins of the 12th-13th c AD. Special techniques describe profile measurements with differential PIXE and mapping of the 3rd c. AD Roman coins.

Kivonat

A tanulmány összefoglalja a Szlovéniában régészeti fémtárgyakon alkalmazott PIXE spektroszkópiai vizsgálatok újabb eredményeit. A réz alapú ötvözetek körében a bemutatott példák őskori bronztárgyakra, római fegyverekre és sárgaréz tárgyakra, középkori lőfegyverekre és a modern kori pénzverésben használt alumínium-bronz ötvözetekre terjednek ki. A vizsgált ezüsttárgyak késő-vaskori kelta éremleletek és középkori ezüstpénzek az i.sz. 12-13. századból. A speciális technikai megoldások közül ismerteti a PIXE segítségével történő profil méréseket és i.sz. 3. századi római pénzérmék elemtérképeit.

KEYWORDS: PIXE, COLORED METALS, NUMISMATICS

KULCSSZAVAK: PIXE, SZÍNEZETT FÉMEK, NUMIZMATIKA

Introduction

Metal objects are relatively well resistant against aging and represent an important part of surviving cultural heritage. Analysis of metals provides us with quite important knowledge about the technological knowledge of ancient people. We can learn about production recipes, supply routes of raw materials, not at last, the metal composition can even apply some dating possibilities. The known examples include the impurity pattern of the Bronze Age alloys, or the introduction of brass into the Roman world. Mechanical properties may answer if the alloys were prepared on purpose, like forming a hard cutting edge and a flexible blade resistant to shocks and twisting. Technically, all this questions may be answered by bulk analysis, but a thick patina layer covering the object surface often hinders access to the bare metal. Sampling is then the obvious solution, but the decision rests with museum curator if the damage caused to the object is worth of the deduced information. Surface-sensitive methods may represent another approach to the problem, especially for the objects made of precious metals (Šmit et al. 2000) and those that were cleaned and polished during the restoration process. For the objects with patina, removing the patina in a small area is often tolerated as the original look of the object is easily restored. Ion beam methods can provide an efficient surface analysis, as they are fast and for metals virtually non-destructive. In this contribution, we shall briefly describe the basic properties of the method of proton-induced X-ray emission analysis (PIXE), specific examples with the combined analysis using proton-induced gamma rays (PIGE), and review the problems that were studied at the facilities of Jožef Stefan Institute in Ljubljana.

Experimental details

The experiments were performed at the Tandetron accelerator with 2.2 MV nominal voltage. Typically, protons of 3 MeV output energy were used and the proton beam was extracted into air through a thin metal foil. Experiments in the air provide simple changing of the analyzed object, fast

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and easy selection of the measuring points, and allow analysis of objects irrespective of their size. Two types of exit windows were generally used in our experiments: an 8 μm aluminum or a 2 μm tantalum foils. The advantage of aluminum is absence of energetic X-ray lines that would enter the detector through scattering, while the advantage of tantalum is its low energy gamma background. Due to stopping in the exit window and in the air gap between the exit window and target, the actual impact energy at the target was about 2.77 MeV. The excited X-rays were detected with a Si(Li) detector of about 150 eV energy resolution at 5.89 keV. As the inner shell ionization cross sections rapidly decrease with the increasing atomic number, absorbers were used to attenuate the X-rays produced in lighter atoms. For most purposes, a 0.3 mm thick aluminum absorber provides good balance between copper and tin X-ray lines in bronzes; however, the disadvantage of this setting is reduced sensitivity for iron, as its lines coincide with the escape lines of copper. For obtaining the concentrations of copper and lighter elements, additional spectrum was measured using a 6 cm air gap between the target and detector as the only absorber. For silver–copper alloys encountered mostly in coins, a 0.1 mm aluminum absorber typically allowed good balance between copper and silver lines, yet allowing sufficient sensitivity to iron. We also experimented with a cobalt foil as a selective absorber for copper X-rays, but were not able to calculate its transmission function precisely enough. X-ray intensities were deduced from the X-ray spectra using the AXIL program (Van Espen et al. 1977), while the elemental concentrations were calculated by the independent parameter method developed in the lab (Šmit et al. 2005). The main feature of this code is correction for the secondary fluorescence and normalization of concentrations to 100%. For the analysis of patinas, it is also possible to treat the target as a mixture of chemical compounds defined by the user. For monitoring the accuracy of the procedures, the brass standard NIST 1107 (containing 1.066±0.015 % Sn) and modern coins of known composition were analyzed periodically as an unknown target. The accuracy of analysis is typically within ± 5%. The normalization to 100% may not work properly if the alloy contains light metals (aluminum or beryllium). These elements are efficiently detected through their gamma lines (see Sec. 3.6). A dedicated numerical procedure was also developed for the measurement with differential PIXE, which allow reconstruction of concentration profiles (see Sec. 3.7).

Examples

Prehistoric bronzes

Archaeological bronzes are, except for certain water finds, thickly covered by patina layer, so sampling or surface polishing is required. In Slovenia, the pioneering work on bronze analysis was done by N. Trampuž Orel using the method of atomic emission analysis (ICP AES) and sampling the objects by drilling (Trampuž Orel 1996). These works resulted in two important results: the impurity pattern for the Ha A and Ha B (Kalakaca horizon) differed. The total amount of impurities is generally smaller than 2% in Ha A period and up to several percent in Ha B, showing the mining transition from oxide copper ores to more involved polymetallic ones. It was further found that the bronze produced varied according to function: the sickles that were sharpened by hammering contained less tin than the objects intended for cutting and thrusting.

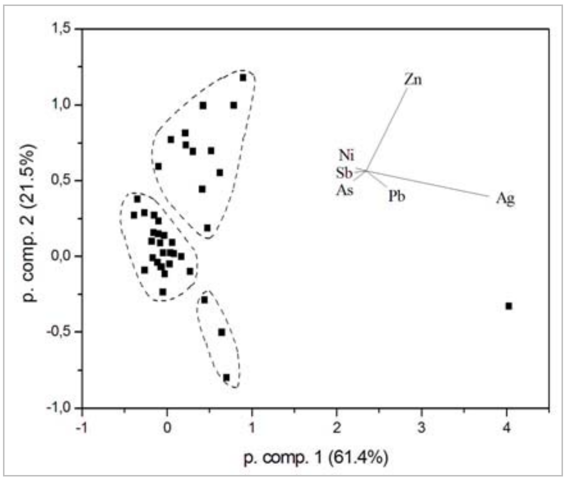

Fig. 1.: Distribution of bronzes from Koszider according to the principal component analysis based on six major impurity elements (Sánta 2011). Three major groups are evident, the main discriminating elements being silver and zinc.

1. ábra: A Koszider korszak bronzainak csoportosítása főkomponens analízissel, hat fő szennyező elem koncentrációja alapján (Sánta 2011). Három csoport egyértelműen elkülönül, a legfontosabb elkülönítő elemek az ezüst és a cink..

Though we analyzed several bronze objects by PIXE preparing the surface by polishing, systematic publication has not appeared yet. The only study that was published in detail is analysis of a small number of samples from south Hungary dated to Middle Bronze Age (Sánta 2011). The impurity

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pattern of bronzes shows three characteristic groups (**Fig. 1.**), which may stimulate finding relation with known ore deposits. For this purpose, the compositional data have to be complemented with the analysis of lead isotopes.

PIXE analysis is particularly efficient for the analysis of iron-reach bronzes known as aes rude, that was circulating in Italy and neighbouring countries since the 6th c. BC. The content of iron typically exceeds several percent, so sufficient precision of the composition is achieved measuring just one spectrum with an aluminum absorber of 0.3 mm thickness.

Roman military equipment

The analysis of Roman military equipment is interesting from the point of technology. It is possible to identify basic materials as well as those used for soldering, riveting, gilding and tinning. Most of the finds we analyzed come from the River Ljubljanica that connected the Roman *municipium* Nauportus, present Vrhnika, with Aemona, now within the borders of present Ljubljana. One of the conspicuous objects analyzed was the medallion of Augustus. It was cast of a very common and cheap lead-tin alloy and silvered on the front side (Istenič 2003). The objects of the so-called Hoard of Vrhnika were made of a qualitative silver alloy containing more than 90% Ag and the objects contained gold inlay (Šmit et al. 2005).

Brass

Most of the Roman objects analyzed were weapons or their parts, like daggers and swords and their scabbards. It was surprising that brass as material was discovered on a scabbard that was traditionally belied to be made of bronze, as the object predated the year 23 BC when the Augustan money reform formally introduced brass for coin nominals of *dupondii* and *sestertii* (Šmit & Pelicon 2000). The archaeologist J. Istenič then initiated a systematic study of Roman bronzes that can precisely be dated on archaeological ground (Šmit et al. 2005). It was found out that brass – as least in the area of Eastern Alps – came into wider use around 60 BC and therefore predates significantly the Roman brass coinage, which appeared in some small issue during the last years of the reign of Julius Caesar (Istenič & Šmit 2007). Brass was further discovered as material of swords scabbards excavated in South-Eastern Slovenia that were made in Late Iron Age style (Šmit et al. 2010). J. Istenič interprets this finding as a matter of cultural relations between the Romans and their barbaric subjects, the Celts in our case. She proposes the objects were made in Roman workshops as gifts for barbaric noblemen who were still attached to their Late Iron Age artistic style (Istenič & Šmit 2014).

Brass objects that occasionally appeared during the first millennium BC were very likely result of using copper ores mixed with zinc minerals. Typically, they contain a few percent Zn, while the brass containing about 20% Zn is result of a demanding cementation process. Around 100 BC brass was widely used for the coins in certain cities of Asia Minor that were or came under the rule of Pontic king Mithradates VI. The king probably used brass coinage as a kind of monopole that helped him paying for his expansionistic politics (Smekalova 2009). The collision with Roman interests induced three major wars, and in 63 BC Mithradates was finally defeated by Pompey and lost his life. During the aftermath period brass gradually spread into the Roman world. In our subsequent analysis we analyzed coins minted by Mithradates VI in Asia Minor (**Fig. 2.**) as well as the brass coins that were used in by Celts in the Gaul during the middle part of the 1st c. BC (Fajfar et al. 2015a). The analysis showed that selenium appears as an important impurity that can point to the ore sources in the eastern part of the classic world, from where the brass spread towards the west.

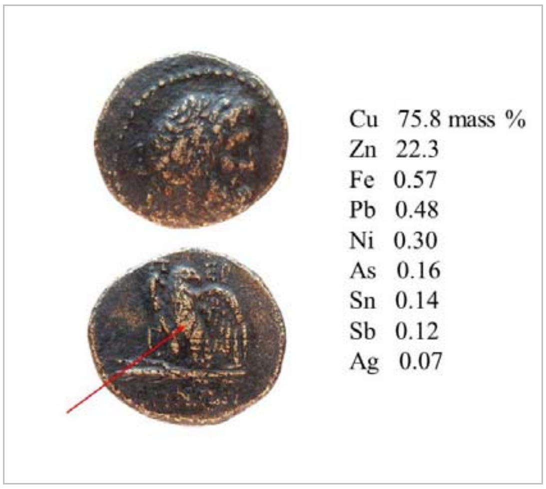

Fig. 2.: Analysis of a 1st c. BC brass coin from Pergamon, measured in the patina-free area on the eagle body (marked with an arrow).

2. ábra: I. e. 1. századi, Pergamonból származó sárgaréz érme kémiai elemzése, a patinamentes helyen mérve (ld. a vörös nyilat)

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Fiery weapons

Among medieval bronzes, we analyzed three fragments that belonged to medieval early fiery weapons (Fajfar et al. 2015b). They were found in the vicinity of three medieval castles and were identified as fragments of the barrels that evidently exploded. Though precise dating and typology were lacking, the barrels very likely represented the earliest fiery weapons, the so-called hand guns or *handgonnes*. They were rather simple weapons that consisted of a metal tube fixed to a plain straight wooden handle. Having no firing mechanism they were usually ignited by a heated iron or a slow-burning match. Most handgonnes did not survive the introduction of powder in granular form that had a much higher explosive effect (Hogg 1996). With our analysis we wanted to identify the material used for manufacturing of the weapons and possibly also to find out what was the reason for their insufficient strength. All three pieces were made of copper alloys; as iron was also commonly used for production of handgonnes, copper alloys were probable selected because of ease of manufacture, as the barrel can be relatively simply produced by casting. According to the surviving records from a castle in Slovenia, iron and copper alloys handguns were equally represented (Lazar 2015). One of the barrels was produced of an alloy with tin and zinc, the so-called gun metal. The reason for its explosion was probably not material strength but improper casting or drilling as the bore was visually rather eccentric. The other two fragments were cast of bronze with a high amount of antimony; virtually the bronze composition was indistinguishable from the alloys used in prehistory. Antimony makes the bronze brittle, the two barrels then exploded because of improper material.

La Tène silver objects and coins

Silver objects spread during the Late Iron Age, together with silver coins since the 2nd c. BC. Analysis of Celtic coins was one of our earliest archaeometric tasks (Šmit & Kos 1984). At that time, we were interested about the net content of silver, as we believed it might explain the systematic weight differences between different archaeological sites. Unfortunately, the coins appeared very inhomogeneous, showing a silver-rich mantle around a base silver core (**Fig. 3.**). This finding discouraged our further work on the coins, as PIXE could only provide the surface concentrations.

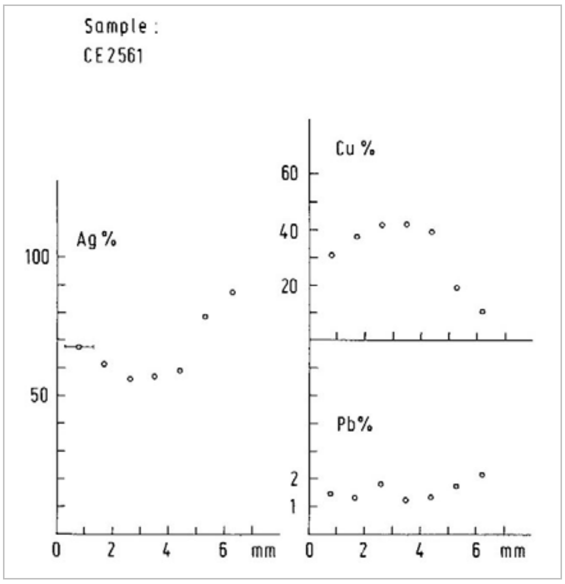

Fig. 3.: Profile scan of a small silver Celtic coin, showing silver-enriched crust and base-silver core (Šmit & Kos 1984). The coin was cut to half and measured by a 1 mm collimated beam from rim to rim.

3. ábra: Profil menti összetétel mérés eredménye kelta érmén. Jól látszik az ezüstben dúsult felület és a belső rész közötti különbség. Az érmét félbevágtuk, és 1 mm-es kollimált sugárral mértük peremtől peremig.

Occasional measurements that we did on some silver objects suggested that the impurity pattern consisting of a set of elements (zinc, tin, gold, lead, bismuth) may be characteristic of the silver source in spite of the objects being inhomogeneous. Our recent analysis involved silver objects discovered on the territory of Slovenia and included votive plaques, fragments of torques and brooches. For comparison, we also analyzed a set of Celtic small silver coins and contemporary Roman *denarii.* Some of the objects were made of a rather pure silver (>98%). Such pure metal was also encountered in some Roman coins, indicating a possible silver source. However, the impurity pattern suggested the source of silver was different for the Roman coins and Celtic silver, indicating the Celts were exploiting silver sources of their own (Laharnar et al. in print).

Medieval silver coins

During the 12th and 13th c. AD, active monetary activity is documented on the territory of the present Slovenia. A number of mints were founded along its eastern border, and their role is speculated to supply silver to the Hungarian kingdom on the east. Several hundred coins were analyzed from different mints, included locations in Carinthia north of the present Slovenian-Austrian border (Šmit & Šemrov 2006). The analysis showed that gold and bismuth were the discriminating elements, so we distinguished the silver between the gold- and bismuth types. The bismuth-type silver was used mainly in the mints of Carinthia and on the eastern border. Though our measurements of a few silver ores did not provide indicative results, we concluded that the bismuth type silver was mined in Carinthia. Part of it was spent in local mints in Carinthia, while the other part followed its commercial route to the eastern mints, from where it was traded further to the east. The eastern mints were abandoned after the 13th c. AD because of two political events: the Mongol invasion in 1241 and the victory of Habsburgs over the Czech king Othakar II. in 1278. Soon after that event, the Viennese pfennig became the leading currency in the area.

Aluminum bronzes

During the first half of the 20th c., different copper-based alloys were introduced for the low-nominal coins. Aluminum bronzes, for example, were found tarnish and wear resistant and non-allergic. Aluminum bronzes are hardly analyzable by PIXE as aluminum X-rays are strongly absorbed in any absorber, including in an air gap of a few centimeters. For analysis, we then used a combined PIXE-PIGE approach, detecting aluminum through its characteristic gamma rays of 844 and 1014 keV (Hirvonen & Lappalainen 1995). The algorithm was essentially the same we use for glass analysis, except that we switched off the option that every element is in its oxide form. Concentrations of aluminum were determined according to the glass standard NIST 620. The examples measured include coins minted around 1940 in Germany, Italy and Yugoslavia; some of them represent finds from the 2nd war world guerilla camps and are thus regarded as historic artefacts. The content of aluminum varied between 6 and 9%. For control purposes, we measured modern euro cents made of the alloy Nordic gold that contains 5% Zn. We reproduced this value within ±3% relative error. Regarding historic artefacts of non-documented origin, measurement of aluminum gamma rays can help to detect fakes.

Differential PIXE

The range of energetic protons in solids is well defined and measurement with a set of impact energies can be used to obtain the concentration profiles at the surface (Šmit & Holc 2004, Šmit 2005). The obstacle of the method is the inner shell ionization cross section that decreases very rapidly with decreasing proton energy. The contribution to the X-ray yield from the end part of the projectile trajectory is minute in comparison with the contribution from the first part, which makes the concentration evaluation algorithms rather sensitive to small variations of the X-ray yields. In our approach, we stabilized the numerical procedure by optimal selection of slices within the target according to the impact energies used.

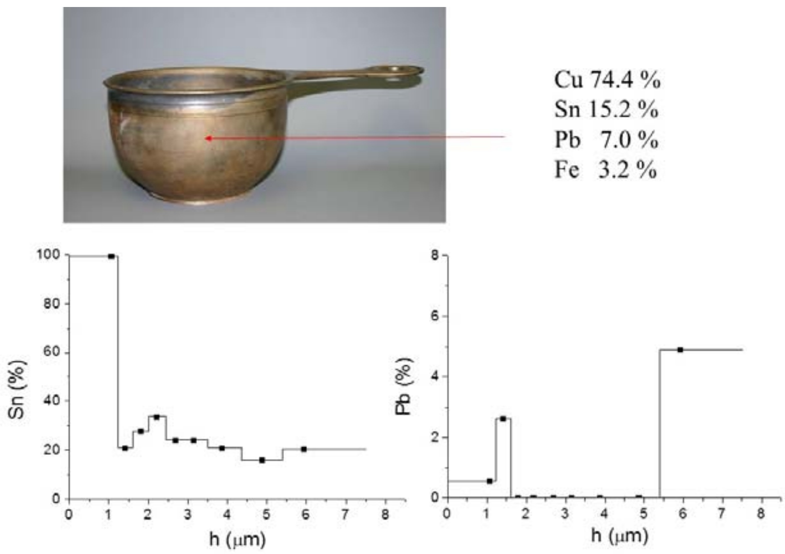

Fig. 4.: A tinned layer on a bronze vessel measured by differential PIXE (Šmit et al. 2008). The bulk composition measured through the layer differs only slightly from the values obtained in the area with the tin layer washed away.

4. ábra: Ónréteg kimutatása egy bronzedényen, differenciális PIXE technikával azonosítottak (Šmit et al. 2008). Az ónréteg alatt mért tömbi összetétel csak kis mértékben különbözik attól, ami az eltávolított ónréteg helyén mérhető.

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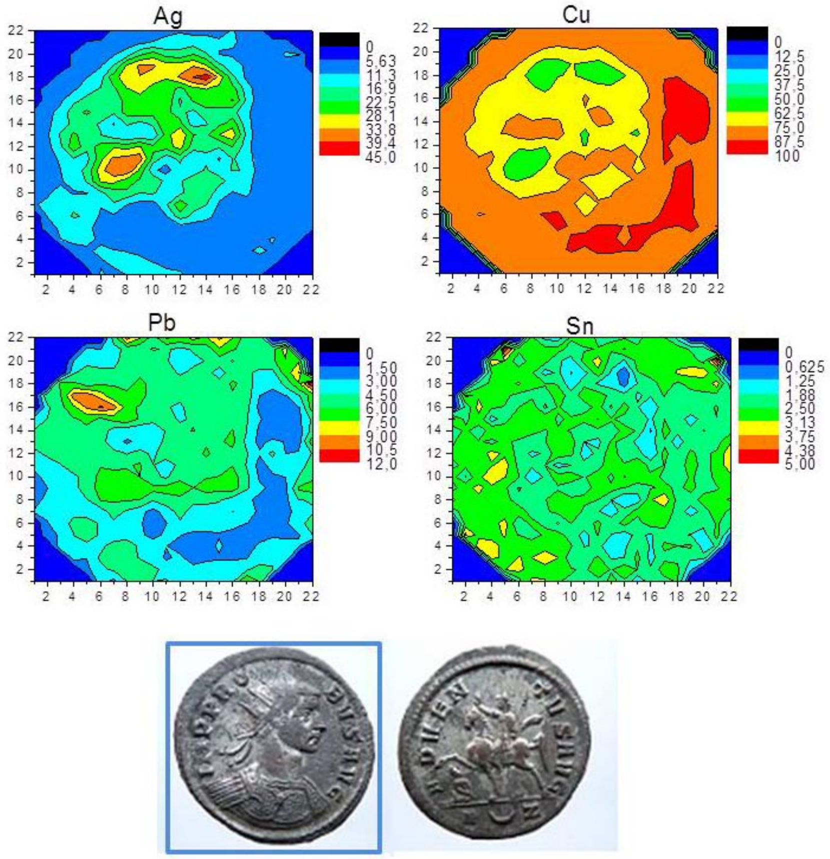

Fig. 5.:
Mapping of the surface of the coin of Probus (mint of Rome, 276-282 AD), showing silvering with a thin silver flush (Fajfar et al. 2015b).

5. ábra:

Vékony ezüstréteggel bevont Probus érme (római veret, Kr. u. 276-282) felszínén végzett elemösszetétel térképezés (Fajfar et al. 2015b)

The technique appeared particularly useful for detection of the gilding techniques. We recognized this during the analysis of gilded layers on the objects from Roman and Early Medieval Period, using a set of nine impact energies between 2.8 and 0.7 MeV (Šmit et al. 2008). Within the layer, we also observed a profile of mercury, which signalized that the technique used was fire or amalgamation gilding (Oddy 1993, von der Lohe 1994). Other types of plating, like silvering or tinning, can be characterized as well (**Fig. 4.**).

For measurement of plated layers, we also developed the method of Rutherford backscattering spectrometry (RBS) in helium atmosphere (Jezeršek et al. 2010). The method proved more accurate for determination of plated layer thickness, but could fail in the detection of mercury; in this case, one has to inspect in addition the PIXE measurement. We further used RBS to detect the intermetallic compounds of copper and tin on the tinned Roman brooch (Jezeršek 2010).

Mapping

Most modern set-ups using in-air beams are now able to do mapping measurements. In our case, this ability was achieved by developing the scanning mode software, as the set-up was initially equipped with xyz stepping motors (Fajfar et al. 2015b). The lateral resolution of the images is about 1 mm, determined by the beam width at half maximum of 0.8 mm (Jezeršek et al. 2010). Scanning measurements were done on the 3rd c. AD Roman coins, which imitated the luster of solid silver (Fajfar et al. 2015b). The coins were partly polished by use, so the mapping revealed which elements belonged to the surface and which to the bulk metal. We showed that the coins minted around 250 AD used combined silvering and tinning, which gave impression of the massive silver, while a coin of around 270 AD showed mere silvering with a thin silver layer (**Fig 5.**).

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Mapping can also reveal the gilding technique. For example, fire or amalgamation gilding results in correlated maps of gold and mercury distributions.

Conclusion

PIXE based on an in-air proton beam can be efficiently used for the determination of coloured metal alloys of the historic periods. The measurement does not alter the objects, though the metals with patina have to be pre-prepared for the measurement by removing a small section of patina to expose the bare metal. The analysis can go beyond point surface measurements and allow rough profiling or mapping of certain areas. Further improvement of the set-up will include the focusing option of the beam, which would allow studies of smaller details and mapping with a higher resolution.

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