PIXE analysis of Late La Tène scabbards with non-ferrous openwork plates (and associated swords) from Slovenia

Žiga ŠMIT, Janka ISTENIČ and Sonja PEROVŠEK

Izvleček

Z metodo protonsko vzbujenih rentgenskih žarkov (PIXE) smo analizirali meče iz 1. stoletja pr. n. št. in pripadajoče nožnice s predrtim okrasom iz Ljubljanice pri Bevkah, s Strmca nad Belo Cerkvijo in iz Verduna (grob 37 in grob 131). Rezultati analiz kažejo, da so pri izdelavi teh predmetov uporabljali železo in medenino.

Ključne besede: latenski meči in nožnice, PIXE, medenina

Abstract

The method of proton-induced X-ray emission (PIXE) was applied for the analysis of late 1st century BC swords and associated scabbards with openwork copper-alloy plates from the Ljubljanica River, Strmec above Bela Cerkev, Verdun grave 37 and Verdun grave 131. The results indicate that iron and pure brass were used in the manufacture of these objects.

Keywords: Late La Tène scabbards and swords, PIXE, brass

1. INTRODUCTION

Analytical methods requiring little or no sampling material are desirable tools for the analysis of archaeological artefacts. The method of proton-induced X-ray emission analysis (PIXE) relies on irradiation of the selected areas by proton beam and detection of characteristic X-rays. Since protons of a few MeV energy penetrate just several 10 μm into the target, and the excited X-rays attenuate in the target itself, the analysis is limited to the very surface layer of about 10 μm. For a quantitative analysis of metals, the non-corroded metal surface has to be exposed.

The procedure was applied to the characterization of metals in Late La Tène swords and associated scabbards from the River Ljubljanica near Bevke, Strmec above Bela Cerkev, Verdun grave 37 and Verdun grave 131. Our main interest was in the characterisation of copper-alloys.

2. THE METHOD

The analytical work was performed on the Tandetron accelerator at the Jožef Stefan Institute in Ljubljana. The measurements were done by the proton beam in air, which provided simple irradiation of the points selected for the analysis (cf. Šmit et al. 2005a). A few such points were prepared for analysis by gently removing the patina and on about 0.1 mm thick superficial metal layer.

The impact proton energy was 3 MeV; however, the protons lose energy in the aluminium exit window (8 μm thick) and the 1.2 cm air gap between the window and target, so the actual impact energy was 2.7 MeV. The Si(Li) X-ray detector was positioned at 45° with respect to the target normal at a distance of 5.7 cm. The X-ray spectra were measured by an absorber of 0.3 mm aluminium, which well attenuated the X-rays up to 10 keV, including the intense K lines of copper (8.04 and

8.9 keV). In this way it was possible to increase the sensitivity for mid-Z elements between silver and antimony to about 200 μg/g. The disadvantage of the thick aluminium absorber is the reduced sensitivity to elements lighter than copper. For silicon X-ray detectors, the most critical is iron, as its X-ray lines coincide with the silicon escape lines of copper. The two sets of lines were separated in the procedure of fitting the spectra, although the distinction of two overlapping Gaussian lines is generally subject to considerable uncertainties. The iron concentrations in our previous work were then uncertain by 0.5 wt. %. To overcome this difficulty we applied a procedure that is based on two sequential measurements in each point, using different absorbers. One measurement is done, as before, with the aluminium absorber of 0.3 mm, while the other exploits the 5.7 cm air gap as the only absorber. The intensities of X-ray lines obtained from the two spectra are then normalized according to the most intense copper K-alpha line, modelling the attenuation effects. A set of values obtained in this way corresponds to a hypothetic measurement without an aluminium absorber, and can be used in our standard codes for evaluation of the concentrations. For metals, the calculation relies on the normalization procedure of setting the sum of all concentrations to unity.

The area of the prepared measurement spot was about 3–4 mm^2, which is slightly larger than the area of our beam with FWHM of about 0.78 mm. By imprecise aiming of the beam there would be the danger of hitting the unprepared area. To avoid this, the beam size was reduced by a diaphragm of 0.3 mm diameter. In order to lessen the beam broadening due to scattering in the air, the diaphragm was positioned about 3 mm from the target. The reduced beam size was appropriate for the measurement of light elements, but it deteriorated the sensitivity to mid-Z elements. The reason for this was intense bremsstrahlung radiation, induced by proton stopping in the diaphragm material. The high energy spectra were then rather measured without the diaphragm, in spite of the broad beam size.

The proton current was about 1 nA and was set to attain a counting rate of about 400 s^{-1}. This value did not completely prevent the pile-up effects of copper K lines, which appear in the spectra as a continuous background extending up to about 17 keV. The pile-up contribution to the spectral background reduced the sensitivity to high Z elements around lead and certain mid-Z elements (arsenic) to about 500 μg/g.

The measuring time was 5–10 minutes for a measurement with the aluminium absorber, and about 3 minutes for a measurement without it. The accuracy of the procedures was checked by analyzing a brass standard NIST 1107 as an unknown sample. The major concentrations were typically reproduced within a few percent, but increased to 10–20% on approaching the detection limits.

3. RESULTS AND COMMENTARY

The investigated objects involved swords and associated scabbards from the River Ljubljanica near Bevke (kept in Muzej in galerije mesta Ljubljana, Inv. No. 510:LJU;32582), Strmec above Bela Cerkev (Kept in the National Museum of Slovenia, Inv. No. P 4371), grave 37 at Verdun near Stopiče (kept in Dolenjski muzej, Novo mesto, Inv. No. A 1776) and from grave 131 at Verdun (kept in Dolenjski muzej, Novo mesto, Inv. No. A 2211). The objects were prepared for analyses in the Conservation Department of the National Museum of Slovenia.

Most of the analyses were made on the scabbard and sword from the River Ljubljanica. The results indicate that its front plate was made of brass containing about 16% zinc (*tab.* and *fig. 1:* spots 1,2). Only very small differences can be observed between the analysis of the prepared and unprepared measurement spots, indicating that there is practically no patina on the brass sheath.

The sword's campanulate hilt-end and knob lining, as well as the lowest rivet on the scabbard's suspension loop plate were made of brass containing a somewhat larger (18–19%) zinc content (*tab.* and *fig. 1:* spots 5,7,8).

Several measurements were made on copper-alloy layers revealed in the iron rungs on scabbard's front by removal of plastic parts added during restoration in 1980 (see Istenič 2010, 138) and by careful removal of corrosion. The results show that the copper alloy was bronze with about 4–7% tin (*tab.* and *fig.1:* spots 11a,12a,13,15). On the underside of the rungs and beneath them (between the rungs and the brass plate) there was a layer of iron corrosion products (*tab.* and *fig. 1:* spots 12b,16).

Restoration work in 2010 also revealed a copper-alloy lining beneath the left and the right iron edge of the laddered chape (between the laddered chape and the back plate and front plate, respectively), at the height of the 9th front rung and 12th to 13th rung on the back. According to measurement results,

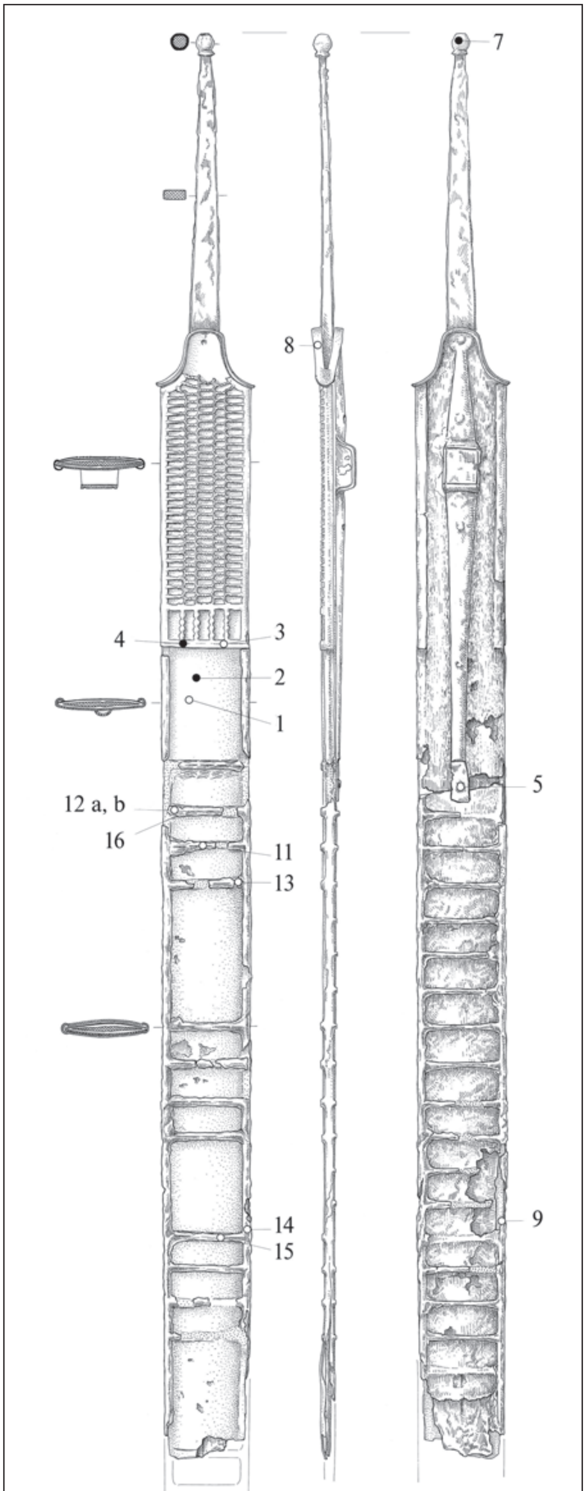

Fig. 1: Sword and scabbard from the River Ljubljanica near Bevke with locations of the areas measured by PIXE: ● prepared area, O unprepared area. Scale 1: 4 (drawing by Ida Murgelj).
Sl. 1: Mesta meritev z metodo PIXE na meču in nožnici iz reke Ljubljanice pri Bevkah: ● mesto, s katerega je bila korozija odstranjena, O mesto, s katerega korozija ni bila odstranjena. M. = 1:4 (risba Ida Murgelj, Narodni muzej Slovenije).

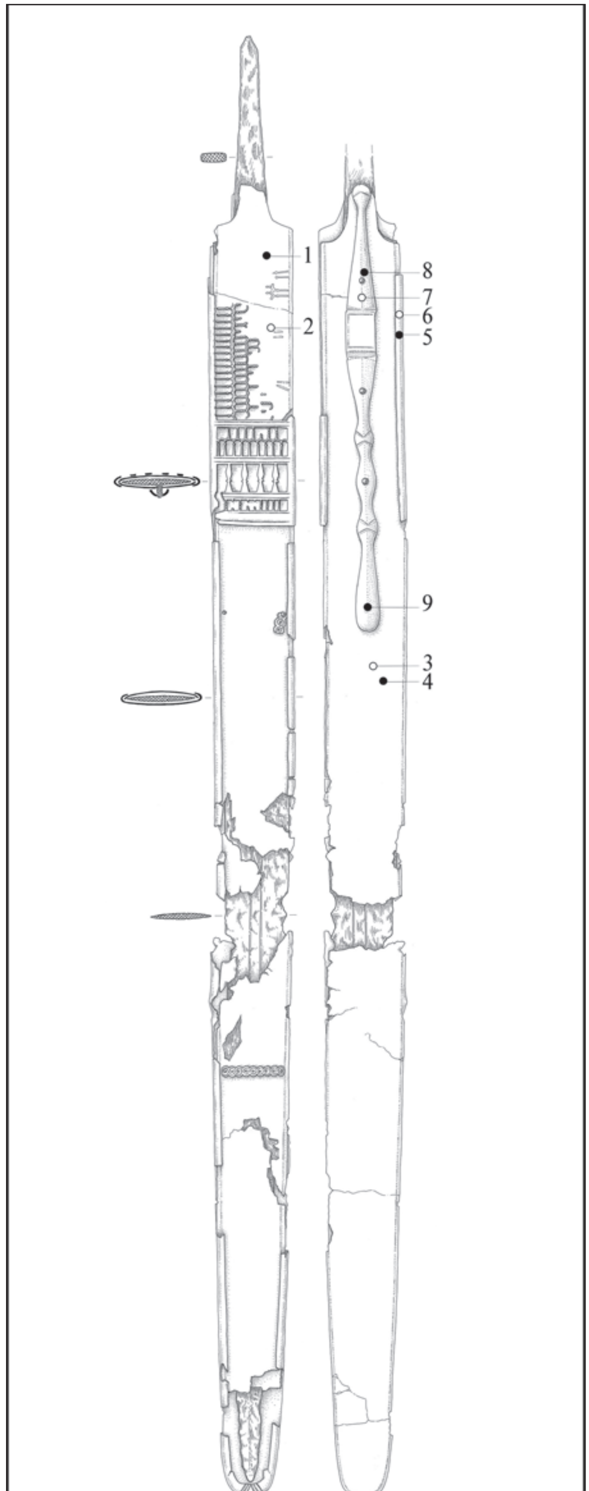

Fig. 2: Sword and scabbard from Strmec above Bela Cerkev with locations of the areas measured by PIXE: ● prepared area, O unprepared area. Scale 1:4 (drawing by Ida Murgelj).
Sl. 2: Mesta meritev z metodo PIXE na nožnici s Strmca nad Belo Cerkvijo: ● mesto, s katerega je bila korozija odstranjena, O mesto, s katerega korozija ni bila odstranjena. M. = 1:4 (risba Ida Murgelj, Narodni muzej Slovenije).

Spot Mesto	Description Opis	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Measure-ment details Meritve - podrob-nosti
1	scabbard, front plate, unprep. sprednja platica nožnice, nepr.	0.62	0.14	81.1	16.7		0.1	0.8		0.68	B
2	scabbard, front plate, prep. sprednja platica nožnice, pripr.	0.42		81.3	16.4		0.1	0.8		1.00	A
3	scabbard, openwork plate, unprep. nožnica, okrasni okov, nepripr.	0.59		81.2	16.8		0.1	0.7		0.71	B
4	scabbard, openwork plate, prep. nožnica, okrasni okov, pripr.	0.41		81.8	16.3		0.1	0.7		0.75	A
5	scabbard, rivet, prep. nožnica, zakovica, pripr.	0.34		78.9	19.1		0.15	1.1		0.47	A
7	sword, knob-lining, prep. meč, obloga gumba na ročaju, pripr.	1.54	0.11	77.8	18.5		0.1	0.9		0.98	A
8	sword, hilt end, unprep., branik ročaja meča, nepr.	1.90	0.11	78.1	18.1		0.1	0.9		0.71	B
9	scabbard, lining beneath the lateral part of laddered chape; unprep. nožnica, podloga pod robnim delom lestvičastega okova	3.57	0.13	90.8	4.60		0.04	0.4		0.42	A
11	scabbard, copper alloy in the 3rd rung; unprep. nožnica, bakrova zlitina v tretji prečki, nepripr.	4.2		87.9	0.49		0.17	7.1	0.09	0.15	C
12a	scabbard, copper alloy in the 2nd rung; unprep. nožnica, bakrova zlitina v drugi prečki, nepripr.	2.98	0.2	92.8	0.47			3.6			A
12b	scabbard, corrosion layer on the underside of the 2nd rung; unprep. nožnica, korozija na spodnji strani druge prečke, nepripr.	93.9		3.5	2.31	0.16		3.6			C
13	scabbard, copper alloy beneath the 4th rung; unprep. nožnica, bakrova zlitina pod četrto prečko, nepripr.	4.14	0.1	88.9	0.86		0.12	5.7		0.11	B, mask
14	scabbard, lining beneath the lateral part of laddered chape; unprep. nožnica, podloga pod robnim delom lestvičastega okova, nepripr.	5.11		88.0			0.20	6.3	0.33	0.11	A
15	scabbard, copper alloy in the 4th rung; unprep. nožnica, bakrova zlitina v deveti prečki, nepripr.	7.13		87.6			0.09	4.7		0.48	B
16	scabbard, beneath the 2nd rung; unprep. nožnica, pod drugo prečko, nepripr.	96.8		1.80	1.19					0.17	B

←

Tab. 1: Elemental concentrations (in wt %) measured by PIXE on the sword and scabbard from the River Ljubljanica given in weight %. Analyses have been carried out on the prepared or unprepared surface (abbreviated prep. and unprep. in the table). In numeration of the measured spots, 6 and 10 were omitted.
Measurement details: A – soft X-ray spectrum was obtained by a narrow beam of 0.3 mm, hard X-ray spectrum by a broad beam of 0,78 mm; B – both soft and hard X-ray spectra were obtained by a broad beam; C – only hard X-ray spectrum by a broad beam was measured.
During the measurement of spot 13, its surrounding was covered by an aluminium foil (mask).
Tab. 1: Elementna sestava (v utežnih %), izmerjena z metodo PIXE na nožnici in meču iz reke Ljubljanice pri Bevkah. Meritve smo naredili na nepripravljeni povšini ali na površini, s katere smo odstranili vrhnji korozijski sloj (v tabeli okrajšano: nepr. in pripr.). Pri številčenju merjenih mest smo izpustili 6 in 10. Način meritve : A – nizkoenergijski spekter izmerjen z zaslonko 0,3 mm, visokoenergijski s širokim žarkom 0,78 mm; B – nizko in visokoenergijski spekter izmerjena s širokim žarkom; C – izmerjen le visokoenergijski spekter s širokim žarkom.

Tab. 2: Elemental concentrations (in wt %) measured by PIXE on the scabbard from Strmec above Bela Cerkev. Analyses have been carried out on the prepared or unprepared surface (abbreviated prep., unprep. in the *table*). For measurement details see *tab. 1*.
Tab. 2: Elementna sestava (v utežnih %), izmerjena z metodo PIXE na meču in nožnici iz Strmca nad Belo cerkvijo. Meritve smo naredili na nepripravljeni povšini ali na površini, s katere smo odstranili vrhnji korozijski sloj (v tabeli okrajšano: nepripr. in pripr.). Podrobnosti o meritvah: glej *tab. 1*!

Spot Mesto	Description Opis	Fe	Ni	Cu	Zn	As	Sn	Pb	Measurement details Meritve - podrobnosti
1	front plate, prep. sprednja platica, pripr.	0.43	0.14	77.5	21.1	0.09	0.5	0.22	A
2	front plate, unprep. sprednja platica, nepripr.	1.31		92.0	4.50	0.20	1.3	0.66	B
3	back plate, unprep. zadnja stranica, nepripr.	2.02		93.4	3.69	0.10	0.5	0.23	B
4	back plate, prep. zadnja patica, pripr.	0.35		76.4	22.3	0.11	0.7	0.19	A
5	openwork plate, prep. okov s predrtim okrasom, pripr.	0.33		77.2	21.4	0.14	0.7	0.24	B
6	openwork plate, unprep. okov s predrtim okrasom, nepripr.	2.30		90.2	4.94	0.26	1.8	0.45	B
7	suspension loop plate, unprep. okov z zanko, patina, nepripr.	2.25		91.1	4.55	0.20	1.7	0.20	B
8	suspension loop plate, prep. okov z zanko, pripr.	0.98		81.1	17.0	0.13	0.6	0.26	A
9	rivet, corrosion layer zakovica, rja	90.8		7.0	1.99	0.05	0.1	0.06	B

the lining on one (right) side was of bronze with about 6% tin (*tab.* and *fig. 1:* spot 14) and on the other (left) side of brass with about 5% zinc (*tab.* and *fig. 1:* spot 9).

Analytical results of the scabbard from Strmec above Bela Cerkev (*tab. 2*) indicate that the front and the back plate, as well as the openwork plate were made of pure brass containing about 21–22% zinc (*tab.* and *fig. 2:* spots 1,4,5). The suspension loop plate is also of pure brass, but with a lower zinc content (*tab.* and *fig. 2:* spot 8). The patina on these plates is well preserved. The results of measurements on the unprepared surface (*tab.* and *fig. 2:* spots 2,3,6,7) showing low percentages of zinc (3–5%) were therefore expected. De-zincification of the corrosion layer on objects made of brass is, in fact usual (Istenič, Šmit 2007, 143).

The measurement of the iron rivet (*tab. 2:* spot 9) showed the presence of copper and zinc, which may indicate diffusion of the corrosion products of brass by the electrochemical processes.

Front plate of the scabbard from Grave 37 at Verdun is of pure brass containing about 21% zinc (*tab.* and *fig. 3:* spot 2). The much smaller zinc percentage measured in the patina was expected (see above). Pure brass with a smaller percentage of zinc was used for the lining of the knob at the end of the sword's tang (*tab.* and *fig. 3:* spot 3).

The sword and its associated scabbard from Grave 131 at Verdun are in poor condition. For this reason we made analysis only on the loose fragment of the sword's and scabbard's end. They indicate pure brass with a very high content of zinc (25.5%) for the front plate (*tab.* and *fig. 4:* spot 2). This is the highest zinc value we encountered in our analyses of Roman brass (cf. Šmit, Pelicon 2000; Šmit et al. 2005b). The upper limit for the zinc content in Roman brass made by cementation process is about 28% (Craddock 1995, 296–298 Craddock, Lambert 1995, 164).

⟶

Fig. 3: Sword and scabbard from grave 37 at Verdun with locations of the areas measured by PIXE: ● prepared area, ○ unprepared area. Scale 1:4 (drawing by Ida Murgelj).
Sl. 3: Mesta meritev z metodo PIXE na meču in nožnici iz gr. 37 v Verdunu: ● mesto, s katerega je bila korozija odstranjena, ○ mesto, s katerega korozija ni bila odstranjena. M. = 1:4 (risba Ida Murgelj, Narodni muzej Slovenije).

Fig. 4: Sword and scabbard from grave 131 at Verdun with locations of the areas measured by PIXE: ● prepared area, ○ unprepared area. Scale 1:4 (drawing by Ida Murgelj).
Sl. 4: Mesti meritev z metodo PIXE na nožnici iz gr. 131 v Verdunu: ● mesto, s katerega je bila korozija odstranjena, ○ mesto, s katerega korozija ni bila odstranjena. M. 1:4 (risba Ida Murgelj, Narodni muzej Slovenije).

Tab. 3: Elemental concentrations (in wt %) measured by PIXE on the sword and scabbard from grave 37 at Verdun. Analyses have been carried out on the prepared or unprepared surface (abbreviated prep. and unprep. in the *table*). For measurement details see *tab. 1.*
Tab. 3: Elementna sestava (v utežnih %), izmerjena z metodo PIXE na meču in nožnici iz groba 37 v Verdunu. Meritve smo naredili na nepripravljeni površini ali na površini, s katere smo odstranili vrhnji korozijski sloj (v tabeli okrajšano: nepripr. in pripr.). Podrobnosti o meritvah: glej *tab. 1*!

Spot Mesto	Description Opis	Fe	Ni	Cu	Zn	Ag	Sn	Pb	Measurement details Meritve - podrobnosti
1	scabbard, front plate, unprep. sprednja platica nožnice, nepripr.	1.64	0.12	92.3	4.56	0.07	1.2	0.09	B
2	scabbard. front plate. unprep. sprednja platica. nepripr.	0.76	0.10	77.8	20.7	0.05	0.5	0.13	B
3	knob-lining. prep. obloga zaključka ročaja. pripr.	0.27	0.10	83.4	15.4	0.09	0.4	0.37	B

Tab. 4: Elemental concentrations (in wt %) measured by PIXE on the scabbard fragments from grave 131 at Verdun. Analyses have been carried out on the prepared or unprepared surface (abbreviated prep. and unprep. in the *table*). For measurement details see *tab. 1.*
Tab. 4: Elementna sestava (v utežnih %), izmerjena z metodo PIXE na meču in nožnici iz groba 131 v Verdunu. Meritve smo naredili na nepripravljeni površini in na površini, s katere smo odstranili vrhnji korozijski sloj (v tabeli okrajšano: nepripr. in pripr.). Podrobnosti o meritvah: glej *tab. 1*!

Spot Mesto	Description Opis	Fe	Ni	Cu	Zn	Ag	Sn	Pb	Measurement details Meritve - pod-robnosti
1	patina	1.14	0.14	87.9	9.31	0.17	1.0	0.32	B
2	no patina brez patine	0.18	0.14	73.3	25.5	0.06	0.6	0.36	A

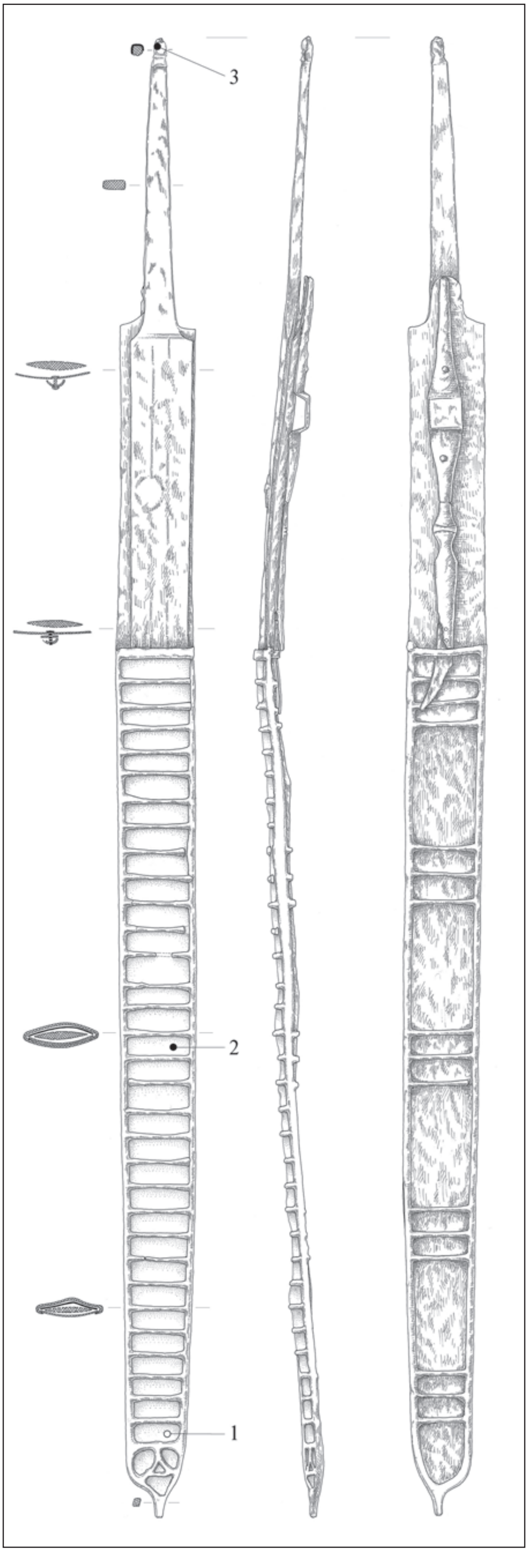

Fig. 3 / Sl. 3

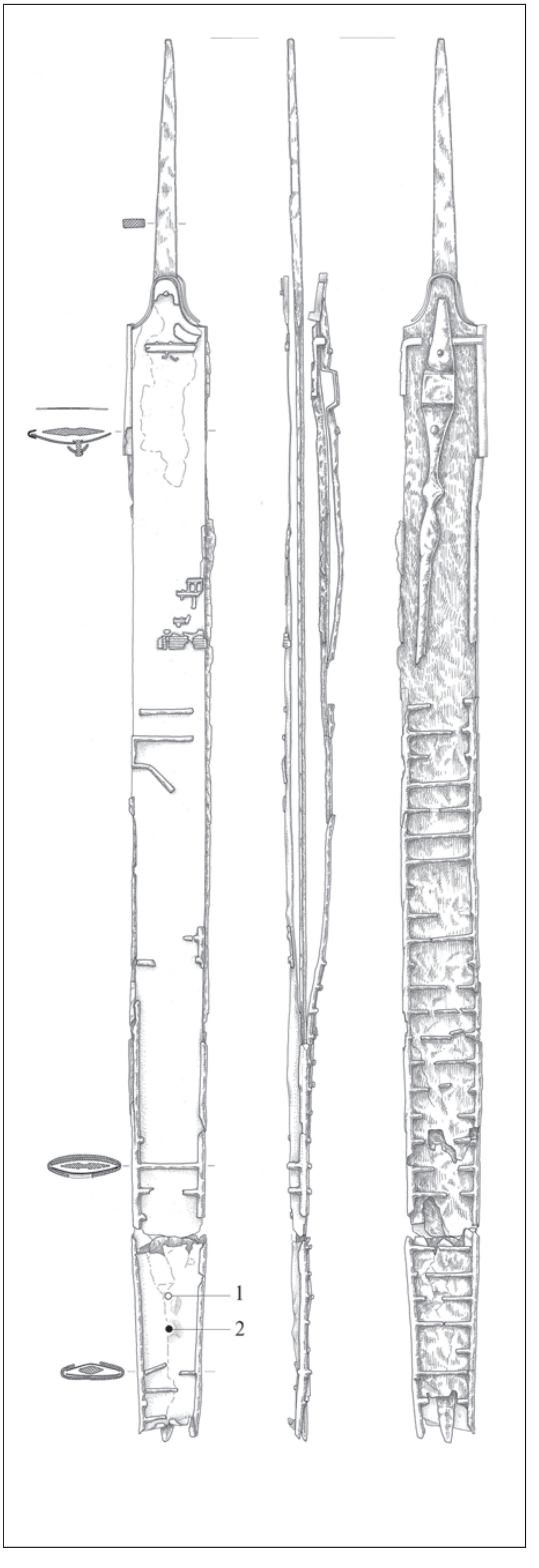

Fig. 4 / Sl. 4

4. CONCLUSION

Analysis of late 1st century BC swords and associated scabbards with openwork copper-alloy plates from the River Ljubljanica, Strmec above Bela Cerkev, Verdun grave 37 and Verdun grave 131 shows an extensive use of pure brass.

From the experimental view, our procedure was upgraded: we combined the soft and hard X-ray spectra for each analyzed spot.

CRADDOCK, P.T. 1995, *Early Metal Mining and Production.* – Edinburgh.

ISTENIČ, J. 2010, Late La Tène scabbards with non-ferrous openwork plates / Poznolatenske nožnice s predrtim okrasnim okovom iz bakrove zlitine ali srebra. – *Arheološki vestnik* 60, 121–164.

ISTENIČ, J. and Ž. ŠMIT 2007, The beginning of the use of brass in Europe with particular reference to the southeastern Alpine region. – In: S. La Niece, D. R. Hook and P. T. Craddock (eds.), *Metals and mines: studies in archaeometallurgy,* 140–147, London.

ŠMIT, Ž. and P. PELICON 2000, Analysis of copper-alloy fitments on a Roman gladius from the river Ljubljanica. – *Arheološki vestnik* 51, 183–187.

ŠMIT, Ž., P. PELICON, J. SIMČIČ and J. ISTENIČ 2005a, Metal analysis with PIXE: the case of Roman military equipment. – *Nuclear Instruments and Methods in Physics Research, Sect B* 239, 27–34.

ŠMIT, Ž., J. ISTENIČ, V. GERDUN, Z. MILIČ and A. MLADENOVIČ 2005b, Archaeometric analysis of Alesia group brooches from sites in Slovenia / Arheometrične analize fibul skupine Alesia s slovenskih najdišč – *Arheološki vestnik* 56, 213–233.

Analize PIXE poznolatenskih nožnic s predrtimi okovi (in pripadajočih mečev) iz Slovenije

1. UVOD

Analitske metode, ki zahtevajo malo ali nič vzorčnega materiala, so zaželeno orodje za preiskave arheoloških predmetov. Metoda protonsko vzbujenih rentgenskih žarkov (PIXE) temelji na obsevanju izbranega mesta s protoni in zaznavanju karakterističnih rentgenskih žarkov. Protoni z energijo nekaj MeV prodrejo le nekaj 10 μm globoko v tarčo, poleg tega se rentgenski žarki v tarči tudi absorbirajo, tako da je analiza omejena le na plitvo površinsko plast debeline približno 10 μm. Za kvantitativno analizo je treba izpostaviti obsevanju nekorodirano kovinsko površino.

Metodo smo uporabili za opredelitev kovin pri poznolatenskih mečih in pripadajočih nožnicah iz reke Ljubljanice pri Bevkah, s Strmca nad Belo Cerkvijo in iz Verduna (grob 37, grob 131). V študiji smo se v glavnem posvetili bakrovim zlitinam.

2. METODA

Analize smo opravili na tandemskem pospeševalniku Inštituta Jožefa Stefana. Za meritve smo uporabili protonski žarek v zraku, ki nam je omogočal enostavno obsevanje na mestih, ki smo jih izbrali za analizo (cf. Šmit et al. 2005a). Nekaj takih mest smo pripravili za analizo tako, da smo previdno odstranili patino in približno 0,1 mm debelo površinsko kovinsko plast.

Energija protonov je bila 3 MeV; ker pa so protoni izgubili nekaj energije v izstopnem okencu iz aluminija (debelem 8 μm) in približno 1,2 cm široki zračni reži med okencem in tarčo, je bila dejanska vpadna energija 2,7 MeV. Si(Li) detektor rentgenskih žarkov je oklepal kot 45° z normalo na tarčo in je bil 5,7 cm oddaljen od nje. Rentgenske spektre smo merili z 0,3 mm debelim aluminijevim absorberjem, ki je močno udušil rentgenske žarke do energije približno 10 keV, vključno z močnimi rentgenskimi žarki bakra (8,04 in 8,9 keV). Na ta način smo povečali občutljivost za srednjetežke elemente med srebrom in antimonom na približno 200 μg/g. Neugodna stran rabe debelega aluminijevega absorberja pa je bila zmanjšana občutljivost za elemente, lažje od bakra. Pri silicijevih rentgenskih detektorjih je najbolj kritičen element železo, saj njegovi rentgenski črti sovpadata s silicijevimi ubežnimi vrhovi bakrovih žarkov. Obe vrsti črt je mogoče ločiti z obdelavo spektrov, vendar je razločevanje dveh prekrivajočih se Gaussovih črt običajno obremenjeno s precejšnjo napako. Železove koncentracije pri našem prejšnjem delu so bile tako negotove za približno 0,5 %. Da bi zmanjšali to napako, smo uporabili postopek, ki je temeljil na dveh zaporednih meritvah na istem mestu, pri čemer smo uporabili različna absorberja. Eno meritev smo tako kot prej opravili z aluminijevim absorberjem debeline 0,3 mm, pri drugi meritvi pa smo kot edini absorber uporabili le 5,7 cm debelo zračno plast. Jakosti rentgenskih črt iz obeh spektrov smo normirali glede na najmočnejšo bakrovo črto, pri čemer smo učinek absorpcije v obeh absorberjih upoštevali računsko. Vrednosti, ki smo jih tako dobili, so ustrezale hipotetični meritvi brez aluminijevega absorberja, tako da smo nadaljnji izračun koncentracij lahko izvedli s programi, ki smo jih uporabljali že doslej. Pri kovinskih tarčah smo v računu uporabili normirni postopek, ki vsoto vseh dobljenih koncentracij postavi na ena.

Površina mest, pripravljenih za meritev, je bila 3–4 mm^2, kar je bilo nekoliko več kot površina protonskega žarka s širino na polovični višini (FWHM) okoli 0,78 mm. Ob netočnem usmerjanju žarka je bila nevarnost, da bi z žarkom zadeli nepripravljeno površino. Da bi se temu izognili, smo površino žarka zmanjšali z zaslonko premera 0,3 mm. Zaslonko smo postavili približno 3 mm od tarče, s čimer smo se izognili razširitvi žarka zaradi sipanja v zraku. Zožen žarek je bil pripraven za merjenje lahkih elementov, vendar je poslabšal občutljivost za srednjetežke elemente. Razlog za to je bilo močno zavorno sevanje, ki so ga protoni vzbujali v zaslonki. Visokoenergijske rentgenske spektre smo zato raje merili brez zaslonke, kljub širšemu žarku.

Tok protonov je bil okrog 1 nA in smo ga uravnavali tako, da smo dosegli hitrost štetja okoli 400 sunkov na sekundo. S tem sicer nismo povsem preprečili kopičenja sunkov (pile-up) pri bakrovih žarkih, kar se je v spektrih pokazalo kot zvezno ozadje do energije približno 17 keV.

Prispevek kopičenja sunkov k ozadju v spektru je zmanjšal občutljivost za težke elemente okoli svinca in nekatere srednjetežke elemente (npr. arzena) na približno 500 μg/g.

Posamezna meritev z aluminijevim absorberjem je trajala 5 do 10 minut, brez absorberja pa okoli 3 minute. Natančnost metode smo preverjali z analizami medeninastega standarda NIST 1107, ki smo ga obravnavali kot neznan vzorec. Koncentracije večinskih elementov smo običajno reproducirali znotraj nekaj odstotkov, vendar pa je napaka narasla na 10–20 %, ko smo se približali meji zaznavanja.

3. REZULTATI IN KOMENTAR

Preiskani predmeti so obsegali meče in pripadajoče nožnice iz reke Ljubljanice pri Bevkah (hrani Muzej in galerije mesta Ljubljana, inv. št. 510:LJU;32582), s Strmca nad Belo Cerkvijo (hrani Narodni muzej Slovenije, inv. št. P 4371), iz groba 37 iz Verduna pri Stopičah (hrani Dolenjski muzej, Novo mesto, inv. št. A 1776) in groba 131 iz Verduna (hrani Dolenjski muzej, Novo mesto, inv. št. A 2211). Predmeti so bili pripravljeni za analize na Konservatorskem oddelku Narodnega muzeja Slovenije.

Večino analiz smo opravili na nožnici in meču iz Ljubljanice. Rezultati kažejo, da je bila sprednja platica nožnice narejena iz medenine z okoli 16 % cinka (*tab.* in *sl. 1:* mesti 1,2). Med analizami na pripravljenih in nepripravljenih mestih opazimo le majhne razlike, kar se dobro ujema z dejstvom, da na nožnici skorajda ni patine.

Branik ročaja meča in obloga gumba na ročaju ter ena zakovica na okovu z zanko za obešanje nožnice so bili narejeni iz medenine, ki vsebuje malo več cinka (18–19 %; *tab.* in *sl. 1:* mesta 5,7,8).

Nekaj meritev smo naredili na plasteh iz bakrove zlitine, ki so se pokazale v železnih prečkah na sprednji strani nožnice, potem ko smo z njih odluščili plastične dele, dodane med restavracijo leta 1980 (glej Istenič 2010, 157), in pazljivo delno odstranili korodirane dele. Rezultati kažejo, da je bakrova zlitina bron s približno 4–7 % kositra (*tab.* in *sl. 1:* mesta 11a, 12a,13,15). Na spodnji strani prečk in med njimi ter medeninasto pločevino smo ugotovili plast železovih korozijskih produktov (*tab.* in *sl. 1:* mesti 12b,16).

Restavratorska dela leta 2010 so razkrila tudi podlogo iz bakrove zlitine pod levim in desnim železnim robom lestvičastega okova (med lestvičastim okovom in pločevino na sprednji oziroma hrbtni strani) v višini devete sprednje prečke ter dvanajste in trinajste prečke na zadnji strani. Po rezultatih meritev je bila ta podloga na eni (desni) strani iz brona z okoli 6 % kositra (*tab* in *sl. 1:* mesto 14), na drugi (levi) pa iz medenine z okoli 5 % cinka (*tab.* in *sl. 1:* mesto 9).

Rezultati analiz na nožnici s Strmca nad Belo Cerkvijo (*tab. 2*) kažejo, da so sprednja in zadnja platica ter okov s predrtim okrasom narejeni iz čiste medenine z okoli 21–22 % cinka (*tab.* in *sl. 2:* mesta 1,4,5). Okov z zanko za obešanje je tudi iz čiste medenine, vendar vsebuje manj cinka (*tab.* in *sl. 2:* mesto 8). Nožnica ima izrazito patino, zato so rezultati meritev na njej (*tab.* in *sl. 2:* mesta 2,3,6,7), ki kažejo majhne vsebnosti cinka (3–5 %), pričakovani. Izluženje cinka iz korozijskih plasti na medeninastih predmetih je namreč običajno (Istenič, Šmit 2007, 143).

Meritve na železni zakovici (*tab. 2:* mesto 9) kažejo prisotnost bakra in cinka, kar lahko razložimo s širjenjem korozijskih produktov medenine z elektrokemijskimi procesi.

Sprednja platica nožnice iz groba 37 v Verdunu je iz čiste medenine, ki vsebuje okoli 21 % cinka (*tab.* in *sl. 3:* mesto 2). Precej manjša vsebnost cinka, ki smo jo izmerili v patini, je v skladu s pričakovanji (glej zgoraj). Čisto medenino z manjšo vsebnostjo cinka pa so uporabili za izdelavo obloge zaključka ročaja meča (*tab.* in *sl. 3:* mesto 3).

Meč in pripadajoča nožnica iz groba 131 v Verdunu sta v slabem stanju. Zato smo opravili analize PIXE le na odlomku nožnice. Meritve na sprednji platici kažejo na čisto medenino z visoko vsebnostjo cinka (25,5 %; *tab.* in *sl. 4:* mesto 2). To je najvišja koncentracija cinka, ki smo jo doslej izmerili na rimskih medeninastih predmetih (cf. Šmit, Pelicon 2000; Šmit et al. 2005b). Zgornja meja za vsebnost cinka v rimski medenini, ki so jo izdelovali s cementacijskim postopkom, je okoli 28 % (Craddock 1995, 296–298; Craddock, Lambert 1995, 164).

4. SKLEP

Analize nožnic s predrtim okrasom iz bakrove zlitine in pripadajočih mečev iz Ljubljanice pri Bevkah, s Strmca nad Belo Cerkvijo ter iz groba 37 in groba 131 v Verdunu kažejo na intenzivno rabo čiste medenine.

Pri raziskavah smo izpopolnili postopek obravnave meritev tako, da smo pri rezultatu upoštevali meritve z mehkimi in trdimi rentgenskimi žarki.

Žiga Šmit
Univerza v Ljubljani
Fakulteta za matematiko in fiziko
Jadranska ulica 19
1000 Ljubljana
ziga.smit@fmf.uni-lj.si

Žiga Šmit
Institut Jožef Stefan
Jamova 39
SI-1000 Ljubljana
ziga.smit@ijs.si

Janka Istenič
Narodni muzej Slovenije
Prešernova 20
SI-1000 Ljubljana
janka.istenic@nms.si

Sonja Perovšek
Narodni muzej Slovenije
Prešernova 20
SI-1000 Ljubljana
sonja.perovsek@nms.si