THE POSSIBILITIES AND LIMITATIONS OF MODERN SCIENTIFIC ANALYSIS OF BRONZE AGE ARTEFACTS IN HUNGARY•

LEHETŐSÉGEK ÉS KORLÁTOK A BRONZTÁRGYAK MODERN MŰSZERES VIZSGÁLATÁBAN MAGYARORSZÁGON

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Abstract

For a long while, the scope of scientific testing of bronze artefacts was limited, with studies focused primarily on the composition, the ratio of alloying agents and impurities, and the presence of trace elements in archaeological objects. From the 1960s, as the technique of spectral (Optical Emission Spectroscopy) analysis became widely available, tens of thousands of objects were sampled (Schubert & Schubert 1963, 1967), but metallographic analyses and the investigations concerning the microstructure were only carried out in a few cases (Szegedy 1954; 1957; Mozsolics & Hegedűs 1963). Despite this, by the direct application of measurements, serious historical and archaeological conclusions were drawn, in relation to raw material sources and metallurgical centres for Bronze Age Europe. As the metallographic thin-sections prepared from prehistoric bronze objects demonstrate, the majority of archaeological bronze artifacts are heterogenous in structure, or even inhomogenous. For this reason, the outcomes of scientific tests must be carried out with the understanding of microstructure in order to interpret the measurements within safe limits. Only scientifically accurate data can be used to draw archaeological-historical conclusions.

Kivonat

A bronztárgyak vizsgálata során a kutatás hosszú ideig csak a régészeti tárgyak anyagának összetételére, az ötvöző és szennyezőanyagok arányára, a különböző nyomelemek jelenlétére volt kíváncsi. Az 1960-as évektől széles körben elérhető spektrumanalízis (optikai emissziós spektrometria) elvégzéséhez tárgyak tízezreiből vettek mintát, de ehhez képest csak elenyésző esetben készítettek csiszolatokat, vizsgálták meg az anyagösszetétel mellett a szövetszerkezetet is. Ennek ellenére jellemzően a mérési eredmények közvetlen átvételével jelentős, történeti-régészeti szempontú következtetéseket vontak le pl. az európai bronzkori nyersanyaglelőhelyekkel, kohászati központokkal kapcsolatban. Az újabban vizsgált bronztárgyak csiszolati képéből látható, a régészeti bronztárgyak többségének szerkezete heterogén, sőt gyakran inhomogén is. Ezért a műszeres mérések adatait alapvetően a szövetszerkezet ismeretében lehet biztonsággal értelmezni, és a hitelesen vizsgált és értékelt adatokból lehet valós régészeti-történeti következtetéseket levonni.

KEYWORDS: BRONZE, BRONZE AGE, ARCHAEOMETALLURGY, METHODS

KULCSSZAVAK: BRONZ, BRONZKOR, ARCHEOMETALLURGIA, MÓDSZERTAN

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The first decades of metal analysis

For a long while, the scope of scientific testing of bronze artefacts was limited, with studies focused primarily on the composition, the ratio of alloying agents and impurities, and the presence of trace elements in archaeological objects. From the 1960s, as the technique of spectral analysis became widely available, tens of thousands of objects were sampled (Schubert & Schubert 1963, 1967), but metallographic analyses and the investigations concerning the microstructure were only carried out in a few cases (Szegedy 1954; 1957; Mozsolics & Hegedűs 1963). Despite this, by the direct application of measurements, serious historical and archaeological conclusions were drawn, in relation to raw material sources and metallurgical centres for Bronze Age Europe.

By 1990s, a new situation began to emerge: the latest generation of instruments and techniques became available in Hungary too, such as the X-ray emission spectroscopy (Költő & Kis Varga 1992) or the neutron activation and laser micro-spectral analysis (Bakos & Borszéki 1989). Some of these tests detected unusually high levels of alloys in archaeological materials for which it was impossible to provide a metallographic explanation (Költő 1996; Cseh 1997) (**Fig. 1.**).

Today we are aware that the problem stemmed from the fact that these artefacts were considered as homogenous entities, and that the surface measurements (which were only concerned with a particular surface area) were extended to the object as a whole. The characteristics of bronze objects, including the grain size, can be altered significantly not only by changing the ratio of alloys, but by cooling, cold or hot working (Kienlin 2010; Szabó 2013). These altered characteristics can then have an effect on the object's microstructure along with the metal surface and corrosion processes (Szabó 1998, 2001, 2010; Kienlin 2010). Therefore it is easy to see, how the increasingly modern scientific techniques – which require very small sample sizes – can produce results which can be misinterpreted, especially in the case of non-homogenous metal alloys with different compositional phases.

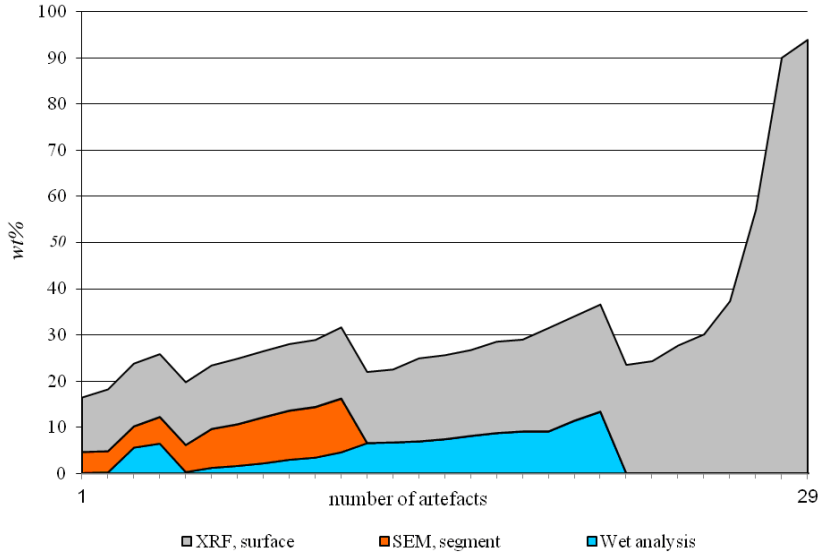

Fig. 1.:

Bronze Age artefacts from the Carpathian Basin tested for tin content by various approaches, both on the microstructural level and on samples taken from the objects' surface (after Szabó 2010, Fig. 1.)

1. ábra:

Kárpát-medencei bronztárgyak óntartalma eltérő módszerekkel, illetve felületen és csiszolaton végzett vizsgálatok alapján (Szabó 2010, 1. ábra nyomán)

Recent examinations: developing laboratory environment and increasing collaboration

In 1996, for the first time in Hungarian research, the composition and microstructure of metal artefacts were examined consistently and simultaneaously on pieces of a bronze depot in the laboratory at the University of Bradford. The original objective of the examination was to understand the relationship between the raw material composition of bronze objects and their use. However, it soon became clear that the measurements published during last decades were not suitable for this enquiry. At the same time, the results of current scientific tests (targeting the microstructure of objects) drew attention to the association between the sampling, the method of analysis and testing instruments, and the production and use of the artefacts, as well as the corrosion processes the object was exposed to (Szabó 1998; 1999; 2001). At this time, these associations only existed on the level of recognition, and no less than two decades had to pass in order to establish the theoretical grounds for these correlations; a process that is still continuing today.

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Table 1.: Research facilities and relevant technologies available for the archaeometrical testing of artefacts in Hungary (listed by scientific technique)

1. táblázat: Régészeti korú fémtárgyak archaeometriai vizsgálatának legfontosabb lehetőségei és helyszínei Magyarországon (módszerek szerint)

Method	Institution
microstructure analysis (thin section)	University of Miskolc, University of Debrecen
SEM-EDS, SEM-EDX (scanning electron microscopy - energy-dispersive X-ray spectroscopy) EMPA/EPMA (electron microprobe analysis)	University of Miskolc, University of Debrecen University of Debrecen,Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)
microstructure analysis (thin sections, polished blocks embedded in Duracryl resin), optical emission spectrometer	Centre for Energy Research (HAS);Research Centre for Natural Sciences (HAS); Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)
NR (neutronradiography, 2D)	Centre for Energy Research, Hungarian Avademy of Sciences (HAS)
NT (neutrontomography, 3D)	Centre for Energy Research (HAS)
PGAA (prompt-gamma activation analysis)	Centre for Energy Research (HAS)
PGAI (prompt-gamma activation imaging)	Centre for Energy Research (HAS)
TOF-ND (Time-of-flight neutrondiffraction, 2D)	Wigner Research Centre for Physics (HAS)
PIGE (proton-induced gamma emission analysis)	Institute for Nuclear Research (HAS)
PIXE (proton-induced X-ray emission analysis)	Institute for Nuclear Research (HAS)
micro-PIXE (proton-induced X-ray emission micronalysis)	Institute for Nuclear Research (HAS)
ED-XRF (energy dispersive XRF analysis)	Budapest University of Technology and Economics
p-XRF (portable X-ray fluorescence analysis)	Institute for Geological and Geochemical Research,Research Centre for Astronomy and Earth Sciences (HAS) Centre for Energy Research (HAS) Budapest University of Technology and Economics
XRD, micro-XRD	Institute for Geological and Geochemical Research,Research Centre for Astronomy and Earth Sciences (HAS)
FTIR (Fourier-transform infrared spectroscopy)	Institute for Nuclear Research, Laboratory of Ion Beam Physics (HAS) Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)
UV-VIS (ultraviolet–visible) spectrometry	Institute for Nuclear Research, Laboratory of Ion Beam Physics (HAS)
secondary neutral mass spectrometry (SNMS)	University of Debrecen, Institute of Physics

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Table 2.: Research facilities and relevant technologies available for the archaeometrical testing of archaeological artefacts in Hungary (listed by institution)

2. táblázat: Régészeti korú fémtárgyak archaeometriai vizsgálatának legfontosabb lehetőségei és helyszínei Magyarországon (intézmények szerint)

Location	Institution	Method	Research fellow
Budapest	Budapesti Neutron Centre (BNC)= Centre for Energy Research (HAS) Wigner Research Centre for Physics (HAS)	PGAA, PGAI, NR, NT, p-XRF TOF-ND	Zsolt Kasztovszky, Zoltán Kis, Boglárka Maróti, László Szentmiklósi, Ildikó Harsányi, Veronika Szilágyi György Káli
Budapest	Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences (HAS)	p-XRF	Zoltán May
Budapest	Budapest University of Technology and Economics	ED-XRF	Iván Gresits
Budapest	Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (HAS)	p-XRF EMPA/EPMA, XRD, micro-XRD FTIR	BernadettBajnóczi Viktória Mozgai Mária Tóth
Miskolc	University of Miskolc, Material Science Institute	XRD, SEM-EDX microstructure analysis (thin section)	Péter Barkóczy, Árpád Kovács
Debrecen	Institute for Nuclear Research, Laboratory of Ion Beam Physics (HAS)	Vacuum & In-air PIXE, micro-PIXE), PIGE, XRF, FTIR, UV-VIS spectrometry	Zsófia Kertész, László Csedreki, Zita Szikszai, Zsófia Török, Imre Uzonyi
Debrecen	University of Debrecen, Institute of Physics	SEM-EDS misrostructure analysis, optical microscopy SNMS	Szilvia Gyöngyösi

However, since the outcomes of the Bradford examinations were made public, archaeological considerations have been taken into account – instead of the pure application of the results – not only during the interpretation of measurements but already at the stages of sampling, and during the planning of scientific testing. In this regard, since the early 2000s, a major step forward was the establishment of the modern laboratory environment with professional staff and cutting-edge technology, where expert consultation taking place between scientists of different fields became the norm (**Table 1-2.**).

At the beginning, the scientific testing of metal artefacts in laboratories were generally carried out within the framework of particular projects targeting a single object or were brought about through the personal arrangements between individual scientists. However, there has been increasing collaboration between archaeologists and

natural scientists including the detailed overview and discussion of measurements. Such collaborations included the metallographic and metallurgical testing of a Copper Age hammer axe, a pair of Bronze Age arm ornaments from Borsodgeszt and a disc-butted axe from Szendrőlád led by Klára P. Fischl, Péter Barkóczy and Árpád Kovács. The microstructure of the samples were examined by optical microscopy, while their average and local composition was tested by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) in the LISA laboratories at the University of Miskolc, where besides the composition of objects, experts were able to shed more light on their production technologies as well (Barkóczy et al. 2011; Török et al. 2013).

The bronze hoards of Hajdúsámson and Téglás were tested by using the technique of proton-induced X-ray emission (PIXE) in the laboratories of Atomki at Debrecen, Hungarian Academy of Sciences (HAS). The examinations took place in the MTA Atomki laboratory in Debrecen conducted by János Dani, Zsófia Török, László Csedreki, Zsófia Kertész and Zita Szikszai. The tests were to map the main components and trace elements, arsenic (As), antimony (Sb), silver (Ag), nickel (Ni), iron (Fe), gold (Au), zink (Zn), manganese (Mn), chromium (Cr) and mercury (Hg, all in ppm) of tin bronzes which could provide clues for identifying differences of raw material and production centres (Dani et al. 2013; Török et al. 2015).

The testing of the hoard from Zalaszabar was also carried out in the LISA laboratories in collaboration with Viktória Kiss. Following the successful collaboration, the scope of the project broadened, and came to include the metallurgy of the Transdanubian Encrusted Pottery culture as a whole involving a series of sites and experts (Kiss et al. 2013). These newly established and successful protocols between archaeologists (particularly Bronze Age scholars) and natural scientists came to serve as benchmarks and led the way for Hungarian research, making it possible to extend the testing and evaluation even further by studying a diverse range of objects.

Further tests were carried out on a number of unique bronze artefacts in the Budapest Neutron Center (BNC) in order to determine production locales and the processes of crafting. The examinations included non-invasive 2D neutron radiography (NR), 3D neutron tomography (ND), while prompt-gamma activation analysis (PGAA) was conducted for the identification of raw materials. The changes induced to the microstructure of bronze objects during the production processes were clearly shown (even without the preparation of micrographs) by time-of-flight neutron diffractometer (TOF-ND) measurements (Kiss et al. 2015). The establishment and dynamic operation of the Lendület/Momentum Mobility Research Group within the Institute of Archaeology of the Research Centre for the Humanities (HAS) marked a turning point in interdisciplinary collaborations (Kiss 2016). Provided its institutional background, social network and financial support, the Research Group was able to maximize its involvement in cutting-edge laboratory projects but was also able to recruit expert scholars from the fields of archaeology and natural sciences. The Group's primary objective is to interpret archaeological contradictions by the development of a range of theoretical frameworks, particularly to better understand phenomena that had previously been observed but were considered as exceptions to the norm. The first outcomes of this research have now been recognized internationally as well (Kulcsár et al. 2015). At the same time, the opportunity rose for the artefacts to be analysed in laboratories both in Hungary and abroad, making it possible to compare measurements taken in different research environments. Here we would like to present the flanged axe from Zalaszabar; an example through which the scientific methodologies, results and the issues around direct interpretation and the potential historical consequences will be illustrated. The Zalaszabar flanged axe was tested in the BNC in Budapest and in the Curt-Engelhorn-Centre for Archaeometry (CEZA) in Mannheim.

Results and questions: possible interpretations of metal analyses

The provenance of raw materials and the recycling of objects are among the pivotal questions of current prehistoric metallurgical enquiries (Radivojević et al 2018). The main impurities and alloys detected in the composition of bronze objects (e.g. silver, arsenic, antimony, nickel and tin), as already mentioned, are generally regarded by current research as indeces for classification and links to mining areas. A series of examinations carried out in the 1960s and 70s (*Studien zu den Anfängen der Metallurgie*, the so-called SAM project of Stuttgart) described 29 metal types (Fig. 2; cf. Junghans et al. 1968, Diagram 1. *Stuttgarter Stammbaum*) which were later re-grouped by Ernst Pernicka and Rüdiger Krause by using cluster-analysis (**Fig. 2.**; Krause 2003, Abb. 39; Kiss 2009a). The CEZA laboratory in Mannheim, led by Ernst Pernicka, is one of the leading centres of European research, focused on locating prehistoric mining areas by the application of composition analyses and lead-isotope measurements of metal artefacts. More recently the centre began testing for tin isotopes as well, in order to identify prehistoric tin sources.

Cluster no.	Copper type	No. of analyses	Trace elements (main elements printed bold)	Class
1	Classic 'Ösenringkupfer'	3804	**As, Sb, Ag**, (Bi), no Ni	Fahlore copper without Ni (IIa)
2	Purest copper	3329	no measurable trace elements	Pure copper (IIIa)
3	With occasional traces of Ag	2740	**As**, no Sb, Ni, Bi	Arsenic copper (Va)
4	Eastern alpine copper	6505	**As, Ni**, Sb, no Bi	Fahlore copper with Ni (Ib)
5		774	**As, Ni,** no Sb, Ag, Bi	Pure copper, law As and Ni contect (IIIb)
6		1275	Sb, As, Ag, no Ni, Bi	Arsenic copper (Vb)
7	Copper with traces of Sb and Ag	522	**Sb, Ag**, no As, Ni, Bi	Antimony copper (IVa)
8	Singen copper	2882	**As, Sb, Ni, Ag**	Fahlore copper with Ni (Ia)
9		32	**Sb, Ni**, no As, Bi	Antimony copper (IVc)
10	Similar to 'Ösenringkupfer'	2929	As, Sb, Ni, Ag, no Bi	Fahlore copper without Ni (IIb)
11		375	**Sb, Ag, Ni**, no As, Bi	Antimony copper (IVb)
12	Fahlore copper without Ag	42	**As, Sb,** no Ag	Arsenic copper (Vc)
13		68	**As, Bi,** scarcely Ni, no As, low Sb	Pure copper (IIIc)
14	Possibly pure copper	82	Ni, Ag, scarcely Sb, no As, Bi	Pure copper (IIId)
15		42		Pure(st) copper (?)
16		2		Pure copper (?)
17	Arsenic copper with Ni, Bi	284	As, Sb, Ni, Bi	Fahlore copper with Ni (Ic)
18		10		?
19	White metal	16	**As, Ni,** Sb, scarcely Bi	Fahlore copper with Ni (Id)
20		110	**As**, Ni, Ag, Bi, no Sb	Arsenic copper (Vd)
21		26	**As, Bi**, scarcely Ag, no Sb, Ni	Arsenic copper (Ve)
22	Unalloyed copper with Ag	40	Ag, As, Ni, scarcely Sb, Bi	Fahlore copper with Ni (Ie)
23	Copper, low Sb and Ag content	20	Sb, Ni, no As, Ag, Bi	Antimony copper (IVd)
24		7		?
25		3		?
27		4		?
28	Copper, Sb and Ag high	7	**Sb, Ag,** Ni, Bi	Antimony copper (IVe)
30		4		?
31		3		?
32		4		?

Fig. 2.: Dendrogram showing the key copper types produced by the cluster analysis of the SAM project *Stammbaum*, based on their occurrance and composition (after Krause 2003, Abb. 39)

2. ábra: A stuttgarti törzsfa klaszteranalízissel csoportosított fő réztípusai gyakoriságuk és elemösszetételük alapján (Krause 2003, Abb. 39 nyomán)

However, there are still several issues to overcome as tin sources show large geographical overlaps making the archaeological interpretation problematic (Nessel et al. 2015, Fig. 5; Brügmann et al. 2017, Abb. 1; Radivojević et al 2018). Similarly to the cluster anaysis of copper groups of the SAM project data (based on the presence or absence of impurities) the University of Oxford's FLAME metallurgy project established 16 metal categories (**Fig. 3.**; Bray et al. 2015, Fig. 1).

The series of tests carried out in Stuttgart on tens of thousand samples already indicated a paradigm-shift in the use of raw materials that had taken place during the 2nd Millennium BC (Schubert & Schubert 1967). In the broader region of Central Europe the artefacts dating to Early Bronze Age (between 2000/1900 and 1600 BC) can be classified into several groups: among these are the pure copper, arsenic copper, and the so-called *Ösenring* copper objects (**Fig. 2.,** Cluster No. 1-3, after Krause 2003) occur in the highest numbers. The latter (*Ösenring* copper*)* was coined after neck rings whose characteristic copper raw material contained high levels of silver, arsenic and antimony, while in the period after 1600 BC, the widespread usage of a copper type rich in arsenic and nickel, the so-called eastern Alpine copper type, is detecteed (Fig. 2, Cluster No. 4). Recent lead-isotope analyses aiming to refine the provenance of copper ore originate the raw material of *Ösenring* copper objects from the region of Slovakia, while the eastern Alpine type copper is suggested to be derived from the mines of Mitterberg (Salzburg region, Austria) (Radivojević et al. 2018, Fig. 7). However, it has to be noted here, that a technological change has also been considered among the explanations for this paradigm-shift (Melheim et al. 2018).

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Copper Category	Copper with...	As	Sb	Ag	Ni
1	None	no	no	no	no
2	As	YES	no	no	no
3	Sb	no	YES	no	no
4	Ag	no	no	YES	no
5	Ni	no	no	no	YES
6	As+Sb	YES	YES	no	no
7	Sb+Ag	no	YES	YES	no
8	Ag+Ni	no	no	YES	YES
9	As+Ag	YES	no	YES	no
10	Sb+Ni	no	YES	no	YES
11	As+Ni	YES	no	no	YES
12	As+Sb+Ag	YES	YES	YES	no
13	Sb+Ag+Ni	no	YES	YES	YES
14	As+Sb+Ni	YES	YES	no	YES
15	As+Ag+Ni	YES	no	YES	YES
16	As+Sb+Ag+Ni	YES	YES	YES	YES

Fig. 3.:

The 16 'copper groups' as defined by the presence/absence of four trace elements (presence is usually taken as greater than 0.1%; after Bray et al. 2015, Fig. 1)

3. ábra:

Négy nyomelem megléte/hiánya alapján meghatározott 16 cluster csoport (általában 0,1% fölött kimutatható nyomelemek; Bray et al. 2015, Fig. 1. nyomán)

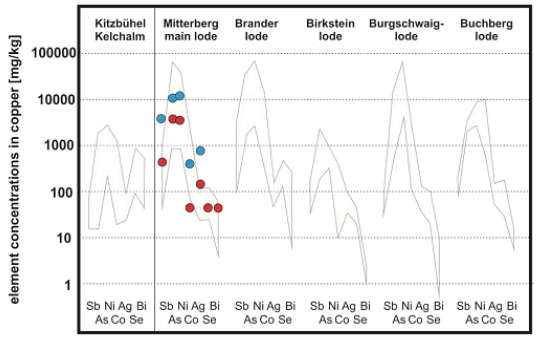

Fig. 4.: The elemental composition of the Hajdúsámson (in red) and the Téglás hoards (in blue) compared with the elemental composition of the eastern Alpine copper mining regions (Pernicka 2013, Fig. 4)

4. ábra: A hajdúsámsoni kincs (pirossal) és a téglási kincs (kékkel jelezve) tárgyainak elemösszetétele a kelet-alpi bányák elemösszetételével összevetve (Pernicka 2013, Fig. 4)

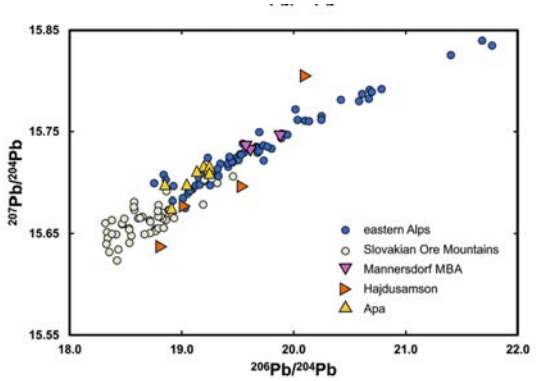

Fig. 5.: Lead isotope analyses of objects from the Hajdúsámson hoard compared with the analyses of assemblages from Austria, Romania, and eastern Alpine copper sources (Radivojević et al. 2018, Fig. 7)

5. ábra: A hajdúsámsoni kincs tárgyainak ólomizotóp elemzési eredménye (Radivojević et al. 2018, Fig. 7)

The classification produced by the cluster analysis of the SAM project's datacluster analysis has been accepted and applied by Hungarian research as well (**Fig. 2.**). According to analyses of a dagger and its rivets' from burial no. 66 of the Early Bronze Age cemetery of Kiskundorozsma, measuring relatively high levels of nickel (4.27 and 5.88%), arsenic (2.16 and 2.45%) besides a low percentage of silver (0.17 and 0.21%), and iron (0.14 and 0.19%), Klára P. Fischl and Gabriella Kulcsár suggested that the raw material could also have contained fahlores with high levels of nickel and arsenic (P. Fischl & Kulcsár 2011).

János Dani argues that the above mentioned swords from Téglás and the artefacts of the Hajdúsámson hoard are – based on trace elements – made of eastern Alpine fahlore copper (Krause 2003, Abb. 39, Cluster no. 4, *Fahlerzkupfer mit Nickel*). Following the system set up by David Liversage, he categorised the raw materials of the Hajdúsámson hoard to the 'AsNi' group and the sword from Téglás to the 'ASN' raw material cluster. Furthermore, while considering Ernst Pernicka's examinations – based on element composition and complementary, the first published Hungarian lead-isotope analysis (**Figs. 4-5.**) – a direct, archaeological-historical link between certain mining regions and the raw material of the Téglás and Hajdúsámson swords has been drawn.

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Table 3.: The elemental composition of the Zalaszabar axe measured by ED-XRF analysis (Kiss et al. 2015, Table 2)

3. táblázat: a zalaszabari balta elemösszetétele az ED-XRF elemzés szerint (Kiss et al. 2015, Table 2)

Inv. nr	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Sn	Sb	Te	Au	Pb	Bi
2010.2.1.82	0.02	0.01	0.074	91	0.2	0.129	0.005	0.175	8	0.127	0.005	0.023	0.028	0.01

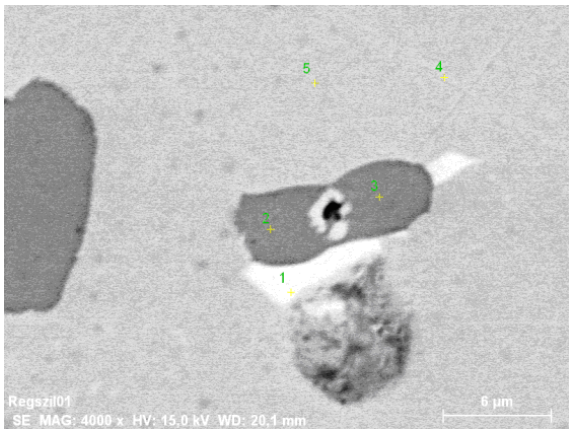
The axes of the Hajdúsámson hoard, the axe of Vámospércs (dating to the same period), along with the hilt of the Téglás sword were linked with the prehistoric mines of the Mitterberg region, south of Salzburg (Austria), that were exploited during the 16th–14th centuries BC. The ore used for the blade of the Téglás sword and an axe from the same hoard could have been mined in the Garam Valley region, Slovakia (Dani et al. 2013; Pernicka 2013).

The Middle Bronze Age hoard of Zalaszabar containing over 80 artefacts was subject to a number of studies (Honti & Kiss 2013; Kiss et al. 2013). One of the artefacts, a flanged axe was made of, according to the ED-XRF analysis testing for 14 elements (**Table 3.**), an ore of high silver, antimony and arsenic content (Kiss et al. 2015). Based on these measurements, the axe was classified as an example of the classic tin bronzes (for more detail on the tin content, see below). Considering the axe's worked edge, the production-technological analysis made by TOF-ND concluded that – although similar objects are still being interpreted as bronze ingots – the Zalaszabar piece was indeed an implement intended for use (see also Kienlin 2010).

Hungarian geologist experts, whose work focuses on the identification of raw materials, have long been drawing attention to fahlores (e.g. tetrahedrite, tennanite) which besides calcopyrite, are the second most frequently occuring minerals in copper deposits. These, however, do not contain nickel in their composition (Anthony et al. 2003; Czajlik 2012, 41, 87-91, 13. ábra). This also highlights the difficulties when it comes to the classification of copper ores based on impurities. The examination of the Zalaszabar axe concluded that 'the raw material could have originated from a fahlore copper deposit given the presence of relatively high levels of arsenic, silver and antimony, where – as the higher iron levels detected in object 2010.2.1.71 demonstrate – calcopyrite minerals could also have occurred' (Kiss et al. 2013). This suggests that different types of ores either intentionally or unintentionally could have been combined during prehistoric metallurgical processes. In this way, ores containing nickel (or other) impurities could have made it into the raw material of prehistoric bronzes.

Our examinations show that artefacts containing nickel either in traces or in a low percentage occur among the Early Bronze Age Bell Beaker, Nagyrév, Kisapostag, and Early Transdanubian Encrusted Pottery assemblages and also among the finds of the Middle Bronze Age Füzesabony Culture (Endrődi et al. 2003; Kiss et al. 2013, Table 1). A range of tests carried out on the Zalaszabar axe also indicated the presence of small amounts of nickel, which is not typical for the *Ösenring* raw material category, characteristic for the metallurgy of the Transdanubian Encrusted Pottery Culture. Furthermore, the results highlighted some issues around sampling and testing methodologies: the object-parts where the sample was taken from and the instruments involved in the examination produced – sometimes significantly – different results. The BNC's handheld XRF measured almost four times higher (45 %) tin content than the measurements by PGAA and time-of-flight neutrondiffraction (TOF-ND), and also by ED-XRF in the Mannheim laboratory. The difference was not so pronounced, when so-called bulk methods were being applied: samples taken from inside, the pure metal part of the object tested by ED-XRF measured 8% tin, while the prompt-gamma activation analysis (PGAA) indicated 90.2% copper, 9.6% tin, 0.18% silver, and 0.056 weight% H content for the axe's raw material. TOF-ND measurements resulted in 7.5±0.5 weight% for tin content. Both PGAA and ED-XRF tests measured corresponding values for copper and silver content, while the significant trace elements determined by the ED-XRF (Fe, Co, Ni, Zn, As, Se, Sb, Te, Au, Pb and Bi) were beyond the detection limit for the PGAA (Kiss et al. 2015). Most recently Boglárka Maróti studied the underlying causes for higher tin values occuring during PGAA tests and worked out a protocol for non-destructive PGAA tests to be carried out on archaeological objects (Maróti et al. 2018). With the validation of the method and according to the new protocol (and the relevant interference corrections) the tin content of the Zalaszabar axe measured at 8,4 +/- 0,4 weight%.

The heterogenous measurements of the same object (i.e. the levels of nickel) raise the question whether the distinction between raw material categories, mining areas, and communication trajectories – often considered as archaeologically and historically conclusive – are truly well founded.



Regszilla Atomic percent (%)						
Spectrum	C	O	S	Ni	Cu	Sn
1	13.53	10.75	-	8.57	48.55	18.060
2	7.86	2.81	24.82	0.75	63.76	-
3	9.090	41.59	-	0.18	35.73	13.41
4	8.90	6.82	-	-	79.36	4.92
5	10.90	3.32	-	1.270	80.33	4.99

Fig. 6.: SEM-EDS analysis of the cauldron sample (Regszil 1a) discovered in the tumulus of Regöly Strupka-Magyar birtok

6. ábra: A Regöly Strupka-Magyar birtokon feltárt tumulusban talált bográcsperem Regszil 1a jelzésű mintájának SEM-EDS elemzése

In relation to the high percentage of tin and nickel, the long-ongoing discussion over when and how alloys entered the copper raw material has to be re-considered. Evidence for tin being used as a direct alloy appears only from the 7th century BC in the Carpathian Basin. More recently a sample taken from the cauldron found in the Early Iron Age tumulus of Regöly was tested by electron microscopy showing a basematrix of Cu-Sn solid solution (Gyöngyösi et al. 2017b). The 'white areas' appearing on the metallographic thin sections indicate a high nickel content, compared to the basematrix which contained a lower percentage of nickel. Nickel is not soluble in tin, it creates an intermetallic compound with a melting point of approx. 900 °C. Some of the SnNi content dissolves into the copper naturally, however the presence of nickel raises the copper's melting point which in turn remains partially solid during the casting process (thus produces a 'white area' on the metallographic thin-sections). In sum, this indicates that the nickel entered the alloy along with the tin (**Fig. 6.**). Unfortunately, due to the lack of evidence so far, the question whether this reflects the appearance of a new technology or these particular objects were imported, cannot be answered at the moment (Gyöngyösi et al. 2017b, Fig. 6) The scientific examinations in relation to Early and Middle Bronze Age artefacts raise the possiblility that differences in nickel content are not always associated with the composition of the copper raw material. Data so far suggests that during the Early and Middle Bronze Age, raw material ingots arrived in the Carpathian Basin in an alloyed form, therefore the alloying process must have taken place in the original mining region (Szabó 1996, 216; Kiss 2009b, 2012). Further research into this enquiry could provide evidence whether the above described paradigm-shift following the 17th century BC was related to the change in exploitation of raw material sources or whether it was due to the introduction of a new technology.

Our examinations clearly show that a distinction has to be made between the amount of alloying agents and contaminants present in a given alloy and how much of these are actually measured. Scientific instruments do not map the object's chemical composition but target and measure one particular physical characteristic which could be informative for the rest of the object's composition. It is possible, in the case of a homogenous solid solutions and chemical compounds, that these two measurements overlap. However, as the metallographic thin-sections prepared from prehistoric bronze objects demonstrate, the majority of archaeological bronze artifacts are heterogenous in structure, or even inhomogenous. For this reason, the outcomes of scientific tests must be carried out with the understanding of microstructure in order to interpret the measurements within safe limits. Only scientifically accurate data can be used to draw archaeological–historical conclusions.

Although the topic of modern scientific instruments and their related protocols are hotly debated both nationally and internationally, this does not mean that there is no relevance or necessity for the testing of archaeological objects. On the contrary, modern scientific testing can provide more accurate and more complex answers to research enquiries. Thus a way forward could be the conceptualisation of more precise questions that are taylored to the abilities of scientific testing methods, and the development of standardised approaches for the testing of archaeological materials, as well as the establishment of wider collaboration for tackling more complex research enquiries would be

desirable (e.g. Gyöngyösi et al. 2017a,b; Kiss et al. 2017a,b; Király et al. 2017; Tarbay et al. 2018).

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