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TIN AND TINNED DRESS ACCESSORIES FROM MEDIEVAL WROCŁAW (SW POLAND). X-RAY FLUORESCENCE INVESTIGATIONS

This paper presents a non-destructive analytical study of selected archaeological artefacts from the Old Town in Wrocław, SW Poland, by energy-dispersive X-ray fluorescence spectrometry. The analysed specimens included dress accessories that decorated both women's and men's clothes in the Middle Ages. Several various metallic artefacts were selected for detailed studies: jewellery (e.g. finger rings) to more utilitarian utensil (functional) items (e.g. knives). All of them were made of tin-lead alloys or were tinned. This research was focused on determining the chemical composition of the artefacts, the identification of similarities and differences between alloys as well as technological aspects of the production. The obtained results suggest that there are many objects with the same chemical composition. It helps to distinguish groups of artefacts (e.g. rings made with the same alloys) or find the parts of one object. The next interesting result is the possibility of determining the presence of tin-plating that was in varied states of preservation (especially for badly damaged artefacts).

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Introduction

Most of what we know about medieval clothing elements and jewellery is from portraits, pictures in manuscripts and artefacts from museum collections. However, this knowledge is focused on precious accessories (and jewellery) that adorned knights and nobles. It was nevertheless important for all social groups to look *fashionable* and to wear jewellery. To the women and men of the Middle Ages dress elements were not only the determinant of social status, but had a religious context as well. The jewellery motifs were often devotional, e.g. crosses and pilgrims' badges (often worn by men on their hats). Women wore pendants, finger rings, belts and brooches, which were often wedding gifts (Kupstas 2000). Clothing accessories were made from very different metals; noble metals (gold and silver) were intended for wealthy men and cheaper metals for the others. The raw material used to produce the latter ones was bronze, tin, lead and/or lead-tin alloy (Koćka-Krenz 1982; Egan & Pritchard 2008). The imitation of noble jewellery is quite intriguing and will be discussed in this paper. After their conservation, several artefacts were selected for detailed studies: jewellery, dress accessories and tools. They were found during an archaeological excavation in the New Market Square in Wrocław, SW Poland. The excavation was connected with the construction of an underground car park, which covered nearly 4000 m^2 in the southern part of the square. The research team, composed of staff and graduate students of several Polish universities (mainly the University of Wrocław) was led by Professor Jerzy Piekalski. The main excavation took place from September 2010 to December 2012. The New Market Square is located in the eastern part of the Old Town of Wrocław. It has a long and varied history, bursting with the rich remains of the past in the form of cultural strata.

Previous studies of medieval archaeology in Wrocław indicate that the beginnings of settlement land use are related to the 11th–12th century and were in the close vicinity of the castle on Cathedral Island. The archaeological and architectural study aimed to determine the true nature of craft production, as well as the layout of the New Market Square in the context of medieval Wrocław. The huge collection of artefacts (11,838 in total, some compact groups of or single ones) is useful in the study of the material culture of medieval Wrocław, as well as its external contacts (Bonar et al. 2013). The condition of the selected artefacts retrieved from archaeological layers was different (specimens covered by corrosion and layers of impurities, sometimes without metallic cores), which made the identification of tin/tinned artefacts difficult. The state of preservation of metal artefacts is a well recognized topic in archaeology and has been the subject of previous papers discussing soil effects on metal objects, e.g. Gerwin & Baumhauer (2000) and Neff et al. (2005). Therefore, artefact conservation prior to archaeometric investigations is very important. Because of the great historical value of the objects in these and previous investigations, there is a need to use non-destructive analytical methods (Bugoi et al. 1999; Janssens et al. 2000).

There are many suitable methods that may be applied in archaeometry: neutron activation analysis (NAA), proton-inducted x-ray emission (PIXE), laser induced breakdown spectroscopy (LIBS) or many types of X-ray spectrometry (X-ray fluorescence (XRF) or scanning electron microscopy with energy dispersive X-ray detection (SEM-EDX)). Many research groups use such analytical techniques, e.g. Linke & Schreiner 2000; Lazic et al. 2005; Šmit & Šemrov 2006; Vlachou-Mogire et al. 2007. The appropriate techniques should be universal, rapid and not too expensive for the institutions that take care of artefacts and store them (e.g. museums, universities and institutes). X-ray fluorescence is one of the aforementioned methods that are often applied in archaeometry projects (Milazzo 2004; Giumlia-

Mair 2005). The selected tin and tinned objects have been investigated by energy-dispersive XRF. The artefacts are an unprecedentedly huge group of metal items (mainly tinned iron-alloys) and come from the collections of the Institute of Archaeology (University of Wrocław). Artefacts of a different function were tinned such as everyday utensils, jewellery and tools. Decorations were made from tin, lead and its alloys including dress accessories and religious elements (pilgrims' signs). The aim of this project was to analyse metal artefacts to identify layers of tin-plating and, in the case of tin-alloys artefacts, to compare the chemical composition of the objects (identify similarities and differences between alloys for different types of items) as well as to recognize technological aspects of the production (also in chronological aspects).

Materials and method

Due to the uniqueness and preciousness as well as the various sizes of the analysed objects, I used point analysis, without sampling, and a Spectro Midex spectrometer. This instrument guarantees rapid, universal, multi-elemental and non-destructive analysis, and is equipped with the large chamber for samples (with the dimensions 540 × 420 × 160 mm that make possible analysis of complete artefacts). It is also possible to choose small areas for analysis (video view system of a sample, the diameter of measurement spot is 0.7 mm, useful for ornaments and details analysis). The configuration is as follows: a 30 W – molybdenum X-ray tube (because of the Mo-tube, the peaks in the range of 16.5–20 keV are discounted), a Si Drift Detector (SDD) with a resolution of 150 eV (relative to the Mn-K alfa line and input pulse density of 1000 cps), and a video system. The disadvantage of the XRF analysis by Midex is the surface character of the measurements (the depth of analysis is only in μm scale) and the incapacity to analyse light elements) (e.g. C, O, S). Since tin and lead are heavy metals, the XRF analysis by Midex is possible, when preparing the representative area on the artefact properly (e.g. by polishing the edge). Several metallic and non-metallic artefacts were selected for archaeometric investigation. Figure 1 presents the selected tin/lead alloy and tinning objects. The analysed items (over 155 objects at the moment: 17 mounts, 2 beads, 5 pendants, 2 hafftels, 18 buckles, 4 diadems, 5 keys, 9 knifes, 4 spurs, 38 finger rings, 44 pilgrims signs and badges and several parts of decorated leather (10 items) were recovered from a stratigraphic layer with a medieval chronology (from the 12th to the 14th century, but the majority of the artefacts were from the 14th century). The stratigraphic layers had various elements, mainly dark-brown mulch mixed with large amounts of humus and organic remains such as small wooden pieces and large wooden construction elements. The artefacts were deposited in the soil for centuries and many of them are corroded. Prior analysis, the surface of artefacts was mechanically cleaned by polymeric tools and then were XRF analysed (Fig. 1).

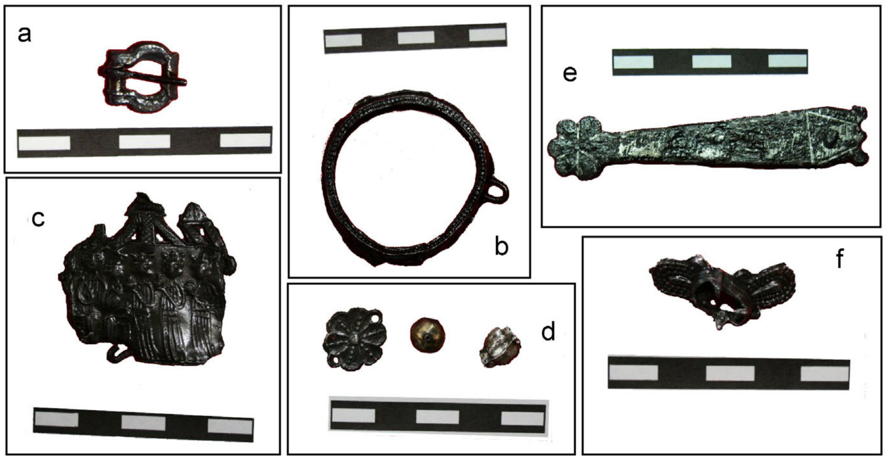

Fig. 1. Photographs of the selected tin and tinned artefacts from Wrocław.

Results and discussion

Tin/lead alloys artefacts

In medieval Europe tin was the alternative raw material used to make jewellery and dress accessories for ordinary people, as was well illustrated for medieval London (Egan & Pritchard 2008). Initially the customers used to buy inexpensive belts with tin or lead elements. Over time, also the nobles started to buy and wear non-precious metal accessories (Giumlia-Mair 2005). Many various tin objects were found in medieval layers. The results of the ED-XRF examinations of the selected artefacts were compared. The chemical composition of many groups of objects was similar. Figure 2 presents the spectra of a few analysed items: mounts, finger rings, diadems and pendants (in the shape of small bells). The comparison of the presented spectra shows that many artefacts have the same metal content. The similarity in the chemical composition of ready products and discovery of incomplete stone moulds (probably for mounts and finger-rings) and tools suggest there must have been craft workshops in the New Market. Also ingots of raw-material (there were almost pure lead) were found.

The close affinity between the metal levels does not only concern the main elements in the alloy (tin and lead), but also trace ones. Three analysed diadems were made from a tin/lead alloy of 61% of tin, 37% of lead, 0.10% of copper, 0.020% of zinc, and 0.10–0.20% of iron. The next interesting group are finger rings. The 38 analysed artefacts are made from various alloys. Two of them are gold (>80% Au), seven are made of copper alloys (70–80% Cu), one is lead (nearly 90% Pb), 28 items are made of tin alloys, twenty are pewter, and eight are almost pure tin. Table 1 presents the metal content of selected finger rings (one representative of each group of finger rings). Figure 2 presents the spectra of

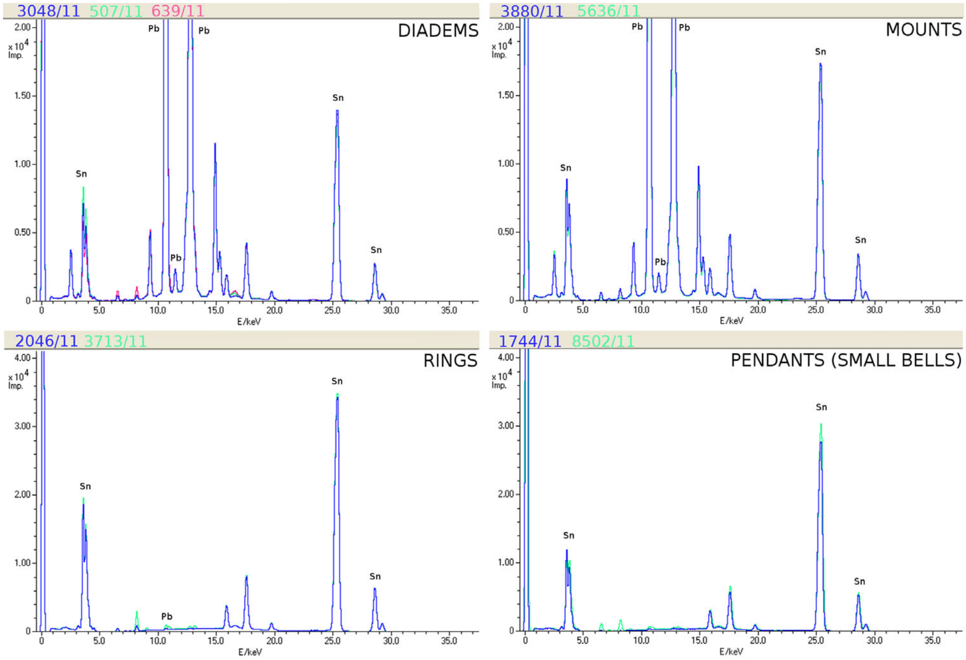

Fig. 2. ED-XRF spectra of the analysed tin-alloys specimens (diadems, mounts, rings and pendants).

tin finger rings (No. 2046/11 and No. 3713/11). We can see that they were made from the same alloy, 98% of tin and small amounts of copper (0.5%), iron (about 0.2%), lead (0.1%) and zinc (0.02%). The pewter finger rings have a more varied chemical composition, the tin and lead content are in the range of 45–65% Sn and 30–50% Pb. In the pewter there are also small amounts of iron, zinc and copper (Table 1). The chronology of the diadems, finger rings and pendants is not broad, the jewellery mostly dates from the 14th century, and rarely from the 13th or 15th century. The high number of tin-alloys preserved and excavated artefacts may be a consequence of the physical properties of non-ferrous metals. For example, the chemical stability of lead and tin causes that they survive general in better condition than iron specimens do. The main and technological useful property is the melting temperature, which is 1083 °C for copper, 1063 °C for gold, 960.8 °C for silver, 327 °C for lead, 232 °C for tin and about 180 °C for tin/lead alloy (Sn/Pb ratio is 60 : 40%) (Bielański 1972). The second important property is hardness of these metals and their alloys. The microhardness of these materials in the Vickers scale is rather low: 3–6 HV for pure lead, 6–10 HV for pure tin, 15–30 HV for pure, cast silver, 40 HV for almost pure gold (23.75 carat gold), 40–50 HV for cast copper and from 50 to 220 HV for various copper alloys, and about 10 HV for Sn-Pb alloys (Scott 1991; Ashkenazi et al. 2011). The hardness is often comparable, for example in gold and copper alloys, all the values for

Table 1. The XRF analysis of selected artefacts from the New Market Square (Wrocław). The metal contents are normalised to 100%

Artefact				Metal (wt. %)						
No.	Photo	Name	Dating	Cu	Zn	Au	Pb	Sn	Ag	Fe
3048/11		Diadem	14th	0.72	0.02	<0.02	36.38	61.41	<0.02	0.12
507/11		Diadem	14th	0.06	0.02	<0.02	36.77	60.80	<0.02	0.12
639/11		Diadem	14th	0.21	0.02	<0.02	36.85	60.68	<0.02	0.36
1336/11		Badge	13th	0.03	0.02	<0.02	26.32	71.91	<0.01	0.11
7691/11		Badge	13th	0.03	0.02	<0.02	27.10	71.06	<0.01	0.08

Table 1. *Continued*

Artefact				Metal (wt. %)						
No.	Photo	Name	Dating	Cu	Zn	Au	Pb	Sn	Ag	Fe
11/10		Badge	13–14th	0.07	0.03	<0.02	0.08	98.59	<0.01	0.11
5336/11		Badge	–	0.04	0.03	<0.02	95.30	<0.10	<0.04	0.17
664/11		Badge	14th	0.08	0.02	<0.02	94.70	0.14	0.04	0.59
5329/11		Badge	14th	0.10	0.02	<0.02	37.60	60.40	<0.04	0.12
2962/11		Badge	14th	0.75	0.02	<0.02	47.70	47.50	<0.02	1.25

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Table 1. *Continued*

Artefact				Metal (wt. %)						
No.	Photo	Name	Dating	Cu	Zn	Au	Pb	Sn	Ag	Fe
3880/11		Mount	14th	0.16	0.02	<0.02	31.28	66.47	<0.02	0.26
4887/11		Mount	14th	0.40	0.02	<0.02	24.90	68.93	<0.02	0.45
8549/11		Mount	14th	0.92	0.02	<0.02	0.21	96.44	<0.01	1.29
355/10		Mount-bulk/layer	14th	0.69	0.02	<0.02	50.84	43.62	<0.02	2.54
3713/11		Finger ring	14th	0.59	0.02	<0.02	<0.12	97.90	<0.01	0.15

Table 1. *Continued*

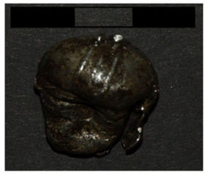
Artefact				Metal (wt. %)						
No.	Photo	Name	Dating	Cu	Zn	Au	Pb	Sn	Ag	Fe
901/11		Finger ring	14th	0.37	0.02	<0.02	40.78	55.66	<0.02	0.75
1766/11		Finger ring	Late medieval	3.57	<0.01	83.48	<0.02	<0.1	12.88	<0.02
3417/11		Finger ring	14th	76.09	19.59	<0.02	1.51	0.80	0.17	0.28
1744/11		Pendant	13th	0.01	0.02	<0.02	<0.02	99.07	<0.01	<0.02
8502/11		Pendant	14th	0.26	0.03	<0.02	0.09	97.50	<0.01	0.83

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Table 1. *Continued*

Artefact				Metal (wt. %)						
No.	Photo	Name	Dating	Cu	Zn	Au	Pb	Sn	Ag	Fe
331/10		Buckle-bulk	Late medieval	0.12	0.04	<0.02	0.07	0.17	<0.01	95.00
		Buckle-layer		0.08	0.05	<0.02	0.18	88.05	<0.01	8.41
9769/11		Buckle-bulk	14th	0.08	0.04	<0.02	<0.003	0.07	<0.01	98.37
		Buckle-layer		0.05	0.07	<0.02	0.55	87.08	<0.01	10.19
7087/11		Buckle-bulk	13th	0.05	0.02	<0.02	0.50	0.97	0.01	96.91
		Buckle-layer		0.11	0.01	<0.02	0.78	34.1	<0.01	48.90
5681/11		Buckle-bulk	13/14th	0.06	0.06	<0.02	0.03	0.32	<0.01	98.12
		Buckle-layer		0.08	0.04	<0.02	0.76	86.9	<0.01	10.91
10299/11		Buckle-bulk	13th	84.27	3.90	<0.02	2.16	6.85	0.08	1.22
		Buckle-layer		74.96	2.83	<0.02	1.36	17.55	0.09	0.83

Table 1. *Continued*

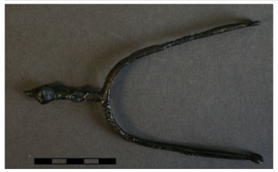
Artefact				Metal (wt. %)						
No.	Photo	Name	Dating	Cu	Zn	Au	Pb	Sn	Ag	Fe
1889/11		Strap fitting-bulk	14th	<0.01	0.02	<0.02	0.11	0.50	0.01	99.15
		Strap fitting-layer		0.08	0.08	<0.02	1.03	85.93	<0.01	10.02
3003/11		Ferrule - bulk	14th	0.03	0.02	<0.02	0.33	7.89	<0.01	85.91
		Ferrule-layer		0.13	0.06	<0.02	0.69	72.5	<0.01	22.52
8466/11		Key-bulk	13th/14th	0.01	0.03	<0.02	0.01	0.05	<0.01	98.54
		Key-layer		0.08	0.08	<0.02	0.22	92.97	<0.01	5.37
9031/11		Key-bulk	14th	0.04	0.02	<0.02	0.01	<0.01	<0.01	98.54
		Key-layer		0.02	0.02	<0.02	<0.02	90.13	0.01	8.87
6866/11		Spur-bulk	12th	0.17	0.05	<0.02	1.18	0.03	0.01	96.44
		Spur-layer		0.82	0.05	<0.02	0.55	94.37	<0.01	3.16

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Table 1. *Continued*

Artefact				Metal (wt. %)						
No.	Photo	Name	Dating	Cu	Zn	Au	Pb	Sn	Ag	Fe
8622/11		Spur	13th	0.08	0.02	<0.02	0.09	0.21	<0.01	98.08
		Spur-decoration		0.04	0.02	<0.02	0.08	91.46	<0.01	7.15
198/11		Handle of the knife (wire)	–	0.05	<0.01	0.85	<0.02	96.6	<0.02	1.85
450/11		Knife-bulk	13th	0.06	0.03	<0.02	0.13	58.9	<0.01	39.7
		Decoration		0.01	0.02	<0.02	0.44	92.8	<0.01	5.56
7031/11		Knife-bulk	Late medieval	0.05	0.02	<0.02	1.67	<0.02	<0.01	96.62
		Decoration		0.08	0.03	<0.02	<0.02	94.93	<0.01	3.96

non-ferrous metals are rather low. It is helpful information, because such soft materials (especially lead and tin) are easy for craft working. The third significant property is chemical passivity of tin, lead and copper. These metals oxidize slowly and often passivate, therefore their surface stays lustrous and shine for a long time. Tin, lead and copper are also less expensive than gold and silver, and at the same time their mechanical properties guaranteed expected quality of ready products. All these listed properties, together with low-melting temperature, were important to craftsmen who produced many items, for example dress accessories by simple casting. The use of the tin-rich alloy (three parts of tin and one part of lead) was widely used in casting and soldering. In manufacturing of finger rings for example, where the liquid metal was involved, tin/lead alloy was deliberately used.

The next group are mounts. The analysed artefacts were selected by their grey and black surface as they were contaminated by corrosion (the copper alloys mounts were not investigated). The analysed mounts were made mainly of various tin and lead alloys; the range of the tin content is from 43% (a tinned iron star-shaped mount – No. 355/10) to 96% (mount No. 8549/11). However, the largest group are mounts made of 60–70% Sn and 30–40% Pb. It is quite similar to the results of the finger rings.

In Table 1 one can see various iron content. That may result from artefact deposition in the soil. Due to the fact the iron is the fifth most common element in the crust and as an active metal can "contaminate" deposited artefacts. Also, the proximity of rapidly corroding iron/steel items can affect other artefacts, which can be observed in iron surface enrichment for tin/lead or copper items.

The next observation is the homogeneity of several analysed tin-alloy artefacts. The archaeological samples are often much corroded, the oxidation layers are thick and the metal core (bulk) is heterogeneous. In this case, XRF analysis helped to find various items made of an identical alloy (for example diadems, which have been already presented) and identify parts of the same object. A very interesting case was that of a little spoon, classified as a badge. The two fragments of the spoon had been retrieved from different stratigraphic layers, a few months apart. However, comparing the macroscopic view (thickness and decorations), it seemed that they could be two fragments of the same spoon (despite the difference in shape). The XRF analysis confirmed this hypothesis (Fig. 3). Artefacts No. 1336/11 and No. 7691/11 had the same chemical composition (71% of tin, 26–27% of lead, 0.03% of copper, 0.02% of zinc and 0.10% of iron), and the difference in shapes was a consequence of their deposition (under the weight of heavy soil layers). Other examples of badges are made mainly of tin-rich alloys. The highest tin content is 98% for two items from New Market Square. It is two ampoules with the following chemical composition of 98.6% Sn, almost 0.1% Pb, Cu and Fe (No. 11/10) and 96.4% Sn, 1% Pb, 0.1% Cu, and 1.6% Fe (No. 38/11). The next group of badge material is almost pure lead. The eight badges are made of an alloy of 94–95% of lead and small amounts of tin, copper and iron

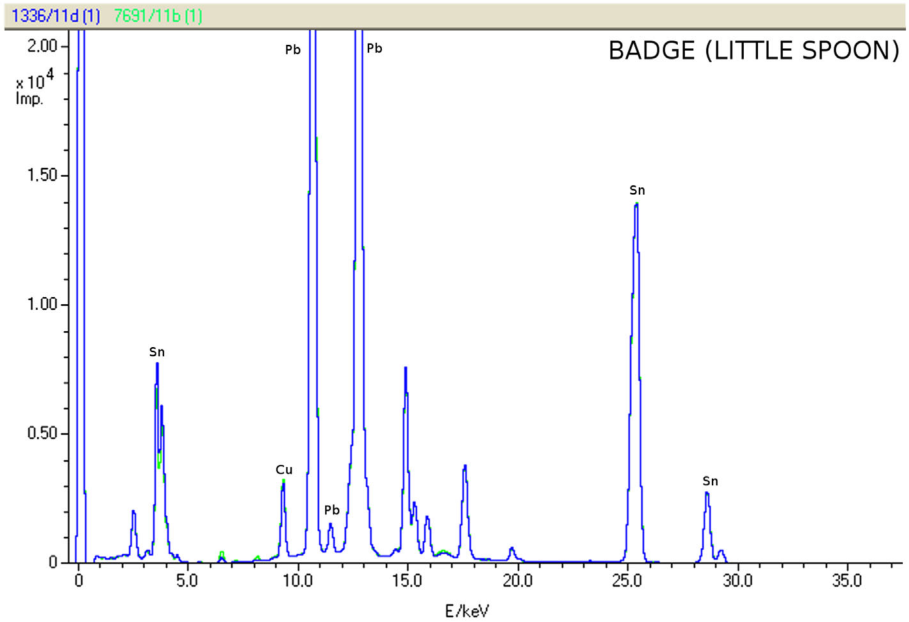

Fig. 3. ED-XRF spectra of the analysed tin-alloy badge (little spoon).

(average of 0.1% Sn, 0.05% Cu and 0.05–0.5% Fe). The largest group of badges (27) are comprised of various pewters, but mostly it was an alloy of 60% of tin and nearly 40% of lead (15 badges). Seven badges are made of an alloy of almost 50% of tin and lead, the rest are made in various Sn/Pb ratios. In Table 1 the elemental composition of a few badges are presented. The application of various tin/lead alloys in badges production was of the same reason like in case of finger rings. The small modification of the tin/lead ratio, does not result in significant changes of the alloy properties. The increasing lead content decreased its hardness which was not desirable for finger rings (which got scratched easily). However, for 8 analysed lead badges, hardness does not seem to be of crucial significance. In this case, the melting temperature of the alloy, which is rather low, seems to be a more important property which made casting of the Sn/Pb alloys easy (Ogden 2007 confirmed, that "Base-metal ornaments were often cast and numerous moulds have survived, including those for the ubiquitous lead Pilgrim badges"). The use of the low-melting alloys had also economic consequences. The cost of preparing molten mixture of metals was not so high like for copper or silver. Another issue influencing application of various alloys is price and reachability of raw-materials. Not only pure metals, but also re-cycled items were used: for example coins, damaged, unfashionable or even stolen items were the important source of gold (Ogden 2007). It is obvious that the craftsmen reused the production waste (e.g. scraps or broken utensils), which resulted in higher variability of the alloy composition.

Tin-plating artefacts

Fig. 4. Photograph of bronze buckle (No. 10299/11).

The tinning had different functions as it was used not only for anticorrosion or protection (copper vessels) (Šmit et al. 2008), but also for decoration. Tinned surfaces become shining and lustrous by simple polishing. In this case, the layers are applied only on the outer surfaces (fronts) of the objects. If the layers have a protective purpose, tin needs to be also applied inside the vessel or on both surfaces (anticorrosion). The tin-plating was done on many different alloys and metals, bronze, silver and iron. In the case of bronze objects, a tin rich surface is a consequence of tin-plating, casting, corrosion processes or artificial patination (Constantinides et al. 2002). Artificial patination should be excluded in this study, because the analysed artefacts came from archaeological excavation and were not conserved before. A good example of tin-plating on bronze is a buckle (Fig. 4).

The bronze does not need to be particularly protected by plating, so in this case the tin rich surface must be a decoration (especially if it is preserved only on the front surface of the buckle). The next analysed buckle has an iron bulk and a tin coating (Fig. 5). In this case, the tinning is both the decoration and the protective coating. On most ferrous objects such as buckles, belt strap-ends or belt mounts the tin layers were bilaterally preserved – see Figure 6.

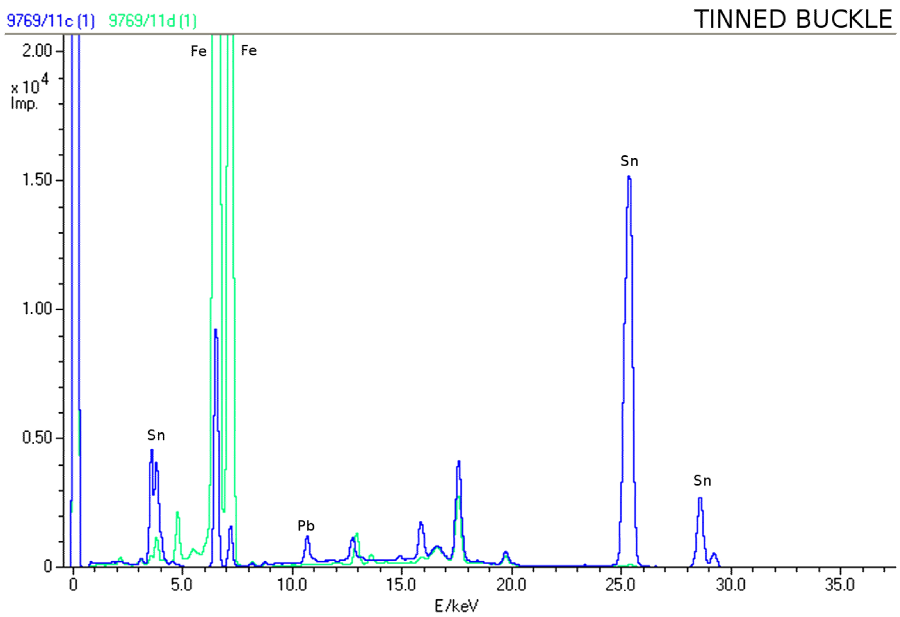

Fig. 5. ED-XRF spectra of iron buckle (No. 9769/11).

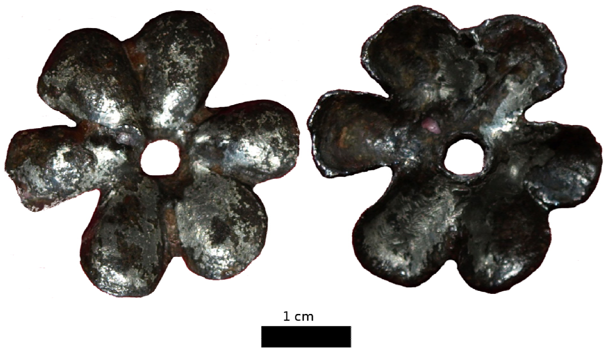

Fig. 6. Photograph of iron mount (No. 1887/11).

It suggests that the tinning was done by dipping the object into molten tin (taking into consideration the varied shapes and surfaces of the analysed items). Dipping objects was one of the possible methods of plating (tinning or bronzing) used since the Roman period. The alternative ways of plating were: folding a metal leaf around the object, hammering an alloy onto the prepared surface, fusion plating (Asderaki et al. 2009), and several other methods of finishing the objects (e.g. De Vries & Smith 2007 for a barbarian axe inlaid with silver, and an inscription on the brass band of the iron helmet).

The tin decorations on the artefacts were usually made by using tin layers, tin-wires or by inserting clout-nails. The analytical difficulties appeared when wire was used in decoration (buckle – No. 7087/11, the handle of knife – No. 198/11), due to the wire's diameters. Very thin wire was identified with the signal of buckle materials (mainly iron) as in Fig. 7. The quantitative analysis (see Table 1) showed that the frame contained about 96% of iron and the decoration had 34% of tin and 48% of iron. The wooden handle of the knife is the easier case. The light elements in wood were not analysed by the XRF spectrometer, because the Midex spectrometer measures in an air atmosphere. The examined wire qualitative chemical composition was iron, mercury, tin and small amounts of lead and it is presented in Fig. 8 and in Table 1.

The presence of mercury indicated a decorative technique which could be a tin-mercury amalgam. Decorating by incrustation enables the making of ornaments of various shapes (spur – No. 8622/11, the blade of knife – No. 450/11). The analysis of long and thin or star-shaped inlays depends on their size and the experience of the researcher. It is possible to put together signals from the blade material and the clout-nails. The measured elemental composition of decorated areas shows the tin as well as the iron amount (see Table 1). The point XRF analysis and good visualization of the analysed part is significant. Figure 9 shows the spectra comparison of the clout-nail analysis (blue line: 92.8% Sn) and the interference of the iron-blade to the clout-nail (red line: 58.9% Sn, 39.7% Fe).

Tinned objects in such quantity, as excavated from numerous features at the New Market Square, were never recorded in the literature on medieval Wrocław, to date. The great number of such finds and their remarkably fine state of

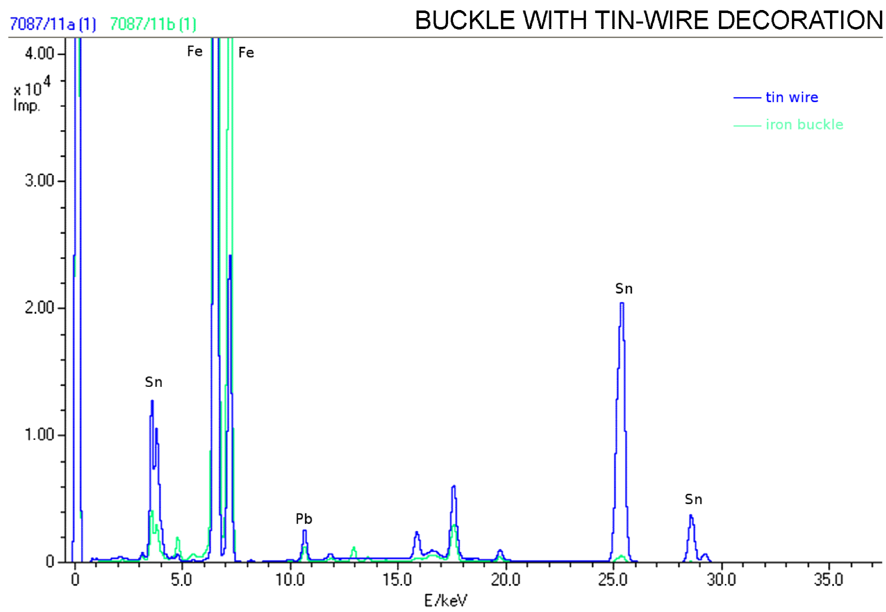

Fig. 7. ED-XRF spectra of iron buckle (No. 7087/11).

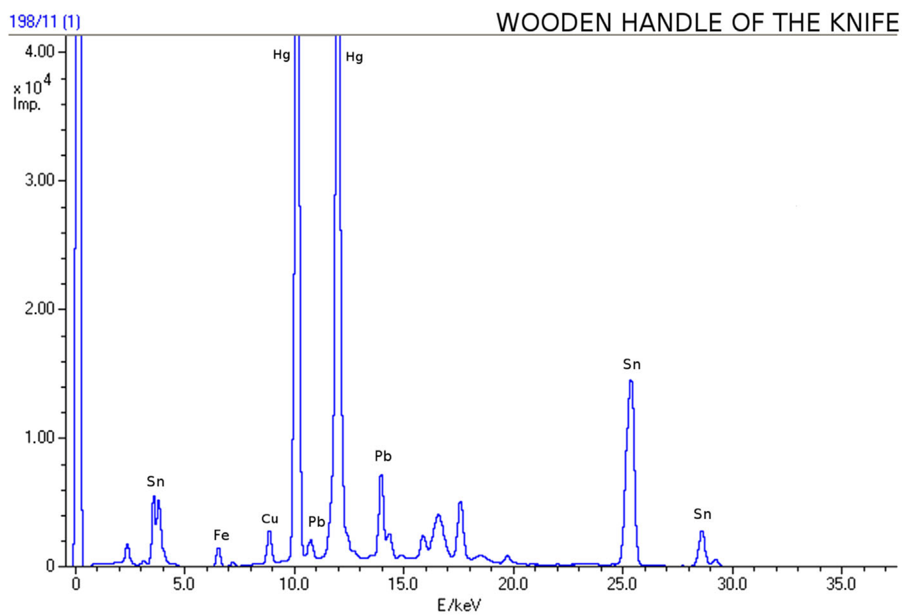

Fig. 8. ED-XRF spectra of knife handle (No. 198/11).

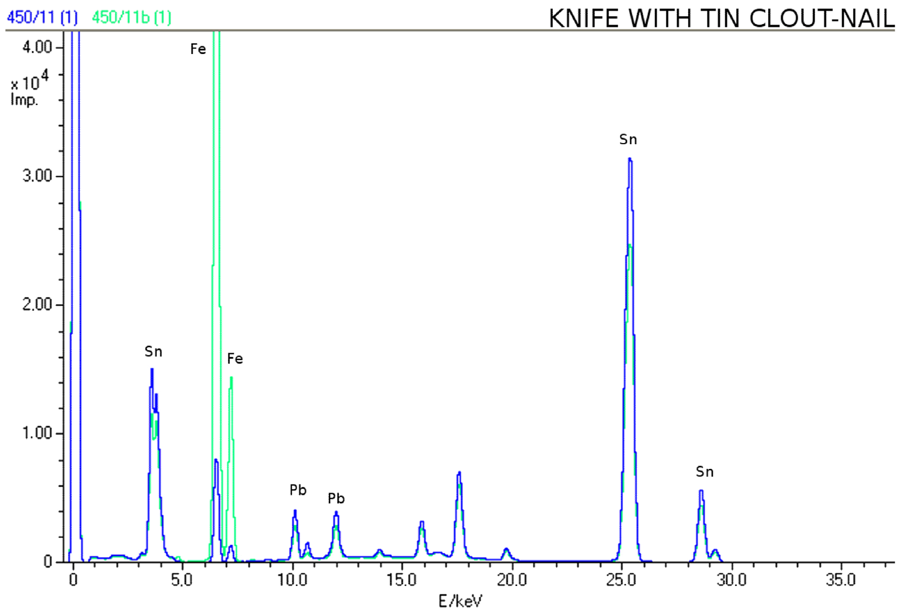

Fig. 9. ED-XRF spectra of knife handle (No. 450/11).

preservation most probably resulted from relatively good deposition conditions. However, the tin coating was preserved very differently on the artefacts. Because tin is soft, layers were often damaged by using items in the past or during deposition (abrasion or corrosion layers). Sometimes mechanical cleaning changed this state and the coating was identified (first intuitively, then analytically). The identification of a tin layer on ferrous items was easier, the difficulties arise in the case of bronze objects, because tin is the main alloy-element. For iron artefacts, tin-plating could be visible with the naked eye as a saved layer or a partly preserved area. The analysis of a large number of artefacts proved that well-preserved tinning is present on artefacts of many different typological groups and used for many different functions: keys, buckles, belt mounts, knives, spurs, parts of weapons, jewellery and many other dress accessories. The X-ray spectra of selected artefacts showed the elemental composition of the ferrous objects and the tin coatings – Figure 10.

When only small areas of tinning are preserved, the analysis is problematic (e.g. the leather belt with ferrule – No. 3003/11, buckle – No. 5681/11).

The difficulties in the identification of tin decoration are especially marked for tin-plated iron artefacts, because both iron and tin are grey in colour. The remains of tinning (very thin layers) were difficult to identify visually, and therefore, the tin coating was often analysed together with a high iron-signal (the results of XRF analyses show that the iron ferrule and buckle has various tin content from nearly 8% to 72% Sn – the ferrule and from 0.32% to 86.9% Sn – the buckle). The analysed buckle (No. 5681/11) was an interesting case. The artefact was very

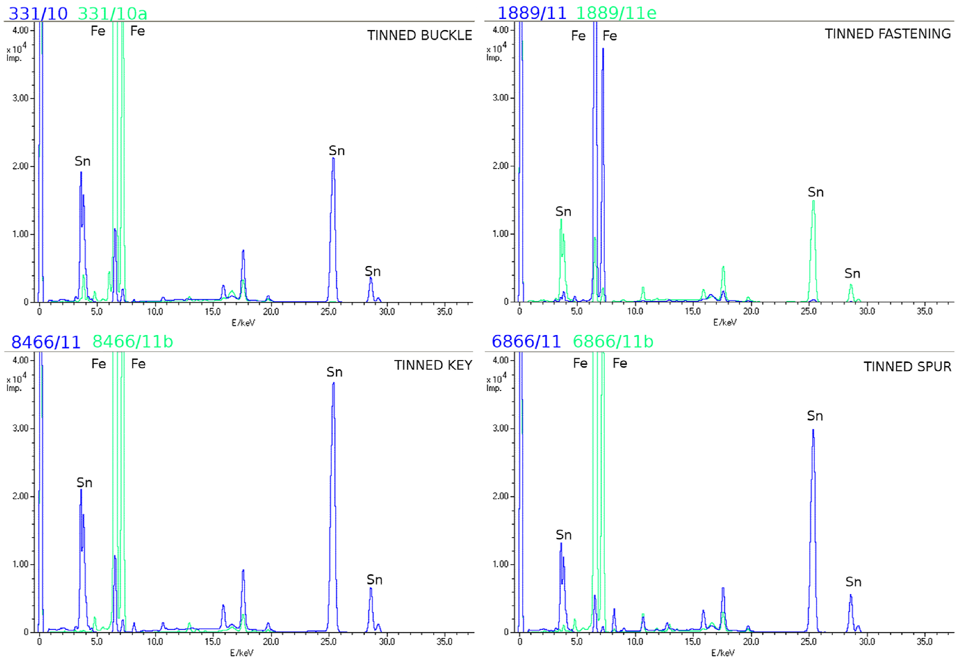

Fig. 10. ED-XRF spectra of well-preserved tinning (iron buckle, iron key, the iron fastening, and iron spur).

light with a silver-grey colour and has been described as a tin-buckle. The XRF spectra showed that artefact was iron-made with a very damaged tin coating (Fig. 11). Therefore, for this buckle, determining the almost pure core was possible, but impossible for the pure tin decoration (the signal of iron was strong; the calculated amount was 10.9% Fe). The XRF spectra of the ferrule before conservation identified only a higher tin signal in iron-artefacts – Figure 11. The differences

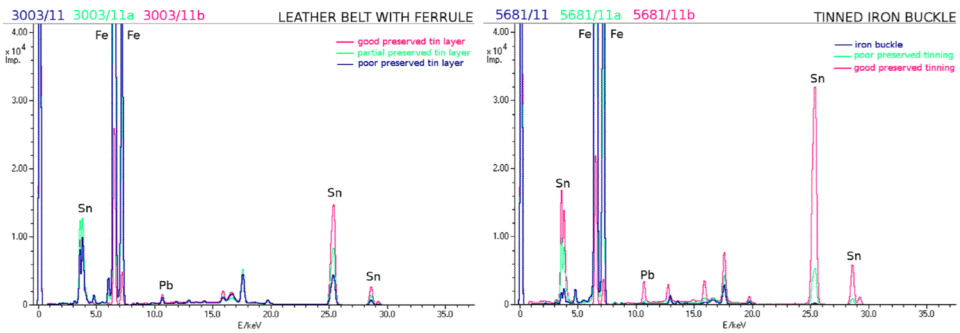

Fig. 11. ED-XRF spectra of poorly preserved tinning on a leather belt with ferrule – No. 3003/11 and buckle – No. 5681/11.

were observed just after conservation (the tannic acid with iron formed a black irontannate complex and the silver-grey tin layer was better visible). The almost pure iron core (the blue line on the XRF spectra) of the ferrule has a weak signal of tin (8% Sn). The tin concentration in other analysed places is higher (20% Sn – green line, 72% Sn – red line).

Conclusions

The tin objects (found in the New Market Square in Wrocław) were a very interesting group of artefacts because of the cardinality. In medieval times, the tin and tin-plated objects (often found in market places) were a very popular alternative to silver jewellery. It could explain the high number of such finds. During previous archaeological investigations of medieval sites in Wrocław, tin or tinned objects were recovered (Kaźmierczyk 1970), but the number was rather small. For example, until the last New Market Square excavation, only four pilgrim signs were known from Wrocław, after 2012 the collection consisted of 31 such objects. For these reasons, it was assumed that a review of such a large group of artefacts would produce new data concerning medieval Wrocław. The XRF examination of tin artefacts yielded interesting results, allowing researchers not only to quickly find parts of crushed artefacts (distributed within an archaeological site), but also facilitated the identification of the differences and similarities of the chemical composition of the studied object. Based on this it will be possible to try to classify artefacts and create a database in the future, grouping objects made of identical alloys. Not all items were made of the same alloy of tin and lead. A wide range of the relative proportions of the two metals cannot be clearly classified in time (because the largest group of artefacts, made of an alloy of tin are dated to the 14th century). Based on the undertaken analyses it cannot be determined that one alloy was characteristic of one group of dress accessories (jewellery, pilgrims' signs and badges and were made of various alloys of tin and lead and also of alloys of many other metals). Further research, however, seems advisable. This allows researchers to enrich as well as to compare the literature on this subject, comparing similar finds of tin/lead items from other towns, regions and countries with the Wrocław finds (an example could be the miniature ampoules from the New Market Square, which are made of tin, just as the ones found in Canterbury Cathedral (Blick 2001). In the future, due to the examination of other finished tin artefacts as well as semi-products (if such items are found in the course of excavations and examined), a craftsman's workshop may be identified. In the case of tin artefacts, previous studies of these coatings in Wrocław were mostly hypothetical (in the 20th century archaeologists often determined artefacts based on macroscopic observations as tin or silver-plated). Therefore, the undertaking of such analyses is important not only for archaeologists and museum staff, but also for conservators. It enables the latter to have an efficient supervision of conservation processes by choosing the proper measures and tools. Additionally, by analytical process control (e.g. by changing the time period or by choosing appropriate research areas) the technology of tinning and its function on a particular artefact can be identified. The tin layer had a protective character mainly for iron artefacts e.g. key and spurs. It was also used to decorate objects (this is confirmed by the tin-rich layer on the surface of the bronze buckle, by tin wire (on buckles) or clout nails (on knife blades). An additional advantage of undertaking a point analysis is an opportunity to examine a selected part of an artefact. For tin items, it is possible to examine separately an object's core (e.g. an iron buckle frame) and decorations (coatings).

Performing archaeometric examinations (including XRF analysis) of archaeological artefacts remains an important part of learning about the past. Despite many studies already published (especially in Europe), it is advisable to conduct further research in this area both for knowledge and conservation reasons. This is particularly important for these archaeological studies, the results of which largely change the state of knowledge as in the case of artefacts from the New Market Square in Wrocław. Undertaking advanced archaeological research in close collaboration with other scientific disciplines (including analytical chemistry) has introduced a number of new variables to the discussion on the late Middle Ages in Wrocław.

Note. All percentages given in alloy compositions are weight percentage.

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Beata Miazga

TINAST JA TINATATUD RÕIVASTE AKSESSUAARID KESKAEGSEST WROCŁAWIST (EDELA-POOLA). RÖNTGENFLUORESTSENTS-SPEKTROMEETRILISED UURINGUD

Resümee

Artikkel on keskendunud keskaegsete tinast ja tinatatud esemete elementanalüüsile. Peamiselt on uuritud rõivaste juures kantavaid metallist aksessuaare. Lisaks hõbedale oli tina ehtematerjalina keskaegses Euroopas vaesema elanik-

konna hulgas laialt levinud. Kokku on uuritud üle 155 eseme, mille hulgas on ripatsid, helmed, peaehted, sõrmused, oimurõngad, nööbid, palverännumärgid, rihma metallosad, pandlad, rihmaotsad- ja naastud, kannused, võtmed, noad ning metalliga kaunistatud nahakatked. Leiud on pärit Wrocławi vanalinnas Uue Turu piirkonnas aastatel 2010–2012 toimunud päästekaevamistelt. Varem Wrocławist teadaolevaga võrreldes koguti nimetatud välitöödelt märkimisväärne kogus tinasulamist ja tinatatud esemeid. Enamik leidudest pärineb 14. sajandist, ehkki on ka varasemaid esemeid.

Esemeid analüüsiti röntgenfluorestsents-spektromeetriga (ED-XRF, Spectro Midex). Eesmärgiks oli kindlaks teha esemete valmistamiseks kasutatud metalli keemiline koostis ja saadud tulemuste põhjal analüüsida sulamitevahelisi sarnasusi ning erinevusi esemetüüpides ja seeläbi uurida tootmise tehnoloogilisi aspekte. Peamine analüüsitav element oli tina, mida esines erineva osakaaluga sulamites (tihti pliiga). Analüüside põhjal ei saa üldistada, et ühe esemetüübi valmistamiseks on kasutatud teatud tüüpi sulamit. Paljude erinevate leidude materjalil on sarnane keemiline koostis. Siiski võib välja tuua, et näiteks teatud peaehete valmistamiseks on kasutatud sarnast sulamit. Lisaks aitas elementanalüüs kokku viia ühe eseme eri kohtadest leitud fragmente.

Uuringu oluline osa oli tuvastada teistest metallidest objektidel tinakihijälgi. Sageli on need halvasti säilinud, mistõttu on neid lihtsa vaatluse abil raske kindlaks teha. Eseme katmisel tinaga on üheks eesmärgiks olnud selle kaitse, eriti rauast objektide puhul. Teiseks võimaluseks on olnud ehte kaunistamine, ja siinkohal on eriti keeruline tuvastada tinatraadist ornamenti esemel, sest traadi läbimõõt on väga väike. Sellised uuringud annavad teadmisi mineviku kohta ja on abiks konserveerimisel.

Võib oletada, et Uuel Turul asus tinaesemeid valmistanud käsitöölise töökoda. Lisaks sarnasusele mitmete esemerühmade valmistamiseks kasutatud sulami koostises viitavad sellele võimalusele kaevamistel leitud kivist valamisvormide katked, tööriistad ja metallkangid, mis olid peaaegu puhtast pliist.