CHARACTERIZATION OF THE FOURTEENTH-CENTURY BELL-CASTING PIT FROM THE OLD TOWN HALL IN SIBIU, ROMANIA

Introduction

During the Middle Ages, the skill of moulding bells was extremely valuable. The craftsmen smelting bells also produced cannons and baptismal fonts (Beşliu 1989). In the long run, the bells were melted when cannons were needed and these were transformed again when the cannons were no longer necessary. For this reason, one preserved only a few old bells.

In this work we have made an analytical investigation by a neutron activation analysis and X-ray fluorescence of a number of pieces found on or near the two structures and the slag layer discovered at the Old Town Hall in Sibiu, Romania, and some bells from the environs of Sibiu in order to answer the question if there is a relationship between these two structures and the slag layer. We also examined the possibility of preparing the alloy for casting the bell in the ogival structure discovered at the Old Town Hall.

Experimental Analysis

The objects which have been analysed are listed in table 1. The metal and slag samples presented in table 1 have been analysed by means of the X-ray fluorescence (XRF) and the neutron activation analysis (NAA) methods. The XRF has been used for a qualitative analysis of the samples and for the quantitative determination of lead, which cannot be observed by the NAA. The objects have been cut with a hard steel knife in order to obtain relatively homogeneous samples. Sample Ie, a piece with a surface of 3 cm^2 from level I, near the loam structure, has been specially prepared (by extracting an evident piece of white metal, which was cut and polished) for the determination of the metal concentration by the XRF. The bells have been sampled by drilling with the discarding of the surface area in order to avoid the corrosion products and other contamination. The resulting quantity of powder was so small that it did not permit the analysis of the lead content by the XRF, so that only the analysis by the neutron activation was possible. The XRF analysis has been performed with the aid of a triple source of Pu^{238} and of 3×33 mCi. The fluorescence X-rays have been detected by a GeHP detector and the characteristic spectra have been counted on a computer with a multichannel analyzer interface. The following elements have been detected: Cu, Fe, Pb and Sn.

Concerning the neutron activation analysis, samples of approximately 10 mg have been cut carefully with a hard steel knife in order to obtain relatively homogeneous samples. These samples have been introduced in polyethylene foils and have been irradiated at the VVR-S Reactor of the National Institute of Physics and Nuclear Engineering at Bucharest-Măgurele, at a rabbit system at a neutron flux of $2.5 \cdot 10^{12}$ neutrons/$cm^2 \cdot s$, for several periods of time: 20 s, 2 min and 30 min. The induced radioactivity in the samples has been detected by a 135 cm^3 GeLi detector (EG&G Ortec) with a 2.7 keV resolution. The samples have been counted after a cooling time of 2 minutes, and again after 1 day, 3 days and 10 days. 14 elements have been noticed: Ag, Al, As, Au, Cu, Ca, Fe, K, Mg, Mn, Na, Sb, Sn and Sc.

Table 1

List of the analysed samples

Ia	Level I
Ib	Level I
Ic	Level I
Id	Level I
Ie	Level I
IIa-s	Level II, surface of the hearth
IIb-s	Level II surface of the hearth
IIc-s	Level II surface of the hearth
IIa	Level II deepness of the hearth
IIb	Level II deepness of the hearth
IIc	Level II deepness of the hearth
Za	Slag layer
Zb	Slag layer
Zc	Slag layer
Zd	Slag layer
C1	Metallic cake, level I
C2	Ash
B1	Bell, medieval, region of Sibiu
B2	Bell, medieval, region of Sibiu
B3	Bell, medieval, region of Sibiu
B4	Bell, XIXth century, region of Sibiu

Results and Discussion

In table 2 one can see the concentration values of the elements detected in the samples of the two structures and the slag layer by the NAA, and the lead content from the XRF analysis. Table 3 shows the results of the NAA for the bell samples. The results are expressed in parts per million (ppm) and when the result was greater than 10 000 ppm, it was given in %. The relative errors of measurements are « 10 % for both the NAA and the Pb content.

Concerning the analyses of the samples shown in table 2, the samples contain tin in relatively high concentrations (2 %–37 %). Sample Ie from level I has the highest content of tin : 36.7 %. We mention the fact that tin as an impurity is rarely found in copper ores (Craddock 1981) and its presence in high concentrations alongside with the copper can be explained only by a deliberate action of alloying. The samples from the loam structure, level II no. IIas, IIbs, IIcs and IIa, IIb, IIc, surface and deepness, have a lower content of copper and tin, but the ratio Sn/Cu (figure 2) is however in the range of the values of this ratio for the samples no. Ia, Ib, Ic, Id from level I as well as for the samples no. Za, Zb, Zc, Zd for the slag. This fact can be explained by a relationship between level I, level II and the slag layer. The iron, in high concentrations in the samples from level II, can be explained by the fact that iron oxides were deliberately added in the melted charge, these acting as fondants. The added iron can be found in slag. As regarding the iron, samples IIas and IIbs are very different from the others : the ratio Fe/Cu is very high, approx. 15 (figure 3). The samples Z, found in the intermediate layer between the two loam structures, known as slag samples, have a concentration of Cu in the range 25–36 %, which is high compared with the usual concentration of Cu in slag of about 4–5 %. In figure 4, the diagram of the ratio Pb/Cu versus the ratio Sn/Cu shows a close relationship between the samples I and II and the slag layer regarding the following elements : Cu, Sn and Pb. We remark a similar composition of the samples Z, of the slag samples with level II, both from the point of view of Fe and the impurities Al, Na, K, Sb and Mn. The content of tin and copper and the concentration of the other minor elements suggest that level I and level II belonged to installations for alloying and casting copper and tin in order to obtain specific objects like bells, statuar art objects or weapons. The sample of ash, C2, approaches the samples from the two installations and the slag. The content of Pb presents a background of concentrations with values not very straggled with a signal of $C_{Pb} =$ 21.8 % from the sample C1. This sample is very different in comparison to the other samples. The significance of sample C1, a piece of metal-cake, remains an unsolved problem due to its high content of lead and silver and the lack of tin ; it may suggest the base mineral for producing the silver, galena, and, by inference, it may suggest the presence of a mint. Initially, it was believed that in this furnace there was prepared the alloy for the coins, but the composition of some binary denars (Beşliu 1987), of silver and copper, with high concentrations of silver, and the presence of silver only in traces in the samples from the two installations eliminate this assumption. Also a NAA analysis of some coins (Beşliu 1987) points out the lack of the element Sn, considered a very important component of the samples. The concentration of zinc for the samples from table 2 was, for the given experimental conditions, < 1 000 ppm.

The analyses of the two loam structures discovered at the Old Town Hall in Sibiu led to the further analysis of some objects of tin alloy, like bells from the neighbourhood of Sibiu. The results of the analyses of four Transylvanian bells, shown in table 3, indicate the similarity of their element composition and also the similarity to the samples from level I, considered as representative for the furnace. The diagram from figure 5, the ratio (Au * 100 + Ag * 10 + Sb + As)/Cu versus the ratio Sn/Cu, shows that the concentration for the samples from level I agrees very well with the four bells. The bells B1, B2 and B3 of the region of Sibiu, from the Middle Ages, have a close pattern composition and bell B4, from the XIXth century, has a somewhat different composition (figures 5 and 6). Also, in table 5 there is shown the composition of two famous bells (Hanson, 1978): the Whitechapel bell and the Christ Church bell, made in the same foundry in London. In comparison, in figure 5 there is represented the composed ratio (Au * 100 + Ag * 10 + Sb + As)/Cu versus the ratio of concentrations Sn/Cu for both Transylvanian bells and the bells made in London. Also, in figure 6 there is shown the composed ratio (Au * 100 + Ag * 10 + Sb + As + Sn)/Cu versus the ratio Fe/Cu for the same bells. Figures 5 and 6 prove that the craftsmen for Transylvanian bells had a smelting formula which was somewhat different from that of the bells made in London.

Conclusions

The analyses of the elements from this study suggest a relationship between level I, the layer of slag and level II and the fact that the different levels preserve traces of an activity of alloying the copper with tin. Also, one can observe the fact that the composition of the alloy for the four bells of the region of Sibiu analysed in this study is very similar to that of the metallic pieces found at the Old Town Hall in Sibiu.

We can conclude that the slags analysed belong to an installation for casting bells. In fact, at level 1 is a fragment of the mould (the bottom of the cope). Near the loam structure there were a lot of slags and also a piece of metal. The mould was set right on the ground, in a pit. Above, near the pit, was a „hearth“, with an ogival form, inclined towards the pit. On its surface the slags can be observed and analysed (level II).

During the casting, the pit was filled with earth and afterwards it became a storage place for slags, fragments of mould etc. (the slag layer).

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Instalaţia de turnat clopote de biserică de la Primăria Veche din Sibiu

(rezumat)

În curtea mare a Primăriei Vechi din Sibiu au fost descoperite resturile unei instalaţii metalurgice pentru turnat clopote. Poziţia şi dimensiunile fragmentului de tipar din lut (miezul) ne determină să căutăm clopotul turnat în acest loc printre cele mai vechi menţionate: clopotul Sfântului Ioan, turnat în 1350, folosit de biserica parohială, clădită în acei ani în stil gotic, „clopotul ceasului“ cu diametrul maxim de 1,50 m, datat în a doua jumătate a secolului al XIV-lea şi „clopotul nopţi“, turnat în 1411, cu diametrul de 1 m.

Instalaţia se compunea dintr-o groapă în care a fost aşezat, pe pământ, tiparul din lut, alcătuit din două părţi: un miez şi o cămaşă, în pământ păstrându-se doar partea de jos a miezului. În partea de sus, în imediata vecinătate s-a aflat o vatră din lut, de forma ogivală, şi înclinată spre marginea gropii. De pe această vatră, aliajul topit se scurgea în tipar. Analizele prin activare cu neutroni efectuate la Institutul de Fizică Măgurele pe fragmente de zgură şi o bucată de metal au dovedit că aliajul folosit la Primăria Veche este cel recomandat pentru turnat clopote sau tunuri în evul mediu, deosebindu-se de aliajul monedelor bătute la Sibiu.

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Table 2

Concentration of the elements in levels I and II, slag, ash and cake, by the NAA and XRF.
The concentrations are expressed in parts per million (ppm), and when the concentration is greater than 10000 ppm, it is given in percents (%).

Sample	Cu	Sn	Fe	Au	Ag	Sb	Al	As	Ca	K	Mg	Mn	Na	Sc	Pb
Ia	43 %	13.9 %	–	49	1 360	9 050	–	4 490	–	–	–	< 30	98	< 7	2.7 %
Ib	70.3 %	14.5 %	–	48	1 180	1.03 %	–	4 800	–	–	–	< 40	200	< 8	4.4 %
Ic	59.6 %	13 %	6.9 %	46	1 200	9 000	970	4 500	–	–	–	< 30	130	< 6	5.5 %
Id	69.9 %	17.6 %	8.1 %	55	710	1.22 %	7 280	5 230	–	–	–	< 70	930	< 20	6.4 %
IIas	4 040	–	6.01 %	< 0.5	< 400	< 800	14.9 %	< 200	2 %	2.15 %	8 %	5 130	1.08 %	25	–
IIbs	4 600	–	4.78 %	< 0.4	< 400	< 300	13.5 %	< 200	1 %	2.8 %	4 %	448	1.1 %	23	–
IIcs	12.9 %	2.15 %	5.56 %	3	310	1 220	1.64 %	400	–	0.2 %	–	102	0.18 %	< 7	3.3 %
IIa	29.6 %	9.78 %	11 %	32	610	7 780	4.4 %	2 900	0.8 %	0.9 %	–	278	0.32 %	11	3 %
IIb	21.2 %	5.02 %	3.3 %	15	910	4 260	7.2 %	1 500	–	1.3 %	–	553	0.64 %	9	1.6 %
IIc	7.37 %	5.0 %	1.2 %	0.7	–	40	13 %	220	1.2 %	1.9 %	–	443	0.82 %	88	0.6 %
Za	32.4 %	5.67 %	8.5 %	19	490	4 480	5 %	2 390	0.7 %	0.85 %	–	973	0.70 %	13	4.0 %
Zb	25 %	3.22 %	6.4 %	13	200	3 690	4.8 %	1 370	0.7 %	2 %	–	748	1.03 %	16	2.2 %
Zc	36.4 %	11.3 %	10 %	6	1 040	9 770	2.2 %	3 680	0.4 %	0.87 %	–	660	1.07 %	6	5.6 %
C1	16.2 %	–	–	1 460	1.4 %	1.1 %	–	2 500	–	500	–	< 2	980	–	22 %
C2	7 210	6.8 %	7.3 %	0.3	< 300	33	–	< 80	–	2.5 %	–	5 270	1.46 %	21	0.09 %

Table 3

Concentration of the elements in the Transylvanian bells, by the NAA.
The concentrations are expressed in parts per million (ppm), and when the concentration is greater than 10000 ppm, it is given in percents (%).

Sample	Cu	Sn	Fe	Au	Ag	Sb	Al	As	Mn	Na	Zn
B1	74 %	19 %	5 000	46	1 580	2.1 %	3 500	7 780	60	880	1 000
B2	71 %	18 %	9 000	42	1 530	2.5 %	2 400	7 010	25	400	500
B3	64 %	16 %	2 500	85	1 950	1.6 %	850	8 700	30	750	400
B4	72 %	14 %	5 900	3	300	0.58 %	4.6 %	1 280	90	1 400	1.7 %

Table 5

Concentration of the elements for the Whitechapel bell and the Christ Church bell, by the XRF (Hanson 1978).
The concentrations are expressed in parts per million (ppm), and when the concentration is greater than 10000 ppm, it is given in percents (%).

Sample	Cu	Sn	Fe	Au	Ag	Sb	As	Pb	Zn
Withechapel Bell	67.87 %	25.67 %	0.06 %	200	1 700	1 100	2 600	2.90 %	1.3 %
Christ Church Bell	76.77 %	21.08 %	0.19 %	0	1 100	100	3 100	0.84 %	0.70 %