Characterisation of Fourteenth-Century Bell-Casting

Pit in Old Town Hall Sibiu, Romania

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1 Introduction

During the Middle Ages the skill of moulding bells was extremely valuable. The craftsmen smelting bells also produced cannons and baptismal fonts (Besliu 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 preserves only a few old bells. An 1507’ bell is used at the Hospital Church in Sibiu. Another bell, dated 1626, is present in the collection of the History Museum from Sibiu, and others bells, remelted several times are in the tower of the Evangelic Church from Sibiu. Installations for moulding or fragments of loam patterns obtained as a result of the moulding of bells are even more rare. Some oven installations have been discovered in Winchester (UK), Leibgott (Denmark), Visegrad (Hungary) (Russel 1990). The similar discovery from the Old Town Hall from
Sibiu, Romania can be linked with the above mentioned examples but also with other uncoveries in the neighborhood: a wooden building from the XIII\textsuperscript{th}-XIV\textsuperscript{th} centuries, a crematory for garbage, and the foundations of the previous buildings, joined after 1470 to form the Old Town Hall.

The installation for smelting copper-alloy discovered in Sibiu in the big inner yard of the Old Town Hall was situated in a pit located near the parochial church. The gothic church was build in the middle of XIV\textsuperscript{th} century and was enlarged at the beginning of XV\textsuperscript{th} century. The two periods and the phases of the construction are linked with the casting of a bell (Roth 1908). The installation was composed of two loam structures. The first one, a hearth on the ground pit at -2.70 m appeared as a circular structure with 1.40 diameter, as shown in Figure 1. The northern part was enlarged. The loam structure is 0.24 m tall and has a narrow ditch in the lower part. Near this structure were uncovered some pieces with an aspect of copper-alloy. The second loam structure has an ogival form with the raised brims and the surface slightly inclined with 3-4\textdegree. Some pieces of metal and slag of copper-alloy have been also found on its surface. Between these two hearths there is a slag layer. The two hearths belonged to a furnace for melting copper-alloy. This furnace is unique but the other archaeological uncoveries in Europe are some pits with stone furnace on which the mould was fixed (Russel 1990).

In this work we have made an analytical investigation by neutron activation analysis and X-ray fluorescence of a number of pieces found on the two hearths and the slag layer discovered at the Old Town Hall from Sibiu, Romania and some bells from the surrounding region of Sibiu to answer the question if there is a relationship between these two hearths and the slag layer. We also examined the possibility of preparing of the alloy for moulding of a bell in the furnace discovered at the Old Town Hall.
2 Experimental Analysis

The objects which have been analysed are listed in Table 1. The samples of metal and slag presented in Table 1 have been analysed by means of the X rays fluorescence (XRF) and neutron activation analysis (NAA) methods. XRF has been used for a qualitative analysis of the samples and for the quantitative determination of lead, which cannot be observed by NAA. The objects have been cut with a hard steel knife in order to obtain relatively homogeneous samples. The sample Ie, a piece with a surface of $3 \text{ cm}^2$ from level I of the oven has been specially prepared (by extracting an evident piece of white metal which was cut and polished) for the determination of concentration of metal by XRF. The bells have been sampled by drilling with discarding of the surface area to avoid the corrosion products and other contamination. The resulting quantity of powder was so small that it did not permit the analysis of lead content by XRF, so that only the analysis by neutron activation was possible. The XRF analysis has been performed with the aid of a triple source of Pu$^{238}$, of 3x33 mCi. The fluorescence X rays have been detected with a GeHP detector and the characteristic spectra have been counted on a computer with a multi-channel analyzer interface. The following elements have been detected: Cu, Fe, Pb and Sn.

As concerning neutron activation analysis, samples of approx. 10 mg have been cut with a hard steel knife with care to obtain relatively homogeneous samples. These samples have been introduced in polyethylene foils and have been irradiated at VVR-S Reactor of National Institute of Physics and Nuclear Engineering Bucharest-Magurele, at a rabbit system at a neutron flux of $2.5 \cdot 10^{12}$ neutrons/cm$^2$·s, for several periods of time: 20 s, 2 min and 30 min. The induced $\gamma$ radioactivity in the samples has been detected by a 135 cm$^3$ GeLi detector (EG & G Ortec) with 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.
3 Results and Discussions

In Table 2 is presented the picture of concentrations of elements detected in samples of the two hearths and the slag layer by the NAA, and the lead content from XRF analysis. The Table 3 shows the results of NAA for the bell samples. The results are expressed in parts per million (ppm) and when the result was greater than 10000 ppm it was given in %. The relative errors of measurements are <10% for both NAA and Pb content.

As concerning the analyses of hearths samples given in Table 2, the samples contain tin in relatively high concentrations [2% - 37%]. The sample Ie, Hearth level I has the highest content of tin: 36.7%. We mention that tin as 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 of the Hearth level II no. IIa, IIb, IIc 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 values of this ratio for the samples no. Ia, Ib, Ic, Id of Hearth 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 Hearth level I, Hearth level II and the Slag layer. Iron, in high concentrations in samples of Hearth level II can be explained by the fact that iron oxides were deliberately added in melted charge, these acting as fondant. The added iron can be found in slag. From the viewpoint of iron, samples IIa and IIb 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 hearths, known as slag samples, have a concentration of Cu in the range 25-36%, which is high compared to 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 hearth samples I and II and the slag layer, from the point of view of elements: Cu, Sn and Pb. We remark a similar composition of samples Z, slag with the Hearth 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 the two hearths level I and level II belonged to a furnace for alloying of copper and tin to obtain specific objects like bells, statuar art objects or weapons. The sample of ash, C2, approaches the samples from the two hearths and 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 with the other samples. The significance of sample C1, piece of metal-cake, remains a question mark 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 was prepared the alloy for the coins but the composition of some binary denars (Besliu 1987), (Table 4), silver and copper, with high concentrations of silver, and the presence of silver only in traces in the samples from the 2 hearths eliminates this assumption. Also a NAA analysis of some coins (Besliu 1987) point out the lack of the element Sn, considered a very important presence in the hearth samples. The concentration of zinc for the samples from Table 2 was for the given experimental conditions $<1000$ ppm. The analyses of the two hearths discovered at Old Town Sibiu led to the further analysis of some tin-alloy objects, like bells from the neighborhood of Sibiu. The results of the analyses of 4 Transylvanian bells shown in Table 3 indicate the similarity of their elemental composition and also the similarity with the samples from the Hearth 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 of Hearth level I agrees very well with the 4 bells. The B1, B2 and B3 bells from the Sibiu region and Middle Ages have a close pattern composition and the B4 bell, XIX century has a somewhat a relative different composition. (Figures 5 and 6). This suggests the possibility that in these hearths was prepared a specific copper-tin alloy for smelting bells. Also, in the Table 5 it is shown the composition of 2 famous bells (Hanson 1978): Whitechapel bell
and Christ Church bell, made in the same foundry in London. For comparison, in Figure 5 it 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 London-made bells. Also in Figure 6 it is represented the composed ratio \((Au*100+Ag*10+Sb+As+Sn)/Cu\) versus the ratio \(Fe/Cu\) for the same bells. Figures 5 and 6 can interpreted that the craftsmen for Transylvanian bells had a smelting formula which is somewhat different of that of London-made bells.

4 Conclusions

The elemental analyses from this study suggest a relationship between Hearth level I, Layer of Slag and Hearth level II and the fact that the hearths preserve traces of an activity of alloying of copper with tin. Also one observes that the elemental composition of the alloy. for the 4 bells from the Sibiu region analysed in this study is very similar with that of the metallic pieces found at the two hearths, discovered at Old Town Hall, Sibiu. We can conclude that at these hearths was prepared a copper-tin alloy for casting bells with the same formula with that of analysed Transylvanian bells.
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| Sample | Description                                      |
|--------|--------------------------------------------------|
| Ia     | Hearth level I                                  |
| Ib     | Hearth level I                                  |
| Ic     | Hearth level I                                  |
| Id     | Hearth level I                                  |
| Ie     | Hearth level I                                  |
| IIa-s  | Hearth level II surface                         |
| IIb-s  | Hearth level II surface                         |
| IIc-s  | Hearth level II surface                         |
| IIa    | Hearth level II deepness                        |
| IIb    | Hearth level II deepness                        |
| IIc    | Hearth level II deepness                        |
| Za     | Slag layer                                      |
| Zb     | Slag layer                                      |
| Zc     | Slag layer                                      |
| Zd     | Slag layer                                      |
| C1     | Metallic cake, found near Hearth level I        |
| C2     | Ash                                             |
| B1     | Bell, medieval, Sibiu region                    |
| B2     | Bell, medieval, Sibiu region                    |
| B3     | Bell, medieval, Sibiu region                    |
| B4     | Bell, XIX century, Sibiu region                 |
Table 2

| Sample | Cu   | Sn   | Fe   | Au  | Ag   | Sb  | Al  | As   | Ca  | K   | Mg  | Mn  |
|--------|------|------|------|-----|------|-----|-----|------|-----|-----|-----|-----|
| Ia     | 43%  | 13.9%| -    | 49  | 1360 | 9050| -   | 4490 | -   | -   | -   | <3  |
| Ib     | 70.3%| 14.5%| -    | 48  | 1180 | 1.03%| -   | 4800 | -   | -   | -   | <4  |
| Ic     | 59.6%| 13%  | 6.9% | 46  | 1200 | 9000| 970 | 4500 | -   | -   | -   | <3  |
| Id     | 69.9%| 17.6%| 8.1% | 55  | 710  | 1.22%| 7280| 5230 | -   | -   | -   | <7  |
| IIas   | 4040 | -    | 6.01%| <0.5| <400 | <800| 14.9%| <200 | 2%  | 2.15%| 8%  | 513 |
| IIbs   | 4600 | -    | 4.78%| <0.4| <400 | <300| 13.5%| <200 | 1%  | 2.8% | 4%  | 448 |
| IIcs   | 12.9%| 2.15%| 5.65%| 3   | 310  | 1220| 1.64%| 400  | -   | 0.2% | -   | 102 |
| IIa    | 29.6%| 9.78%| 11%  | 32  | 610  | 7780| 4.4% | 2900 | 0.8%| 0.9% | -   | 278 |
| IIb    | 21.2%| 5.02%| 3.3% | 15  | 910  | 4260| 7.2% | 1500 | -   | 1.3% | -   | 555 |
| IIc    | 7.37%| 5.0% | 1.2% | 0.7 | -    | 40  | 13% | 220  | 1.2%| 1.9% | -   | 443 |
| Za     | 32.4%| 5.67%| 8.5% | 19  | 490  | 4480| 5%  | 2390 | 0.7%| 0.85%| -   | 973 |
| Zb     | 25%  | 3.22%| 6.4% | 13  | 200  | 3690| 4.8% | 1370 | 0.7%| 2%  | -   | 748 |
| Zc     | 36.4%| 11.3%| 10%  | 6   | 1040 | 9770| 2.2%| 3680 | 0.4%| 0.87%| -   | 660 |
| C1     | 16.2%| -    | -    | 1460| 1.4% | 1.1%| -   | 2500 | -   | 500 | -   | <2  |
| C2     | 7210 | 6.8% | 7.3% | <300| 33   | -   | <80 | -    | 2.5%| -   | -   | 527 |
Table 3

| Sample | Cu  | Sn  | Fe  | Au  | Ag  | Sb  | Al  | As  | Mn  | Na  | Zn  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| B1     | 74% | 19% | 5000| 46  | 1580| 2.1%| 3500| 7780| 60  | 880 | 1000|
| B2     | 71% | 18% | 9000| 42  | 1530| 2.5%| 2400| 7010| 25  | 400 | 500 |
| B3     | 64% | 16% | 2500| 85  | 1950| 1.6%| 850 | 8700| 30  | 750 | 400 |
| B4     | 72% | 14% | 5900| 3   | 300 | 0.58%| 4.6%| 1280| 90  | 1400| 1.7%|
| Coin                | Code         | Provenance   | Ag, % | Cu, % |
|---------------------|--------------|--------------|-------|-------|
| Matei Corvin Denar  | T.1285/4641  | Sibiu        | 69.2  | 30.8  |
| Transylvania Denar  | T.1285/2455  | Sibiu        | 35.8  | 64.2  |
| XV century Denar    |              | Saliste, near Sibiu | 94.5  | 5.5   |
| Leopold I piece     | T.1285/3762  |              | 57.0  | 43.0  |
| Sample                  | Cu     | Sn     | Fe  | Au | Ag | Sb | As  | Pb       | Zn    |
|------------------------|--------|--------|-----|----|----|----|-----|----------|-------|
| Whitechapel Bell       | 67.87% | 25.67% | 0.06% | 200 | 1700 | 1100 | 2600 | 2.90%    | 1.3%  |
| Christ Church Bell     | 76.77% | 21.08% | 0.19% | 0   | 1100 | 100  | 3100 | 0.84%    | 0.70% |
FIGURE CAPTIONS

Figure 1. Schematic drawing of the Hearth level I of the bell casting pit from Old Town Hall, Sibiu, Romania

Figure 2. Ratio of the Sn and Cu concentrations for the two hearths, slag and Transylvanian bells.

Figure 3. Ratio of the Fe and Cu concentrations for the two hearths, slag and Transylvanian bells.

Figure 4. Diagram of Pb/Cu concentration ratio versus Sn/Cu concentration ratio for the two hearths and slag.

Figure 5. Diagram of composed concentration ratio \((Au*100+Ag*10+Sb+As)/Cu\) versus Sn/Cu concentration ratio for the Hearth level I, Transylvanian bells and Whitechapel bell (WB) and Christ Church bell (CCB)

Figure 6. Diagram of composed concentration ratio \((Au*100+Ag*10+Sb+As+Sn)/Cu\) versus Fe/Cu concentration ratio for Transylvanian bells and Whitechapel bell (WB) and Christ Church bell (CCB)
TABLE CAPTIONS

Table 1. List of analysed samples.

Table 2. Concentration of elements in hearths levels I and II, slag, ash and cake, bye 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 (%).

Table 3. Concentration of elements in Transylvanian bells, bye NAA. The concentrations are expressed in parts per million (ppm), and when the concentration is greater than 10000 ppm it is given in percents (%).

Table 4. Composition of some coins from Sibiu region by gamma transmission (Besliu 1987)

Table 5. Concentration of elements for Whitechapel bell and Christ Church bell, bye 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 (%).
Figure 2
Figure 5

\[
\frac{(\text{Au}^*100+\text{Ag}^*10+\text{Sb}+\text{As})}{\text{Cu}}
\]
Figure 6

Transylvanian Bells

London Bells

Fe/Cu

$\frac{(Au*100+Ag*10+Sb+As+Sn)}{Cu}$