Neutron activation and X-ray fluorescence analyses of Early Roman Age Bohemian artifacts

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Abstract. Composition of more than 500 metallic artifacts was studied by means of INAA and XRF, including 404 objects of copper alloys. Analyses proved not only use of specialized bronze alloys in the imported Roman vessels, but also use of very pure brass with average content of 20% zinc in the production of decorative brooches, especially in the 1st century A.D. These artifacts were evidently made on the Bohemian territory, but raw brass was probably imported from the Roman provinces. Common products are mostly made of mixed materials possibly recycling old objects and using local raw materials.

1. Introduction
The earliest metallic products were made of pure copper or arsenic copper containing often probably unintentionally not only arsenic but also substantial content of antimony, silver, and sometimes nickel. This type of raw copper continued to be used even in the Early Bronze Age in the production of tin bronze. This type of raw copper disappeared during the EBA and for production of tin bronze the relatively pure copper was then used. But bronze was for a long time discussed in the Czech archaeology as only one phenomenon: alloy of copper and tin.

Many deposits from Late Bronze Age contained up to hundreds of cakes and formless pieces of metal. Archaeologists regarded them as melted scrap–metal of old bronze artifacts but intensive research in 90’s disproved this opinion about recycling origin of those objects based on the observation that some cases of them contained pieces of old broken products. In fact, it was probably a new imported type of raw copper without tin from quantitatively very different deposits than in Early Bronze Age. The next quantitative stage was in the La Tène age, when leaded bronze appeared with the high content of lead. It should be explained by the import of Roman technology [1].

First, but very inaccurate, spectral analyses of 37 of the artifacts from the Teutonic graveyard in Třebusice were made approximately in 70’s in the laboratories of the Institute of Archaeology in Prague. The new type of alloy – brass – was reported.

The milestone in the research of Roman and Teutonic metallurgy of non–ferrous metals in our territory were two research projects of two significant Bohemian (i.e. Czech) excavations at Dřífovo-Pičhora (archaeological research between 1896 and 1905; with more than 150 graves from older Roman age) and Třebusice (archaeological research between 1921 and 1963; from the end of the 1st century B.C. to the 3rd century A.D.). In both of the project, the cooperation of archaeologist and nuclear physicist was very powerful. Due to this type of
cooperation more than 500 artifacts of the Roman and Teutonic origin from Bohemian territory have been analysed. Very large research of the similar topic has been made simultaneously in Germany [3],[4], so it is possible to compare the data on the international level.

2. Analytical methods

2.1. X-ray fluorescence analysis

The radioactive source $^{241}\text{Am}$ of a ring shape was used for the excitation of characteristic X-ray radiation. There is a sketch of our apparatus — especially the source part — in figure 1. It is one of the typical setup for this type of XRF, described e.g. in [5]. The advantage of this setting is its ability to eliminate the influence of surface irregularities on the intensity of signal of individual elements in the sample. The $^{241}\text{Am}$ source is covered by very thin layer which enabled to use for excitation not only the 59.5 keV line from the decay of americium, but also the X-ray lines at 14 and 18 keV from the transitions in $^{237}\text{Np}$. The more complex character of excitation radiation had a negative impact on the growth of background in the measured spectra and the radiation’s interference with analytical peaks somewhat lowered detection limit of some elements. On the other hand, this had an advantage of comparable sensitivity of determination of both metals with low energy characteristic radiation (Fe, Ni, Cu, Zn, As, Pb) and heavier metals (Ag, In, Sn, Sb) in the course of single measurement event.

The collimator, made of lead and tin alloy, between the sample and the detector limited the sample’s analyzed segment to a ring with diameter of approximately 3.5 mm.

2.1.1. Sensitivity and reliability of the determination  
The above described system of sample measurement enable to determine the presence of elements with Z higher than chromium. Light metals such as, for instance, aluminium or magnesium could not be determined. During the usual measuring time – fifteen minutes – the detection limits of elements from mangan to zinc amounted to some 0.1%, for heavier metals several hundredths of percent (after the

Figure 1. Sketch of the source part of XRF apparatus; A: X–Ray source, B: shielding box with collimator, C: additional shielding, D: Cadmium plate with thin foil
background corrections). No element displayed a detection limit lower than 0.02%. In the case of lead–arsenic the situation is complicated by the fact that their main analytical peaks have almost the same energy.

Resulting errors depend on a number of factors and may be only roughly estimated. In the case of standard materials the measured contents diverged within the range of 5% to 10% rel. from those which were certified. Serious component of errors which is difficult to estimate consists of the contribution of non-homogeneities and changes on objects surfaces, especially the degree of their corrosion.

2.1.2. Influence of non-homogenity and corrosion Because XRF-analysis is a surface method and influence of inner heterogenity of the artifact itself and in many cases the corrosion of it is very serious. Some material from soil (i.e. iron) can be absorbed on the surface. Scratching away this layer is usually not allowed. Another problem is heterogenity of the artifact.

2.2. Neutron activation analysis

A LVR 15 experimental reactor of the Nuclear Research Institute at Řež with neutron fluence rate of \(8 \cdot 10^{13} \text{ cm}^{-2} \text{s}^{-1}\) was used for the exposure of samples to neutrons. Irradiation time was 4 hours (reactor performance 9 MW).

Samples in the form of dust, clippings and, in few instances, of small cut-off pieces were weighted and sealed into polyethylene capsules, than packed to the aluminium foil, and finally putted to the aluminium irradiating tube. The standards, like pieces of pure metals, synthetic multielementary standards, and gold monitors were added to the irradiating tube. Spectra measurements by HPGe detector of an 100 cm\(^3\) volume with a relative efficiency of 22\% did usually take place at following times:

(i) three days after irradiation, exposition 2 – 5 minutes;
(ii) 7 – 10 days after irradiation, exposition 20 – 40 minutes;
(iii) 25 – 40 days after irradiation, exposition 40 – 70 minutes.

The NAA enables identification of a number of elements, in some very sensitively instances. A high sensitivity may nonetheless be detrimental to the determination of many other elements.

2.3. Sample preparation

The preparation of samples for INAA was, of course, necessary. The 1 mm thin drill was used to take sample from artifact. This was a two phase process. The first phase was to route a surface layer to the raw material and than take s sample directly from the deep of the artifact. Some artifacts were to thin for this process, so there was possibility to cut a piece of it, if its shape was like plate. In some cases (less than 25\%) there was no possibility to take a sample from the artifact.

3. Results

Total number of measured artifacts from Dobřichov-Pičhoro and Třebusice was 404. All of them were non–destructively measured by XRF. Samples for more precious neutron activation analysis were taken from more than 75\% of them. The most artifacts measured by NAA were different types of brooches (127 pcs.), than parts of vessels (54 pcs.). Drinking horns and their components (36 pcs.) and different types of belt parts (39 pcs.) were not so dominant, but their total number was not negligible. 26 pieces of different type of ferrules and 23 pieces of artifacts pertaining to arms (parts of swords and shields) represented the rest.
3.1. Type of material sorting

Research of artifact composition was mainly aimed to the alloys of copper, or silver. The pure copper without any alloying metal was not presented, so in the sorting to the material groups were to the copper group inserted artifacts with the total concentration of alloying metal under 3% and none of them over 1%. The number of this cases was very low (8 pcs.).

The transparent categorization of types of artifacts to the type of material group could be seen in table 1 (total numbers). For this purposes not only accurate NAA data were used, but also the estimation of data of artifacts measured only by XRF. Accurate classification of all artifacts measured by NAA to the concentration intervals of zinc, tin, and lead content are in table 2 and on the charts at figure 2.

Concentrating our attention to the zinc alloys, the brasses, it is possible to say, that to the brooches production was used, in approximately 3/4 of cases, the very high quality brass with impurities of tin or lead usually much less then 1%. Only a little part of brooches was made of tin or tin–lead bronze. Some brooches were made of the brass of the worse quality with more than 1% of tin, or with only low concentration of zinc. The similar situation is in the case of belt parts and pats of arms, only the relative concentration of pure brass is there much lower. It seems, that probably the pure brass material was used for only the brooches production and

### Table 1. Categorization of types of artifacts to the type of material groups

| Material       | Type of artifact | brooches | drinking horns | parts of belt | sundry | utensils | arms | Total sum |
|----------------|------------------|----------|----------------|---------------|--------|----------|------|-----------|
| Copper         |                  | 0        | 0              | 1             | 4      | 1        | 2    | 8         |
| brass, Zn>15  |                  | 101      | 0              | 16            | 12     | 1        | 8    | 138       |
| brass, Zn<15  |                  | 2        | 1              | 6             | 4      | 1        | 0    | 14        |
| brass, Zn>Sn  |                  | 19       | 2              | 15            | 8      | 0        | 5    | 49        |
| bronze, Sn>Sn |                  | 1        | 0              | 2             | 6      | 3        | 1    | 13        |
| bronze, Sn<5  |                  | 0        | 0              | 2             | 1      | 2        | 2    | 7         |
| bronze, Sn    |                  | 15       | 8              | 12            | 11     | 34       | 6    | 86        |
| bronze, Sn + <10 Pb |              | 6        | 15             | 4             | 12     | 9        | 0    | 46        |
| bronze, Sn + >10 Pb |            | 1        | 12             | 0             | 0      | 11       | 0    | 24        |
| gun metal     |                  | 3        | 5              | 2             | 6      | 0        | 3    | 19        |
| **Total sum** |                  | 148      | 43             | 60            | 64     | 62       | 27   | 404       |

### Table 2. Summary of percentage concentration of the group of artifacts in the intervals of zinc, tin, and lead content.

| Interval | Zn | Sn | Pb | Zn | Sn | Pb | Zn | Sn | Pb | Zn | Sn | Pb |
|----------|----|----|----|----|----|----|----|----|----|----|----|----|
| 0-2      | 0.0| 100| 98.8| 39.4| 81.3| 21.1| 50.0| 81.6| 95.9| 6.1| 59.2| 85.7| 2.9| 20.0|
| 2-4      | 0.0| 0.0| 0.0| 1.2| 3.0| 27.3| 0.0| 2.6| 15.8| 10.5| 0.0| 2.0| 8.2| 17.1| 1.1|
| 4-6      | 0.0| 0.0| 0.0| 0.0| 0.0| 9.1| 21.2| 3.1| 5.3| 0.0| 2.6| 2.0| 8.2| 10.2| 0.0| 11.4| 20.0|
| 6-8      | 0.0| 0.0| 0.0| 0.0| 0.0| 3.0| 6.1| 6.3| 5.3| 15.8| 5.3| 0.0| 38.8| 0.0| 2.9| 28.6| 11.4|
| 8-10     | 0.0| 0.0| 0.0| 0.0| 0.0| 12.1| 15.2| 6.3| 5.3| 5.3| 0.0| 0.0| 24.5| 6.1| 0.0| 2.9| 20.0| 11.4|
| 10-12    | 0.0| 0.0| 0.0| 0.0| 0.0| 6.1| 9.1| 0.0| 10.5| 5.3| 0.0| 0.0| 6.1| 2.0| 0.0| 17.1| 0.0|
| 12-14    | 1.2| 0.0| 0.0| 15.2| 3.0| 3.1| 7.9| 5.3| 0.0| 0.0| 2.0| 2.0| 0.0| 2.9| 2.9|
| 14-16    | 2.4| 0.0| 0.0| 9.1| 0.0| 0.0| 7.9| 2.6| 0.0| 0.0| 2.0| 4.1| 0.0| 0.0| 5.7|
| 16-18    | 17.9| 0.0| 0.0| 3.0| 0.0| 0.0| 7.9| 0.0| 0.0| 0.0| 0.0| 18.4| 0.0| 0.0| 20.0|
| 18-20    | 35.7| 0.0| n/d| 0.0| 0.0| 0.0| 2.6| 0.0| n/d| 0.0| 0.0| n/d| 0.0| 0.0| n/d|
| 20-22    | 20.2| 0.0| n/d| 0.0| 0.0| 0.0| 10.5| 0.0| n/d| 0.0| 0.0| n/d| 0.0| 0.0| n/d|
| 22-24    | 17.9| 0.0| n/d| 0.0| 0.0| 0.0| 2.6| 0.0| n/d| 0.0| 0.0| n/d| 0.0| 0.0| n/d|
| 24-26    | 4.8| 0.0| n/d| 0.0| 0.0| 0.0| 7.9| 0.0| n/d| 0.0| 0.0| n/d| 0.0| 0.0| n/d|
| >26      | 0.0| 0.0| n/d| 0.0| 0.0| 0.0| 2.6| 0.0| n/d| 0.0| 0.0| n/d| 0.0| 0.0| n/d|
Figure 2. Graphic summary of percentage concentration of the group of artifacts in the intervals of zinc, tin, and lead content

to the another types of artifacts the zinc was included as a product of recycling of old artifacts.

In the rest of artifacts (parts of drinking horns and utensils), zinc was very rare. The typical alloy of drinking horns was tin or leaded bronze. The material typical for utensils was tin bronze or bronze with lead. Also the bronze utensils from Roman sites (Kempten, Augsburg, Haltern, and Saalburg) were made of a tin bronze [6].

3.2. Minority admixtures in alloys
As a minority admixtures were marked elements which are presented in the copper alloys in concentrations up to tenths of percent and they were probably not added knowingly. Some of the elements could be in some prehistoric ages presented as a majority components (i.e. As-Sb-Ag-Ni in Early Bronze Age; Pb, in last centuries B.C.). Alloys originally from Roman imperium are significant with both high specialization and very low concentrations of unpremeditated admixtures. This was proved by many of analyses (atomic absorption with sensitivity of hundredths of percent) made by J. Rieder.

Neutron activation analysis helped us to determine in all studied artifacts the most common admixtures like: arsenic, silver and antimony on the level of tens of ppm, so it was possible to
Table 3. Summary of percentage minority alloys concentration of the group of artifacts in the intervals of silver, arsenic, and antimony content.

| Interval     | Brass brooches | Non-brass brooches | Belt parts | Utensils | Drinking horns |
|--------------|----------------|-------------------|------------|----------|---------------|
|              | Ag  | As  | Sb  | Ag  | As  | Sb  | Ag  | As  | Sb  | Ag  | As  | Sb  | Ag  | As  | Sb  |
| 0.00-0.02    | 32.1| 59.5| 51.2| 3.1 | 15.6| 15.6| 7.9 | 28.9| 31.6| 6.1 | 8.2 | 8.2 | 0.0 | 2.9 | 0.0 |
| 0.02-0.04    | 20.2| 20.2| 20.2| 0.0 | 28.1| 12.3| 7.9 | 21.1| 10.5| 16.3| 18.4| 8.2 | 0.0 | 14.3| 0.0 |
| 0.04-0.06    | 15.5| 11.9| 11.9| 15.6| 31.3| 9.4 | 15.8| 36.8| 7.9 | 34.7| 28.6| 14.3| 20.0| 17.1| 2.9 |
| 0.06-0.08    | 13.1| 3.6 | 8.3 | 9.4 | 9.4 | 6.3 | 10.5| 2.6 | 10.5| 28.6| 10.2| 10.2| 14.3| 25.7| 8.6 |
| 0.08-0.10    | 2.4 | 3.6 | 7.1 | 12.5| 6.3 | 18.5| 7.9 | 5.3 | 26.3| 0.0 | 6.1 | 12.2| 14.3| 14.3| 25.7| 8.6 |
| 0.10-0.12    | 3.6 | 1.2 | 0.0  | 3.1 | 6.3 | 3.1 | 7.9 | 2.6 | 2.6 | 4.1 | 10.2| 12.2| 8.6 | 5.7 | 17.1|
| 0.12-0.14    | 3.6 | 0.0 | 1.2  | 3.1 | 3.1 | 12.5| 15.8| 0.0 | 2.6 | 6.1 | 4.1 | 8.2 | 8.6 | 2.9 | 14.3|
| 0.14-0.16    | 0.0 | 0.0 | 0.0  | 0.0 | 0.0 | 6.3 | 5.3 | 0.0 | 0.0 | 0.0 | 0.0 | 5.7 | 0.0 | 5.7 | 8.6 |
| 0.16-0.18    | 0.0 | 0.0 | 0.0  | 12.5| 0.0 | 0.0 | 2.6 | 0.0 | 2.6 | 2.0 | 4.1 | 4.1 | 2.9 | 0.0 | 8.6 |
| 0.18-0.20    | 2.4 | 0.0 | 0.0  | 3.1 | 0.0 | 3.1 | 5.3 | 0.0 | 0.0 | 0.0 | 0.0 | 2.0 | 2.9 | 2.9 | 8.6 |
| 0.20-0.25    | 3.6 | 0.0 | 0.0  | 3.1 | 0.0 | 9.4 | 5.3 | 0.0 | 0.0 | 0.0 | 0.0 | 2.0 | 0.0 | 5.7 | 0.0 |
| 0.25-0.30    | 1.2 | 0.0 | 0.0  | 6.3 | 3.1 | 0.0 | 2.6 | 0.0 | 2.6 | 0.0 | 4.1 | 6.1 | 5.7 | 0.0 | 2.9 |
| 0.30-0.35    | 0.0 | 0.0 | 0.0  | 3.1 | 0.0 | 0.0 | 2.6 | 0.0 | 2.6 | 0.0 | 4.1 | 8.6 | 0.0 | 2.9 | 8.6 |
| >0.35        | 2.4 | 0.0 | 0.0  | 25.0| 0.0 | 3.1 | 2.6 | 0.0 | 2.6 | 2.0 | 6.1 | 8.2 | 8.6 | 8.6 | 2.9 |

explore the differences on this low level. Our attention was aimed to the brooches, divided into two subgroups in accordance with the zinc and tin concentration, drinking horns, belt parts, and utensils. The summary of numbers of artifacts contained Ag, As, and Sb are in table 3, in graphical view at figure 3.

Brass brooches Almost one third of all brooches contained silver in the interval between 0.001 and 0.02%. In the interval under 0.1% there were more than 80% of artifacts with approximately exponentially decreasing count in the intervals. The much more lower concentrations were measured in the case of arsenic and antimony. In the 60% of the brooches there was a concentration of As less than 0.02% and 99% was under 0.1%. The antimony concentration was in 51% less than 0.02% and 99% was under 0.1%. The total sum of all admixtures was in the most of the cases under 0.05%. So, it is possible to say that for the production of this type of the artifact pure copper was used.

Non–brass brooches Concentrations of minority admixtures in this type of brooches were higher. The concentration of silver was only in 3% of artifacts at lower level than 0.02% compared with 32% in the brass brooches. Only 41% of samples had silver admixture under 0.1% with maximum at 0.07%. Concentrations of silver in the rest of artifacts were in the range 0.1 – 0.35, and more than 25% of them were over this level. Concentration of arsenic was in 91% under the 0.1% level with the peak at approximately 0.04%. In the antimony case there is 53% of brooches under 0.1%.

Parts of belts The concentration of the minority admixtures was nearly the same as in the case of the non–brass brooches. It is possible to say, that a similar material was used for producing this type of artifact.

Utensils Utensils and their parts contained slightly more admixtures than brass brooches. The concentration of silver was in 85% cases under 0.1% with the maximum at 0.05%. The similar situation as in with silver appears in arsenic concentrations, where 72% of them were under 0.1% with maximum at 0.05%. The more wider distribution of antimony up to the 0.35% was observed (only 37% under 0.1%). This substantial difference between utensils and brass
brooches could be explained by the higher concentration of lead in the utensils. More than one third of utensils had the concentration of lead higher than 10%.

**Drinking horns** The concentration of arsenic is approximately the same as in the another types of artifacts. The so wide distribution of silver and antimony could be explained in the same way as in the case of utensils.

The comparison of our measurements of minority admixtures (Ag, As, Sb) in the material from Třebusice and Dobřichov–Píčora sites showed close similarity with the measurements of the artifacts from the early Roman settlement Haltern [7].

4. Conclusions
The performed metallographic analyses have changed the existing point of view on the present archaeometallurgical research in the territory of Bohemia. Two different aspects of metals were considered: the macroelementary composition and minor admixtures. Obtained data helped to the archaeologists to hypothesize about metallurgy not only in the territory of today’s Bohemia but also for the so called central European barbaricum. We were, for example,
able to prove that ancient brass was delivered to the territory of today’s Bohemia, mainly because of brass artifacts production; or to hypothesize that the artifacts were produced on this territory, which could be deduced from the concentration of brooches specific for this territory.

This type of interdisciplinary research showed as the advantages of cooperation of physicists and archaeologists.

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