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**Expert report of the X-ray fluorescence analysis of objects from Slovak
archaeological sites:**

**Bratislava, Devínska Nová Ves, Hronský Beňadik, Komárno,
Košice - Krásna, Radzovce, Rusovce, Streda nad Bodrogom,
Vištuk and Záhorská Bystrica**

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RÖNTGEN FLUORESCENT ANALYSIS OF ARCHAEOLOGICAL OBJECTS

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The selection of analyzed objects from the depositories of the Danube Museum in Komárno and the Archaeological Museum of the Slovak National Museum in Bratislava was prepared by Mgr. András Csuthy, PhD., PhDr. Juraj Bartík, Ph.D. and Mag. Dr. phil. Beate Maria Pomberger. The composition of the alloys of the objects was investigated by the X-ray fluorescence method.

Method and methodology of work

X-ray fluorescence analysis (ED-XRF) is a method of non-destructive detection of the chemical composition of objects. It is based on the measurement of X-rays aroused by irradiation of an object under investigation. ED-XRF is especially suitable for the analysis of macroelements, or even some trace elements. X-ray fluorescence spectrometry is a relative analytical method because the measured quantity must relate to the composition of the sample by calculations or by comparison with standards. The actual measurement is performed from the surface of the examined object, in which the concentration values (Wt% - weight percent) of individual elements are determined by a spectrometer.

Object analyzes were performed with a hand-held X-ray fluorescence spectrometer DELTA CLASSIC + from Olympus from the USA, which is intended for non-destructive quantitative analyzes of archaeological objects, precious metals and precious metal alloys. The analyzer determines the percentage of up to 29 elements (Au, Pd, Ag, Pt, Ir, Rh, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Zr, Nb without leaving traces), Mo, Hf, W, Re, Pb, Sn, Bi and Sb).

DELTA CLASSIC + measures only the surface of the examined material and therefore does not guarantee the homogeneity of the chemical composition of the measured material in the whole volume. It provides only information on the composition of the surface layer of the object at the given examined place, while the depth of penetration of the X-ray beam is given by the chemical composition of the material. Therefore, it is very important to choose the place on the studied object where the spectral analysis will be performed. If the material is gold-plated or clad or otherwise surface-treated, possibly with corrosion, then the chemical composition does not correspond to the weight percentages in the whole volume, but to the weight percentages in the measured surface layer at a given measuring point.

For objects that have a spherical, resp. the rounded shape can affect the positioning of objects, so it is important to choose the appropriate geometry of such samples. The results of the measurements are presented in the form of tables. Above them is the object, a link to the illustration and location, the grave number and the incremental number of the object. The table shows the name of the object and the average weight percentages of metals (Wt%) measured in the individual artifacts examined. Below the table follows a verbal description of the composition of the investigated alloy determined by ED-XRF analysis. Note: Pictures of objects are taken from a group image and are for illustrative purposes only.

RESULTS OF MEASUREMENTS OF SPECTRAL ANALYZES

Table 1 Pellet bell (Fig. 1)
Devínska Nová Ves Grave 796 InvNr. AP968

Artifact	Cu	Ga	Sn	Pb
Pellet bell	27,01	3,40	13,09	56,50

Lead bronze pellet bell. It contains a thick layer of Pb and Ga oxides in the patina.



Fig. 1. Pellet bell. Grave 796. InvNr. AP968.



Fig. 2. Pellet bell. InvNr. AP12073.

Table 2 Pellet bell (Fig. 2)
Záhorská Bystrica InvNr. AP12073

Artifact	Fe	Cu	Zn	Ga	Ag	Sn	Pb
Pellet bell	1,03	45,37	0,96	1,60	1,75	31,18	18,11

Lead bronze pellet bell. In the patina are oxides of Fe, Zn, Ga and Ag.

Table 3 Pellet bell (Fig. 3)
Záhorská Bystrica InvNr. AP12438

Artifact	Cu	Ga	Ag	Sn	Pb
Pellet bell	49,55	1,49	0,48	31,16	17,32

Lead bronze pellet bell. In the patina are oxides of Ga and Ag.



Fig. 3. Pellet bell. InvNr. AP12438.



Fig. 4. Pellet bell. InvNr. AP501.

Table 4 Pellet bell (Fig. 4)
Devínska Nová Ves Grave 412 InvNr. AP501

Artifact	Fe	Cu	Zn	Ag	Sn	Pb
Pellet bell	0,98	81,97	0,83	0,45	8,08	7,69

Lead bronze pellet bell. In the patina are oxides of Fe, Zn and Ag.

Table 5 Pellet bell (Fig. 5)
Záhorská Bystrica Grave 208 InvNr. AP14098

Artifact	Cu	Zn	Ag	Sn	Pb
Pellet bell	55,82	0,96	0,41	32,56	10,24

Lead bronze pellet bell. In the patina are oxides of Zn and Ag.



Fig. 5. Pellet bell. InvNr. AP14098.



Fig. 6. Pellet bell. InvNr. AP482.

Table 6 Pellet bell (Fig. 6)
Devínska Nová Ves InvNr. AP482

Artifact	Fe	Ni	Cu	Zn	Ag	Sn	Pb
Pellet bell	0,24	0,10	86,55	1,56	0,32	8,30	2,93

Bronze pellet bell with a mixture of lead. In the patina are oxides of Fe, Ni, Zn and Ag.

Table 7 Pellet bell (Fig. 7)
Devínska Nová Ves Grave 765 InvNr. AP926

Artifact	Cu	Zn	Ag	Sn	Pb
Pellet bell	76,80	1,63	0,50	16,40	4,67

Bronze pellet bell with a mixture of lead. In the patina are oxides of Zn and Ag.



Obr. 7. Pellet bell. Grave 765.
 InvNr. AP926.



Obr. 8. Pellet bell. Grave 804.
 InvNr. AP982.

Table 8 Pellet bell (Fig. 8)
Devínska Nová Ves Grave 804 InvNr. AP982

Artifact	Fe	Cu	Zn	Ag	Sn	Pb
Pellet bell	0,43	85,35	0,93	0,39	5,75	7,17

Lead bronze pellet bell. In the patina are oxides of Fe, Zn and Ag.

Tab. 9 Pellet bell (Fig. 9)
Rusovce InvNr. AP21001

Artifact	Cu	Zn	Ga	Ag	Sn	Pb
Pellet bell	63,40	2,40	1,35	1,86	15,22	15,78

Lead bronze pellet bell. In the patina are oxides of Zn, Ga and Ag.



Fig. 9. Pellet bell. InvNr. AP21001.



Fig. 10. Pellet bell. InvNr. AP21002.

Table 10 Pellet bell (Fig. 10)
Rusovce InvNr. AP21002

Artifact	Ni	Cu	Zn	Ga	As	Ag	Sn	Pb
Pellet bell	0,14	69,60	1,41	1,05	1,24	1,43	12,72	12,40

Lead bronze pellet bell. In the patina are oxides of Ni, Zn, Ga, As and Ag.

Table 11 Bell (Fig. 11)
Bratislava, Židovská ul. InvNr. HF23165

Artifact	Fe	Ni	Cu	Zn	Sn	Pb
Bell	0,23	0,12	68,87	20,61	9,91	0,25

Brass bell with a mixture of tin. In the patina are oxides of Fe, Ni and Pb.



Fig. 11 Bell. InvNr. HF23165.

Table 12 Bell (Fig. 12)
Radzovce InvNr. HF26051

Artifact	Fe	Ni	Cu	Zn	Pb	Bi
Bell	0,24	0,48	79,94	13,71	5,03	0,61

Brass bell with a mixture of lead. In the patina are oxides of Fe, Ni and Bi.



Fig. 12. Bell. InvNr. HF26051.



Fig. 13. Bell. InvNr. HF26052.

Table 13 Bell with heart (Fig. 13)

Radzovce InvNr. HF26052

Artifact	Fe	Ni	Cu	Zn	As	Sn	Sb	Pb
Bell	0,90	0,20	74,61	1,76	0,61	18,57	0,98	2,38
Heart bell	95,99	0,00	4,01	0,00	0,00	0,00	0,00	0,00

Bronze bell with a mixture of lead. In the patina are oxides of Fe, Ni, Zn, As and Sb. Iron heart of bell.

Tab. 14 Bell (Fig. 14)

Vištuk InvNr. AP76204

Artifact	Fe	Ni	Cu	Zn	Sn	Pb
Bell	1,06	0,12	67,42	12,23	11,24	7,92

Brass-bronze bell with lead. In the patina are oxides of Fe and Ni.



Fig. 14. Bell. InvNr. AP76204.



Fig. 15. Bell. InvNr. AP9445.

Table 15 Bell (Fig. 15)

Rusovce, InvNr. AP9445

Artifact	Fe	Cu	Zn	Sn	Pb
Bell	0,89	78,80	1,28	12,96	6,06

Bronze bell with a mixture of lead. In the patina are oxides of Fe and Zn.

Table 16 Bell (Fig. 16)
Komárno InvNr. AP13771

Artifact	Cu	Zn	Sn	Pb
Bell	82,25	1,35	9,48	6,92

Bronze bell with a mixture of lead. In the patina are oxides of Zn.



Fig. 15. Bell. InvNr. AP13771.



Fig. 16. Bell. InvNr. AP13772.

Table 17 Bell (Fig. 17)
Komárno InvNr. AP13772

Artifact	Fe	Cu	Zn	Ga	Sn	Pb
Bell	0,29	73,45	0,66	1,60	4,59	19,42

Lead bronze bell. In the patina are oxides of Fe, Zn and Ga.

Table 18 Bell (Fig. 18)
Streda nad Bodrogom InvNr. AP32157

Artifact	Fe	Cu	Zn	Ga	Sn	Pb
Bell	0,58	75,80	4,60	1,06	5,03	12,93

Lead bronze bell with a mixture of zinc. In the patina are oxides of Fe and Ga.



Fig. 18. Bell. InvNr. AP32157.



Fig. 19. Bell. InvNr. AP32107.

Table 19 Bell (Fig. 19)

Košice – Krásna Inv. č. AP32107

Artifact	Fe	Ni	Cu	Zn	Sn	Pb
Zvonček	0,79	0,11	76,76	5,04	14,74	2,57

Bronze bell with a mixture of zinc and lead. In the patina are oxides of Fe and Ni.

Table 20 Bell (Fig. 20)

Hronský Beňadik InvNr. AH57416

Artifact	Fe	Cu	Zn	Ga	As	Sn	Sb	Pb
Bell - fragment	0,95	67,22	0,67	1,29	3,27	2,08	12,31	12,20

Fragment of a bronze bell with an admixture of antimony and lead. In the patina are oxides of Fe, Zn a Ga.



Fig. 20. Fragment of bell. InvNr. AH57416.

Table 21 Bell

Devín InvNr. 1812

Artifact	Fe	Cu
Bell	98,51	1,49

Iron bell. Cu oxides are in the patina.

Table 22 Fragment of pellet bell - 1 (Fig. 21)

Komárno-Lodenice Grave 36 InvNr. A5314

Artifact	Fe	Cu	Zn	As	Ag	Sn	Au
Fragment of pellet bell - 1	0,48	83,76	0,87	1,06	0,98	12,56	0,29

Bronze fragment of a pellet bell. The obverse of the pellet bell was gilded. The patina contains oxides of Fe, Zn, As, Ag and Fe.

Table 23 Fragment of pellet bell - 2 (Fig. 21)
Komárno-Lodenice Grave 36 InvNr. A5314

Artifact	Cu	Zn	As	Ag	Sn	Au	Pb
Fragment of pellet bell - 2	91,86	1,48	0,45	0,61	4,80	0,36	0,45

Bronze fragment of a pellet bell. The obverse of the pellet bell was gilded. The patina contains oxides of Zn, As, Ag and Pb.



Fig. 21. Fragment of pellet bells and rivet. Grave 36. InvNr. A5314.

Table 24 Fragment of pellet bell - 3 (Fig. 21)
Komárno-Lodenice Grave 36 InvNr. A5314

Artifact	Fe	Cu	Zn	As	Ag	Sn	Au	Pb
Fragment of pellet bell - 3	1,56	71,22	1,01	1,63	0,81	18,20	1,02	4,55

Bronze fragment of a pellet bell. The obverse of the pellet bell was gilded. The patina contains oxides of Fe, Zn, Ag and As.

Table 25 Fragment of pellet bell - rivet (Fig. 21)
Komárno-Lodenice Grave 36 InvNr. A5314

Artifact	Fe	Ni	Cu	Zn	As	Ag	Sn	Pb
Rivet - 4	0,37	0,18	76,92	1,07	1,26	1,11	18,70	0,39

Bronze rivet. The patina contains oxides of Fe, Ni, Zn, Ag, As and Pb.

Table 26 Pellet bell (Fig. 22)
Komárno-Lodenice Grave 65 InvNr. A5396

Artifact	Mn	Fe	Cu	As	Sn	Au
Pellet bell	0,26	93,35	4,22	0,20	1,63	0,35

Bronze pellet bell with traces of gilding. The surface of the pellet bell is coated with strong corrosion of iron; oxides of Mn and As are also in the patina.



Fig. 22. Pellet bell. Grave 65. InvNr. A5396. Obr. 23. Pellet bell. Grave 65. InvNr. A5397.

Table 27 Pellet bell (Fig. 23)

Komárno-Lodenice Hrob 65 InvNr. A5397

Artifact	Mn	Fe	Cu	Zn	Sn	Au	Pb
Pellet bell	0,11	31,89	62,98	1,01	2,91	0,40	0,81

Bronze pellet bell with traces of gilding. The surface of the pellet bell is coated with strong corrosion of iron; oxides of Mn, Zn and Pb are also in the patina.

Table 28 Pellet bell (Fig. 24)

Komárno-Lodenice Grave 71 InvNr. A5418

Artifact	Cu	Zn	Ag	Sn	Pb
Pellet bell	97,81	0,71	0,57	0,64	0,27

Copper pellet bell. In the patina are oxides of Zn, Ag, Sn and Pb.



Fig. 24. Pellet bell. Grave 71. InvNr. A5397.

Table 29 Pellet bell - 1 (Fig. 25)

Komárno-Lodenice Grave 79 InvNr. A5490

Artifact	Cu	Zn	Ag	Sn	Pb
Pellet bell - 1	90,57	0,94	1,24	3,94	3,31

Bronze pellet bell with a mixture of lead. In the patina are oxides of Zn and Ag.



Obr. 25. Hrob 79. Pellet bells. Inv. č. A5490.

Table 30 Pellet bell - 2 (Fig. 25)

Komárno-Lodenice Grave 79 InvNr. A5490

Artifact	Cu	Zn	As	Ag	Sn	Au	Pb
Pellet bell - 2	90,48	1,12	0,62	1,19	5,70	0,33	0,56

Bronze pellet bell with traces of gilding. In the patina are oxides of Zn, As, Ag and Pb.

Table 31 Pellet bell (Fig. 26)

Komárno-Lodenice Grave 86, InvNr. A5638

Artifact	Ni	Cu	Zn	As	Sn	Pb
Pellet bell	0,16	72,18	0,67	1,44	18,10	7,45

Bronze pellet bell with a mixture of lead. In the patina are oxides of Ni, Zn and As.



Fig. 26. Pellet bell. Grave 86. InvNr. A5638.

Table 32 Pellet bell (Fig. 27)

Komárno-Lodenice Grave 91 InvNr. A6052

Artifact	Fe	Cu	As	Sn
Pellet bell	96,37	2,80	0,26	0,57

Iron pellet bell. In the patina are oxides of Cu, As and Sn.



Obr. 27. Pellet bells. Grave 91. InvNr. A6052 a A6053.

Table 33 Pellet bell (Fig. 27)
Komárno-Lodenice Grave 91 InvNr. A6053

Artifact	Fe	Cu	As	Ag	Sn	Sb	Au	Pb
Pellet bell - 2	92,44	5,33	0,00	0,00	2,23	0,00	0,00	0,00
Metal sleeve on the pellet bell - 2	0,00	75,46	0,85	1,05	21,02	0,75	0,23	0,64

Iron pellet bell. In the patina are oxides of Cu a Sn. Bronze sleeve with possible gold plating; in the patina are oxides, As, Sb and Pb.

Table 34 Fragments of pellet bell (Fig. 28)
Komárno-Lodenice Grave 101 InNr. A5859

Artifact	Fe	Cu	Zn	As	Sn	Pb
Fragment of pellet bell	0,45	90,51	4,47	0,82	1,95	1,80

Brass fragments of pellet bell with tin. In the patina are oxides of Fe, As and Pb.



Obr. 28. Fragments of pellet bell. Grave 101. InvNr. A6070.

Table 35 Pellet bell (Fig. 29)
Komárno-Lodenice Grave 110 InvNr. A6070

Artifact	Fe	Cu	As
Pellet bell	96,99	2,85	0,16

Iron pellet bell. In the patina are oxides of Cu and As.



Fig. 29. Pellet bell. Grave 110. InvNr. A6070.

Table 39 Pellet bell - 1 (Fig. 30)

Komárno-Lodenice Grave 107 InvNr. A5813

Artifact	Cu	Zn	Ag	Sn	Pb
Pellet bell - 1	90,31	0,96	0,71	6,37	1,65

Bronze pellet bell. In the patina are oxides of Zn, Ag and Pb.

Table 39 Pellet bell - 2 (Fig. 30)

Komárno-Lodenice Grave 107 InvNr. A5813

Artifact	Cu	Zn	Ag	Sn	Pb
Pellet bell - 2	94,63	0,65	2,10	2,06	0,57

Bronze pellet bell. In the patina are oxides of Zn, Ag and Pb.

Table 39 Pellet bell - 3 (Fig. 30)

Komárno-Lodenice Grave 107 InvNr. A5813

Artifact	Cu	Zn	Sn	Pb
Pellet bell - 3	92,95	0,58	4,12	2,35

Bronze pellet bell with a mixture of lead. In the patina are oxides of Zn.



Obr. 30. Hrkálky. Grave 107. InvNr. A5813.

Table 39 Pellet bell - 4 (Fig. 30)

Komárno-Lodenice Grave 107 InvNr. A5813

Artifact	Cu	Zn	Sn	Pb
Pellet bell - 4	90,69	2,59	4,67	2,05

Bronze pellet bell with a mixture of lead. In the patina are oxides of Zn.

Table 40 Pellet bell - 1 (Fig. 41)

Komárno-Lodenice Grave 121 InvNr. A5771

Artifact	Cu	Zn	Ag	Sn	Pb
Pellet bell - 1	91,29	0,70	0,37	3,92	3,72

Bronze pellet bell with a mixture of lead. In the patina are oxides of Zn and Ag.

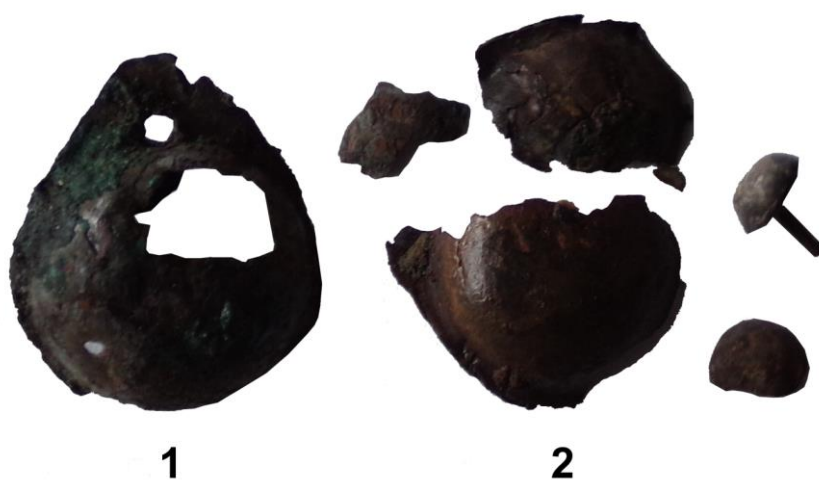


Fig. 41. Pellet bells. Grave 121. InvNr. A5771.

Table 41 Pellet bell - 2 (Fig. 41)

Komárno-Lodenice Grave 121 InvNr. A5771

Artifact	Fe	Cu	Zn	As	Ag	Sn	Au	Pb
Pellet bell - 2	1,07	68,09	1,46	1,73	2,56	23,16	0,35	1,58

Bronze pellet bell with traces of gilding. In the patina are oxides of Fe, Zn, As, Ag and Pb.

Table 42 Pellet bell – 1 (Fig. 42)

Komárno-Lodenice Grave 149 InvNr. A6103

Artifact	Fe	Cu	As	Sn
Pellet bell - 1	94,34	4,54	0,21	0,91

Iron pellet bell. In the patina are oxides of Cu, Sn and As.



Obr. 42. Hrkálky. Hrob 149. Inv. č. A6103.

Table 42 Pellet bell – 2 (Fig. 42)

Komárno-Lodenice Grave 149 InvNr. A6103

Artifact	Fe	Cu	As	Sn
Pellet bell - 2	95,38	3,98	0,24	0,40

Iron pellet bell. In the patina are oxides of Cu, Sn and As.

Table 44 Pellet bell (Fig. 43)

Komárno-Lodenice Grave 153 InvNr. A6117

Artifact	Cu	Zn	Ge	As	Ag	Au	Pb
Pellet bell – gilded surface	76,01	0,76	1,63	0,00	0,59	20,67	0,35
Pellet bell - body	98,75	0,64	0,00	0,37	0,00	0,00	0,24

Gilded copper pellet bell. In the patina are oxides of Zn, Ge, As, Ag a Pb.



Fig. 43. Pellet bell. Grave 153. InvNr. A6117

Table 45 Pellet bell (Fig. 44)

Gajary

Artifact	Fe	Cu	Zn	Sn	Pb
Pellet bell	3,31	64,71	2,30	23,92	5,76

Bronze pellet bell with a mixture of lead. In the patina are oxides of Fe and Zn.



Fig. 44. Pellet bell. Gajary.

Conclusion

Based on the results of spectral analysis, individual alloys of objects were identified: bronze and brass alloys, but also objects made of copper and iron. Measurements showed that the bronze objects contained, in addition to the main components (copper and tin), a mixture of lead and zinc. In addition to the main components (copper and zinc), brass objects also contained an admixture of tin and lead. The studied bronze and brass alloys are manifested by the dispersion of the content of zinc, lead and tin, so that they are sometimes difficult to clearly identify as bronze or brass.

The presence of silver, arsenic and antimony is related to the fact that copper ores are polymetallic. Oxides of Cu, Pb, Sn, As, Zn, Ag, Ga and Fe often occurred in the patina of individual objects as a result of long-term storage of objects in the ground.

When interpreting the results obtained by X-ray fluorescence analysis, it must be taken into account that they are the product of the current alloy analysis. They therefore provide only qualitative information on the composition of the metals from which the artifact was made and on its surface treatment. In the case of gilded objects, it is assumed that the technology of thermal gilding and plating has been used.

The obtained results confirm the important role of non-destructive analytical methods in the archaeological interpretation of artifacts in terms of their composition, origin of raw materials and production technologies.

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