ANNALS OF THE NÁPRSTEK MUSEUM 22 • PRAGUE 2001



APPENDIX 1 Technical Analyses

ELEMENT COMPOSITION OF *BIDRI* ARTICLES Jaroslav Frána and Nafaâ Reguigui

The metal composition of the surveyed group of Indian utility and decorative articles was analysed at the Nuclear Spectroscopy Department of the Nuclear Physics Institute in Řež. In general, zinc is known to be the basic material of *bidri* ware. The individual items of the group in question were analysed here with the use of two methods: namely, X-ray fluorescence analysis (XRFA), and instrumental neutron activation analysis (INAA). XRFA. Annular radioactive source ²⁴¹Am irradiating the surface of a given object at an angle of 40° was used to achieve the excitation of characteristic radiation of the elements contained in the material under survey. Characteristic radiation emitted at an angle of 90° was detected by a semiconductor Si(Li) detector with a resolution of 170 eV (5.9 keV), and the spectrum was stored into a multichannel analyzer (MCA). The examination of each object involved tentative qualitative testing of different sections of the surface, followed by choice of the section best suited for quantitative analysis.¹

INAA. Samples for activation analysis were obtained by drilling of material from a small, cleaned section of the surface, in a normally unexposed part of a given object. At a drilling-hole diameter of 1 mm, the amount of material used did not exceed 1 mm³ (sample masses ranged from 0.14 to 7.6 mg). In certain items, samples were taken from several functionally different sections. Those samples were first subjected to XRFA. Subsequently, they were sealed in PE foils and irradiated simultaneously with corresponding element standards during a period of four hours, in LWR-15 reactor at Řež, at a neutron flux rate of $8x10^{13}n \text{ cm}^{-2}\text{s}^{-1}$. Spectra of the

¹ For a more detailed description of analytical conditions and evaluation of results, see Frána-Jiráň-Maštalka-Moucha 1995, p. 145.

resultant radioactive isotopes were measured by HPGe detector with a relative efficiency of 22% and energy resolution of 1.85 keV (1333 keV). The first measurement was made between three and four days after irradiation, the following one 20 days after irradiation, with the spectra stored in an 8K MCA. Upon the evaluation of spectral lines the content ratios of the individual elements were calculated by comparison of the element standards and the samples.

The table of results (Appendix 2, Table) lists both INAA and XRFA results (the latter being indicated in italics). Where data from several sections of an object were obtained, these are separated by thin lines, whereas different objects are separated from each other by bold lines. No significant differences were revealed between the results obtained by the two methods employed, albeit obviously INAA was proven to be much more sensitive and accurate for all elements with the exceptions of lead and bismuth whose detection is beyond its capacity. For the INAA results, parameters of error were derived not exceeding 5% of value. In XRFA the inevitable rate of incertitude ranges from 5% - 10% of value, as evidenced by measurment of cleaned surfaces of the reference standards. However, in view of the fact that the actual articles under survey were measured without previous cleaning, errors caused by the presence of corrosive layers and impurities on surface may actually be substantially greater (XRFA works on surface layers of up to a mere several micrometres deep, especially as regards lighter metals). For the type of XRFA employed in this particular case, the detection limit of the elements listed in the tables was approximately 0.1%.

The content of zinc in the vessels ranged between 90% and 95%. An important admixture was invariably represented by copper whose content ranged from 0.6% - 6.2%. In most cases, the presence of lead was detected, its content varying up to a maximum of 5.5%, and occasionally there were admixtures of tin. In several cases small admixtures of iron were found; however, as its detection level was a mere 0.1%, its presence in a larger number of samples cannot be ruled out. Some of the objects were found to contain comparatively significant amounts of cadmium (up to almost 0.5 percent), which could be interpreted as a possible clue to the origin of the zinc ore. Apart from *huqqa* base No. A 9951 (Fig. 5), whose lip was made of silver with small admixture of copper, increased amounts of silver were detected in another two cases: namely, in *huqqa* base No. 13 772 (Fig. 8), over 3%; and mirror No. 13 402 (Fig. 14), 0.38% Ag. None of the examined articles was found to contain nickel and chromium;

the detected amounts of arsenic, gold, cobalt and antimony, never exceeding the order of hundredths of percent, are evidently insignificant.

Special cases were represented by cosmetic box No. 53 780 (Fig. 1), and the bottom of *huqqa* base No. 13 771 (Fig. 9). In both of these articles, analyses revealed the approximate composition of the alloy employed in their making as a mixture of zinc, tin and lead. In the case of the cosmetic box, the elaborate decorative pattern covering its entire surface prevented sampling those parts of the object which would have provided unquestionable material, and the actual sample was probably obtained from a section contaminated by tin-lead solder, also likely the sole material used in the making of the bottom of the second vessel.

The analyses have demonstrated that the simultaneous use of the two methods makes it possible to determine the contents of the individual with a detection limit 0.1% or better. The sole exception concerns detection of aluminium, where samples would have to be measured immediately after several minutes of irradiation. The matrix could nondestructively show the presence of trace quantities of Ag, As, Cr, Ni and Sb, to the levels of 0.01%; Co, 0.001%; and Au, 0.0001%.

Bibliography:

Frána, J., Jiráň, L., Maštalka, L., Moucha, V. 1995: Artifacts of copper and copper alloys in prehistoric Bohemia from the viewpoint of analyses of element composition. Památky archeologické - Supplementum 3, 127 - 294 (Institute of Archaeology, Prague).

object	inv.no.	part	origin	sample	m g	Ag	As	Au	Cd	Co	Cu	Fe	Sb	Sn	Zn	Рb
1. Cosmetic	53870	body, inside	Deccan	NpM 1	5.01	0.022	0.003	0.00023	0.007	0.0003	1.1	0.19	0.018	28.31	26.13	44.2
DOX											1.9		0.100	14.50	39.30	44.2
2. Salver	2183/7 Vu 165	bottom	Deccan	NG 1	5.14	0.016	0.020	0.00018	0.123		5.8				92.9	
		/							0.1		6.7				91.7	0.7
3. Huqqa base	49693	neck, inside	Deccan	NрМ За	0.59		0.141	80000.0	0.472	0.0006	3.8	0.72	0.005		94.89	
									0.300		3.7				96.00	
3. Huqqa base	49693	bottom	Deccan	NрМ 3b	0.78		0.001	80000.0	0.456	0.0005	3.8	0.50	0.005		94.47	0.8
											3.9				95.40	0.8
4.Huqqa base	2183/7	neck, inside	Deccan	NG 2	6.14	0.004	0.006	0.00014	0.032	0.0003	4.0	0.22	0.003		94.7	
	Vu 2919								0.060		4.6				93.3	0.9
5.Huqqa base	A 9951	neck, inside	Deccan	NpM 4a	4.80	93.4	0.015	0.03088			6.3		0.019		0.00	0.3
						91.8					7.5				0.20	0.3
5.Huqqa base	A 9951	collar	Deccan	NpM 4b		1.550	0.002	0.00046	0.005	0.0010					96.14	1.7
						5.200					0.1				93.10	1.7
6.Huqqa base	3573/1	neck, inside	Deccan	NG 3	6.53	0.067	0.009	0.0046	0.175		5.2				94.7	
	Vu 331								0.1		6.2				92.1	0.7
7.Bottle, surahi	13574	foot	Deccan	NpM 8a	1.38	0.009	0.016	0.00019	0.129	0.0013	6.0	2.02	0.003	1.26	90.16	0.4
											6.0	2.20		0.40	91.00	0.4
7. Bottle.	13574	neck.inside	Deccan	NpM 8b	0.16	0.000	0.001	80000.0	0.166	0.0338			0.001	2.95	96.85	
											0.2				99.80	

APPENDIX 2 Table: Element Composition of *Bidri* Ware

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8. Huqqa base	13772	bottom	Purnea	NpM 2b	0.72	3.333	0.007	0.00137	0.112	0.0019	2.6		0.013	2.72	85.69	5.5
						2.700					2.5			1.00	88.30	5.5
8. Huqqa base	13772	neck, inside	Purnea	NpM 2c	2.13	0.076	0.006	0.00029	0.135	0.0002	2.7	0.42	0.007	1.14	93.30	2.2
											2.7			0.50	94.60	2.2
8. Huqqa base	13772	foot	Purnea	NpM 2a	7.32	0.168	0.015	0.00008	0.264				1.874	8.08		89.6
													2.100	8.40		89.6
9. Huqqa base	13771	bottom	Purnea	NpM 5b	7.56	0.004	0.006	0.00002	0.025	0.0005	0.4	0.12	0.632	46.15	10.26	42.4
											0.5		0.600	39.80	16.60	42.4
9. Huqqa base	13771	spout	Purnea	NpM 5a	4.12	0.003	0.008	0.00002	0.113	0.0006	2.7		0.020	1.65	93.88	1.6
											2.9			0.30	95.30	1.6
10. Bottle, surahi	13544	neck, inside	Purnea	NpM 9a	2.28	0.004	0.011	0.00005	0.089	0.0004	4.1		0.010	1.39	91.33	3.1
											4.3			0.70	91.90	3.1
11. Salver	A 5627	bottom	Lucknow	NpM 7	2.31	0.004	0.017	0.00006	0.018	0.0003	4.4		0.001		93.74	1.8
											4.8				93.40	1.8
12. Salver	43580	bottom	Lucknow	NpM 6	1.10	0.004	0.017	80000.0	0.022		4.2		0.001		93.42	2.3
											4.4				93.30	2.3
13. Bottle, surahi	13401	neck, inside	Hydarabad	NpM 10a	0.45		0.013	0.00008	0.030	0.0007	3.9		0.001		93.67	2.4
											4.3				93.30	2.4
13. Bottle, surahi	13401	lid	Hydarabad	NpM 10b	0.63		0.005	0.00003	0.029	0.0006	3.0				94.87	2.1
											3.0				94.80	2.1
14. Mirror	13402	bottom	Hydarabad	NpM 11	4.20	0.382	0.104	0.00009		0.0005	6.2				93.32	
						0.300					6.7				93.00	