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CHEMICAL COMPOSITION OF BUCKLES DATED FROM 3TH TO THE 7TH CENTURIES AD FOUND IN NORTH-EASTERN BULGARIA

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ABSTRACT

The archaeological belt accessories are important chronological indicators, thus, can be very useful when studying some historical periods. As being subject to fashion, they carry potential information about social status, gender and ethnicity of the owner as well as about commercial connections and production centers. Archaeometric investigations of the development of belt accessories from the Great Migration Period in Bulgaria lags significantly considering the large amount of finds of this kind. In this study a set of 60 buckles from North-Eastern Bulgaria dated from the 3rd to the 7th centuries AD were investigated using inductively-coupled-plasma atomic-emission-spectrometry (ICP-AES) and inductively-coupled-plasma mass-spectrometry (ICP-MS) to check similarities or differences between them. The results show that these belt accessories were made of various kinds of copper alloys such as bronze, brass, or nearly pure copper.

KEYWORDS: bronze buckles, Great Migration Period, chemical composition, ICP-AES, ICP-MS.

1. INTRODUCTION

In the past, belt accessories have played a very important role in people's daily lives. During the Great migration of peoples in South-Eastern Europe many interactions took place between population groups of different origins (Huns, Gotts, Slavs, proto-Bulgarians, etc.) Their cultural, trade, and social contacts reflected on the composition and manufacturing technology of the metal alloys used for different purposes.

Since the beginning of the twentieth century and almost to its end, most of the authors have not paid much attention to the materials used for the manufacture of the archaeological buckles found in Bulgaria. The finds have been rather mentioned than studied for their elemental composition. In most publications belt accessories have been discussed along with other metal objects such as jewelry, tools, hinges, fittings, nails, etc. (Ovcharov, 1984). Several Bulgarian finds were included from foreign authors in their publications related mostly to the whole territory of the Roman Empire or different parts of it. For example Sommer and Büllinger included the set of Kaylaka in Pleven (Sommer, 1984; Büllinger, 1969); Kazanski included tiles and trims with inlays along with buckle and two trims from Sadovets, as well as buckles with Christian inscriptions from the Varna Museum (Kazanski, 1994), etc.

As in the rest of Europe, in Bulgaria archaeometric investigations of belt accessories from the Great Migration Period are still in the very initial stage or even missing. Several publications dealing with the composition of copper alloys from the same period can be found, where incidental analyses of buckles are included (Craddock et al., 2010, Aparaschive et al., 2012). There is only one publication considering a small number (8) of buckles of a particular type – eagleheaded, dated to the Great Migration period in Bulgaria (3rd-7th c. AD) when most of the brass produced have been used primarily for the manufacture of buckles (Kuleff et al., 2002).

The aim of this study is to determine the chemical composition of buckles from Eastern Bulgaria dated to the Great Migration Period as well as to enlarge the data on bronze-made items from the Balkan peninsula (Iliev et al., 2007; Giumlia-Mair, 2009; Bonev et al., 2015). On the basis of the chemical composition data and its statistical treatment we obtain analytical results, which we use to suggest possible differences in the chemical content of the finds in dependence of the geographical region. As next step we also make an attempt to verify if there are chronological differences between the buckles from the same region.

2. MATERIALS AND METHODS

The materials studied included 60 copper alloy buckles dated from the 3rd to the 7th centuries AD (the Great Migration Period or Late Antiquity and Early Medieval period in Bulgaria). A short description of the analyzed buckles according to the place of their discovery, chronology and type are listed in Table 1, while a map of Bulgaria with the locations of several archaeological museums in Eastern Bulgaria is presented in Figure 1.

Table 1. Description of the specimens analyzed in this study.

3000.YM: Chance find, in the Regional History Museum Yambol. Bronze buckle, moulded; length 5.05 cm, width 2.9 cm. Second half of 6th c.-beg. of 7th c.
3002.NZ: Karanovo, municipality Nova Zagora in the Historical Museum of Nova Zagora. Bronze strap-end, attached to belt by one rivet; length 3,45 cm, max. width 3,0 cm.2nd-4th c.
3003.NZ: Karanovo, municipality Nova Zagora, in the Historical Museum of Nova Zagora. Bronze buckle, plate attached to belt by two rivets; length of plate 2,9 cm, width of loop 3,9 cm. 3th-4th c.
3004.NZ: Lyubenets, municipality Nova Zagora in the Historical Museum of Nova Zagora. Bronze buckle, plate attached to belt by two rivets; length 4,35 cm, width of loop 3,7 cm. 4th c.
3005.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze plate of buckle, openwork, moulded; length 2,4 cm, width 2,7 cm. Second half of 6th c.-beg. of 7th c.
3008.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by three rivets; length 3,95 cm, width of loop 2,8 cm. 4th c.
3009.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by two rivets; length of loop 2,55 cm, width of loop 3,65 cm. 3th-4th c.
3010.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by three rivets; length of plate 2,5 cm, width of loop 2,8 cm. 4th c.
3011.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by two rivets; length of plate 2,75 cm, width of loop 2,8 cm. 2nd-4th c.

3012.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by three rivets; length of plate 2,7 cm, width of loop 3,5 cm. 3th-4th c.
3012a.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze tongue of buckle; length 2,3 cm, width 0,8 cm. 3th-4th c.
3013.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by three rivets; length of plate 2,75 cm, width of loop 3,45 cm. 4th c.
3014.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by three rivets; length 5,9 cm, width of loop 4,85 cm. 4th c.
3015.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by two rivets; length 3,8 cm, width of loop 3,4 cm. 3th-4th c.
3015a.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze tongue of buckle – 3015.STZ, length 2,4 cm, width 0,5 cm. 3th-4th c.
3016.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, moulded; length 3,7 cm, width of loop 1,8 cm. Second half of 6th c.-beg. of 7th c.
3017.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by two rivets; length of plate 2,6 cm, width of loop 4,1 cm. 4th c.
3018.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze strap-end, attached to belt by two rivets; length 4,5 cm, max. width 2,1 cm. 4th c.
3019.STZ: Stara Zagora, in the Regional History Museum Stara Zagora. Bronze buckle, plate attached to belt by two rivets; length 7,2 cm, width of loop 7,7 cm. Second half of 4th – beg. of 5th c.
3027.VAR: Chance find, in the Archaeological museum Varna. Bronze buckle, moulded; length 4,1 cm, max. width of loop 4,1 cm. Second half of 6th c.-beg. of 7th c.
3028.VAR: Chance find, in the Archaeological museum Varna. Bronze plate of buckle, moulded, openwork; length 2,8 cm, width 2,7 cm. Second half of 6th c.-beg. of 7th c.
3029.VAR: Chance find, in the Archaeological museum Varna. Bronze buckle, moulded; length 3,45 cm, max. width of loop 3,65 cm. Second half of 6th c.-beg. of 7th c.
3030.VAR: Chance find, in the Archaeological museum Varna. Bronze buckle, moulded; length without tongue 2,9 cm, max. width 1,35 cm. Second half of 6th c.-beg. of 7th c.
3031.VAR: Chance find, in the Archaeological museum Varna. Bronze buckle, moulded; length 3,8 cm, max. width of loop 4,6 cm. Second half of 5th c.- 6th c.
3031a.VAR: Chance find, in the Archaeological museum Varna. Bronze tongue of buckle, moulded; length 4 cm, max. width 1,5 cm.Second half of 5th c.- 6th c.
3032.VAR: Chance find, in the Archaeological museum Varna. Bronze loop of buckle, moulded; length 2,9 cm, width 3,2 cm. Second half of 6th c.-beg. of 7th c.
3033.VAR: Chance find, in the Archaeological museum Varna. Bronze plate of buckle, moulded, openwork; length 4,1 cm, max. width 2,95 cm. Second half of 6th c.-beg. of 7th c.
3034.VAR: Chance find, in the Archaeological museum Varna. Bronze plate of buckle, moulded; length 3,7 cm, width 2,45 cm.Second half of 6th c.-beg. of 7th c.
3035.VAR: Chance find, in the Archaeological museum Varna. Bronze loop of buckle; length 2,15 cm, width 2,7 cm. 4th c.
3036.VAR: Chance find, in the Archaeological museum Varna. Bronze loop of buckle, moulded; length 2,7 cm, width 4,5 cm. Second half of 5th c.- 6th c.
3037.BLA: Late antique fortress near Byala, Varna district. Bronze buckle, moulded, openwork; length 3,6 cm, width 2,3 cm. Second half of 6th c.-beg. of 7th c.
3038.BLA: Late antique fortress near Byala, Varna district. Bronze buckle, moulded; length 5,75 cm, width 3,55 cm. Second half of 6th c.-beg. of 7th c.
3039.BLA: Late antique fortress near Byala, Varna district. Bronze plate of buckle, moulded, openwork; length 3,1 cm, width 2,5 cm. Second half of 6th c.-beg. of 7th c.
3040.BLA: Late antique fortress near Byala, Varna district. Bronze plate of buckle, moulded, openwork; length 2,65 cm, width 2,45 cm. Second half of 6th c.-beg. of 7th c.

3041.BLA: Late antique fortress near Byala, Varna district. Bronze buckle, moulded; length 3,1 cm, width 2,5 cm. Second half of 6th c.-beg. of 7th c.
3042.BLA: late antique fortress near Byala, Varna district. Bronze loop of buckle, moulded; length 3,1 cm, width 4,7 cm. Second half of 5th c.- 6th c.
3043.BLA: Late antique fortress near Byala, Varna district. Bronze buckle, moulded; length 4,85 cm, width 2,8 cm. Second half of 6th c.-beg. of 7th c.
3044.BLA: Late antique fortress near Byala, Varna district. Bronze tongue of buckle, moulded, there are a decoration imitative cells for inlay; length 4 cm, diameter of the round part 1,5 cm. Second half of 5th c.- 6th c.
3045.BLA: Late antique fortress near Byala, Varna district. Bronze mould for the casting of plate of buckles; length 3,4 cm, width 4,6 cm. Second half of 5th c.- 6th c.
3047.RZG: Abrittus near Razgrad in the "Abrittus" museum. Bronze buckle, moulded, openwork; length 4,3 cm, max. width 2,9 cm. Second half of 6th c.-beg. of 7th c.
3048.RZG: Abrittus near Razgrad in the "Abrittus" museum. Bronze buckle, plate attached to belt by two rivets; length 4,3 cm, width 3,4 cm. 4th c.
3049.RZG: Abrittus near Razgrad in the "Abrittus" museum. Bronze strap-end, attached to belt by two rivet; length 2,15 cm, max. width 2,1 cm. 4th c.
3050.RZG: Abrittus near Razgrad in the "Abrittus" museum. Bronze buckle, plate attached to belt by two rivets; length 3,74 cm, width 4,2 cm. 4th c.

The sampling was performed by scraping a small amount of shavings from the back surface of the metal objects using small drills. Surface layers were pre-treated to avoid the penetration of preservative chemicals into the samples. Elemental analysis of the buckle samples was performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, *Perkin Elmer Optima 7000 DV*) and inductively coupled plasma-mass spectrometry (ICP-MS, *Perkin Elmer ELAN DRC-e*). Applying both analytical techniques the concentrations of 14 elements were determined (As, Bi, Co, Cd, Cu, Fe, Mn, Ni, P, Pb, Sb, Se, Sn, and Zn). Approximately 20 mg of each sample were initially dissolved in "aqua regia" and diluted to a volume of 50 ml. An external calibration strategy using well characterized matrix-matched standards and standard reference materials with similar chemical and physical properties (e.g. BAM 228) was chosen for the analysis of the archaeological samples. Precision of the method was estimated using the SR-criteria according to McFarren et al., 1970. Results show SR values below 25% for all of the measured elements which is an excellent agreement between analytical data and certified values.

Statistical treatment of the analytical data obtained was performed using the *Statistica 10* software. All of the results for the elemental composition of the investigated copper alloy buckles were subjected to cluster analysis.

3. RESULTS

3.1 Elemental composition

Analytical data of the elemental composition obtained for the investigated copper alloy buckles are listed in Table 2. The concentration of copper for the investigated samples is in the range of 70 and 99%, but for the majority of the buckles this element varies between 75 and 85% with average value of 82% (Figure 2). It is noteworthy that four belt accessories are made of nearly pure copper and all of them are found in the close regions of Stara Zagora and Nova Zagora (Figure 1).

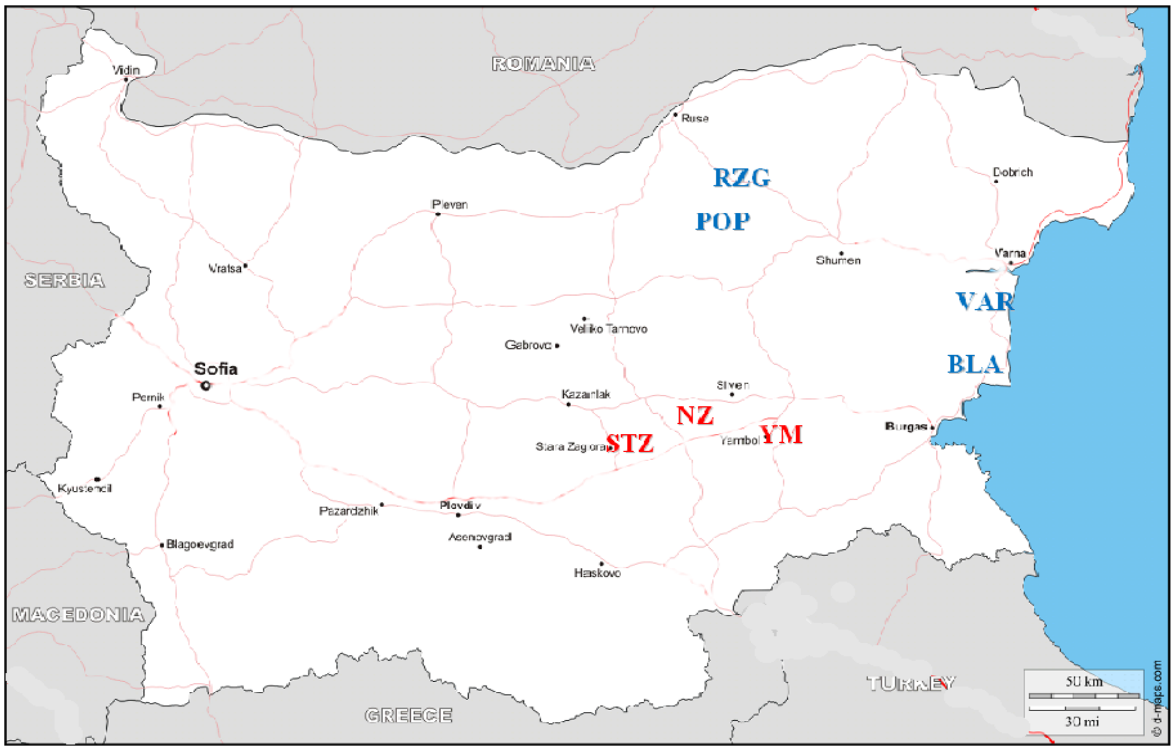

Figure 1. Map of Bulgaria with the sampling sites regions pointed: BLA – Byala, Varna Region; NZ – Nova Zagora, Sliven Region; POP – Popovo, Targovishte Region; RZG – Razgrad Region; STZ – Stara Zagora Region; VAR – Varna Region; YM – Yambol Region.

Table 2. Total percentage of the elemental composition of the belt accessories studied.

Sample	Cluster	As	Cd	Fe	Pb	Mn	Ni	Se	P	Zn	Sn	Sb	Bi	Co	Cu
3015.STZ	3	<0.001	0.001	0.078	0.19	0.006	0.011	<0.001	0.041	0.104	0.038	0.001	0.001	<0.001	99.5
3012.STZ	3	0.009	0.007	0.060	0.23	0.001	0.015	<0.001	<0.001	0.259	0.032	0.004	0.007	0.001	99.4
3015a.STZ	3	<0.001	<0.001	0.129	0.25	0.006	0.007	<0.001	0.146	0.097	0.035	<0.001	0.001	<0.001	99.3
3013.STZ	4	0.039	0.007	0.243	0.59	0.003	0.109	<0.001	0.041	16.6	0.353	0.003	0.001	0.029	81.9
3012a.STZ	4	0.073	<0.001	0.040	0.64	0.001	0.183	<0.001	<0.001	11.8	0.169	0.006	0.001	0.009	87.1
3010.STZ	4	0.389	0.004	<0.001	0.68	<0.001	0.353	<0.001	0.084	14.2	0.143	0.019	0.005	0.003	84.1
3009.STZ	3	<0.001	<0.001	<0.001	0.74	<0.001	0.028	<0.001	0.036	0.047	0.099	0.003	0.001	0.001	99.3
3056.POP	1	0.252	<0.001	0.268	0.77	0.004	0.092	<0.001	0.034	10.5	0.353	0.118	0.013	0.026	87.5
3035.VAR	1	0.149	<0.001	0.494	0.85	0.001	0.079	<0.001	<0.001	11.6	2.89	0.127	0.002	0.005	83.8
3011.STZ	2	0.029	<0.001	0.346	0.86	0.008	0.020	<0.001	0.475	5.56	0.272	0.021	0.001	0.003	92.5
3049.RZG	1	0.079	<0.001	0.131	0.87	<0.001	0.047	<0.001	0.037	4.11	6.98	0.071	0.002	0.006	87.7
3066.POP	1	0.058	<0.001	0.080	0.98	0.001	0.034	0.028	0.031	1.18	4.96	0.101	0.004	0.003	92.5
3014.STZ	4	0.220	<0.001	0.085	1.01	0.001	0.097	<0.001	0.007	13.4	0.748	0.051	0.009	0.003	84.3
3004.NZ	4	<0.001	<0.001	0.216	1.04	<0.001	0.026	<0.001	<0.001	11.3	0.217	<0.001	<0.001	0.007	87.2
3045.BLA	1	0.255	<0.001	0.118	1.07	<0.001	0.091	<0.001	<0.001	0.656	4.22	0.162	0.009	0.018	93.4
3038.BLA	4	0.113	<0.001	0.093	1.09	0.001	0.064	<0.001	0.045	19.8	0.072	0.069	0.003	0.003	78.6
3051.RZG	4	0.050	0.004	0.068	1.29	<0.001	0.055	<0.001	0.031	14.2	0.177	0.045	0.003	<0.001	84.0
3057.POP	4	0.013	<0.001	0.094	1.32	0.001	0.042	<0.001	0.085	20.5	0.320	0.019	0.002	<0.001	77.6
3047.RZG	1	0.245	0.001	0.264	1.34	0.001	0.112	<0.001	0.073	4.34	3.02	0.128	0.016	0.008	90.4
3058.POP	4	0.119	<0.001	0.155	1.39	<0.001	0.086	<0.001	<0.001	11.5	0.801	0.043	0.009	0.003	85.9
3063.POP	4	0.359	0.003	0.268	1.73	0.001	0.092	<0.001	0.019	15.8	1.122	0.089	0.004	0.015	80.5
3000.YM	4	0.067	<0.001	0.063	1.79	<0.001	0.091	<0.001	<0.001	22.4	0.032	0.005	0.001	0.006	75.5
3044.BLA	4	0.242	0.001	0.104	1.86	<0.001	0.068	0.021	0.084	23.1	1.142	0.057	0.002	0.018	73.2
3033.VAR	4	0.116	<0.001	0.061	1.98	0.003	0.073	0.030	0.002	19.0	0.035	0.030	0.006	0.001	78.6
3043.BLA	4	0.167	0.001	0.215	2.10	0.001	0.079	<0.001	<0.001	25.1	0.113	0.044	0.004	0.008	72.1
3019.STZ	4	0.028	<0.001	0.248	2.27	<0.001	0.041	<0.001	<0.001	15.4	0.169	0.008	0.001	0.001	81.8
3052.RZG	4	0.184	0.001	0.335	2.35	<0.001	0.109	<0.001	0.016	14.5	0.583	0.044	0.002	0.017	81.8
3032.VAR	4	0.113	0.001	0.120	2.37	0.001	0.037	<0.001	0.014	18.8	0.143	0.089	0.001	0.001	78.3
3061.POP	4	0.268	<0.001	0.201	2.45	0.001	0.086	0.015	0.044	14.9	0.137	0.031	0.006	0.037	81.8
3054.RZG	2	0.054	<0.001	1.769	2.50	0.012	0.029	<0.001	0.388	11.9	0.994	0.034	0.004	0.001	82.4
3031a.VAR	1	0.149	<0.001	0.211	2.55	0.002	0.085	<0.001	0.038	17.9	0.927	0.123	0.003	0.001	78.0

3060.POP	4	0.120	<0.001	0.134	2.74	0.001	0.059	0.017	<0.001	23.8	0.444	0.049	0.005	0.006	72.5
3031.VAR	4	0.110	<0.001	0.052	2.86	0.001	0.050	<0.001	0.009	20.7	0.597	0.100	0.003	0.001	76.1
3039.BLA	4	0.189	0.004	0.129	3.00	0.001	0.051	0.025	<0.001	21.7	0.456	0.034	0.007	0.009	74.8
3005.STZ	4	0.475	0.001	0.119	3.03	0.002	0.051	<0.001	0.027	22.6	0.072	0.024	0.003	0.004	73.5
3003.NZ	2	0.037	<0.001	0.229	3.21	0.010	0.030	<0.001	0.629	6.08	1.662	0.013	0.001	0.002	88.1
3008.STZ	4	0.036	<0.001	0.309	3.59	0.001	0.060	<0.001	0.087	0.179	0.893	0.041	<0.001	0.030	94.8
3034.VAR	4	0.181	<0.001	0.156	3.84	0.002	0.088	0.029	0.006	23.8	0.211	0.047	0.007	0.006	71.5
3040.BLA	4	0.203	<0.001	0.126	3.94	<0.001	0.076	<0.001	<0.001	22.8	0.679	0.036	0.017	0.002	72.1
3002.NZ	3	<0.001	<0.001	0.081	4.05	0.001	0.044	<0.001	0.062	0.008	0.652	0.001	0.004	<0.001	95.1
3028.VAR	4	0.128	<0.001	0.080	4.07	0.001	0.051	<0.001	0.046	25.6	0.120	0.088	0.003	<0.001	69.7
3062.POP	4	0.182	0.001	0.216	5.91	0.001	0.179	<0.001	0.014	19.7	0.134	0.022	0.007	0.006	73.6
3018.STZ	1	0.206	<0.001	0.111	6.06	<0.001	0.065	<0.001	<0.001	8.62	2.453	0.061	0.007	0.007	82.4
3041.BLA	4	0.121	<0.001	0.926	6.45	<0.001	0.082	<0.001	<0.001	13.1	3.71	0.044	0.003	0.059	75.6
3017.STZ	1	0.060	0.013	0.022	6.49	<0.001	0.072	<0.001	0.092	4.93	3.98	0.011	0.002	0.010	84.3
3037.BLA	4	0.296	<0.001	0.158	6.60	0.002	0.043	<0.001	0.013	22.4	0.188	0.089	0.007	0.003	70.2
3067.POP	1	0.069	<0.001	0.401	7.16	<0.001	0.040	<0.001	0.026	9.03	2.07	0.048	0.002	0.001	81.2
3065.POP	1	0.103	<0.001	0.165	8.33	<0.001	0.067	<0.001	0.019	0.251	7.66	0.113	0.002	0.005	83.3
3030.VAR	1	0.168	<0.001	0.189	9.01	0.001	0.106	0.017	<0.001	11.6	3.80	0.088	0.004	0.005	74.9
3027.VAR	1	0.216	<0.001	0.238	9.05	<0.001	0.100	<0.001	<0.001	7.11	6.04	0.139	0.008	0.009	77.2
3042.BLA	1	0.063	0.014	0.163	9.39	<0.001	0.058	<0.001	0.006	6.16	5.72	0.062	0.001	0.022	78.3
3059.POP	1	0.091	<0.001	0.066	9.79	<0.001	0.067	<0.001	0.025	2.29	4.67	0.103	0.001	0.005	82.9
3064.POP	1	0.223	<0.001	0.147	10.07	<0.001	0.072	<0.001	0.007	10.5	3.87	0.066	0.006	0.007	75.2
3036.VAR	1	0.155	<0.001	0.137	10.19	<0.001	0.047	<0.001	<0.001	1.66	6.62	0.107	0.002	0.017	81.1
3050.RZG	1	0.085	<0.001	0.283	10.69	<0.001	0.047	<0.001	<0.001	8.12	1.96	0.159	0.003	0.002	78.7
3016.STZ	1	0.077	<0.001	0.096	10.71	0.001	0.107	<0.001	<0.001	9.83	0.832	0.014	0.001	0.007	78.3
3029.VAR	1	0.173	<0.001	0.173	11.12	<0.001	0.123	0.040	0.037	16.8	0.902	0.078	0.008	0.004	70.5
3048.RZG	1	0.401	<0.001	0.159	12.36	<0.001	0.073	<0.001	0.013	5.47	5.14	0.101	0.008	0.009	76.3
3053.RZG	1	0.396	0.001	0.204	13.34	<0.001	0.060	0.027	0.017	4.22	2.47	0.135	0.028	0.013	79.1
3055.POP	1	0.331	<0.001	0.087	15.31	0.001	0.115	<0.001	<0.001	1.73	4.29	0.086	0.006	0.011	78.1

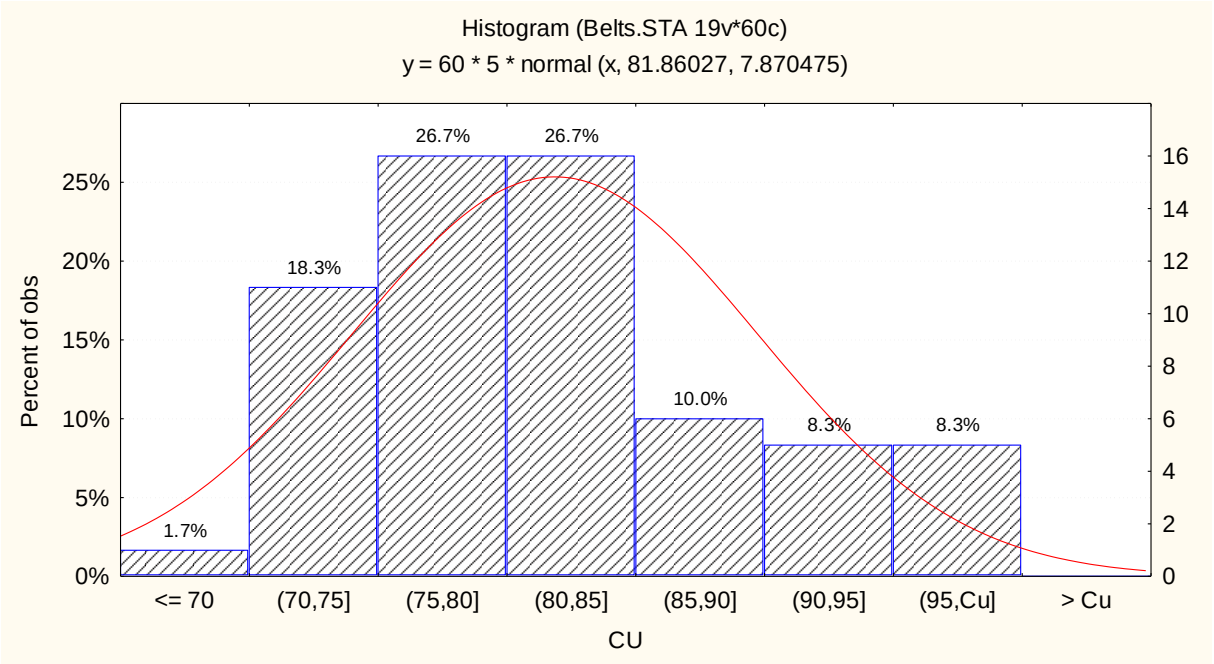

Figure 2. Histogram of copper distribution for the samples.

Concentration of lead varies from 0.19% up to 15%, but the majority of the finds (approximately 65%) have Pb content below 4%. Due to the presence of lead in ore the melting point of the alloy decreases and the melted metal achieves higher fluidity. Therefore higher amount of Pb in the bronze alloy causes better properties of the smelted metal and improves the process of casting (Scott, 1991). It should be pointed out that even a lead content of slightly more than 3% does not necessarily show intentional adding to the alloy. It can originate from the copper ore. When the concentration of Pb exceeds 5% it cannot be dissolved in copper which causes cracking of the final produced metal object. Therefore the metal is not workable through hammering in these cases.

Figure 3 shows a scatter plot of two dimensional distribution of the investigated samples according to the contents of tin and zinc. A significant number of the buckles studied are made of brass. The content of Zn for approximately 58% of all investigated finds is up to 10%. Twenty five of the belts accessories (or 45% of all samples) show Zn concentration between 5 and 10%, while all of the rest finds contain less than 5% of Zn. The zinc content gradually decreases in the case of multiple assimilation of the metal alloys. The low zinc content is therefore evidence that the craftsmen either used scrapped items, or added lead, bronze or brass to the copper alloy.

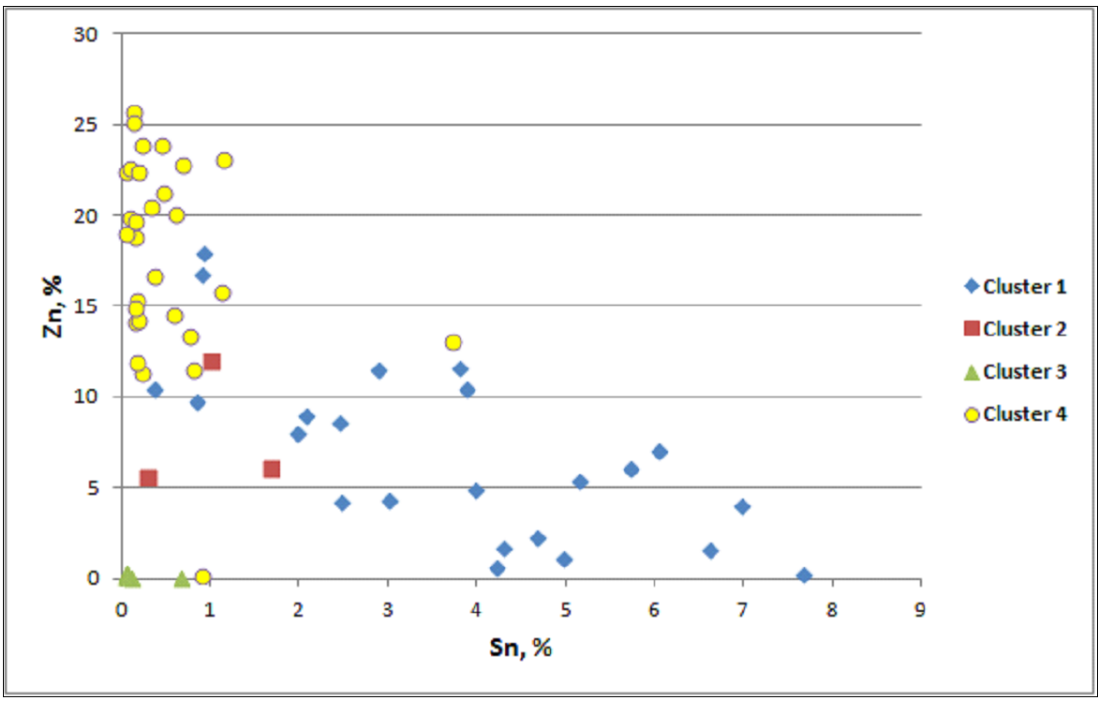

Figure 3. Sn vs. Zn concentrations plot. The distribution of the findings in four groups according to the cluster analysis performed is shown. Significant differences in the Sn/Zn concentrations for the four clusters are notable (see part 3.2).

Four of the samples (3027.VAR, 3030.VAR, 3042.BLA and 3048.RZG) with respectively low zinc concentrations (5.47%-11.66%) have lead contents between 9.01% and 12.36 % and also show high tin levels (3.80%-6.04%). This alloy, the so-called leaded red brass, could indicate mixing of brass with some scrap bronze. These finds are dated from the second half of the 6th century to the beginning of the 7th century AD, the second half of the 5th century AD to the 6th century AD, and the older one is from the 4th century AD respectively. All of them origin from North-Eatern Bulgaria. The specimens represent different types – these from Varna region have similar typology and dating, but the rest are not similar even in dating, typology and geographical region.

The intentional addition of arsenic (up to 3%) and tin (up to 5%) to the alloy aims to achieve lighter shade of the bronze alloy. In our case, however, finds showing level of As more than 1% are in fact missing. In addition, only 17% of the samples have Sn content up to 5% and all of these specimens were found in North-Eastern Bulgaria.

Concentration of Ni above 2% in the alloy increases its strength and therefore minerals containing nickel have been usually added to the metal artifacts made by casting in antiquity. In our case, however, Ni concentrations rarely exceed 0.1% which means that additional amount of nickel was not intentionally included to the metal finds, as seen from Figure 4. On the other hand, lead has been most probably intentionally added during the production process of many of the specimens which increases the plasticity of the alloy (the Pb content reaches 11%). Therefore we may assume that the majority of the metal buckles studied were made by forging.

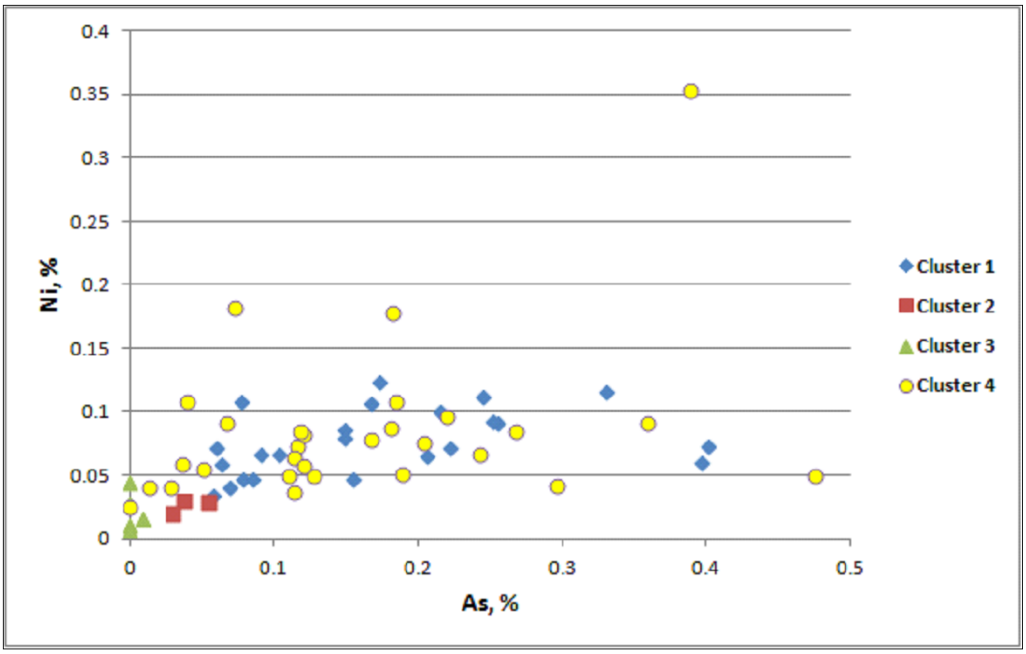

Figure 4. As vs. Ni concentrations plot.

3.2 Clustering classification

Individual results were treated by hierarchical cluster analysis, based on the Ward's method algorithm and the squared Euclidean distance. The resulting dendrogram is presented in Figure 5. On the basis of the similarity in the chemical composition the investigated samples were grouped in four clusters and the average concentrations of lead, zinc and tin for obtained clusters are presented in Figure 6. Cluster analysis results show good agreement with the geographical discrimination of the studied specimens (Table 3). The artifacts made of Pb-bronze or brass are almost equal in number and are very good distinguished by clusters 1 and 4, including the majority of the specimens analyzed (Table 3, Figures 3, 6). As mentioned before, it is noteworthy that the buckles from the Stara Zagora Region are made of nearly pure copper. Moreover, the specimens discovered in the southern part of East Bulgaria show greater variety in their alloy type (including Pb-bronzes, mixed alloys, brass, brass with higher lead content and pure copper) compared to those from Northeastern Bulgaria.

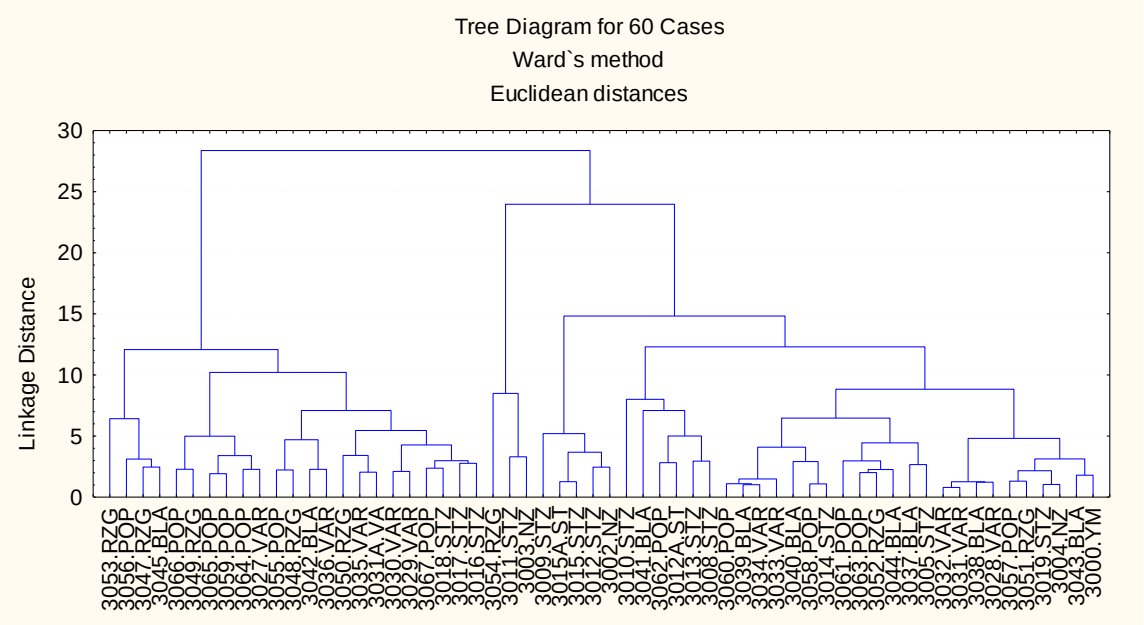

Figure 5. Dendrogram of obtained cases of the belt accessories studied.

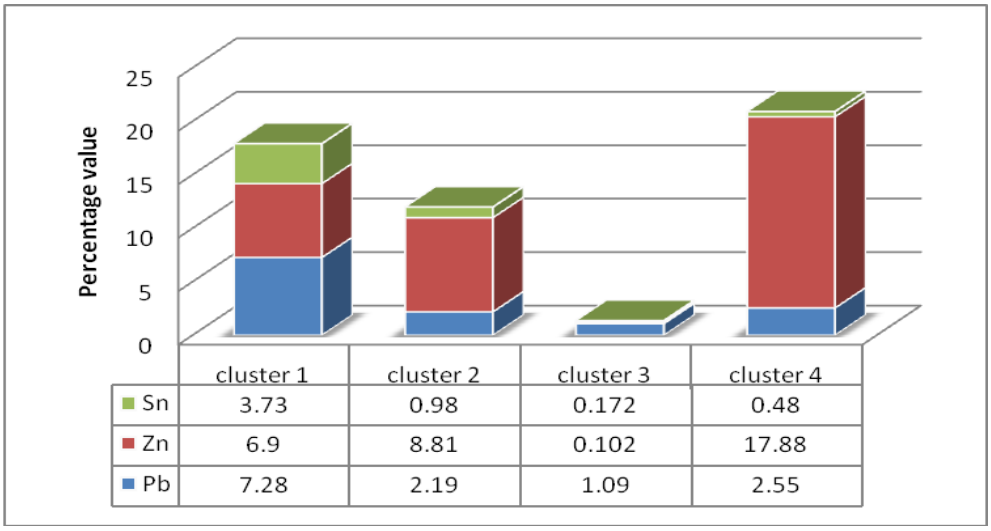

Figure 6. Cluster percentage value of average concentrations of Pb, Zn and Sn.

Table 3. Type of alloy for the majority of the members of each cluster obtained.

Cluster	*Total share of the members of each cluster (italic – NE Bulgaria; bold – SE Bulgaria)*							*Type of alloy for the majority of the members*
	BLA	*POP*	*RZG*	*VAR*	**NZ**	**STZ**	**YM**	
Cluster 1	*2*	*7*	*5*	*6*	**-**	**3**	**-**	Leaded bronze with addition of Sn; red brass
Cluster 2	-	-	*1*	-	**1**	**1**	**-**	Mixed alloy
Cluster 3	-	-	-	-	**1**	**3**	**-**	Nearly pure copper
Cluster 4	*7*	*6*	*2*	*5*	**-**	**7**	**1**	Brass with higher lead content

The tin concentration in the cluster 1 specimens rarely exceeds 5%, however, this amount is sufficient for the alloy to be considered as bronze. On the other hand, the zinc content in many of the studied buckles from that group is significant (higher than 7%) and for that reason they can be considered as made of brass and leaded (tin-) bronze alloy as well. Such conclusions suggest that the finds belonging to cluster 1 were probably made by melting of older bronze objects to which some zinc has been added. Unlike them, the buckles from the other three clusters (including nearly all specimens from South Bulgaria and approximately the half of the samples from the North Bulgaria, Table 3) do not contain significant amount of tin. Therefore they have been made most likely by melting of older brass/bronze artifacts or using newly prepared brass alloy. As an exception of that group we may note again the specimens from the Stara Zagora museum, made of pure copper.

3.3 Chronology and territorial distribution of the samples belonging to the four clusters

The tested buckles are divided into four chronological groups (see Fugures 7-9) according to their period of circulation.

The First chronological group comprises the period from the end of the 3rd to the end of the 4th century AD. It includes belt fittings from all clusters, however, the largest number of samples from this period belongs to cluster 1. This chronological group includes a great variety of belt fittings types – buckles, frames, appliqués and belt tips. All buckles that possess well preserved plates belong to a homogeneous group with elliptical to oval shaped plates. Two of the three belt tips in cluster 1 are also of one and the same type – the so called amphora-shaped. The territorial distribution of the samples in the first group indicates that the majority of them come from Northeastern Bulgaria and the Stara Zagora region (Figure 1).

The Second chronological group comprises a period from the second half of the 4th century to the beginning of the 5th century AD. This group partially coincides in time with the first chronological group, but it comprises types of buckles that appear and spread after the middle of the 4th century up to the first decades of the 5th century. It includes buckles only from cluster 4.

A Third chronological group comprises the period from the second half of the 5th century to the end of the 6th century. It includes buckles from clusters 1

and 4 that both contain an almost equal number of samples from that period. Among the specimens from this group are buckles, ripped frames, prongs and a matrix for a clay mould for casting. The territorial distribution indicates that the samples from Northeastern Bulgaria predominate as only one sample in the group comes from Southeastern Bulgaria.

The fourth chronological group comprises the period from the second half of the 6th century to the beginning of the 7th century. Like the previous group, it includes belt accessories from clusters 1 and 4. In this case, however, the samples belonging to cluster 4 are almost twice in number than those from cluster 1. The fourth chronological group includes buckles and buckle plates. Only one of the buckles is of the type used for belt pouches. The rest are for belt fastening. Samples come from Popovo, Varna, Byala (Varna Region), Yambol and Stara Zagora. The territorial distribution indicates that the samples from Northeastern Bulgaria predominate, as only two samples in the group come from Southeastern Bulgaria.

The four clusters were defined according to similarity of the chemical composition of the tested samples of belt fittings. The first, third and fourth chronological groups are represented in cluster 1. An emerging trend indicates a peak of the 4th century samples compared to those from the 5th to the beginning of the 7th century. Clusters 2 and 3 include samples from the first chronological group only. All chronological groups are represented in cluster 4. The trend of increment in number of belt fitting samples in the chronological groups is the opposite of that in cluster 1. Those from the second half of the 6th century to the beginning of the 7th century AD reach a notable peak in comparison to the samples from the other periods. The trends that have been outlined refer only to the samples taken from the region of Eastern Bulgaria. The results should not be considered to be universally valid without comparison with samples from other regions of Bulgaria.

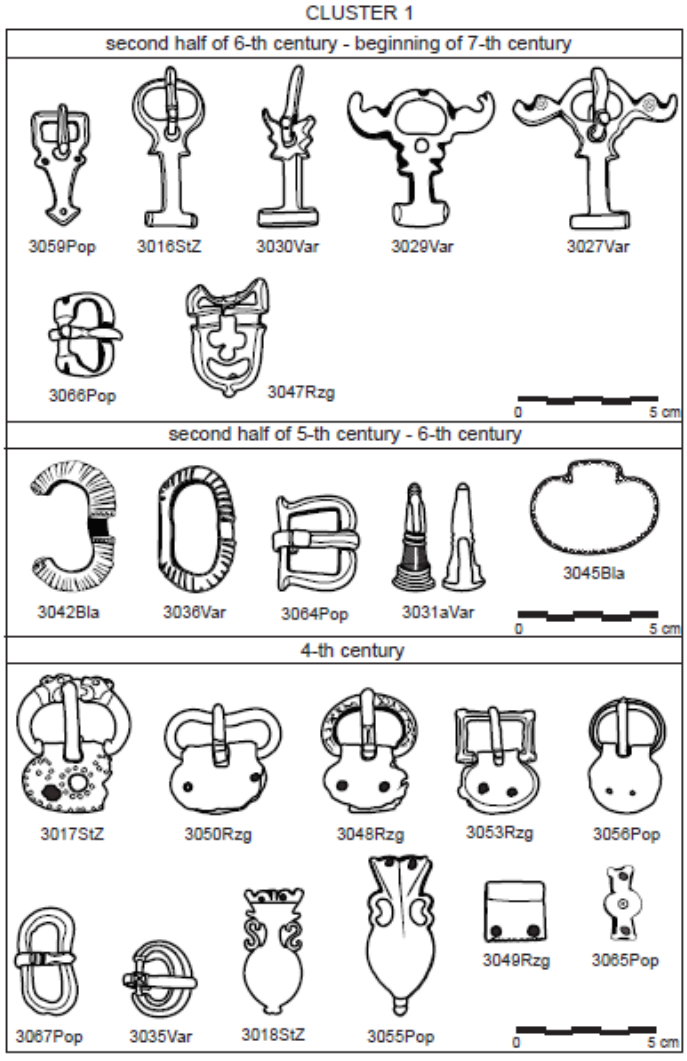

Figure 7. Chronology distribution of the members in cluster 1.

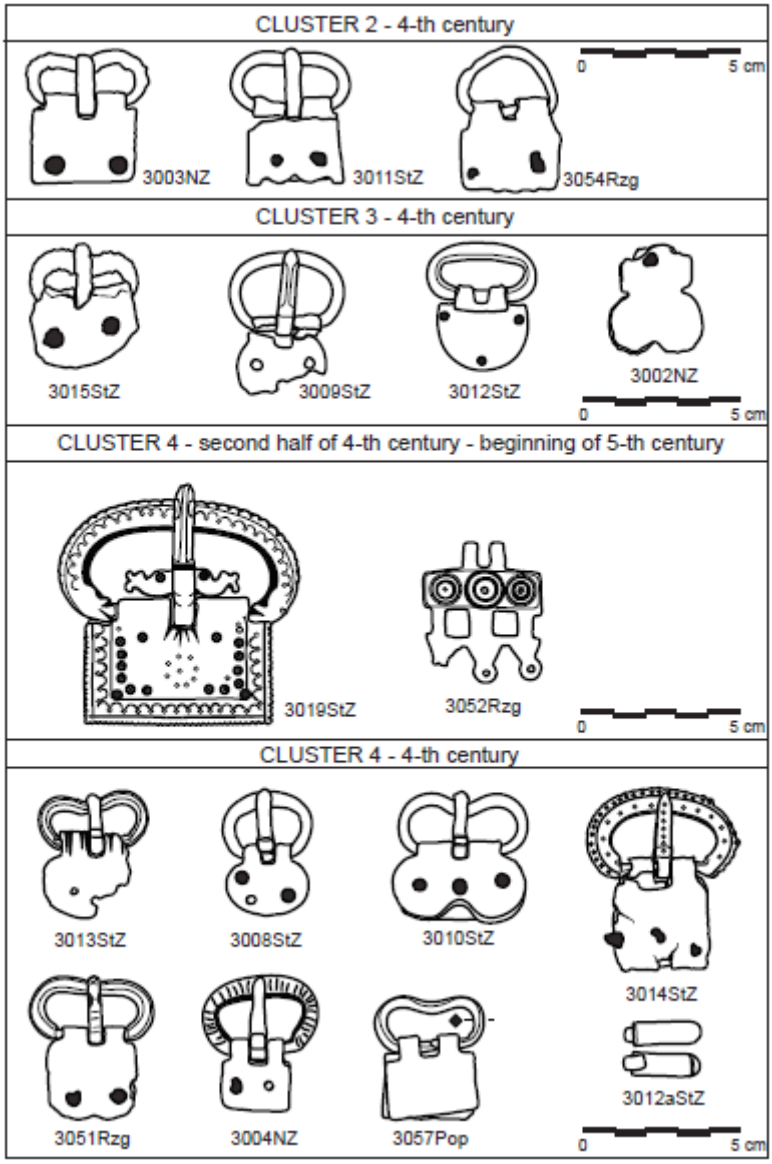

Figure 8. Chronology distribution of the members in clusters 2 and 4.

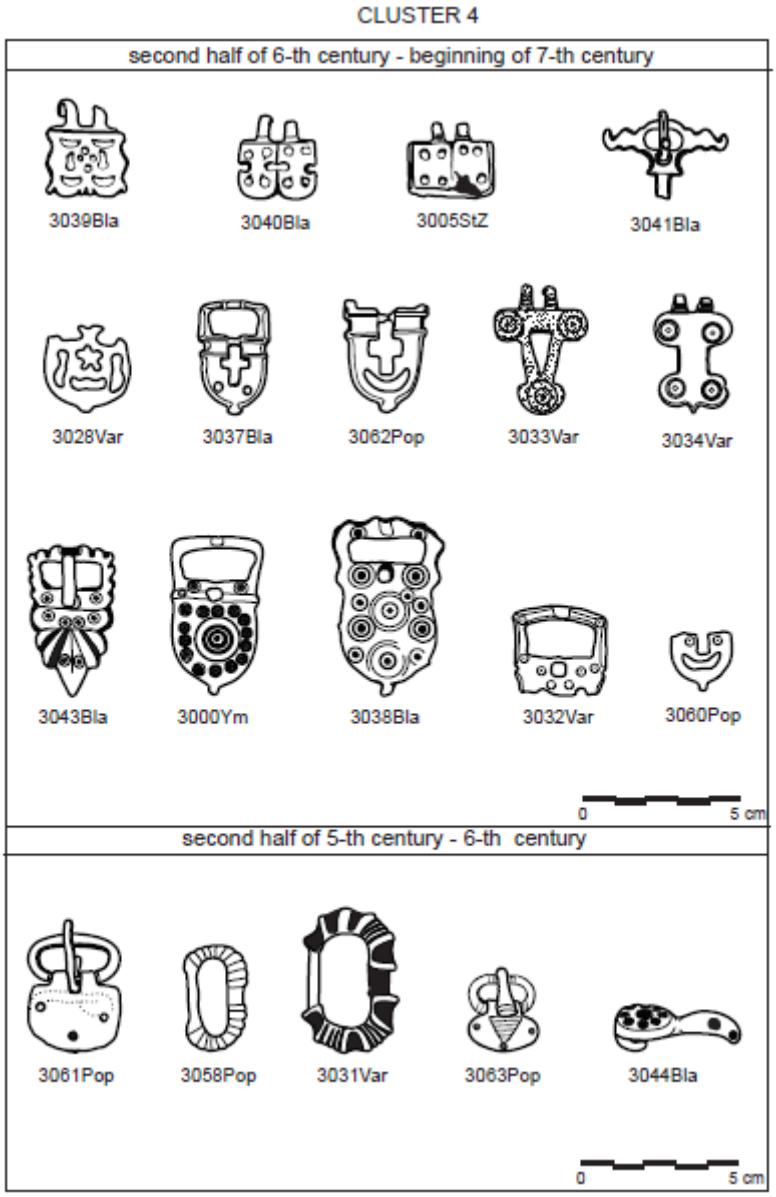

Figure 9. Chronology distribution of the members in cluster 4 (cont.).

4. DISCUSSION

The copper alloy buckles studied here date from the end of the 3rd to the beginning of the 7th century AD. This historical period is characterized by cultural changes in the Balkan Region (and Europe as well) and considerable contacts between, and movement into, areas that were using different alloy types.

A significant part of the buckles analyzed were made of bronze, or leaded (-tin) bronze. There are also specimens made of mixed alloys containing both of tin and zinc, which make up approximately 25% of the total, or brass (almost 50% of the total). Even the so-called red brass and nearly pure copper alloys are encountered. It appears that the analyzed samples from Bulgaria have a diverse background.

The previously investigated buckles from Bulgaria are dated to the 5th-7th centuries AD. They include the so-called eagle-head buckles, made of brass and two of them are characterized by an unusually high concentration of silver (Kuleff et al., 2002). Other previously studied contemporary copper-based buckles originate from different parts of Europe: the Carpathian basin (Gradcock et al., 2010; Aparaschivei et al., 2012), East Europe (Dnepar region, Saprykina, 2014), North-Western Europe (La Niece and Cowell, 2010) and England (Skinner and Ozgenc, 2004). Based on the results of these studies we can summarize that all of the specimens analyzed show a great variety of copper alloys used for their preparation. It seems that during the Great Migration period people from different parts of Europe

used brass very intensely and even replaced bronze by brass. We have to notice, however, that bronze was still in use predominately in the Western part of Europe during the epoch under discussion (La Niece and Cowell 2010; Skinner and Ozgenc 2004), while in the Byzantine Empire in East Europe brass was already prevalent (Saprykina, 2014; Gradcock et al., 2010). On the other hand typical brass (with zinc content between 15% and 30%) is very rare among the finds of that age. The most widespread alloy composition found after the analyses consists of four main components (Cu-Zn-Pb-Sn) – leaded bronze, tin bronze, gunmetal, brass, red brass or leaded brass. Our results shows that at the beginning of the 3rd century AD in the nowadays area of North-Eastern Bulgaria leaded bronze was the preferred copper alloy. Over time, however, bronze was replaced by brass or leaded brass. We have to notice that there is an evidence of the use of brass in the Bulgarian territory at times prior to the ones officially accepted (Bonev et al., 2015). It was recently reported about some evidences of using the brass before Christ for production of fibulae (Istenić and Šmit, 2007). This fact confirms the assumption that the ancient craftsmen were searching for aesthetic effect by using brass – this alloy is similar to gold in color. The reuse of older bronze materials from the Roman period in Bulgaria is not surprising considering the fact that the Bulgarian territory was a part of the Byzantine Empire. The peak of usage of brass alloys is dated to the 7th century AD. Some authors describe the possible origin of the artifacts made of brass found in Western Europe or other parts of Eastern Europe (the Dnepar Region) with trade contacts from the Byzantine world across the Black Sea (Gradcock et al., 2010; Saprykina, 2014).

5. CONCLUSION

As widespread finds, buckles are quite appropriate for both archaeological and archaeometric investigations. The archaeometric investigation of different types of copper alloy buckles dated from the beginning to the final stage of the Migration Period in Europe reveals that finds were made of bronze or brass with different chemical composition that could be chronologically correlated. Additionally there are buckles made of other multi-element alloys or nearly pure copper. However, the preferred alloy in the 4th century AD was bronze with a high lead content and inclusions of tin. The finds from the second half of the 6th century to the beginning of the 7th century AD show a notable peak for preferable alloys - brass, or even red-brass. This conclusion is made only for the samples found on the territory of the present day North-Eastern Bulgaria.

The metalworking practices and the level of skills attained seem to be comprehensive and competent. Differences in the elemental composition of the specimens could be as a result from chronological reasons or/and place of manufacture. However, question about the metal alloys used during the Migration Period in Europe is still open and future investigations of similar artifacts found in different parts of Europe would be very beneficial. Therefore, the next step of the presented here investigation will be chemical and metallographic analysis of series of buckles from other parts of Bulgaria aiming to establish chronological, territorial and type-dependant differences of the alloys used.

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