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CHARACTERIZATION OF THE CHEMICAL COMPOSITION OF MEDIEVAL GLASS FINDS FROM SOUTH BULGARIA

Valentina Lyubomirova*[1], Žiga Šmit[2,3], Helena Fajfar[2], Boika Zlateva[1], Rumyana Djingova[1,] Ivelin Kuleff[1]

[1]University of Sofia, Faculty of Chemistry and Pharmacy, 1, James Bourchier blvd., BG-1164-Sofia, BG
[2]University of Ljubljana, Faculty of Mathematics and Physics, Jadranska 19, SI-1000 Ljubljana, Slovenia
[3] Jožef Stefan Institute, Jamova 39, POB 3000, SI-1001 Ljubljana, Slovenia

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Corresponding author: Valentina Lyubomirova (vlah@chem.uni-sofia.bg)

ABSTRACT

PIXE and PIGE were used for determination of 23 elements in 50 glass samples excavated in Zlatna Livada – South Bulgaria (dated 11th-12th century AD). Elemental concentrations show that the analyzed fragments belong to soda-lime-silica glasses. Cluster analysis and bivariate plots indicate the use of *natron*, *plant ash* and *mixed alkalis* as well as production according Near East and Roman-province recipes. The metal oxides responsible for coloration were also investigated. The blue and blue-green colors are due either to CoO or to high concentration of FeO (blue: 3.3-6.3%, blue-green: 1.23-2.83%), melted in reducing atmosphere. The melting under oxidizing environment determined the higher oxidation state of iron oxide and the green color of some of the glasses (0.7-3.4% Fe_2O_3). Different shades of brown color are due to the high concentration of Fe_2O_3 (2.4-4.9%) and Mn_2O_3 (0.3-0.7%) melted in oxidizing atmosphere. Discoloration of the glasses is achieved by the presence of high amount of MnO (0.6-2%). A comparison to other medieval Bulgarian glasses was performed.

KEYWORDS: Medieval glass bracelets, PIXE, PIGE, glass technology.

1. INTRODUCTION

Investigation of the chemical composition of medieval glasses, and its relation to broader aspects of the processes of production, the choice of raw materials and provenance has been the subject of a number of recently published studies for Italian (Brianese et al. 2005; Genga et al. 2008; Cagno et al. 2010; 2012a,b; Silvestri and Marcante 2011), Slovenian (Smit et al. 2002; 2012), Romanian (Bugoi et al. 2013), Spanish (Ortega-Feliu et al. 2011; Kunicki-Goldfinger et al. 2014), French (Lombardo et al. 2013; Kunicki-Goldfinger et al. 2014), English, German, and Dutch (Kunicki-Goldfinger et al. 2014), Portuguese (Delgado et al. 2011), Serbian (Radičević, 2009) and Bulgarian (Bezborodov and Marinov 1958; 1959; 1961a; Kuleff et al. 1985a,b; Kuleff et al. 1988; Djingova and Kuleff 1992; Kuleff and Djingova 1994; Detcheva 2010; 2014; Georgieva et al. 2010a,b; 2014) glass objects. Glass is usually formed from quartz (silica) and sodium or potassium rich flux plus a calcium compound as stabilizer at temperature above 1000°C (Wedepohl and Simon 2010). Elemental analyses of major and minor components of glass reflect the compositional signature of the ingredients: e.g. alumina vs. lime content identifies the raw material of the former used, potash vs. magnesia – the source of flux used (Genga et al. 2008; Freestone et al. 2008). Additionally, the contents of transition metals as Co, Mn, Cu, Fe are indicative for intentional addition of coloring agents to the glass (Kuleff and Djingova 2002).

Different compositions of medieval glass have been measured in recent studies. The type of sand has been established according to the Al_2O_3 content: below 2.5% - siliceous pebbles and Al_2O_3 higher than 2.5% - quartz sand (Cagno et al. 2010). The studied glass objects are divided mainly in two groups with respect to the possible source of flux (Sayre and Smith 1961). *Low-magnesia, low-potash glasses* where the oxides of potassium (K_2O, potash) and magnesium (MgO, magnesia) are below 1.5%. Such glasses were characteristic of the Roman world and were the dominant glass type from the middle of the 1st millennium BC until the 9th century AD (Freestone et al. 2008). Glasses of this type are generally termed *natron* glasses. At present the only recognised sources of such material in the ancient world are in Egypt (Freestone et al. 2008). Later, *natron* became scarce (Shortland et al. 2006) and is found in a limited number of glass samples (Smit et al. 2002; 2012; Freestone et al. 2008; Genga et al. 2008; Silvestri and Marcante 2011; Cagno et al. 2012b). A new source of soda-rich *plant ash* replaced *natron* as a flux (Brianese et al. 2005; Smit et al. 2002; 2012; Freestone et al. 2008; Genga et al. 2008; Cagno et al. 2010, 2012a,b; Wedepohl and Simon 2010; Ortega-Feliu et al. 2011; Silvestri and Marcante 2011; Bugoi et al. 2013). The new type of glass, termed as *high magnesia high-potash glass* had K_2O and MgO content higher than 2.0 %.

Archaeological excavations in villages and necropolis have proved that glass was known, and used in Bulgarian territories as early as 6th - 7th centuries BC (Kuleff et al. 1985a; 1988). The beginning of a systematic study of the Bulgarian medieval glass is set by Bezborodov and Marinov (Bezborodov and Marinov 1958; 1961a,b). According to Djingov (1975) the use of glass objects declined during the 7th to 8th century, and as a result the local manufactoring ceased. The intensive development of the Bulgarian state during the 9th to 10th century resulted in the advance of material culture, in particular, of production and trade of glassware. The ruins of medieval glassworkshops (Djingov 1963; 1965; Doncheva-Petkova and Zlatinova 1978), from Pliska (Bezborodov and Marinov 195; 1959; 1961a; Kuleff et al. 1988; Djingova and Kuleff 1992; Kuleff and Djingova 1994), Preslav (Djingov 1963; 1965; Bezborodov and Marinov 1958; 1959; 1961a; Kuleff et al. 1985a,b; Kuleff and Djingova 1994), Tarnovo (Bezborodov and Marinov 1961b; Georgieva 1974), Gabrovo (Koicheva 1990), Stara Zagora (Yankov 1983), Hissar (Zaprianov 1967) proved the local production during the existence of the first and the second Bulgarian states (7th to 10th century AD). Glass fragments of beads and bracelets dated to 11th to 12th century AD found by archaeological excavations in medieval villages and necropolis indicate that different ornaments were also produced along with decoration of churches, monasteries, and palaces (Detcheva et al. 2010; 2014; Georgieva et al. 2010a,b; 2014). All medieval glass artifacts, imported or locally produced, regardless of their type – window glass, goblets,

vessels (Kuleff et al. 1985a,b; Djingova and Kuleff 1992; Kuleff and Djingova 1994), bracelets (Kuleff et al. 1985a,b; Djingova and Kuleff 1992; Kuleff and Djingova 1994; Detcheva 2010; 2014; Georgieva et al. 2010a,b;2014) refer to the group of soda-lime-silica glasses. However, different sources of alkalis (*natron* or *plant ash*) were used, depending on the type of object, the place and the time of production.

A limited number of papers deal with the chemical composition of medieval Bulgarian glasses and refer mainly to archeological sites in the North and North-East part of Bulgaria. This localization narrows the knowledge about the chemical composition of medieval glasses from other parts of the country. Recently a few papers reported results from the analysis of a limited number of samples from the southern regions of Bulgaria (Detcheva et al. 2014; Georgieva et al. 2014).

In the present work the results from the chemical analysis of 50 medieval glass samples, excavated in Zlatna Livada (central South Bulgaria), using the analytical techniques of PIXE (particle induced X-ray emission) and PIGE (particle induced gamma emission) are presented.

Zlatna Livada is located close to the town of Chirpan in central South Bulgaria (lat. = 42.2°, long. = 25.4°). The settlement is preliminarily dated by archaeological finds to the 11th – 12th century AD (Herries et al. 2008).

The aim of the present study is to investigate the technology and the raw materials used for the production of glass objects excavated in Zlatna Livada (central South Bulgaria) after determination of 23 elements by PIXE and PIGE and to compare the glasses with other medieval Bulgarian glass finds.

2. MATERIALS AND METHODS

2.1 Samples

In the present investigation 43 pieces of bracelets, 6 pieces of vessels and 1 piece of handle cup found during excavations in the site "Medieval village and necropolis" in the area of Byalata voda, Zlatna Livada, near Chirpan in South Bulgaria were analyzed. The glass bracelets and vessels represent only fragments (not entire objects) which are different in size and cross-section. The bracelets have different color, dominated by blue, green and brown in different shades. Some of the fragments are colorless and translucent with a greenish or pink tint. They can be grouped in three main groups according cross-section - circular, flat and rectangular. The round bracelets are monochrome, with smooth or twisted surface, or with a curled spiral strand of another color on the body. The flat bracelets are also monochrome and smooth or with straight grooves of one or more alternating colors. In most cases the glasses are well preserved, without many weathered areas. Description of the investigated glass samples is given in Table 1. For easier reference only the digital number as a sample identification is used throughout the text.

2.2 Instrumentation

The analysis of the investigated glass finds was carried out in Slovenia – at the tandem accelerator of the Jožef Stefan Institute in Ljubljana. A proton beam of 3MeV nominal energy in air was used. Applying a combined PIXE/PIGE method elements heavier than silicon were analyzed according to their characteristic X-rays, detected by a Si (Li) detector of 160 eV resolutions at 5.89 keV.

The proton energy at the target, after passing an 8 μm aluminum window and a 1.1 cm air-gap, was 2.70 MeV. The air gap between the target and X-ray detector was 5.7 cm, which acted as an efficient absorber of intense silicon X-rays. The precise values of the air-gaps were determined by measurement of a series of single element and simple chemical compound targets, using the argon signal from air for normalization. The beam size at the target had a Gaussian profile of 0.8 mm full-width at half maximum (Jezeršek et al. 2010).

Using air as the only absorber provided good sensitivity for the elements between silicon and iron. Typical measurement times were 300-500 seconds at a proton current of < 1 nA. Sensitivity for mid-Z elements was improved to about 5 mg kg^{-1} by an aluminum absorber of 0.1 mm thickness, and increasing the proton current to a few nA. by the AXIL code. The line intensities of two spectra were combined into one set of input Spectral deconvolution was performed.

Table 1 Description of the samples

Sample code	Color	Sample	Description
G-801.ZLL	light brown	bracelet	translucent, iridescent, flat, five straight cannelures on the surface
G-802.ZLL	colorless, pale pink tint	bracelet	translucent, no iridescence, round, furrowed
G-803.ZLL	colorless, pale greenish tint	bracelet	translucent, no iridescence, round, forrowed
G-804.ZLL	colorless, pale pink tint	bracelet	translucent, no iridescence, round, furrowed
G-805.ZLL	light blue	vessel	translucent, iridescent, smooth
G-806.ZLL	blue-green	vessel	translucent, iridescent, smooth
G-807.ZLL	brown	bracelet	translucent, iridescent, round, furrowed
G-808.ZLL	colorless, pale greenish tint	vessel	translucent, no iridiscence, smooth
G-809.ZLL	colorless, pale greenish tint	handle	translucent, no iridescence, rectangular, smooth
G-810.ZLL	colorless, greenish tint	vessel	translucent, iridiscent, smooth
G-811.ZLL	dark brown	bracelet	translucent, iridescent, flat, smooth
G-812.ZLL	brown	bracelet	opaque, no iridescence, round,smooth
G-813.ZLL	dark green	bracelet	opaque, iridescent, round, smooth
G-814.ZLL	dark green	bracelet	opaque, iridescent, flat, smooth
G-815.ZLL	colorless, greenish tint	bracelet	translucent, iridescent, rectangular, smooth
G-816T.ZLL	colorless, pale yellow tint	vessel	translucent, iridescent, smooth
G-816B.ZLL	blue	bracelet	translucent, iridescent, flat, smooth
G-817.ZLL	blue-green	bracelet	translucent, no iridescence, flat, smooth
G-818.ZLL	blue-green	bracelet	transparenr, iridescent, round, furrowed
G-819.ZLL	brown-redish	bracelet	opaque, iridescent, flat, five straight cannelures on the surface, the three inner stratified with white stripes
G-820.ZLL	dark blue	bracelet	opaque, iridescent, round, smooth with a curled spiral strands of brown and white color on the surface
G-821.ZLL	brown-redish	bracelet	opaque, no iridescence, round, twisted with a curled spiral strands of dark brown color on the surface
G-822.ZLL	brown-redish	bracelet	opaque, no iridescence, round, smooth
G-823.ZLL	light brown-redish	bracelet	opaque, no iridescence, round, smooth
G-824.ZLL	blue	bracelet	translucent, iridescent, flat, smooth
G-825.ZLL	blue	bracelet	translucent, iridescent, round, smooth
G-826.ZLL	dark blue	bracelet	opaque, iridescent, round, twisted
G-827.ZLL	colorless, pale greenish tint	vessel	translucent, no iridescence, smooth
G-828.ZLL	dark brown	bracelet	translucent, iridescent, rectangular, furrowed
G-829.ZLL	dark green	bracelet	opaque, iridescent, flat, smooth
G-830.ZLL	blue-green	bracelet	translucent, iridescent, flat, smooth
G-831.ZLL	dark brown	bracelet	translucent, iridescent, round, furrowed
G-832.ZLL	green	bracelet	translucent, iridescent, rectangular, smooth
G-833.ZLL	dark blue	bracelet	translucent, iridescent, round, twisted
G-834.ZLL	dark blue	bracelet	opaque, no riridescence, rectangular, smooth
G-835.ZLL	brown-redish	bracelet	translucent, iridescent, round, smooth
G-836.ZLL	dark blue	bracelet	opaque, iridescent, flat, eight straight cannelures on the surface, stratified with two white (at the two sides) and one red (in the middle) stripes
G-837.ZLL	dark blue	bracelet	opaque, iridescent, round, twisted with a curled spiral strands of dark brown color on the surface
G-838.ZLL	green	bracelet	translucent, no iridescence, five straight cannelures on the surface, the middle one stratified with red stripe
G-839.ZLL	dark blue-black	bracelet	opaque, no iridescence, round, smooth
G-840.ZLL	light brown-redish	bracelet	opaque, no iridescence, round, smooth
G-841.ZLL	blue-green	bracelet	opaque, iridescent, round, smooth surface
G-842.ZLL	dark blue	bracelet	opaque, iridescent, flat, two red inserted stripes on the surface
G-843.ZLL	brown-greenish	bracelet	translucent, iridescent, round, furrowed
G-844.ZLL	deep blue	bracelet	translucent, iridescent, round, smooth surface with a curled spiral strand of white color
G-845.ZLL	dark blue	bracelet	opaque, iridescent, rectangular, smooth
G-846.ZLL	colorless, pale greenish tint	bracelet	translucent, no iridescence, rectangular, flat
G-847.ZLL	colorless, pale greenish tint	bracelet	translucent, no iridescence, rectangular, furrowed

G-848.ZLL	green	bracelet	translucent, no iridescence, round, flat
G-849.ZLL	green	bracelet	translucent, iridescent, round, furrowed

data using the iron line for normalization and computed values for filter transmission.

The concentrations of Na, Mg and Al were determined from the intensities of gamma rays excited by inelastic proton scattering. A 2 μm thick tantalum foil on a brass nozzle was used as a proton exit window in order to avoid background gamma production above 100 keV. Due to proton stopping in the window and air, the actual target impact energy was 2.74 MeV. The number of incident protons was measured by a thin wire mesh intersecting the beam in front of the exit window. The transmission of the mesh was 59%. Gamma rays were detected by a 40% intrinsic germanium detector. The gamma lines used in the analysis were 440 keV for Na, 585 keV for Mg, and 844 and 1014 keV for Al. Line intensities were determined by the GRILS program of the GANAAS software package. The most critical measurement was that of Mg, as its content in *natron* type glass is typically below 1.6%. The detection limit for magnesium is limited by the strong Compton background produced by the intensive sodium lines of 1634 and 1636 keV, and by interference of its 585 keV line with the 583 keV line from the natural background. The intensity of the natural background line was reduced by lead shielding and a high relative count rate of proton-induced gamma rays. The count rate of the 583 keV line was also measured and the detected gamma intensities corrected for the contribution of the natural background. The detection limit for Mg under this configuration was about 0.2%. For gamma measurement, the proton current was 2-3 nA and the collected dose was about 5 μC for the sample, and 15 μC for the standard. The elemental concentrations were calculated by a code developed in the lab that considers the matrix effects for production of gamma rays and X-rays simultaneously. As the matrix effects are Z-dependent, an iterative procedure was applied. In thick targets, the density has no effect. If the atoms are less densely spaced, the protons simply go deeper.

As calibration standards both NIST 610 and NIST 620 were used. The sum of all metals oxides was normalized to unity. For control purposes, the sum of metal oxides was also calculated with respect to the argon yield from the air. Differences up to 20% between the two values were tolerated and resulted in about 5% uncertainties of major elements; however, the uncertainty in the concentrations of minor elements and those near to detection limits may be 10-15%. The concentrations of Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, Br, Sr, Zr, Ag, Sn, Sb, Ba, Pb were evaluated and are given (mostly in oxide form) in Table 2.

3. RESULTS AND DISCUSSIONS

3.1 Statistical analysis

The analytical data were subjected to cluster, factor, correlation and discriminant analyses using STATISTICA 7.0 software package. The individual results of the analysis of the glass bracelets from Zlatna Livada are presented in Table 2. Although 23 elements were determined, not all of them were used in the statistical analysis. The concentrations of CoO, Ag, SnO_2, Sb_2O_3, BaO in most of the samples, are below the limit of detection and were not included in the statistical evaluation. Besides the values for Fe_2O_3, CuO and MnO were also excluded from the mathematical interpretation. Previous studies have demonstrated that, when different colored glasses are being investigated, coloring agents should be omitted, otherwise the resulting classification is according to color (Djingova and Kuleff 1992). The rest of the elements were treated by hierarchical cluster analysis, based on the Wards method algorithm and the squared Euclidean distance. Fig. 1 presents the resulting dendrogam, where the formation of three major clusters is visible.

Factor analysis indicated that three factors were responsible for the formation of the three clusters. The first factor was loaded with Na_2O, MgO and K_2O (type of flux used), the second one with Al_2O_3 and TiO_2 (the type of sand used – quarz sand or quarz pebbles) and the third factor with CaO, NiO and SrO (network stabilizer alkaline earth oxides). Parallel correlation analysis was performed to further reveal dependences between the elements.

Table 2 Analytical data (wt. %) of the investigated glass finds

sample	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO
801	12.9	2.19	3.27	68.0	0.59	0.40	1.76	7.01	0.09	0.56	1.97	<0.003
802	15.5	3.13	1.80	68.9	0.56	0.63	1.89	6.51	0.05	0.60	0.38	<0.003
803	12.1	3.57	2.63	67.6	0.44	0.88	2.49	7.93	0.11	1.41	0.71	<0.003
804	14.2	3.55	1.33	69.5	0.54	0.71	1.92	7.11	0.06	0.58	0.39	<0.003
805	14.6	1.92	2.61	67.8	0.69	0.69	1.83	7.22	0.09	0.64	1.62	0.041
806	13.5	1.24	2.80	68.7	0.65	0.69	1.49	7.91	0.10	0.78	1.86	<0.003
807	13.3	2.39	2.68	69.7	0.60	0.63	1.77	7.57	0.07	0.59	0.52	<0.003
808	13.5	3.76	2.10	67.6	0.58	0.91	2.53	7.58	0.08	0.75	0.51	<0.003
809	13.4	3.00	2.82	67.0	0.66	0.74	2.14	8.33	0.08	0.94	0.60	<0.003
810	14.7	0.32	3.86	68.5	0.47	1.05	0.67	7.88	0.08	1.82	0.58	<0.003
811	13.5	2.12	3.21	67.2	0.54	0.51	1.74	7.28	0.14	1.95	1.49	<0.003
812	14.4	0.26	2.68	65.9	0.71	0.70	1.24	6.63	0.10	0.47	4.93	0.027
813	11.3	2.24	2.23	68.7	0.59	0.68	2.10	7.93	0.10	0.67	3.39	<0.003
814	14.3	1.76	2.66	68.7	0.67	0.70	1.36	6.84	0.11	0.51	2.16	<0.003
815	13.1	1.76	2.93	66.8	0.69	0.60	2.07	8.28	0.14	2.04	1.38	<0.003
816B	13.4	2.07	1.95	69.5	0.65	0.79	1.67	7.61	0.09	0.72	1.10	0.041
816T	16.6	<0.2	2.04	73.4	0.68	0.93	0.58	5.26	0.06	0.01	0.33	<0.003
817	14.8	<0.2	2.51	70.6	0.67	0.69	1.17	7.09	0.11	0.77	1.23	<0.003
818	14.4	1.16	2.42	70.0	0.62	0.76	1.47	6.63	0.08	0.51	1.74	0.029
819	14.0	2.21	2.93	65.0	0.52	0.58	1.71	7.36	0.13	0.70	3.60	<0.003
820	13.6	2.29	3.57	64.6	0.08	0.43	1.89	8.00	0.13	0.72	3.93	<0.003
821	13.4	2.16	3.27	65.9	0.55	0.58	1.87	7.67	0.12	0.74	2.93	<0.003
822	14.2	1.58	3.93	67.2	0.54	0.60	2.12	5.50	0.15	0.33	3.25	<0.003
823	12.9	2.36	2.85	64.6	0.55	0.55	1.75	8.17	0.11	0.73	2.47	<0.003
824	12.8	1.68	2.31	70.4	0.58	0.76	1.66	7.53	0.08	0.77	1.06	0.071
825	13.0	2.36	2.72	69.5	0.62	0.66	2.20	6.49	0.08	0.68	1.18	0.056
826	13.4	2.11	3.57	66.8	0.55	0.60	1.60	6.91	0.14	0.62	3.59	<0.003
827	13.1	3.38	1.84	68.2	0.52	0.77	2.31	8.49	0.07	0.78	0.52	<0.003
828	13.3	2.95	2.31	67.2	0.66	0.55	1.83	8.16	0.09	1.91	0.76	<0.003
829	13.8	2.14	2.36	66.8	0.20	0.58	1.86	8.26	0.08	0.86	2.46	<0.003
830	15.6	1.58	1.95	68.7	0.72	0.89	1.18	7.05	0.08	0.53	1.53	0.022
831	13.8	2.29	2.17	67.0	0.09	0.42	2.16	8.68	0.08	1.89	1.04	<0.003
832	14.8	1.76	2.48	69.3	0.58	0.66	1.29	6.48	0.08	0.52	1.67	0.021
833	14.8	2.17	1.71	69.5	0.59	0.91	1.31	6.76	0.06	0.53	1.46	0.083
834	13.4	1.86	2.32	67.0	0.59	0.66	1.90	7.68	0.13	0.82	3.33	<0.003
835	14.3	2.50	2.42	67.2	0.09	0.41	1.54	8.83	0.09	1.12	1.08	<0.003
836	13.8	1.86	2.61	66.1	0.66	0.68	1.75	7.37	0.15	0.76	3.90	<0.003
837	12.4	2.21	3.29	65.9	0.63	0.57	1.64	7.58	0.16	0.81	4.32	<0.003
838	14.0	2.84	2.40	67.8	0.66	0.63	1.86	8.13	0.07	0.57	0.74	<0.003
839	13.9	2.60	2.23	65.7	0.57	0.57	1.83	7.88	0.16	0.63	3.65	<0.003
840	13.5	2.62	2.76	64.8	0.52	0.52	1.94	8.42	0.10	0.73	2.42	<0.003
841	13.8	2.49	2.46	66.5	0.04	0.35	2.05	7.67	0.12	0.77	2.83	<0.003
842	14.3	1.99	3.12	65.3	0.07	0.45	1.77	7.67	0.16	0.74	4.03	<0.003
843	13.6	2.52	3.16	65.9	0.11	0.42	1.77	9.08	0.08	1.69	1.12	<0.003
844	15.1	1.71	2.93	68.7	0.61	0.78	1.08	6.59	0.12	0.50	1.21	0.056
845	13.6	1.69	2.80	66.5	0.59	0.47	1.67	7.14	0.15	0.76	4.16	<0.003
846	13.8	3.47	1.79	67.8	0.56	0.92	2.24	8.13	0.07	0.95	0.38	<0.003
847	12.2	3.50	3.02	68.7	0.47	0.52	2.35	7.28	0.10	0.85	0.80	<0.003
848	13.9	2.34	2.32	67.8	0.55	0.52	2.00	8.41	0.12	0.60	1.15	<0.003
849	14.4	2.12	2.23	68.9	0.51	0.51	1.52	7.82	0.10	0.52	0.92	<0.003

Table 2 Continued

sample	NiO	CuO	ZnO	Br	SrO	ZrO_2	Ag	SnO_2	Sb_2O_3	BaO	PbO
801	<0.001	0.94	0.01	0.002	0.092	0.017	<0.1	<0.01	<0.001	<0.001	0.15
802	0.001	<0.0005	0.01	0.005	0.041	0.003	<0.1	<0.01	<0.001	<0.001	0.006
803	0.001	<0.0005	<0.001	0.002	0.091	0.009	<0.1	<0.01	<0.001	<0.001	0.004
804	0.001	<0.0005	<0.001	0.004	0.042	0.004	<0.1	<0.01	<0.001	<0.001	0.003
805	<0.001	0.12	0.05	0.003	0.058	0.006	<0.1	<0.01	<0.001	<0.001	0.12
806	<0.001	0.12	0.02	0.003	0.082	0.008	<0.1	<0.01	<0.001	<0.001	0.13
807	<0.001	0.01	<0.001	0.003	0.059	0.007	<0.1	<0.01	<0.001	<0.001	0.05
808	0.001	0.03	0.01	0.003	0.051	0.006	<0.1	<0.01	<0.001	<0.001	0.05
809	<0.001	0.05	0.01	0.004	0.070	0.010	<0.1	<0.01	<0.001	<0.001	0.15
810	0.002	<0.0005	<0.001	0.001	0.071	0.003	<0.1	<0.01	<0.001	<0.001	0.001
811	<0.001	0.07	0.01	0.002	0.076	0.010	<0.1	<0.01	<0.001	0.05	0.13
812	<0.001	1.64	0.03	0.003	0.055	0.000	<0.1	<0.01	<0.001	<0.001	0.22
813	<0.001	0.04	0.01	0.003	0.053	0.016	<0.1	<0.01	<0.001	<0.001	0.05
814	0.003	0.07	0.01	0.002	0.083	0.010	<0.1	<0.01	<0.001	<0.001	0.10
815	0.004	0.04	0.01	0.002	0.144	0.011	<0.1	0.03	<0.001	<0.001	0.07
816B	<0.001	0.06	0.07	0.003	0.060	0.003	<0.1	<0.01	<0.001	<0.001	0.09
816T	<0.001	<0.0005	<0.001	0.002	0.047	0.004	<0.1	<0.01	0.23	<0.001	0.01
817	0.001	0.09	0.02	0.002	0.065	0.007	0.132	<0.01	<0.001	<0.001	0.17
818	<0.001	0.15	0.01	0.004	0.059	0.006	<0.1	<0.01	<0.001	<0.001	0.04
819	0.001	0.92	0.04	0.002	0.067	0.008	<0.1	0.07	<0.001	<0.001	0.14
820	<0.001	0.45	0.02	0.003	0.063	0.015	<0.1	0.04	<0.001	<0.001	0.10
821	0.001	0.64	0.02	0.003	0.063	0.015	<0.1	0.06	<0.001	<0.001	0.12
822	<0.001	0.61	0.01	0.002	0.052	0.008	<0.1	0.04	<0.001	<0.001	0.12
823	0.005	2.74	0.02	0.001	0.115	0.009	<0.1	<0.01	<0.001	<0.001	0.13
824	<0.001	0.08	0.12	0.003	0.065	0.007	0.018	<0.01	<0.001	<0.001	0.07
825	<0.001	0.09	0.13	0.002	0.055	0.004	<0.1	<0.01	<0.001	<0.001	0.10
826	<0.001	0.10	0.01	0.003	0.062	0.013	<0.1	0.04	<0.001	<0.001	0.09
827	0.001	0.02	<0.001	0.003	0.052	0.010	<0.1	0.03	<0.001	<0.001	0.01
828	0.004	0.03	0.01	0.002	0.148	0.011	<0.1	<0.01	<0.001	<0.001	0.06
829	0.001	0.07	0.01	0.003	0.083	0.005	<0.1	<0.01	<0.001	<0.001	0.45
830	0.002	0.13	0.02	0.003	0.057	0.009	<0.1	<0.01	<0.001	<0.001	0.07
831	0.002	0.06	0.01	0.003	0.168	0.008	<0.1	<0.01	<0.001	<0.001	0.14
832	0.001	0.08	0.02	0.003	0.059	0.006	<0.1	<0.01	<0.001	<0.001	0.06
833	<0.001	0.10	0.01	0.004	0.044	0.004	<0.1	<0.01	<0.001	<0.001	0.02
834	0.001	0.15	0.02	0.003	0.072	0.012	<0.1	0.05	<0.001	<0.001	0.11
835	0.002	0.07	0.01	0.002	0.179	0.009	<0.1	0.03	<0.001	<0.001	0.15
836	0.001	0.11	0.02	0.003	0.070	0.013	<0.1	<0.01	<0.001	<0.001	0.13
837	0.002	0.13	0.01	0.003	0.104	0.018	<0.1	0.07	<0.001	<0.001	0.11
838	0.002	0.03	0.01	0.003	0.101	0.009	<0.1	<0.01	<0.001	<0.001	0.06
839	0.001	0.06	0.01	0.002	0.091	0.022	<0.1	<0.01	<0.001	<0.001	0.14
840	0.003	1.39	0.02	0.002	0.117	0.013	<0.1	<0.01	<0.001	<0.001	0.13
841	0.001	0.64	0.01	0.002	0.123	0.015	<0.1	0.07	<0.001	<0.001	0.12
842	<0.001	0.12	0.02	0.002	0.072	0.016	<0.1	<0.01	<0.001	<0.001	0.14
843	0.002	0.25	0.01	0.003	0.167	0.010	<0.1	<0.01	<0.001	<0.001	0.10
844	<0.001	0.11	0.13	0.002	0.042	0.009	<0.1	0.04	<0.001	<0.001	0.19
845	<0.001	0.31	0.02	0.002	0.072	0.011	<0.1	<0.01	<0.001	<0.001	0.12
846	0.001	<0.0005	<0.001	0.004	0.048	0.004	<0.1	<0.01	<0.001	<0.001	0.002
847	0.001	0.03	0.01	0.003	0.055	0.012	<0.1	<0.01	<0.001	<0.001	0.01
848	0.002	0.07	0.01	0.002	0.144	0.009	<0.1	<0.01	<0.001	<0.001	0.08
849	0.002	0.05	0.01	0.001	0.124	0.005	<0.1	<0.01	<0.001	<0.001	0.12

To a great extent agreement was established between the three statistical procedures. Worth mentioning are the positive correlations between K_2O and MgO and respectively the negative correlations K_2O-Na_2O, the three oxides forming factor 1. Significant positive correlation was established between Al_2O_3 and TiO_2 (factor 2), and CaO - SrO, SrO - NiO (factor 3). The positive correlations between A_2O_3 and TiO_2 shows that Ti is correlated with Al-bearing minerals. The correlation between Ni and Sr is an indication that this correlation is a dilution effect; Sr is generally assumed to come with the lime; Ni is related to clays or heavy minerals.

The negative correlation between Na_2O and K_2O shows that investigated glasses are a mixture of soda-based (high Na, low K) and non-soda *plant ash*-based (high K, low Na) glasses. The two-dimensional plot after discriminat analysis (Fig. 2) confirmed the results from the cluster analysis.

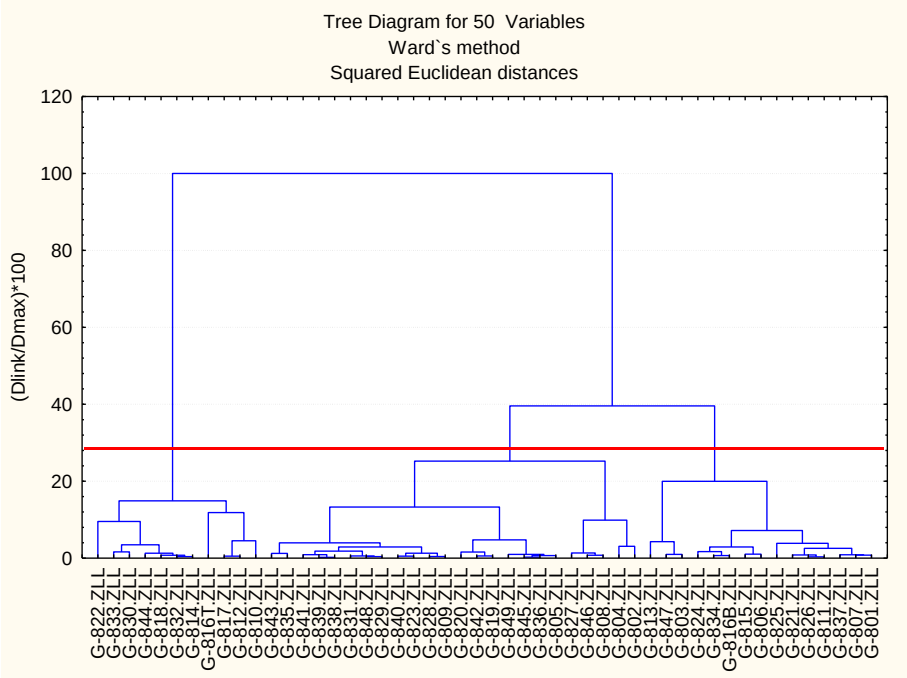

Figure 1 Dendrogram from the cluster analysis of the samples without the values for FeO, CuO and MnO

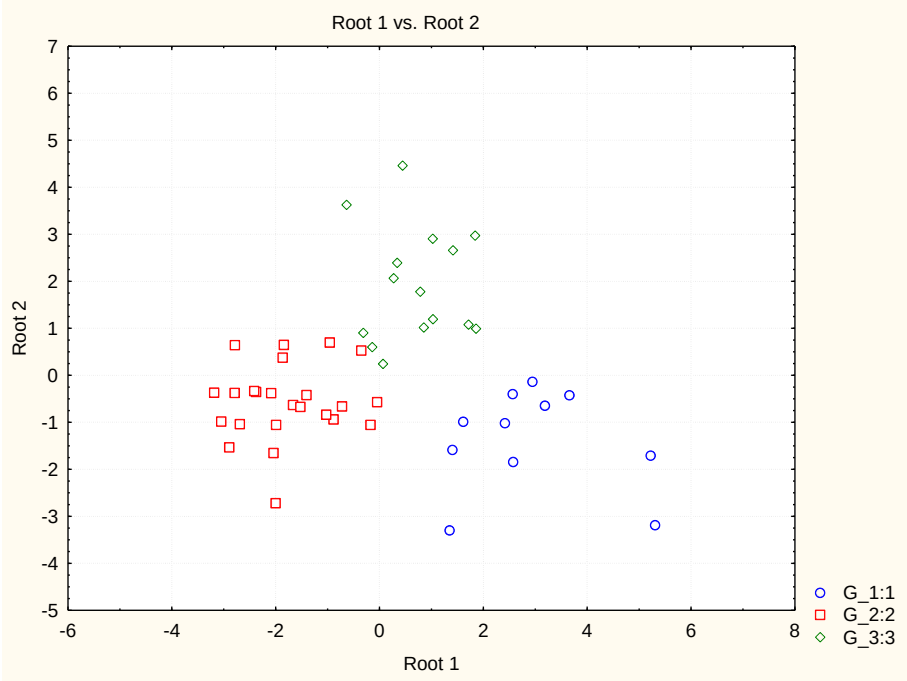

Figure 2 Two-dimensional plot after discriminat analysis of the samples without the values for FeO, CuO and MnO

3.2 Bulk glass composition

The analytical results are presented as oxides in mass percent in Table 2. All samples are essentially composed of SiO_2 (from 64.6 to 73.4%), Na_2O (from 11.3 to 16.6%) and CaO (from 5.3 to 9.1%). The glasses may be defined as Na_2O-CaO-SiO_2 (soda-lime silica) glasses since the three major components add up to 90% from the overall composition.

The content of K_2O is between 0.6 to 2.5% and none of the investigated glass fragments is made of potassium glass. MgO content is in the range from <0.2% (in samples 816T and 817) to 3.8%.

3.3 Raw materials

Potential sources of silica include quarried siliceous minerals and rocks such as vein quartz, chert and quartzite, as well as quartz pebbles of these materials and sand (Freestone 2006). The Al_2O_3 content varies between 1.3-3.9% indicating that quartz sand was used, instead of the alternative quartz pebbles material used as former (Freestone et al. 2009; Genga et al. 2008). The relatively high aluminum and the wide interval of iron content (0.33-4.93%) indicate the use of impure sand or mixed silica sources as raw materials (Artioli, 2010).

The relatively high amount of SrO (0.05-0.07%) is probably derived from bioaccumulation phenomena of marine organisms and the use of coastal sand may be assumed (Freestone et al. 2003).

3.4 Fluxing agents

All investigated glasses are of the soda-lime silica type. Considering the MgO and K_2O bivariate plot (Fig. 3) the type of flux is unambiguously determined. Less than half of the samples fall into two well known categories.

The low MgO and K_2O content (both inder 1.5%) in some of the samples indicate that *natron* was probably used as a flux, following medieval production technology (Silvestri and Marcante 2011). These samples may be classified as *"low magnesia-low potash" glasses.*

Another group has relatively high magnesia and high potash (typically more than 2% of each oxide) (Freestone 2005) and was most probably made using *plant ash* as a source of soda thus characterized as "*high-magnesia high-potassium oxide glass*". The ratio of Na_2O/K_2O in this group of samples would suggest that the glasses were made with sodium rich ashes from halophytic plants (like Salsola soda, Salsola kali, Salicornia herbacea and Kalidium capsicum) instead of *natron* (Bezborodov 1975).

Fig. 3 indicates that the majority of the analyzed glass bracelets fall between the two distinct groups of typical *natron* and *plant ash* glasses. The MgO and K_2O concentrations are lower than those indicating the use of *plant ashes*. This group of glass bracelets can be classified as intermediate type of glass called "*mixed natron-plant ash*" category.

The distribution of the samples from the *natron* group shows that they could be divided into two subgroups. The samples from the first one have very low concentrations of both MgO and K_2O and the second one with concentrations of the oxides about 1.5%. The comparison of the *natron* glass samples to the late and post-Roman groups of *natron* type glass of Levantine origin (Freestone 2005; 2006) shows relatively close values of both oxides to the Levantine I group (Israel, primary workshop) (Freestone 2005) and to Levantine, Bet She'an group (Israel, secondory workshop) (Freestone 2006). Furthermore, the first subgroup has closer values to the samples from Pliska (9^{th}-10^{th} century AD) and the second one to the samples from Preslav (9^{th}-10^{th} century AD) (Djingova and Kuleff 1992), Mezek and Stambolovo (11^{th} century AD) (Georgieva et al. 2014). This result indicates that different sources of the mineral trona were concomitantly available in Bulgaria during medieval times.

The *plant ash* group shows a correlation to the *plant ash*, Banias group with probable primary source from Syria-Palestine (Freestone 2006). The *plant ash* group could be also divided into two subgroups: the first one with MgO concentration higher than 3% and K_2O concentration between 2 and 2.5%. High concentrations of MgO (between 3 and 4%) was found in *plant ash* medieval bracelets from Drastar castle, near to the city of Silistra, Bulgaria dated to 11^{th}–13^{th} century AD (Georgieva et al. 2010a,b). In the Drastar samples, however the concentration of K_2O is below 2% and the concentration of MgO is about 4%, classified as high-magnesia glasses (HMG) which is probably due to the fact that magnesium-containing carbonates (as dolomite) were used as raw materilas by the glassmakers (Georgieva et al. 2010a).

The second *plant ash* subgroup comprises of colorless glasses with pale greenish or pink tint and has MgO concentration lower than 2.5% and K_2O concentration around 2%. Similar *plant ash* bracelets were studied in (Georgieva et al. 2014) from Stambolovo necropolis and Mezek castle, South-East Bulgaria dated to 11^{th} century AD. Therefore it may be assumed that several types of *plant ashes* were used for the production of the *plant ash* bracelets in Bulgaria and at

least two types for the fragments from Zlatna Livada.

The third group, the "*mixed natron-plant ash*", contains 27 bracelet fragments and is rather dispersed. Similar category of glass had been previously identified in artifacts found in Levantine and Italian sites and dated to the 9th-11th century AD (Dussart et al. 2004; Henderson et al. 2004; van der Werf et al. 2009; Arletti et al. 2010; Silvestri and Marcante 2011), and Romanian bracelets dated to 11th-13th century AD which furthermore look stylistically similar (Bugoi et al. 2013). It is also noteworthy that the Banias, Early Islamic group (Freestone, 2006) is located right between the *plant* and the *mixed natron-plant ash group*. Therefore, the key question is whether the mixed group of bracelets was produced from raw materials, recycled natron glass or both?

The sources of *plant ash* glass can be traced by plotting the relative fraction of Na_2O and K_2O in the total content of alkali and alkaline earth oxides (Smit et al. 2012). In Fig. 4 the values for all samples are displayed, showing the distribution of the three groups, together with the medieval Bulgarian glass bracelets, mentioned above. Fig. 4 shows well separated *plant-ash* and *mixed natron-plant ash* groups. The distribution of the samples from the *plant ash* group from Zlatna Livada shows again the formation of two subgroups, which confirms the assumption made for the presence of two types of *plant ash* flux.

The separation of the *mixed natron-plant ash* from the *plant ash* group leads to two assumptions. One of the reasons might be that different type of plant species were used as a flux, or the majority of the glass bracelets are produced by recycling *natron* glass cullet in combination with a certain proportion of Levantine *plant ash* glass.

The discrimination of production centres of *natron* based glasses is usually traced by the plot of CaO vs Al_2O_3 (Fig. 5), as they reflect the amounts of lime (in the form of shell or limestone) and feldspar in the sands used to make the glasses. Each group therefore reflects the use of a different source of sand and production in a different location (Freestone et al. 2008). Al_2O_3 appears in the final glass composition as a sand contaminant, while CaO originates either from the use of calcareous sand, from the shell addition to the glass batch or from the calcium contained in the *plant ashes* (Freestone 2006). The results in the present study indicate very close concentrations of both oxides in the three groups of glasses which would lead to mixing and overlapping of the samples. Along with the concentrations of CaO and Al_2O_3, most of the oxides have intermediate average concentrations in the samples from the *mixed natron-plant ash* group compared to the *natron* and *plant ash* group (see Table 2). The result could be accepted as evidence that the majority of the *mixed natron-plant ash* glass bracelets in the present study are manufactored by recycling a *natron* glass cullet and *plant ash* glass chunks.

3.5 Glass norm

The ratio of alkali oxides (Na_2O+K_2O) to alkaline earth oxides (CaO+MgO) was also used to propose the so called "recipe norm" (Ščapova 1990). The dependence of the MgO + CaO content on norm is approximately hyperbolic according to (Smit et al. 2002), which was confirmed for the investigated glasses (Fig. 6). In general, three recipes for glassmaking were simultaneously used in the past independantly of the place of production (Ščapova, 1990). The glasses with alkali oxides to alkaline earth oxides ratio about 1.5 were produced according to the so called Near East recipe norm; those with a ratio about 2.0-2.5 – according to the Roman-province norm and those with a ratio about 3 – according to the Roman-capital recipe norm.

Fig. 6 presents a comparison of the investigated glass bracelets with other medieval glasses from Bulgaria of different origin – from Pliska and Preslav (Djingova and Kuleff 1992), Stambolovo and Mezek (Georgieva et al. 2014), and Drastar castle (Georgieva et al. 2010b).

The ratio of $Na_2O+K_2O/CaO+MgO$ proved that the glass bracelets from the *plant ash* and the majority of the *mixed natron-plant ash* group were produced according to the so-called Near East recipe norm (ratio around 1.5), while for all the *natron* (except samples 816T and 806), three mixed glasses (802, 822 and 833) the Roman province recipe norm (ratio around 2.0–2.5) was used.

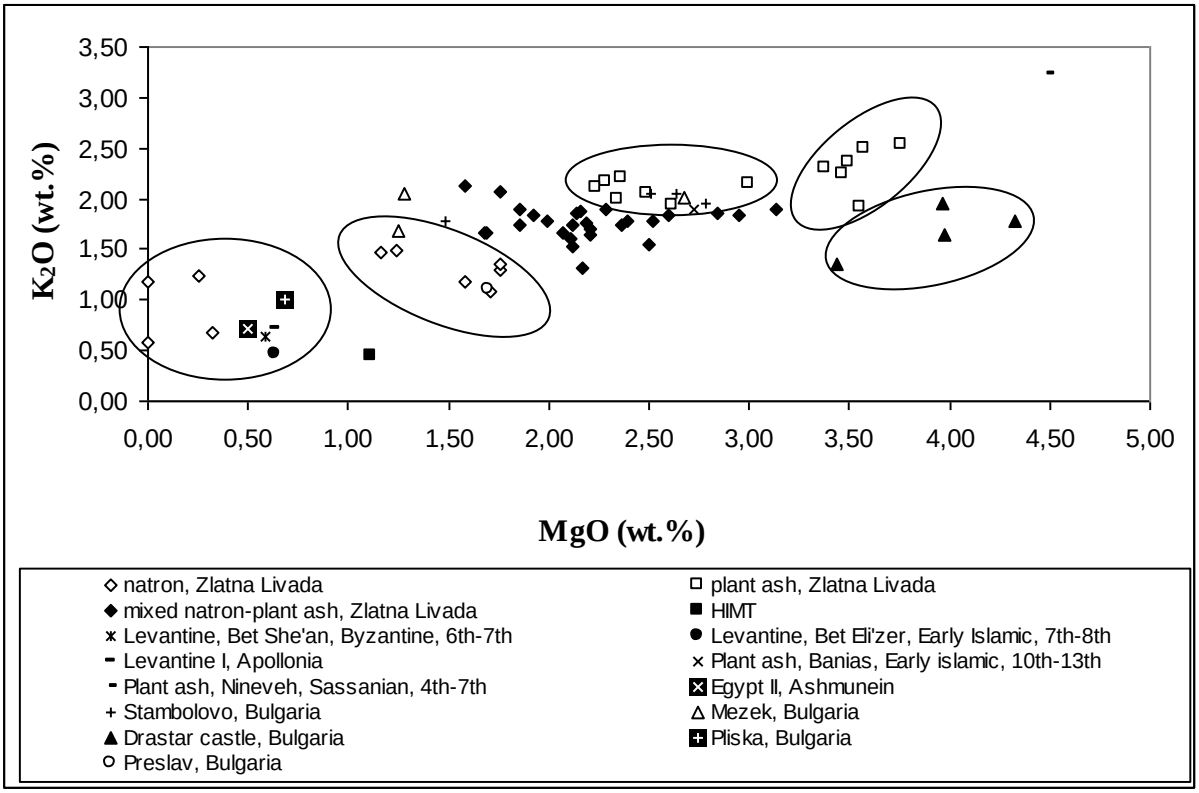

Figure 3 MgO and K_2O content (in weight %) in the analyzed glass fragments

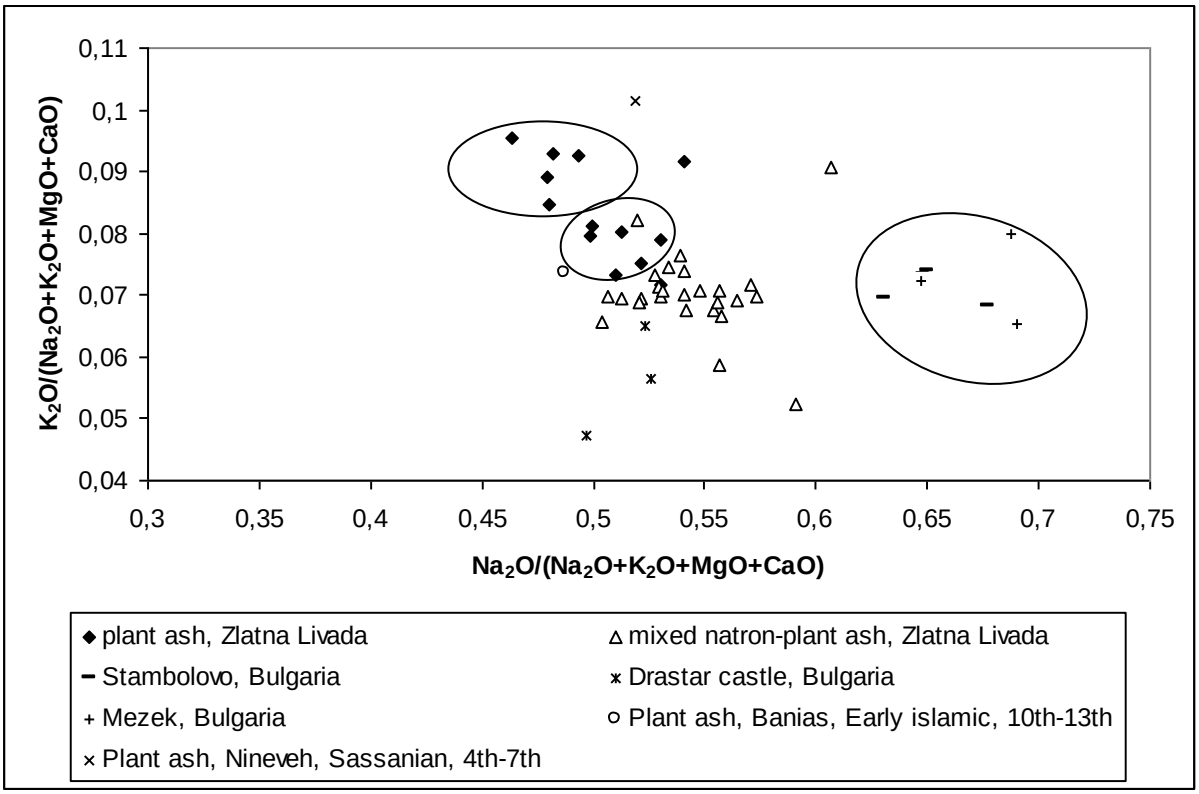

Figure 4 Distribution of the glasses according to the relative contents of Na and K oxides

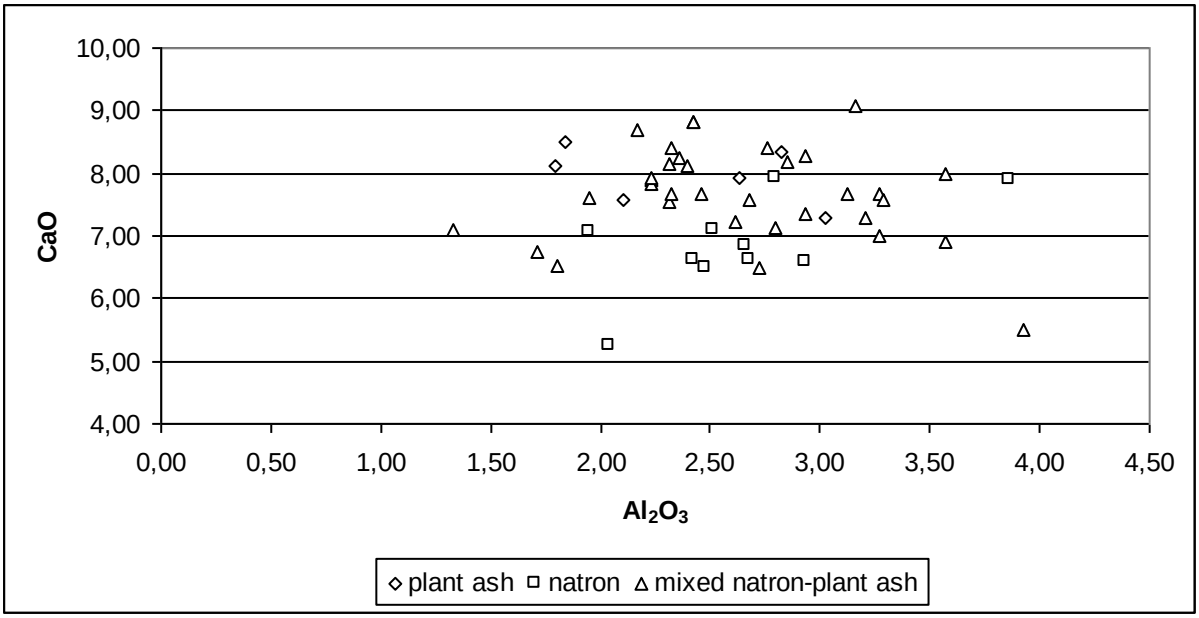

Figure 5 Concentrations of CaO (wt.%) and Al_2O_3 (wt.%) for the glass fragments

The Roman-capital recipe norm (ratio around 3) was used only for one sample from the *natron* group (816T). This is the only sample in which a measurable concentration of Sb_2O_3 was found. Furthermore, compared to the other samples, higher concentration of SiO_2, lower concentration of CaO and SrO and higher concentration of Cl was determined, which is an indication of different type of sand used. Similar translucent glass fragments have been investigated in (Genga et al. 2008), originating from the archaeological site of Siponto (Foggia, Italy).

The medieval Bulgarian glasses investigated earlier from Preslav (Djingova and Kuleff 1992) and Drastar castle (Georgieva et al. 2010b) were produced using the Near East recipe norm. The Roman-capital recipe was used for the production of glasses found in Pliska (Djingova and Kuleff 1992), Stambolovo and Mezek (Georgieva et al. 2014). Part of the the glass objects found in Pliska, Mezek and Stambolovo were also produced according to the Roman-Province recipe norm. It was previously established that in the same way as in the Byzantine Empire (Ščapova 1990), glass was produced using different ancient recipes simultaneously (Djingova and Kuleff 1992). This result indicates the strong influence both from the Roman Empire and the Near East traditions on the glass making technology in medieval Bulgaria.

The Roman-province recipe norm was used for the glasses made in Aquileia (Italy), Philippi and Patras (Greece), and Poitieres (France) (Georgieva et al. 2010b).

3.6 Coloring agents

Over time, a wide range of methods to color glass were discovered. The most common coloring agents in ancient glass are transition metals as Co^{2+}, Mn^{2+} or Mn^{3+}, Cu^{2+}, Fe^{2+} or Fe^{3+}. The addition of Co-bearing ores is traditionally added to obtain blue color glasses (Mirti et al. 2002). Manganese oxide (MnO) is usually added to produce pink to purple color, copper oxide (CuO) for turquoise, or green and cobalt oxide (CoO) for blue color (Mirti et al. 2002). Ancient glassmakers produced glass of different colors not only by using different chromophores, but also by modifying the redox conditions in the kiln (Mirti et al. 2002). Deliberate additions of iron gave a range of blue, green or brown colors, depending on the whether the conditions were oxidizing or reducing, and in large amounts could appear black. The iron content of the glass, as a component within the sand, results in a range of natural colors, from an aqua blue-green in low concentrations to a more saturated green and blue in concentrations above 1%. The presence of iron in reducing atmosphere leads to a greenish-blue color of the glass which becomes clear blue when the

amount of Fe^{2+} is about the half of the total iron content. The blue color becomes deeper with enhancing the Fe^{2+}/Fe^{3+} ratio, Fe^{2+} only renders glass blue color. Adding Mn_2O_3 to the glass melt results in a redox reaction: $Mn^{3+} + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$. As a result, the strong blue color of Fe^{2+} disappears and is replaced by a yellowish color of Fe^{3+}. The addition of manganese oxide to the glass melt allows the producers to avoid undesirable natural tints (Rehren and Cholakova, 2010).

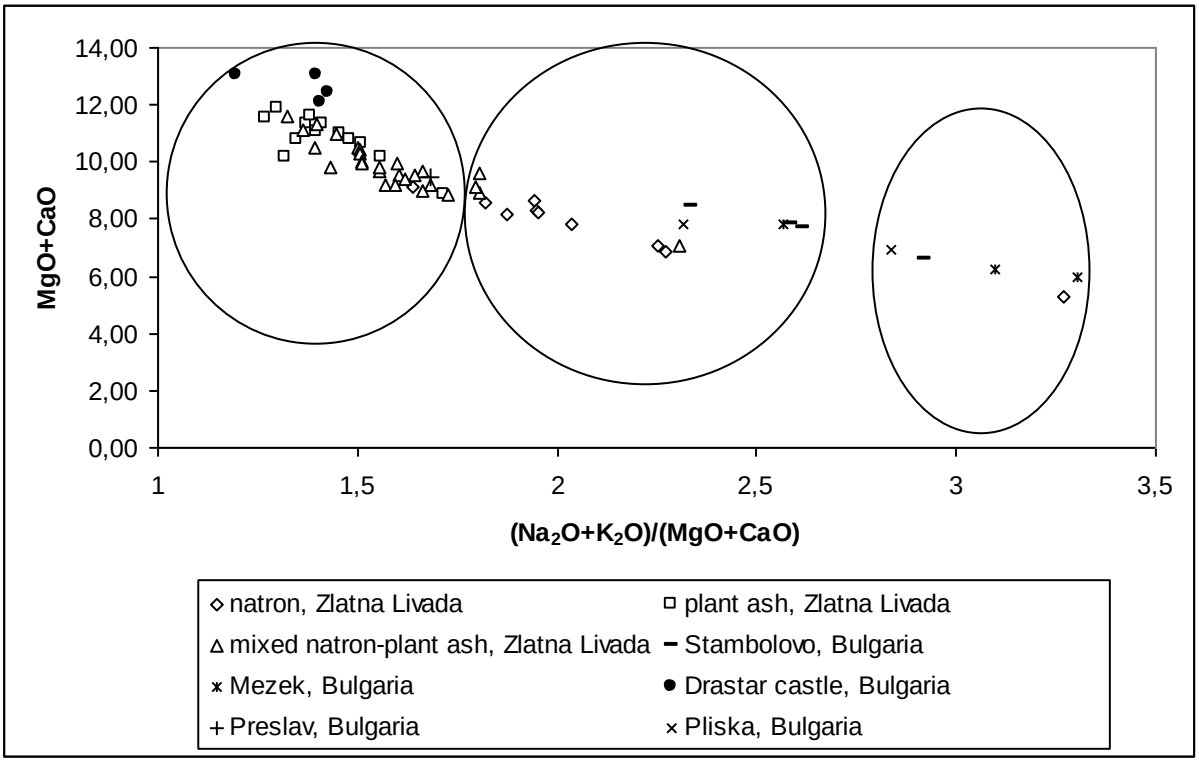

Figure 6 Content of divalent metal oxides with respect to the glass norm $(Na_2O+K_2O)/CaO+MgO$

The values for Cu, Mn, Fe and Co reported in the literature as minimum concentrations necessary to produce glass coloration are: Cu – 0.6%; Mn – 0.5%; Fe_2O_3 = 0.25 %, CoO = 0.02 % (Kuleff and Djingova 2002). As mentioned above, the glasses analysed in the present work were opaque (around 36%) and translucent. Apart from the above mentioned classification, the samples can be separated into several groups with respect to their color as given in Table 3.

The results presented in Table 3 show that the amounts of Co and Cu (usually responsible for the blue coloration of glass) in the fragments from group 1a are far below the minimum concentrations necessary to produce glass coloration. The dark blue color of the glass fragments from this group can be attributed to their high iron content (3.3-6.3% FeO), melted at reducing atmosphere. The concentration of Sb_2O_3 is below the limit of detection. Therefore, most probably the opacity of the glass material is due to the presence of tin oxide (SnO_2) and/or the reduction of CuO to Cu_2O.

The blue color of the fragments in group 1b is due to CoO (0.041-0.083%) which is known to be a very strong chromophore. Additionally, the relatively high iron concentration (1.1-1.6% FeO), melted at reducing atmosphere could also contribute to the blue color.

The relatively high concentration of iron oxide (2.4-3.4% Fe_2O_3) - about five times exceeding manganese oxide (0.51-0.86% MnO) in the samples from group 2a causes their opacity and dark green color, indicating that in this case the melting was carried out in oxidizing environment (Bamford, 1977). The green to light green color of the glass fragments in the samples from group 2b is due to the lower concentration of iron oxide (0.6-1.7% Fe_2O_3) compared to group 2a. Similar glass coloration, depending on the

Fe_2O_3 and MnO concentrations was determined by Cagno et al. (2012b).

Although the concentration of CuO in group 1 (blue glasses) is lower than the the minimum concentrations necessary to produce glass coloration, it can be noticed that in most of the samples it's content is one order of magnitute higher than in the green ones which suggests that it may be responsible for the blue color of the glasses. The blue-green color of the fragments from group 3 is due to the high concentration of iron oxide: 2.83% FeO in the opaque (group 3a) and between 1.23 and 1.86% FeO in the translucent glass samples (group 3b), melted in reducing atmosphere. In two of the samples (818 and 830) a measurable concentration of CoO was detected, which could also be responcible for the blue color. CoO could be added on purpose to color the glass or its presence is a result of recycling of colored glass of various composition, diluting the color.

Although brown color is related to ferrisulfide chromophore (Schreurs and Brill 1984), sulfur was not established after PIXE analysis. The metal oxide concentration (Table 3) shows that the different shades of brown color are due to the high concentration of Fe_2O_3 (2.4-4.9%), Mn_2O_3 (0.3-0.7%), which combinations in oxidizing atmosphere result in yellow, light to dark-brown and even black colors according to Detcheva et al. (2010). The addition of CuO (0.6-2.7%) gives reddish tint to the glasses. Since the brown opaque group glasses are also the group with the highest CuO contents, the presence of CuO is most likely the cause for the opacity.

The colorless glasses were obtained by the presence of high amount of MnO (0.6-2%), from 1.5 to 3 times higher than the corresponding amount of Fe_2O_3. In this case most probably pyrolusite (MnO_2) was purposely added as a decolorizer. Only in the colorless sample 816T Sb_2O_3 was used as a decolorizer, typical for some types of roman glass. This sample is an evidence that recycled roman glass was incorporated in the medieval glass production (Foster and Jackson 2010; Hiusman et al. 2009).

Table 3 Grouping of the glass samples, according to their color and its relation to the concentrations of FeO, CuO, MnO and CoO

color	sample	color	Fe_2O_3	CuO	MnO	CoO	group
blue	839	dark blue-black	6.35	0.06	0.63		1a opaque
	837	dark blue	4.32	0.13	0.81		
	845	dark blue	4.16	0.31	0.76		
	842	dark blue	4.03	0.12	0.74		
	820	dark blue	3.93	0.45	0.72		
	836	dark blue	3.9	0.11	0.76		
	826	dark blue	3.59	0.10	0.62		
	834	dark blue	3.33	0.15	0.82		
	805	light blue	1.62	0.12	0.64	0.041	1b translucent
	833	deep blue	1.46	0.10	0.53	0.083	
	844	deep blue	1.21	0.11	0.5	0.056	
	816B	blue	1.10	0.06	0.72	0.041	
	824	blue	1.06	0.08	0.77	0.071	
	825	blue	1.18	0.09	0.68	0.056	
green	813	dark green	3.39	0.04	0.67		2a opaque
	814	dark green	2.16	0.07	0.51		
	829	dark green	2.36	0.07	0.86		
	832	green	1.67	0.08	0.52	0.021	2b translucent
	848	green	1.15	0.07	0.6		
	849	green	0.92	0.05	0.52		
	838	green	0.74	0.03	0.57		
blue-green	841	blue-green	2.83	0.64	0.77		3a opaque
	806	blue-green	1.86	0.12	0.78		3b translucent
	818	blue-green	1.74	0.15	0.51	0.029	
	830	blue-green	1.53	0.13	0.53	0.032	
	817	blue-green	1.23	0.09	0.77		
brown	812	brown	4.93	1.64	0.47	0.027	4a opaque
	819	brown-redish	3.6	0.92	0.7		
	822	brown-redish	3.25	0.61	0.33		
	821	brown-redish	2.93	0.64	0.74		

	823	light brown-redish	2.47	2.74	0.73		
	840	light brown-redish	2.42	1.39	0.73		
	801	light brown	1.97	0.94	0.56		4b translucent
	811	dark brown	1.49	0.07	1.95		
	843	brown-greenish	1.12	0.25	1.69		
	807	brown	0.52	0.01	0.59		
	835	brown-redish	1.08	0.07	1.12		
	831	dark brown	1.04	0.06	1.89		
	828	dark brown	0.76	0.03	1.91		
colorless	815	colorless, greenish tint	1.38	0.04	2.04		5 translucent
	810	colorless, greenish tint	0.58	<0.0005	1.82		
	803	colorless, pale greenish tint	0.71	<0.0005	1.14		
	809	colorless, pale greenish tint	0.60	0.05	0.94		
	808	colorless, pale greenish tint	0.51	0.03	0.75		
	847	colorless, pale greenish tint	0.80	0.03	0.85		
	827	colorless, pale greenish tint	0.52	0.02	0.78		
	802	colorless, pale pink tint	0.38	<0.0005	0.6		
	804	colorless, pale pink tint	0.39	<0.0005	0.58		
	846	colorless, pale greenish tint	0.38	<0.0005	0.95		
	816T	colorless, pale yellow tint	0.33	<0.0005	0.01		

4. CONCLUSIONS

The bulk glass chemical composition data from the analyses of 43 pieces of bracelets, 6 pieces of vessels and 1 piece of handle cup from Zlatna Livada was determined using simultaneous external PIXE-PIGE methods. All analyzed fragments were identified as soda-lime-silica glass type. According to the sources of flux (the ratio of K_2O vs. MgO) the glass fragments were divided into "*natron*", "*plant*" and "*mixed natron-plant ash*" type.

Further the results from the present study can be summarized as follows:

i. For the production of the *natron* group of bracelets Roman-province recipe norm was used;

ii. The *plant ash* group and the *mixed natron-plant ash* group of fragments were produced following Near East recipe norm.

The comparison to literature data indicates that during the period 7th -13th century AD, the medieval Bulgarian glasses were soda-lime–silica type. Two recipe norms and three types of flux were simultaneously used. This reflects the complex influence of Near East, Byzantine and Roman traditions of glass production on Bulgarian craftsmen as well as the trade relations to different medieval centres from where probably glass ware were imported.

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