

Archaeometric investigation of roman glass finds from Bulgaria

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Introduction

Glass finds discovered in the European part of the Roman Empire are usually referred to as Roman glasses while the glass from the Near East and Egypt is considered separately although it has been produced in the same period of time. One of the reasons for this classification is that glass production in Egypt and the Near East has had a long tradition while the knowledge of glassmaking has been introduced in the Roman Empire from Mesopotamia and Egypt and is considered as new for the territories of Italy and the Eastern provinces. The territory of present Bulgaria belongs to these regions. The lack of enough chemico-technological investigations of Roman glass excavated in Italy was recognized in the literature in the early 80-ies (e.g. Goffer, 1980) and it was recently compensated by the investigations carried out by Casoli&Mirti (1992) and Verita&Toninaga (1990). This lack is still more valid for the glass, excavated on Bulgarian territory where only a sporadic information exists which does not provide an answer to the questions concerning the technology of glassmaking. It is worth mentioning that the finds from that period are numerous (see e.g. Kabakhciewa, 1987; 1996; 1997; 1997a; Mincev, 1986; 1988; 1989; 1990; 1992) and there are direct evidences for glass production in Bulgaria in the period 1st - 5th century AD (Kabakhciewa, 1987; 1996; 1997; 1997a;). Therefore the aim of the present study is to investigate glass finds from the Roman period in Bulgaria using Instrumental Neutron Activation Analysis (INAA). The method for analysis is described in Kuleff et al., (1984; 1988) and Kuleff&Djingova (1990). Thus data for the chemical composition of glasses from the Roman period in Bulgaria will be obtained for the first time and the results might be used for initial conclusions about the technology of glass production.

Experimental

1. Material. Twenty six glass finds, referred to the Roman period, were subjected to analysis. Nine from the finds were excavated in the glass-workshop in the Roman town Oescus (the workshop is dated to the first half of 3rd - first half of 4th century AD). Three of them represent glass from glassmelting tubs excavated in the workshop. The 10 finds from Varna and the 5 finds from the Roman villa Armira belong to the 2nd - 4th century AD, while the two finds from Kaliakra are dated to the 4th - 6th century AD. A short description of the finds is given in Table 1 and the investigated sites are presented in Fig. 1.

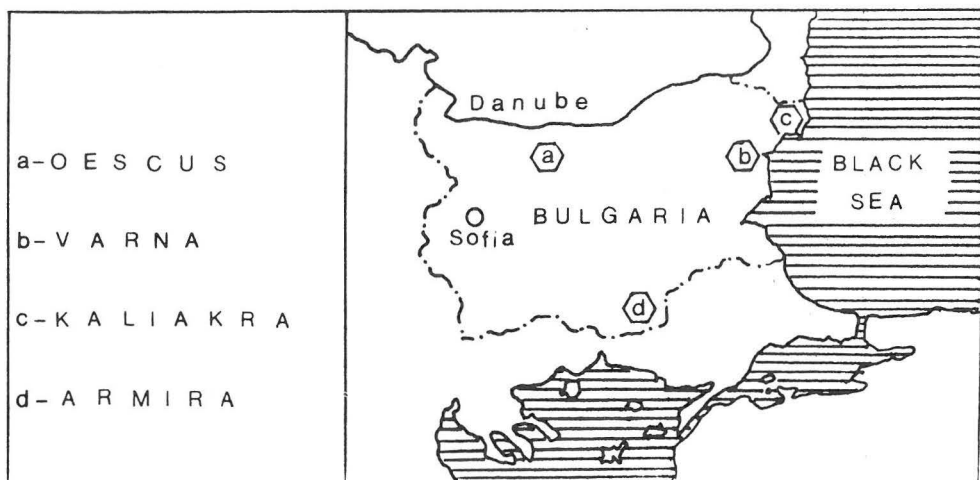


Fig. 1: Map of Bulgaria showing the location of the samling places.

2. Method of analysis. To remove surface contamination the glass samples are carefully washed with tap water, detergent and brush and rinsed with deionized water. Thus the thin iridescent weathering layer (if present) is removed. The samples are placed between polyethelene plates, crushed and homogenized in an agate mortar.

INAA (Kuleff et al., 1984; 1988; Kuleff&Djingova, 1990) and energy dispersive X-ray fluorescence analysis (ED XRFA) have been used for the analysis of the investigated glass finds. INAA was used to determine the content of Al, As, Ba, Ca, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, La, Mg, Mn, Na, Rb, Sb, Sc, Sm, Ta, Th, Ti, V, and Yb in the samples after two irradiations with pile and one with epithermal neutrons and six measurements (twice after each irradiation) (Kuleff et al., 1984; Kuleff&Djingova, 1990). The gamma-spectra were measured with a HP Ge detector (energy resolution 1.9 keV and efficiency 15 % for 1332.5 keV gamma line of ^{60}Co) connected to a 4096 channel pulse height analyser (Canberra 35 +).

ED XRFA was used for determination of the content of lead and sodium in some of the investigated samples. Excitation was done by X-rays produced by a tube: voltage 30 kV; current 0.15 mA, Ag anode and filter rhodium.

The obtained analytical data (Table 2) were subjected to cluster analysis using the program package of Brookhaven National Laboratory (Sayre, 1988). The following subprograms were used:

- CONDIST = for calculation of distance coefficient matrix using squared mean Euclidean distance;

- AGCLUS = for aggregative hierarchical clustering using „nature’s group“ as clustering method. The cluster size is defined as the mean of the distances between all pairs of points within the cluster, not just pairs of distinct items, i.e. the „diagonal“ entities of the dissimilarities matrix are included in the mean and the size is multiplied by the number of specimens within the cluster. Clustering proceeds by joining in sequence those clusters for which the new cluster would have a minimum net increase in size over the combined sizes to the clusters to be merged.

Table 1: Description of the investigated glass samples.

Lab.code	Description	Colour	Date c. AD	Excavation site
52.OES	Fragment, disc form, thick folded rim	deep green	IV-VI	Oescus
53.OES	Glass from glassmelting tub	green	III-IV	Oescus
54.OES	Fragment of bracelet	colourless slight yellow	II-IV	Oescus
56.OES	Fragment of window glass	colourless slight yellow	III-IV	Oescus
57.OES	Fragment of vessel (cup ?)	colourless slight yellow	III-IV	Oescus
58.OES	Fragment of window glass	colourless	III-IV	Oescus
59.OES	Fragment of window glass	colourless slight green	III-IV	Oescus
60.OES	Glass from glassmelting tub	colourless slight yellow	II-IV	Oescus
61.OES	Glass from glassmelting tub	slight blue-greenish	II-IV	Oescus
62.VAR	Fragment of unguentarium in the form of a bell	colourless	II-III	Varna
63.VAR	Fragment of vessel (cup ?)	colourless	II-III	Varna
64.VAR	Fragment of unguentarium	green	I-II	Varna
65.VAR	Fragment of unguentarium	colourless slight yellow	II-III	near Varna
66.VAR	Fragment of bottle-flask	colourless slight yellow	III-IV	Varna
67.VAR	Fragment of unguentarium	colourless	III	Varna
68.VAR	Fragment of unguentarium in the form of a ball	colourless	III	Varna
69.VAR	Fragment of jug (ionohoe)	colourless slight greenish	III	Varna
70.VAR	Fragment of unguentarium	colourless	IV-VI	Varna
71.VAR	Fragment of unguentarium in the form of a bell	colourless	II-III	Varna
72.KAL	Fragment of wheel beaker	slight greenish	IV-VI	Kaliakra
73.KAL	Fragment of window glass	slight yellowish	IV-VI	Kaliakra
74.ARM	Fragment of window glass	colourless slight yellowish	II-IV	Armira
75.ARM	Fragment of window glass	colourless slight yellowish	II-IV	Armira
76.ARM	Fragment of window glass	colourless	II-IV	Armira
77.ARM	Fragment of window glass	colourless blueish	II-IV	Armira
78.ARM	Fragment of the botom of bottle	colourless greenish	II-IV	Armira

Table 2: Concentration of determined elements ($\mu\text{g/g}$) in investigated samples of Roman glasses

Element	52.OES	53.OES	54.OES	56.OES	57.OES
Al_2O_3 (%)	2.61 ± 0.08	2.15 ± 0.25	2.06 ± 0.34	2.31 ± 0.06	2.32 ± 0.08
As	242 ± 5	<4	14 ± 2	5 ± 1	<4
Ba	67 ± 3	660 ± 50	417 ± 40	390 ± 80	240 ± 180
Br	9.3 ± 1.9	1.9 ± 0.5	2.4 ± 0.4	2.1 ± 0.3	3.9 ± 0.8
CaO (%)	5.81 ± 0.32	7.22 ± 0.84	6.41 ± 0.50	8.27 ± 0.50	7.56 ± 0.75
Ce	16.6 ± 1.6	15.5 ± 1.6	95.0 ± 1.5	11.6 ± 1.1	13.2 ± 1.7
Cl (%)	0.87 ± 0.09	1.93 ± 0.23	0.20 ± 0.19	2.60 ± 0.45	2.51 ± 0.43
Co	11.5 ± 1.8	4.0 ± 0.5	16.6 ± 0.8	3.0 ± 0.5	6.0 ± 0.3
Cr	16 ± 5	19 ± 3	81 ± 4	11 ± 4	12 ± 3
Cs	0.26 ± 0.06	< 0.1	0.70 ± 0.09	0.25 ± 0.09	0.55 ± 0.08
Cu	6410 ± 520	130 ± 20	330 ± 50	220 ± 30	215 ± 30
Dy	< 3	4.0 ± 1.0	3.0 ± 1.0	2.0 ± 1.5	2.3 ± 1.1
Eu	0.13 ± 0.02	0.66 ± 0.08	1.43 ± 0.18	0.58 ± 0.06	0.46 ± 0.09
Fe_2O_3 (%)	0.99 ± 0.03	0.59 ± 0.03	5.58 ± 0.13	0.41 ± 0.03	0.46 ± 0.03
Hf	2.1 ± 0.2	1.3 ± 0.2	5.9 ± 0.2	1.3 ± 0.1	1.3 ± 0.2
K_2O (%)	0.9 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	0.5 ± 0.1	0.9 ± 0.1
La	13.8 ± 1.5	8.7 ± 0.4	41.3 ± 1.9	6.2 ± 0.6	5.9 ± 0.6
Lu	-	0.11 ± 0.03	0.46 ± 0.04	0.23 ± 0.04	0.08 ± 0.02
MgO (%)	0.44 ± 0.03	0.52 ± 0.03	1.93 ± 0.03	0.79 ± 0.03	0.54 ± 0.03
Mn	2730 ± 40	1480 ± 140	11520 ± 440	2160 ± 30	4250 ± 130
Na_2O (%)	23.6 ± 0.5	21.5 ± 0.3	21.5 ± 0.4	22.6 ± 0.3	21.6 ± 0.8
Nd	7 ± 2	4 ± 1	41 ± 2	30 ± 2	34 ± 3
Rb	< 20	45 ± 6	125 ± 9	18 ± 4	35 ± 5
Sb	122 ± 8	2500 ± 40	3.2 ± 0.1	2960 ± 50	2000 ± 30
Sc	1.7 ± 0.3	1.5 ± 0.1	15.0 ± 0.5	1.1 ± 0.1	1.2 ± 0.1
Sm	2.1 ± 0.1	1.5 ± 0.1	8.3 ± 0.2	1.2 ± 0.2	1.3 ± 0.1
Ta	0.11 ± 0.03	0.11 ± 0.03	0.09 ± 0.04	1.10 ± 0.08	1.14 ± 0.09
Th	1.6 ± 0.1	1.4 ± 0.3	14.4 ± 0.4	0.6 ± 0.2	0.5 ± 0.2
Ti	840 ± 120	660 ± 140	4020 ± 420	480 ± 160	410 ± 160
V	26.1 ± 4.6	15.2 ± 1.7	120 ± 5	13.6 ± 2.9	25.1 ± 1.4
Yb	0.9 ± 0.1	0.6 ± 0.1	3.3 ± 0.2	< 0.6	< 0.5

Table 2: (continuation)

Element	58.OES	59.OES	60.OES	61.OES	62.VAR
Al ₂ O ₃ (%)	2.02±0.17	2.15±0.06	2.26±0.11	2.31±0.06	1.93±0.06
As	<4	<4	<3	<3	<6
Ba	350±40	640±50	280±90	480±70	760±60
Br	1.7±0.6	3.3±0.5	3.3±0.6	3.8±0.5	1.5±0.5
CaO (%)	7.48±0.55	7.36±0.53	7.52±0.54	7.98±0.54	5.73±0.36
Ce	10.5±1.1	13.3±0.7	14.7±0.5	16.0±0.6	5.3±1.3
Cl (%)	1.83±0.38	2.39±0.40	2.63±0.44	2.47±0.42	2.80±0.19
Co	2.2±0.5	4.2±0.1	5.4±0.2	4.8±0.2	2.2±0.3
Cr	8±1	9±1	13±1	12±1	14±1
Cs	0.25±0.08	0.52±0.05	0.86±0.07	0.91±0.09	0.53±0.07
Cu	162±45	150±50	200±70	200±60	400±90
Dy	2.3±0.4	2.3±0.4	2.0±0.4	1.9±0.4	2.0±0.4
Eu	0.57±0.05	0.50±0.06	0.82±0.12	0.93±0.12	0.59±0.09
Fe ₂ O ₃ (%)	0.36±0.04	0.50±0.03	0.44±0.04	0.49±0.03	0.23±0.02
Hf	1.6±0.1	0.9±0.3	1.6±0.2	1.7±0.2	1.4±0.2
K ₂ O (%)	0.6±0.1	0.7±0.1	0.6±0.1	0.5±0.1	<0.5
La	6.6±0.4	6.0±0.6	6.9±0.5	4.4±0.4	6.4±0.4
Lu	-	0.11±0.04	0.45±0.05	0.23±0.04	0.08±0.02
MgO (%)	0.41±0.03	0.58±0.02	0.53±0.03	0.44±0.06	0.36±0.02
Mn	174±20	1950±50	2020±40	2080±40	105±20
Na ₂ O (%)	22.9±0.4	21.6±0.8	22.2±0.5	21.3±0.8	23.7±0.9
Nd	10±2	9±1	12±1	6±2	8±1
Rb	70±8	<5	33±5	12±1	40±5
Sb	4420±50	2470±70	3110±90	2400±80	5300±80
Sc	1.0±0.1	1.2±0.1	1.2±0.1	1.2±0.1	0.6±0.1
Sm	1.3±0.1	1.1±0.1	1.4±0.2	0.7±0.1	1.2±0.1
Ta	0.07±0.01	<0.04	0.14±0.01	0.25±0.03	<0.05
Th	0.8±0.1	0.6±0.1	1.0±0.1	1.1±0.1	1.5±0.2
Ti	470±20	590±20	690±20	600±20	440±20
V	10.7±0.9	13.4±1.1	15.2±1.2	15.2±1.1	4.7±0.5
Yb	<0.6	<0.4	<0.8	<0.5	<0.6

Table 2: (continuation)

Element	63.VAR	64.VAR	65.VAR	66.VAR	67.VAR
Al ₂ O ₃ (%)	1.98±0.06	2.45±0.06	2.26±0.09	2.15±0.08	2.47±0.08
As	<4	4±1	<0.5	22±2	<0.5
Ba	260±50	470±30	340±50	460±40	410±40
Br	5±2	16.4±3.6	14.7±3.2	20.3±1.7	13.7±1.1
CaO (%)	5.76±0.46	7.42±0.62	8.27±0.60	10.11±1.02	9.51±0.99
Ce	12.0±0.1	14.7±0.2	13.7±0.3	13.1±0.31	2.1±0.4
Cl (%)	2.97±0.60	2.20±0.40	2.04±0.35	1.82±0.25	1.75±0.30
Co	4.0±0.4	16.9±0.5	7.8±0.3	8.1±0.2	9.1±0.2
Cr	11±1	18±1	11±1	15±1	14±1
Cs	1.53±0.18	1.02±0.12	1.19±0.12	0.58±0.09	2.00±0.10
Cu	400±90	510±130	190±60	270±80	250±100
Dy	<1.5	3.1±0.3	1.5±0.7	3.0±0.9	2.7±0.9
Eu	0.81±0.08	0.75±0.15	0.50±0.09	0.51±0.09	0.61±0.07
Fe ₂ O ₃ (%)	0.26±0.02	1.52±0.07	0.27±0.02	0.72±0.04	0.37±0.03
Hf	2.6±0.2	2.0±0.2	0.7±0.1	2.5±0.2	0.6±0.1
K ₂ O (%)	0.5±0.1	<0.4	<0.4	< 0.3	<0.3
La	6.8±0.4	7.0±0.2	6.2±0.2	7.3±0.2	8.1±0.2
Lu	0.11±0.02	0.16±0.03	0.07±0.01	0.17±0.02	0.13±0.02
MgO (%)	0.46±0.07	1.63±0.05	0.39±0.03	1.24±0.04	0.48±0.03
Mn	68±7	13900±450	2050±70	7200±120	6730±100
Na ₂ O (%)	12.3±0.4	5.6±0.2	4.2±0.3	5.5±0.3	4.0±0.3
Nd	30±2	1.8±0.2	<1.5	<1.5	46±5
Rb	50±6	22±2	6±1	14±1	<1
Sb	5580±50	560±9	6.4±0.2	113±10	107±7
Sc	0.6±0.1	2.4±0.1	0.7±0.1	1.6±0.1	1.0±0.1
Sm	1.2±0.2	1.8±0.1	1.5±0.1	1.8±0.1	1.6±0.1
Ta	<0.05	0.26±0.05	0.23±0.3	<0.04	0.26±0.06
Th	<0.9	1.3±0.1	0.9±0.1	0.9±0.1	1.3±0.1
Ti	555±60	1330±230	330±40	1040±100	560±90
V	6.2±1.1	58±5	15.3±1.7	21±2	25±3
Yb	<0.4	<0.3	0.5±0.1	0.3±0.1	0.6±0.1

Table 2: (continuation)

Element	68.VAR	69.VAR	70.VAR	71.VAR	72.KAL
Al ₂ O ₃ (%)	1.89±0.06	2.68±0.08	2.49±0.09	2.63±0.13	-
As	<1	<0.5	<0.5	<0.5	<0.8
Ba	<120	500±70	380±50	680±70	473±50
Br	<3	21±2	6.4±1.4	28±3	4.4±1.3
CaO (%)	7.98±0.87	10.82±1.09	10.00±0.74	7.94±0.60	7.3±0.7
Ce	13.7±0.9	14.2±0.7	14.1±0.9	13.2±0.7	13.3±1.9
Cl (%)	2.24±0.44	1.47±0.39	1.78±0.31	2.35±0.40	6400±400
Co	7.9±0.6	14.8±1.1	9.2±0.9	4.7±0.8	10.1±0.4
Cr	11±1	14±1	15±1	3±1	13.4±1.1
Cs	2.8±0.1	3.1±0.2	1.2±0.2	1.0±0.2	0.7±0.1
Cu	225±90	250±90	200±40	200±30	309±100
Dy	<3	<2	<3	<2	<25
Eu	0.68±0.07	0.54±0.06	0.46±0.05	0.57±0.09	0.37±0.10
Fe ₂ O ₃ (%)	0.44±0.07	0.90±0.11	0.71±0.14	0.51±0.05	0.79±0.03
Hf	2.4±0.1	1.5±0.1	1.5±0.1	1.3±0.1	1.1±0.2
K ₂ O (%)	0.5±0.1	< 0.4	<0.5	0.5±0.1	0.6±0.1
La	5.6±0.2	6.6±0.2	8.2±0.3	8.2±0.5	7.4±1.1
Lu	0.06±0.01	0.18±0.02	0.10±0.01	0.08±0.02	0.13±0.03
MgO (%)	0.49±0.03	0.81±0.04	0.95±0.06	0.64±0.02	1.0±0.4
Mn	118±12	6830±130	3560±50	2200±30	8900±300
Na ₂ O (%)	9.8±0.4	4.9±0.3	4.8±0.3	8.6±0.4	16.4±0.5
Nd	<2	8±1	<1.5	<2	<2
Rb	<3	<2	6±1	<4	8±2
Sb	3720±120	140±15	64±4	3420±130	240±16
Sc	0.9±0.1	1.6±0.1	1.4±0.1	1.2±0.1	4.4±0.1
Sm	1.3±0.1	1.9±0.2	1.5±0.1	1.4±0.1	1.4±0.2
Ta	<0.05	0.38±0.07	0.26±0.06	<0.06	0.13±0.01
Th	0.9±0.1	0.7±0.1	0.9±0.1	1.7±0.1	0.6±0.1
Ti	210±70	1460±170	1100±100	450±80	1100±250
V	6.7±1.6	26±2	22±1	17±2	32.9±1.6
Yb	0.3±0.1	0.5±0.1	0.5±0.1	<0.3	0.7±0.1

Table 2: (continuation)

Element	73.KAL	74.ARM	75.ARM	76.ARM
Al ₂ O ₃ (%)	-	-	-	-
As	<35	<34	<35	<37
Ba	495±65	515±75	462±48	485±84
Br	2.7±0.6	2.2±0.2	<6	1.5±0.9
CaO (%)	8.0±0.7	5.3±0.6	6.4±0.6	8.4±0.7
Ce	13.0±1.8	10.9±1.5	<5	19.8±2.8
Cl	3600±400	6500±600	6300±400	5900±400
Co	8.8±0.5	9.4±0.7	2.7±0.7	11.1±0.5
Cr	15.7±1.3	15.2±1.2	<5	33.7±2.7
Cs	0.45±0.04	0.35±0.04	2.1±0.1	0.47±0.04
Cu	225±80	<150	<150	190±80
Dy	<20	<30	<20	<20
Eu	0.28±0.08	0.30±0.10	<0.2	0.36±0.10
Fe ₂ O ₃ (%)	0.77±0.03	0.33±0.04	0.36±0.07	0.66±0.02
Hf	1.6±0.2	0.8±0.2	<0.5	1.3±0.2
K ₂ O (%)	-	-	-	2.6±0.8
La	7.7±0.6	6.2±0.7	7.1±0.5	11.9±1.4
Lu	0.10±0.01	0.43±0.12	<0.1	0.11±0.03
MgO(%)	1.2±0.5	-	-	-
Mn	1220±400	7100±300	2300±100	12800±500
Na ₂ O(%)	13.2±0.5	14.2±0.7	14.9±0.5	14.2±0.7
Rb	12±2	<4	<4	<4
Sb	132±6	1.3±0.2	4100±80	1.5±0.3
Sc	1.7±0.1	0.9±0.1	1.7±0.1	0.5±0.1
Sm	1.4±0.1	1.3±0.2	1.4±0.2	2.3±0.2
Sr	380±60	380±90	350±80	330±80
Ta	0.13±0.02	0.13±0.1	<0.1	<0.1
Tb	<0.2	0.3±0.1	2.2±0.4	<0.2
Th	0.9±0.1	0.7±0.1	<0.4	1.6±0.2
Ti	1000±200	<500	<500	<500
V	35.9±2.4	38.5±3.5	12.3±2.2	35.7±4.9
Yb	0.42±0.03	0.46±0.05	0.70±0.16	0.65±0.14

Table 2: (continuation)

Элемент	77.ARM	78.ARM
Al ₂ O (%)	-	-
As	<30	<25
Au	0.007±0.002	<0.005
Ba	505±80	584±40
Br	1.1±0.3	3.3±0.9
CaO (%)	9.8±2.2	10.6±1.7
Ce	10.3±1.5	14.5±1.0
Cl	4500±400	7000±50
Co	3.2±0.2	5.3±0.5
Cr	11.3±0.9	38.5±5.7
Cs	0.34±0.04	<0.04
Cu	<100	340±60
Dy	<15	<10
Eu	0.3±0.1	1.3±0.1
Fe ₂ O ₃ (%)	0.30±0.02	1.34±0.23
Hf	0.9±0.2	1.7±0.2
K ₂ O (%)	1.8±0.6	1.5±0.5
La	5.3±0.7	6.6±1.3
Lu	<0.1	<0.1
MgO(%)	-	-
Mn	2100±100	2245±110
Na ₂ O(%)	11.3±0.4	15.5±0.7
Rb	<5	<4
Sb	0.9±0.2	2430±150
Sc	0.5±0.1	1.7±0.2
Sm	2.2±0.1	1.1±0.2
Sr	380±70	390±80
Ta	<0.1	1.9±0.2
Tb	<0.1	<0.1
Th	0.9±0.1	1.7±0.2
Ti	<300	1130±280
U	2.4±0.2	2.1±0.2
V	21.2±2.2	16.3±3.2
Yb	0.4±0.1	<0.1

Results and Discussions

The results from the INAA are presented in Table 2. Each value is a mean of 3 independent determinations and is characterized by the respective standard deviation.

The first impression in studying the data in Table 2 is the considerably low Na_2O content (4.0 - 5.6 %) of some of the finds from Varna. (These results have been proven by ED XRFA and classical analytical methods.) This low concentration of Na_2O is not compensated by higher K_2O concentration, which is below 0.5 % in these finds and is far below the necessary one for potassium glass. Similar results are reported by Liritzis et al. (1995). This fact poses the question: what is compensating the deficiency of alkali oxides in the investigated glasses? One possibility is the change of alkali oxides with lead by which the so called lead glass is obtained. This technology is known for Roman glasses, originating from Egypt (Bezborodov, 1969).

The Oescus glasses have K_2O concentration in the interval 0.5-0.9 %, which is slightly higher than the typical one for Na-Ca-Si Roman glass (e.g. Bezborodov, 1969; Caley, 1962; Shtapova, 1983; Verita & Toninaga, 1990), but still in the interval, characteristic for sodium glass.

Since INAA is an inappropriate analytical method for the determination of lead, ED XRFA was used for the analysis of lead in the glass finds from Varna. The results are presented in Table 3 and the concentrations are within the typical interval for lead in Na-Ca-Si Roman glass (e.g. Baxter et al., 1995; Bezborodov, 1969; Caley, 1962; Sayre, 1968; Sayre & Smith, 1961; Verita & Toninaga, 1990). Therefore the investigated Roman glasses, excavated in Varna have been produced neither of potassium nor of lead glass.

Extremely low alkali concentration have been determined by Liritzis et al. (1995) in Roman glasses from Patras. The paper of Liritzis et al. (1995) reports concentration of Na_2O for one of the samples amounting to 1.2 %! Additionally Cox & Ford (1989) communicate data showing more than twofold decrease in the concentrations of Na_2O and K_2O in the surface layer of glass corroded over a period of 240 years. These results (Liritzis et al., 1995 and Cox & Ford, 1989), the evidence of strong corrosion and the very thin walls (less than 1 mm) of the glass finds from Varna investigated in this work give us the argument to presume that the low concentration of Na is a result of leaching by the soil solution and the investigated glasses are really Na-Ca-Si.

These facts might be accepted as an additional prove of our proposal that mostly trace elements and microelements should be used in the classification of archaeological glasses on the basis of similarity of their chemical composition (Djingova & Kuleff, 1991; 1992; Kuleff et al., 1985). Using this approach the investigated 26 finds of Roman glass were subjected to cluster analysis, without taking into account the concentrations of macroelements. Table 4 presents the membership of the 6 clusters, formed on the basis of similarity in the chemical composition.

With the exception of 52.OES (dated to the 4th - 6th century AD) and 54.OES, the finds from Oescus form one stable group while the finds from Varna, Kaliakra and villa Armira are distributed among the rest of the clusters. This is not unexpected since the finds from Varna, Kaliakra and Armira cannot be referred to a definite production centre on the one hand and on the other hand imported materials from different regions are very typical for the fortresses and towns along the sea coast. The formation of a common group of finds from Kaliakra and villa Armira (cluster 4) presents certain interest. A probable explanation might be the import from one and the same production centre most probably in Constantinople. Finds from Armira are forming another cluster and are present among the outliers which is an indication that the glass has been imported from diffe-

rent production centres to Armira. This result is an indirect prove of the archaeological data, which do not indicate any local production of glass in Armira (Kabakhchieva, 1997b).

The classification of the investigated finds permits the correct determination of the chemical profile of the glass produced in the Roman town Oescus during 3rd - 4th century AD. Among the members of cluster 1 (Table 4 and Table 1) are 3 finds of melted glass, excavated in the glassworkshops in Oescus. Table 5 presents the mean values of the concentrations of the investigated elements for cluster 1, which actually represent the chemical profile of Roman glass made in Oescus.

One of the basic questions answered by chemical analysis of ancient glass is the revealing of the recipe, used for the glassmaking. One of the possible approaches is proposed by Shtapova (1983), which uses the ratio alkali oxides to alkaline earths oxides to reach the conclusion that three recipes have been simultaneously used in the Roman Empire, independently of the place of production. Using this approach it may be stated that in the production of Oescus glass natural soda has been used (the ratio $[Na_2O] : [K_2O]$ is bigger than 20) and a recipe according which $([Na_2O] + [K_2O]) : ([CaO] + [MgO]) = 2.9$. (For more see Shtapova, 1983). Of course this result cannot answer the question where the natural soda has been imported from?

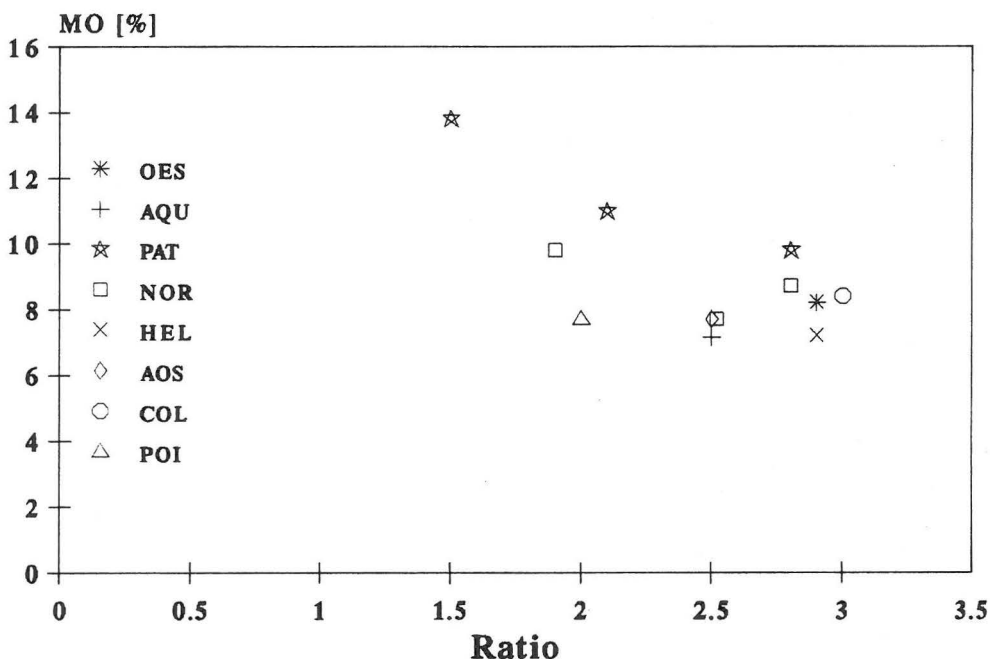


Fig.2: The ratio $([M_2O]) : ([MO])$ vs MO in Roman glasses from Bulgaria and other European countries. $[M_2O] = ([Na_2O] + [K_2O])$; $[MO] = ([CaO] + [MgO])$

AQU = Aquilea (Verita & Toninaga. 1990);

AOS = Aosta (Casoli & Mirti. 1992);

COL = Colchester (Baxter et al..1995);

HEL = Helgoe (Sanderson & Hunter. 1982);

OES = Oescus (this work);

PAT = Patras (Liritzis et al.. 1995);

POI = Poitiers (Velde & Gendron. 1980)

Table 3: Concentration of lead ($\mu\text{g/g}$) in samples of Roman glasses from Varna.

Sample	62.VAR	65.VAR	66.VAR	68.VAR	69.VAR	70.VAR
Pb	140	430	65	110	130	2560

Table 4: Membership of the samples in clusters

Cluster	Samples member of the cluster
1	53.OES. 56.OES. 57.OES. 58.OES. 59.OES. 60.OES. 61.OES.
2	63.VAR. 68.VAR.
3	66.VAR. 69.VAR. 70.VAR.
4	72.KAL. 73.KAL. 75.ARM.
5	65.VAR. 67.VAR.
6	74.ARM. 77.ARM.
outlier	52.OES. 54.OES. 62.VAR. 64.VAR. 71.VAR. 78.ARM.

Table 5: Mean concentrations of the Roman glass, produced in Oescus.

Element	$\bar{O} \pm s$	RSD (%)	Element	$\bar{O} \pm s$	RSD (%)
Al_2O_3 (%)	2.22 ± 0.11	5.1	La	6.4 ± 1.3	20.3
As	<4	-	Lu	0.16 ± 0.08	50.0
Ba	406 ± 195	48.0	MgO (%)	0.54 ± 0.12	22.2
Br	2.9 ± 0.9	32.1	Mn	2020 ± 1200	59.4
CaO (%)	7.63 ± 0.37	4.8	Na_2O (%)	21.6 ± 1.3	6.0
Ce	13.4 ± 2.2	16.4	Nd	15 ± 12	81.8
Cl (%)	2.32 ± 0.37	15.9	Rb	33 ± 22	71.4
Co	4.0 ± 1.7	42.5	Sb	2850 ± 790	27.8
Cr	11.6 ± 3.7	31.8	Sc	1.2 ± 0.1	8.3
Cs	0.45 ± 0.27	59.0	Sm	1.2 ± 0.2	16.7
Cu	179 ± 39	21.8	Ta	0.4 ± 0.7	175
Dy	2.4 ± 0.7	30.7	Th	0.8 ± 0.4	50.0
Eu	0.63 ± 0.18	28.5	Ti	547 ± 120	21.9
Fe_2O_3 (%)	0.46 ± 0.07	15.9	V	15.0 ± 4.4	29.3
Hf	1.3 ± 0.3	23.0	Yb	0.6 ± 0.1	16.7
K_2O (%)	0.7 ± 0.2	28.5			

Figure 2 presents a comparison of the Oescus glass with other European Roman glasses in respect to the recipe used for their production (Baxter et al., 1995; Bezborodov, 1969; Caley, 1962; Casoli & Mirti, 1992; Christie et al., 1979; Liritzis et al., 1995; Sanderson & Hunter, 1982; Sanderson et al., 1984; Velde & Gendron, 1980; Verita & Toninato, 1990). There is no correlation between the recipe and the place of production. The glass in Aquilea and Aosta (Italy), in Germany, in Patras (Greece), in Komarov (Ukraina), in Potiers (France) as well as the major part of the investigated Roman glasses from Norway are made according to the recipe ratio 2 - 2.5. In the same time the glass made in Colchester (Britain), Helgoe (Sweden), Oescus (Bulgaria) and a small part of the investigated Norwegian glasses are made according to the recipe ratio 3.0. One sample from Patras is made according to the recipe ratio 1.5, which is more usual for the glass produced in the Near East.

The concentrations of such macrocomponents as Fe_2O_3 , MgO , Al_2O_3 , TiO_2 in Oescus glass are within the intervals, typical for Roman glass.

It is interesting to discuss the concentrations of antimony and manganese since their use for decolouration of glass is very important and an indication for the technological level of glass production. Figure 3 presents the distribution of the investigated finds in respect to the content of Mn and Sb. It shows that the Oescus glasses have relatively higher concentrations of Mn

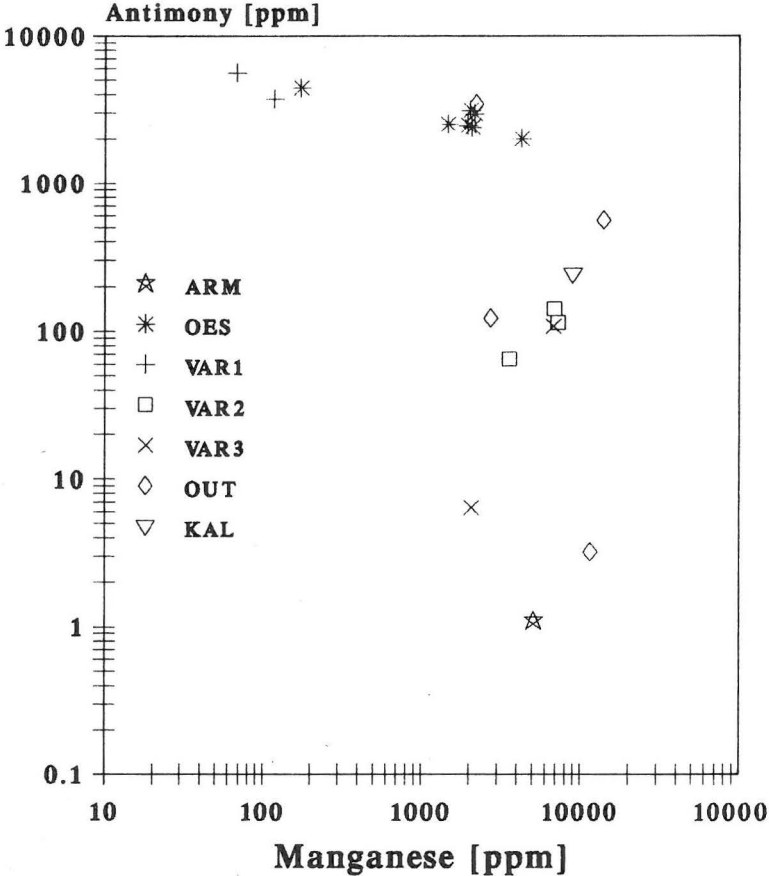


Fig. 3: Concentration of manganese vs concentration of antimony in Roman glasses from Bulgaria.

and Sb in comparison to the glasses from Varna, Kaliakra and Armira. This result is an indication that for the decolouration of the glass in Oescus both Sb and Mn have been used.

Recently Velde and Hochuli-Gysel (1995) investigating glasses from the 1st-3th century reached a conclusion that there is a certain dependance Sb/Fe in Gallo-Roman glass. The glasses of Oescus do not have any correlation between the two elements so no connection between intentional use of Sb in dependance of the concentration of Fe can be found in this case.

Therefore the simultaneous use of antimony and manganese as decolourants according to Sayre (1968) corresponds to the technological methods, known during 2nd - 4th century AD and is characteristic for the production tradition in Italy (see Sayre, 1968; Shtapova, 1983). Therefore this is an indication that glass production in Oescus developed in close contacts to Italy and under the influence of the Roman tradition. An indirect evidence of this assumption may be found in the paper of Dimitrova-Milceva (1996) where archaeological evidences based on stamped Terra sigillata are presented for the contacts between the Roman province Moesia (Oescus and other Roman towns in the region) and North and Middle Italy.

On the other hand the glass finds from Varna are produced using either only Sb (VAR-1) or only Mn (VAR-2, VAR-3, KAL) (see Fig.3). This approach is more characteristic for the Near East tradition and we presume that the finds are probably imported from the Near East. Such a result is not unexpected since Varna is situated on the Black sea and it has been a well known trade centre. Additional indication in this respect is the presence of some typological similarity of glass vessels excavated in Varna to vessels from Syria, Palestina and Asia Minor (see Mincev, 1988, 1989, 1990, 1992).

Since all investigated finds from Oescus are colourless no conclusion is possible about the use of colouring agents in Oescus.

The only find (52.OES) with bright green colour is not belonging to the local groups and therefore is not included in Table 5. Its colour is due to the high concentrations of copper (0.64 %) and iron (0.99 %).

Conclusion

The present investigation permits the characterization of the chemical profile of the glass, produced in the Roman town Oescus (3rd - 4th century AD) by determination of 30 elements and interpretation of the analytical data using multivariate analysis. Additionally archaeological finds from Roman glass, excavated in Varna, Kaliakra (Black sea coast) and villa Armira (near Ivailovgrad) are chemically characterized. The comparison of the analytical data to results for other Roman glasses from Europe enabled the establishment of the technological methods used in Oescus; the recipe ratio 1:3 and of Sb and Mn for decolouration. The conclusion reached is that glass production in Oescus developed under the influence of Italian tradition, while in Varna the near East import probably had major importance.

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ABSTRACT

Using INAA and ED XRFA the content of Al, As, Ba, Ca, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, La, Mg, Mn, Na, Pb, Rb, Sb, Sc, Sm, Ta, Th, Ti, V, and Yb in 26 glass finds from Roman time excavated in Bulgaria were determined. Investigated samples were classified according to the similarity in the chemical composition (cluster analysis). The chemical profile of the glass production in the Roman town Oescus has been obtained. On this basis the recipe used by the production of glass in Oescus has been evaluated. The use of Mn and Sb for decolouration of glass was discussed.

KEYWORDS: GLASS, ROMAN TIME, BULGARIA, CHEMICAL ANALYSIS, INAA, ED XRFA, CLUSTER ANALYSIS.