STUDIES ON ANCIENT ROMAN GLASS USING MICRO-PIXE AND SEM-EDS

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The goal of the experiment was to determine the Roman glass production technology – from paste (glass "clay") recipes to colorants and opacifiers - at the beginning of First Millennium A.D. Glass consists of four principal components: - A former which is the matrix of the glass – this is Silica (SiO_2) exploited in the form of siliceous sand by the Romans; - An alkali flux to lower temperature at which the silica melts: natron (a sodium mineral coming from Egypt) in Roman glass, sodium-rich plants or ash from wood containing potash (K_2CO_3) in medieval times; - A stabilizer to stop the glass dissolving in water and increase corrosion resistance – the most effective is lime (CaO); - A colorant or opacifier, mainly metallic oxides.
Our study was focused on the presence of Na or K as fluxes, of Ca, Al, Mg and of Mn, Fe, Cu, Zn, Pb, As, Sb metallic oxides.
In the present work we discuss the possibility to identify all the important glass components during the same irradiation using PIXE – two detectors, illustrating with the case of Roman glass pieces found in ancient cities from Moesia Inferior (now Dobroudja). The samples) were mainly recipients fragments found in Tropaeum Traiani, Ulmetum, Oltina, Harsova settlements (glass chips dated IIIrd-Vth Centuries AD) – see Figure 1.

Fig. 1. Roman glass from Tropaeum Traiani

The first experiment was performed at Bucharest TANDETRON (see Fig.2): 2.7 MeV protons, approx. 2-3 nA, one millimeter beam diameter to obtain compositional values not influenced by micro-local corrosion and also to allow the analysis on the narrow edge of the cut samples to totally avoid corrosion aspects. We used two detectors: one for Low Energy (analyzing Na, Mg, Al, Si, Cl, K, Ca) and other for High Energy (for Ti to U region). The experiment was initially performed in vacuum on small glass sherds fixed with a carbon adhesive tape on a stainless steel holder (see Fig.3). The final version is an "in-air" - but really in a helium flow (1.2-1.5 l/min) – measurement (see Figs.4,5). The composition was calculated using GUPIX software.

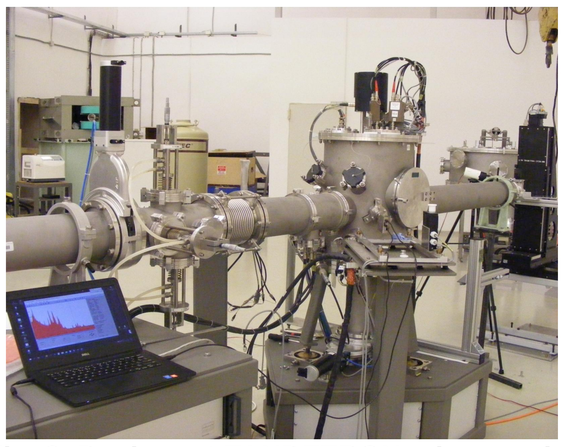

Fig. 2. Bucharest TANDETRON micro-probe

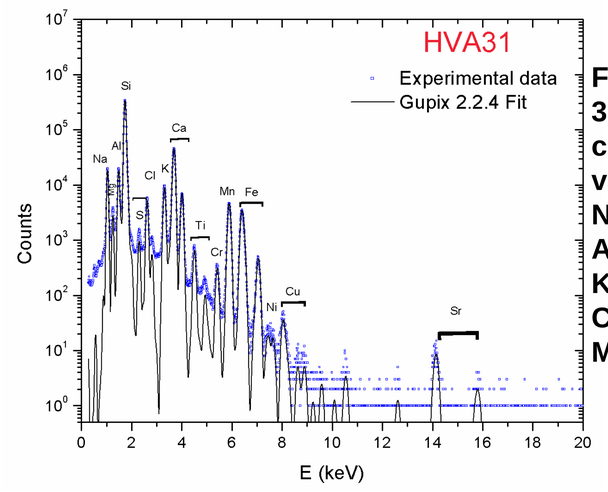

Fig.3. Harsova HVA 31 sample. Some concentration values: Na_2O 12.39%, Al_2O_3 3.97%, K_2O 1.44%, CaO 7.66%, MnO 1.64%

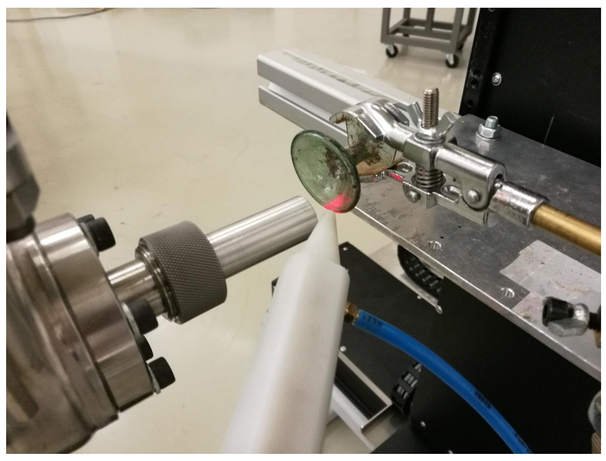

Fig.4. In air (helium flow) measurement

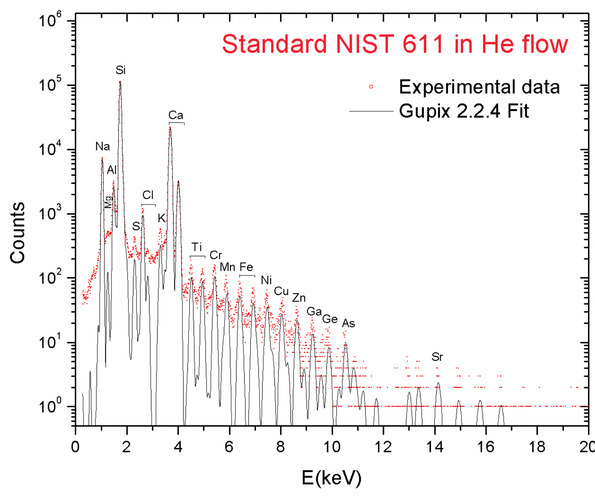

Fig.5. Some concentration values: Na_2O 14.10%, Al_2O_3 1.85%, K_2O 0.16%, CaO 11.10%, MnO 620ppm

To verify the PIXE results on low Z elements a supplementary EDS (Energy-Dispersive X-ray Spectroscopy) analysis was performed based on a Scanning Electron Microscope (*SEM*) Zeiss EVO MA15 with Energy Dispersive X-ray Spectroscopy (*EDS*) module provided by Thermo Scientific. The settings we used during analysis were: electron accelerating voltage EHT - 15 kV, curent *I* - 850 pA and working distance WD - 10.5 mm.

In the case of Harsova-Carsium glass (HVA31 sample) – see Figure 6 and Table 1: the segregation of Al and K in relation to Na and Ca was observed in one selected area – see Fig.7.

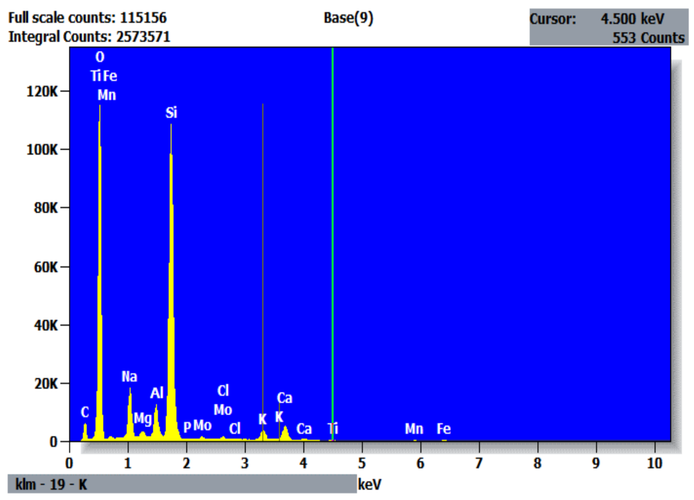

Fig. 6. HVA31 SEM-EDS spectrum

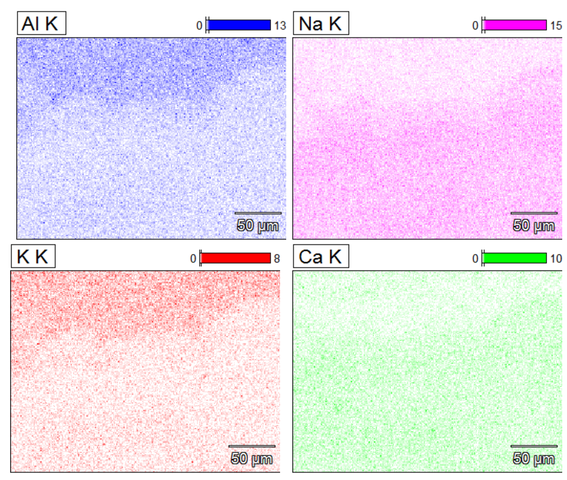

Fig.7. HVA 31 , Al, K, Na, Ca segregation

Element	Base(9)			
	Intensity	Net Counts	Weight %	Atom %
C K	0.00	14142	6.47	9.97
O K	0.00	677696	57.17	66.14
Na K	0.00	117219	6.55	5.27
Mg K	0.00	7817	0.24	0.18
Al K	0.00	72912	1.95	1.34
Si K	0.00	933490	23.00	15.16
P K	0.00	0	0.00	0.00
Cl K	0.00	10637	0.33	0.17
K K	0.00	37806	1.20	0.57
Ca K	0.00	52327	1.84	0.85
Ti K	0.00	1660	0.08	0.03
Mn K	0.00	3516	0.24	0.08
Fe K	0.00	5670	0.42	0.14
Mo L	0.00	13212	0.51	0.10
			100.00	100.00

Table 1. SEM-EDS composition (weight% and atomic% values)

A micro-PIXE experiment was performed using 2 MeV protons at AN2000 LNL microprobe, obtaining elemental maps and point spectra. To verify the performances of Roman glass technology elemental maps were acquired.
In the case of Altinum-Oltina glass (AO5 sample); – see Figure 8: the segregation of Mn in relation to Si was observed in one selected area.

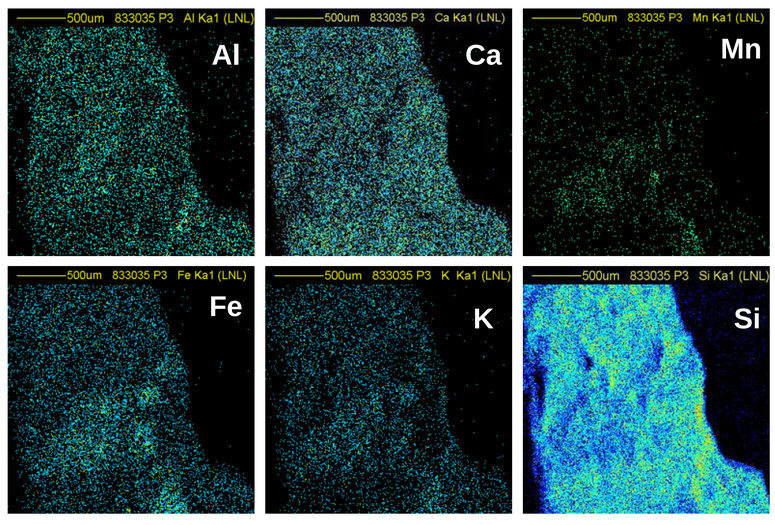

Fig. 8. Sample Altinum-Oltina - AO5 (500 µm x 500 µm)

The main results of our analyses are:
- all the samples are soda–lime-silica glass type (strong presence of Calcium and reduced presence of Potassium) with relevant quantities of Antimony or Manganese (to obtain glass transparency) and Lead.
- there are two recipes for transparency: a Manganese-based and an Antimony-based
- as colorants (green nuances) iron and copper oxides are used
- in air (helium flow) PIXE, SEM-EDS and micro-PIXE (elemental maps) must be used as complementary method to obtain a complete characterization of glass items.

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