STUDIES ON ANCIENT ROMAN GLASS USING PIXE AND SEM-EDS

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\textbf{Abstract.} The goal of the experiments was to study which analytical methods can be used in the best way to compositionally characterize the Roman glass production technology – from paste (glass “clay”) recipes to colorants and opacifiers – in the 1\textsuperscript{st} Millennium A.D. Our conclusion is in air (helium flow) PIXE, SEM-EDS and micro-PIXE (elemental maps) can give a complete characterization of glass items.

\textit{Key words:} Roman glass, in-air PIXE, micro-PIXE, SEM-EDS.

\section{1. INTRODUCTION}

The goal of the experiments was to study how PIXE and SEM-EDS can be used in the best way to compositionally characterize the Roman glass production technology – from paste (glass “clay”) recipes to colorants and opacifiers – in 1\textsuperscript{st} Millennium A.D.

Glass consists of four principal components [1, 2]:

– A former which is the matrix of the glass – this is Silica (SiO\textsubscript{2}) exploited in the form of siliceous sand (quartz) mixed with alumina (typically 2.5%) and lime (about 8%) by the Romans;

– An alkali flux to lower temperature at which the silica melts: only soda (sodium carbonate) as natron (a sodium mineral coming from Egypt, a naturally occurring salt found in dry lake beds around Wadi El Natrun) in Roman glass, sodium-rich plants or ash from wood containing potash (K\textsubscript{2}CO\textsubscript{3}) in medieval times;

– A stabilizer to stop the glass dissolving in water and increase corrosion resistance – the most effective is lime (CaO), in Roman Period lime as shell particles;

– A colorant or opacifier, mainly metallic oxides.

Ancient Roman glass is a soda-lime glass. It was made from silicon, sodium and calcium oxides, with the addition of potassium, magnesium and aluminum oxides [3]. Sometimes a characteristic pale blue-green color is caused by iron oxide, an impurity – see Fig. 1.

Colorless glass was produced by adding antimony or manganese oxides [3]. The use of manganese as de-colorant was a Roman invention first noted in the Imperial period.

In the first millennium AD the Roman economy was highly structured and centralized [4, 5]. So, large primary glass workshops on the Syro-Palestinian coast and in the Egyptian Nile-delta were able to make up to several tons of raw glass. The south-eastern Mediterranean is a strategic location in proximity of the raw materials: calcareous sand (mainly from shells) and mineral soda. The melting temperature of sand was difficult to be reached with ancient furnace technologies, hence, other substances, called flux, were added to reduce the needed melting temperature. This capability was found in Natron, a mixture of sodium salts obtained from lakes with a high rate of evaporation. The primary produced raw glass were subsequently crushed into large irregular chunks to ship it throughout the entire Roman empire to supply the secondary workshops where the raw glass got re-melted and shaped into market ready objects – vessels in our case. In these secondary workshops the glass was often de-colored. The sodium-rich, calcium poor glass composition from Egypt was ideally suited for de-colorising with antimony. The calcium-rich Syro-Palestinian glasses were de-colorised with manganese, not antimony.

An excellent study on compositional identification of 6th Century AD glass from the Lower Danube (Serdica, Dichin and Odartsi settlements in Bulgaria) was published by Cholakova et al. [6]. Recently, a similar study on Early Byzantine glass windowpane shreds from Jelica Mountain in Serbia was published by Balvanovic et al. [7].

Fig. 1 – Roman glasses from Tropaeum Traiani.
2. REGIONAL SETTING – ARCHAEOLOGICAL BACKGROUND

The analyzed glass is specific for the Roman-Byzantine world from the 4th–7th Centuries AD (especially fragments of simple wine-glasses). These were discovered by archaeologists in various settlements fortifications (and their surroundings) in Dobroudja-Constanța County (formerly Scythia Minor or Moesia Inferior): Tropaeum Traiani (Adamclisi), Ulmetum (Pantelimonul de Sus), Altinum? (Oltina) and Carsium (Harşova). Although these fragments are not spectacular or rarely constitute rarities, they bring a valuable historical and archeological contribution on the knowledge of realities of the crafts and commercial links from Late Roman and Early Byzantine era.

Until now, with the exception of the “capital” of Dobroudja – Tomis (where only traces of some few workshops were un-earthed), ancient glass-workshops are not certified in Scythia Minor. However, it has been suggested the possibility of their existence in the context of numerous discoveries of household and religious glassware fragments [8].

The samples we analyzed were mainly recipients fragments found in Tropaeum Traiani – Civitas Tropaensium, Ulmetum, Altinum, Carsium settlements (glass chips dated 4th–7th and in the context of 10th Centuries AD).

Civitas Tropaensium was a Roman castrum situated in Scythia Minor in modern Constanța County, Romania. Its site is now the modern settlement of Adamclisi. It was colonized with Roman veterans of the Dacian Wars, was the largest Roman city of Scythia Minor and became a municipium around 200 AD. In 109 AD, a monument named Tropaeum Traiani was built to commemorate the Roman Empire’s victories over the Dacians. The majority of glass fragments from Tropaeum Traiani came from archaeological researches carried out in the southern district, sector C [9], in an imposing Domus type late-Roman aristocratic edifice (4–6th Century AD). The existing fragments of 10 simple glasses suggest a small warehouse discovered in a small room, under several steps leading to the first floor of the building.

Ulmetum settlement is located in the central part of Dobroudja, on the northwestern edge of Pantelimonul de Sus. The objective, represented by a Roman-Byzantine fortification, had a strategic role on road that protected freight and merchandise transport between the Roman towns of Noviodunum and Marcianopolis [10].

Located in the southeastern part of Constanța County, Oltina (Altinum site ?) is known from important discoveries belonging to pre-Roman, Roman, Byzantine and early medieval periods. The analyzed glass fragments came from “Capul Dealului” hill, located at the limit of Satu Nou and Oltina, where there is an early medieval fortification site with a wave and a ditch [11].

The city of Carsium / Harşova is the result of several phases of habitation, presenting itself today as a complex of vestiges: a camp built by Ala (Gallorum) Flaviana (Vespasianus or Trajan’s order) replaced by a fortress of Constantin the
Great, destroyed by the Huns in 434 BC substantially restored in the sixth Century under Justinian [12]. The investigated glass fragments originate either from an early medieval level or from a layer composed of mixed materials (Roman, early medieval and late medieval) from a Roman Byzantine level under a dwelling.

3. MATERIALS AND METHODS

Our study was focused on the presence of Na or K as fluxes, of Sb or Mn as de-coloring agents (to obtain a transparent glass) and of Ca, Al, Mg, Fe, Cu, Zn, Pb, As metallic oxides. A special attention was given to manganese and antimony, de-colorants used to annihilate the green pale aspect induced by iron oxide (antimony is a stronger de-colorant than manganese – producing a more truly colorless glass) and rarely used together.

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 Moesia Inferior (now Dobrudja) – see Chapter 2.

The first experiment was performed at the Bucharest 3 MV Tandetron™ [13] (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 recently cut samples to totally avoid corrosion aspects. We used two detectors: one for Low Energy – Amptek SDD with a polymer window (analyzing Na, Mg, Al, Si, Cl, K, Ca) and other for High Energy Amptek SDD with a 8 microns Be window (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 (2 l/min) – measurement (2.9 MeV on the target, approx. 2 nA, approx. 1 mm beam diameter) using an Amptek X-123 SDD Complete X-Ray Spectrometer with Silicon Drift Detector (SDD) – 12.7 microns Be window. The composition was calculated using GUPIX version 2.2.4.
In a second experiment, to study the homogeneity of composition for light elements a supplementary investigation was performed using a SEM (Scanning Electron Microscope) Zeiss EVO MA15 coupled with an EDS (Energy Dispersive X-ray Spectroscopy) module provided by Thermo Scientific. The settings for our analysis were: electron accelerating voltage – 15 kV, current I – 850 pA and working distance (sample – detector) 10.5 mm [14].

In a third experiment we used micro-PIXE method with 2 MeV and 1 nA proton beam at AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy [15], obtaining elemental maps and point spectra. The characteristic X-rays were measured with a Canberra HPGe detector (180 eV FWHM at 5.9 keV). The quantitative analysis was performed using the GUPIXWIN software. To verify the performances of Roman glass technology elemental maps were especially acquired.

4. RESULTS AND DISCUSSION

A very important result, both for in vacuum and in-air PIXE measurements, is the good detection of sodium, the flux exclusively used by Romans. Some concentration values for Harșova HVA31 sample: Na₂O 11.60%, MgO 1.04%, Al₂O₃ 4.09%, SiO₂ 69.60%, SO₃ 0.33%, Cl 0.81%, K₂O 1.50%, CaO 8.17%, TiO₂ 0.16%, MnO 1.25%, Fe₂O₃ 1.15%, SrO 712 ppm, PbO 226 ppm – see Fig. 4. The presence of manganese suggests it was used as de-colorant.

![Fig. 4 – Harsova HVA31 sample – in vacuum measurement.](image)

As concerning in-air (helium flow 2 l/min) experiment (2.9 MeV on the target, approx. 2 nA, approx. 1 mm beam diameter) we illustrate with two samples:
– Harsova HVA32: Na\textsubscript{2}O 8.65%, MgO 0.66%, Al\textsubscript{2}O\textsubscript{3} 3.71%, SiO\textsubscript{2} 76.45%, SO\textsubscript{3} 0.25%, Cl 0.86%, K\textsubscript{2}O 0.91%, CaO 7.64%, TiO\textsubscript{2} 0.067%, MnO 0.16%, Fe\textsubscript{2}O\textsubscript{3} 0.46%, SrO 370 ppm, PbO 0 ppm, Sb\textsubscript{2}O\textsubscript{5} 1.87 – see Fig. 5, antimony as de-coloriser.

– Tropaeum Traiani TT6b: Na\textsubscript{2}O 5.33%, MgO 1.49%, Al\textsubscript{2}O\textsubscript{3} 6.24%, SiO\textsubscript{2} 74.67%, SO\textsubscript{3} 0.26%, Cl 0.66%, K\textsubscript{2}O 0.52%, CaO 7.99%, TiO\textsubscript{2} 0.012%, MnO 1.22%, Fe\textsubscript{2}O\textsubscript{3} 0.93%, SrO 1835 ppm, PbO 1391 ppm, manganese as de-coloriser – see Fig. 6.
Generally speaking, the analyzed Roman glass samples are in our case based even on manganese or on antimony de-colorants (never mixed!). The absence of pieces having a mix of manganese and antimony suggests the absence of re-melting of glass chunks, a procedure well spread in large Roman workshops.

In the case of SEM-EDS analysis an example is Harșova-Carsium glass – HVA31 sample (X spectrum in Fig. 7 and Table 1): the segregation of aluminum and potassium in relation to Na and Ca was observed – see Fig. 8 – an explanation can be the difference between used minerals: one containing aluminum and potassium, the other one containing sodium and calcium (probably natron). This segregation could also be an indicator of a local not so very high-skilled workshop. Concentration values are different from PIXE because the SEM-EDS analyzed layer is approx. 2–3 microns and at the surface in-homogeneities are often present.

![Fig. 7 – Harsova HVA31 sample, SEM-EDS spectrum.](image)

**Table 1**

The SEM-EDS composition (weight% and atomic% values)

<table>
<thead>
<tr>
<th>Element</th>
<th>Net Counts</th>
<th>Weight (%)</th>
<th>Atom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>677696</td>
<td>57.17</td>
<td>66.14</td>
</tr>
<tr>
<td>Na</td>
<td>117219</td>
<td>6.55</td>
<td>5.27</td>
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<tr>
<td>Mg</td>
<td>7817</td>
<td>0.24</td>
<td>0.18</td>
</tr>
<tr>
<td>Al</td>
<td>72912</td>
<td>1.95</td>
<td>1.34</td>
</tr>
<tr>
<td>Si</td>
<td>933490</td>
<td>23.00</td>
<td>15.16</td>
</tr>
<tr>
<td>P</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl</td>
<td>10637</td>
<td>0.33</td>
<td>0.17</td>
</tr>
<tr>
<td>K</td>
<td>37806</td>
<td>1.20</td>
<td>0.57</td>
</tr>
<tr>
<td>Ca</td>
<td>52327</td>
<td>1.84</td>
<td>0.85</td>
</tr>
<tr>
<td>Ti</td>
<td>1660</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn</td>
<td>3516</td>
<td>0.24</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe</td>
<td>5670</td>
<td>0.42</td>
<td>0.14</td>
</tr>
<tr>
<td>Mo</td>
<td>13212</td>
<td>0.51</td>
<td>0.10</td>
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</table>
During the third micro-PIXE experiment using 2 MeV protons at AN2000 LNL microprobe elemental maps and point spectra were obtained. To verify the performances of Roman glass technology elemental maps are a good indicator. So, in the case of Altinum-Oltina glass (AO5 sample) – see Fig. 9, the segregation of manganese and iron in relation to silicon, aluminum and calcium was observed. An explanation could be manganese (de-coloriser) was added separately to melted glass and non-homogeneously dissipated in the “paste”.

Fig. 8 – Harsova HVA31 sample, SEM-EDS map spectra – Al, K, Na, Ca segregation.

Fig. 9 – Altinum-Oltina sample AO5 – micro-PIXE map spectra (500 mm × 500 mm).
5. CONCLUSION

The main results of our three experiments 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).

– as known, there are two Roman recipes for transparency: a manganese-based one and an antimony-based one – most probably the manganese-based recipe is local.

– as colorants (green nuances) impurities of iron and copper oxides are the reason.

– only five samples are from glass de-colorised with antimony: two from Tropaeum Traiani, one from Altinum, one from Ulmetum, one from Carsium. The radio antimony/manganese is from 3 to 15, suggesting no role for manganese in de-colorisation.

– thirty-three samples are from manganese de-colorised with manganese: twenty four from Tropaeum Traiani, five from Ulmetum, two from Altinum, two from Carsium.

– ten samples have a green-pale aspect, due to iron impurities: five from Tropaeum Traiani, three from Carsium, one from Ulmetum, one from Altinum.

– 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.

Because there are no data about glass furnaces in Dobroudja, our results suggest the analyzed glass items were imported from secondary workshops dealing with Syro-Palestinian glass (most probably in the Balkans). Only few items have provenance workshops dealing with Egypt glass, most probably luxury objects. We intend to continue our study for more samples from all the Roman settlements from Dobroudja (Moesia Inferior) to try to obtain the glass circulation pattern in this region during 1st Millenium AD.

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REFERENCES


