Romanian Reports in Physics, Vol. 63, No. 4, P. 912–922, 2011

ION BEAM ANALYSIS STUDIES OF ANCIENT GLASS BRACELETS DISCOVERED IN BUCHAREST*

R. BUGOI[1*], I. POLL[2], GH. MĂNUCU-ADAMEŞTEANU[2], T. CALLIGARO[3], L. PICHON[3], C. NEELMEIJER[4], F. EDER[5]

[1]"Horia Hulubei" National Institute for Nuclear Physics and Engineering, PO BOX MG-6, Măgurele 077125, Romania, E-mail: bugoi@nipne.ro
[2]The Museum of Bucharest city, B-dul I.C. Brătianu 2, Bucharest 030174, Romania
[3]Centre de Recherche et de Restauration des Musées de France (C2RMF), CNRS UMR 171, Palais du Louvre, 75001 Paris, France
[4]Helmholtz-Zentrum Dresden-Rossendorf (HZDR), PO BOX 510119, Dresden D-1314, Germany
[5]Atominstitut, Stadionallee 2, 1020 Vienna, Austria

Received March 1, 2011

*Abstract***.** Eight fragments of glass bracelets from the XVIII-XIXth centuries discovered in Bucharest were analyzed using external IBA methods (PIXE-PIGE) at AGLAE tandem accelerator, C2RMF, Paris and at HZDR tandem accelerator, Dresden. The investigated objects had different glass recipes, indicating their manufacturing in several workshops. Cupric oxide was the blue cromophore for all analyzed glass fragments.

Key words: historical glass, glass bracelets, compositional analysis, IBA, PIXE, PIGE, Bucharest.

1. INTRODUCTION

The typological assignation for ancient glass artifacts is a rather complicated process, because certain physical and chemical aspects must be taken into consideration. Namely, when a glass object is buried for a long time, a loss of alkaline compounds through leaching takes place, and silica enrichment occurs; glass might also become opaque because fine layers of hydrated silica are formed on its surface. Both the manufacturing context (composition, fusion temperature) and the burial environment (humidity, temperature) play important roles in the weathering phenomena of glasses. Weathering can take place because of the long period of time the archaeological glass objects spent in ground, exposed to high humidity [1]. The progressive destruction of glass is a result of hydrolysis and crystallization, during which solubilization phenomena occur, causing alkali leaching and the shift of salts towards the surface where they lodge in thin layers. If

* Paper presented at the National Symposium of Archaeometry, 28–29 October 2010, Bucharest, Romania.

such a glass is transferred into a dry environment, surface iridescence and exfoliation may take place; glass surface becomes opaque. The iridescence of ancient glass can be explained as diffraction phenomena occurring on the surface of the hydrated silica layers, light being selectively refracted on the microscopic irregularities of the glass surface [2].

Knowledge of the chemical composition of ancient glass artifacts might help to their proper classification. Hints regarding ancient manufacturing technologies can be revealed by finding out the bulk recipe of archaeological glass objects. In addition, by studying the composition of such archaeological items one can try to establish whether the objects were manufactured in a single or in several workshops and if the same technique was used for their production.

In this paper, the results of investigations on some glass bracelets fragments discovered in archaeological excavations performed in Bucharest area, dated to the XVIIIth and XIXth centuries, are reported.

Previous research papers [3-8] on glass objects from different historical periods indicate that the combination of external Ion Beam Methods (IBA), namely Proton Induced X-ray Emission (PIXE) and Proton Induced Gamma-ray Emission (PIGE) is an excellent approach for compositional studies of ancient glass objects, providing accurate results and the almost complete recipe for these kind of artifacts.

Eight glass bracelets fragments discovered in several archaeological sites from Bucharest were analyzed using external PIXE-PIGE techniques in two European laboratories – namely C2RMF in France and HZDR in Germany – in order to determine their bulk composition. Prior to the IBA measurements, the glass bracelets fragments were examined with an optical microscope.

2. INVESTIGATED OBJECTS

Glass bracelets represent a category of finery that was rarely found in excavations performed in Bucharest area. Such objects seem to have been used for the first time during the Geto-Dacian period: an unpublished dark-blue bracelet fragment, with a triangular cross-section and decorated with an incised motif, was discovered in a settlement dated to the IInd–Ist centuries B. C. on *Ziduri între Vii* Street by Dinu V. Rosetti.

On the nowadays Romanian territory, glass bracelets seen to have been in use from the IInd century A. D. until the IVth century A. D.; they reappeared in the Xth century – when they seemed to have been very popular, but disappeared altogether in the XIIIth century.

After a long period of absence, glass bracelets appeared again in excavations for the XVIIIth century sites. However, from the XVIIIth century onward, a reduced number of such objects was found. In any case, the main type of such adornment was the blue colored bracelet with triangular cross-section, decorated with ribs [9, 10].

The bracelets fragments studied in this paper were discovered in excavations made in Bucharest. Some of them were found in storages found on Colței Street

and Stavropoleos Inn. These deposits belonged to different merchants which were engaged in trading common pottery (plates, jugs, cups, etc.), but also in selling tiles, porcelain and glass ware, some of them imported from different European centers [11, 12]. Another group of bracelets was found in the funerary inventory buried in the tombs investigated at Udricani Church, while another one came from Cărămidarii de Jos Church [13].

Historical records mention that some glass craftsmen were active in Bucharest during the second half of the XVIIIth century and at the beginning of the XIXth century; however, little is known about the precise nature of the products they manufactured. Ostrov and Nufăru were the only places in Romania where the manufacture of glass bracelets was documented as being performed at the beginning of the XXth century [14].

As the written records of that period mention the existence of glass workshops without specific reference to glass bracelets manufacture, and since the bracelets discovered in Bucharest show perfect analogies with the ones from other archaeological sites in Romania (Brăila, Nufăru), a way of tackling the issue of glass bracelet manufacturing centers was to study the composition of glass bracelets fragments.

The precise assignation of the eight fragments of glass bracelets measured by IBA methods – see Fig. 1 – is the following: fragments no. 1 and no. 2 were discovered in excavations at Stavropoleos Inn, fragments no. 3, no. 4 and no. 5 were found on Colței Street 8, fragment no. 6 in General Florescu Street, fragment no. 7 was excavated at Udricani Church, while fragment no. 8 was discovered at Cărămidarii de Jos Church.

All bracelets are of different shades of blue, ribbed and with triangular cross-section, except for bracelet fragment no. 7, whose surface is smooth (without ribs) and flat.

3. SAMPLE PREPARATION

Glass consists of different components, namely formers, fluxes and stabilizers, each of them playing a different role. The former constitutes the bulk of glass and is normally silica (SiO_2). Fluxes are added to the former to lower the melting temperature of the silica. Most common fluxes are the oxides of the alkali metals Na and/or K (*i.e.* soda-Na_2O and potash-K_2O) and less frequent Pb (PbO). Since glass made of silica and alkali oxides only would not be stable at all owing to the solubility of the composing oxides, lime (CaO) plays the role of stabilizer, making the glass more durable [15-17].

Throughout history the main sources of glass raw materials were sand or quartz pebbles (SiO_2), natron, plant ash, potash (K_2O) – generally from tree ashes, and lime ($CaCO_3$) from marine shells and/or plant ashes. These raw materials contain impurities such as MgO, Al_2O_3, P_2O_5, TiO_2, Fe oxides etc.

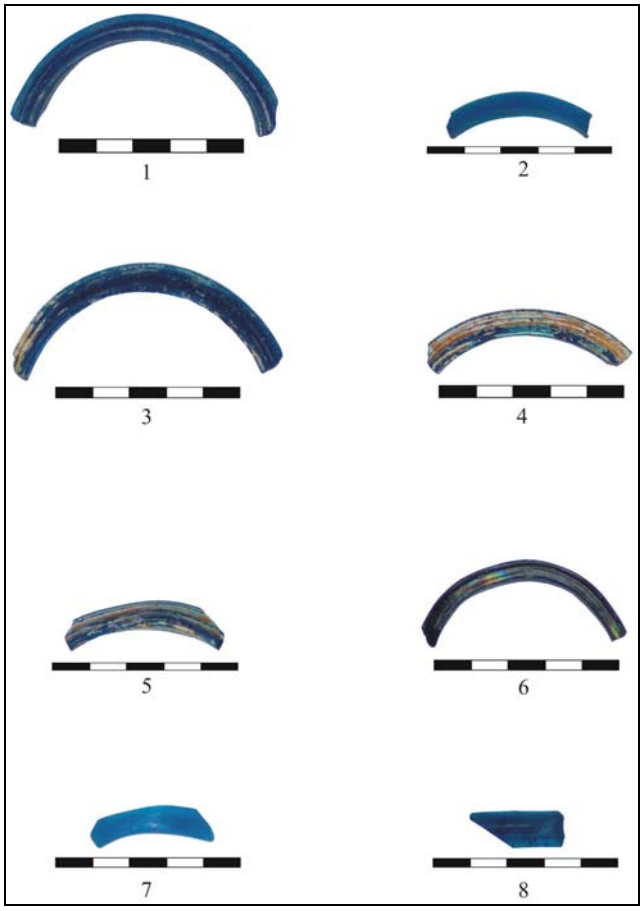

Fig. 1 – Investigated glass bracelets fragments, found in Bucharest excavations at: Stavropoleos Inn (no. 1 and no. 2), Colței Street 8 (no. 3, no. 4 and no. 5), General Florescu Street (no. 6), Udricani Church (no. 7), Cărămidarii de Jos Church (no. 8).

As already mentioned in the Introduction, silicate materials are affected by weathering phenomena. Exposure to humid environments generates altered layers on the glass object surfaces. Glass corrosion represents the selective leaching of alkali ions (Na^+, K^+) and to some extent also of alkaline earths (Ca^{2+}, Mg^{2+}), and the incorporation of water components from the humidity of the ambient environment. Glass corrosion actually consists of very complex reactions [18]; in all cases a surface layer is formed which is depleted in network modifiers and enriched in hydrogen or hydrogen-bearing species. Typical corrosion layer thicknesses are in the range of a few nanometers up to some hundred microns [19].

Taking into account the long period of time during which the investigated bracelets fragments were buried in humid soil (hundreds of years), it is obvious that a relatively thick layer of corrosion products had been formed on the bracelet

fragments surfaces (roughly estimated to several tens of μm). Such a thick corrosion layer is of the same order of magnitude as the range of the incident protons used for glass investigations (approximately 85 μm for 3 MeV protons in a soda-lime-silica glass matrix and 125 μm for 3.85 MeV protons in the same kind of matrix).

Therefore, in order to perform an accurate analysis of the bulk glass cleaned surfaces had to be put in the front of the proton beam. Consequently, before IBA experiments, the cross-sections of the glassy fragments were wet polished using SiC papers of different grits followed by alcohol cleaning, and thus flat and fresh glass zones were exposed to the proton beam. Though not completely not-destructive – as it would have been the ideal scientific investigation of archaeological artifacts – this solution implied just the removal of the corrosion products that otherwise would have precluded the determination of correct bulk glass composition.

4. EXPERIMENTAL

Five bracelets fragments (fragments no. 1, no. 2, no. 3, no. 4 and no. 5) were measured using external IBA at the AGLAE accelerator [20] using a 3 MeV external proton beam focused to 50 μm, with current intensities of hundreds of pA and acquisition times of aproximately 2 minutes. The measurement region was flushed with a 2.5 l/min stream of helium gas. For PIXE signals acquisition, two Si(Li) detectors were used – Low-Energy PIXE detector (LE-PIXE) for major elements ($12 \leq Z \leq 26$), and High-Energy PIXE (HE-PIXE) detector, of higher efficiency, for trace-elements ($Z > 26$). In front of the HE-PIXE Si(Li) detector a 50 μm Al filter was used to improve the detection limits for the trace-elements in the glass matrix. A HPGe detector was employed for PIGE, particularly for the detection of the 440 keV gamma-rays promptly emitted by the Na atoms within the glasses.

The glass fragments were analyzed in most of the cases on 200×200 μm^2 areas on the cross-sections of the bracelets.

Several glass standards – alkaline and lead glasses (BRILL from Corning Museum of Glass, BGIRA – British Glass Industry Research Association) and DR-N geo-standard from Centre de Recherches Pétrographiques et Géochimiques, Nancy were used to obtain quantitative results for PIGE (Na quantification) and to check the accuracy of the PIXE results.

PIXE quantitative results were obtained by running the GUPIX software [21-23], assuming the targets being thick and homogeneous and that all elements – except for Cl – were present as oxides. For Na_2O quantification, PIGE data were used for Na_2O quantification. Namely, the intensity of the 440 keV prompt gamma line

from the archeological glass fragments spectra was compared to the intensity of the same gamma line emitted by the certified glasses which were measured under the same experimental conditions as the archaeological samples.

Other three bracelets fragments (fragments no. 6, no. 7 and no. 8) were analyzed at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Germany, using an experimental set-up that is principally similar to the one at AGLAE. The detailed description of the external beam experimental arrangement from HZDR, previously used for many archaeometrical applications is given in [24]. The 4 MeV proton beam from the tandem accelerator of HZDR is extracted through a 3 μm thick Havar® exit window into a volume delimited by the adjusted sample surface and the surrounding detectors, volume that was flushed with He. The on-target proton beam energy was 3.85 MeV, and the analyzed areas were around 1 mm^2. Two Si(Li) detectors of different efficiencies, namely LE-PIXE (12.5 mm^2 area, filtered by 4 μm of Mylar® and a 1 mm diameter Ta diaphragm) and HE-PIXE (80 mm^2, filtered by 1.3 mm Acrylic) were employed to detect the characteristic X-rays emitted by the target atoms for the elements with Z>13. A HPGe detector (60% relative efficiency) was used to provide quantitative information for the light elements – particularly Na, Mg, Al, and Si – via the detection of the corresponding prompt-induced gamma-rays (440 keV, 1369 keV, 1014 keV and 1779 keV).

Long acquisition times (~ 20 minutes live time) were used to obtain spectra of good statistics. The beam current intensities had the order of hundreds of pA.

Synthesized glass samples of known composition were measured before analyzing the archaeological samples, and the corresponding results were used for PIGE data calibration.

The procedures used for PIXE-PIGE data quantification of glass materials used in HZDR, also based on the GUPIX software, are detailed in reference [5].

No damage due to glass irradiation was observed during and after the analysis. This was mainly due to the low values of proton beam currents and to the fact that the samples were analyzed in external beam, and not in vacuum.

As quality assurance strategy, some measurements on a set of samples were made in both laboratories – C2RMF and HZDR. A relatively good agreement between the quantitative results obtained for both experimental runs was obtained, fact that stimulated the joint presentation of the results in the same publication.

The compositional results for all analyzed samples, expressed as oxides (except for Cl), and in units of wt% for major and minor elements, and μg/g for trace-elements, and normalized to 100%, are given in Table 1. The overall combined uncertainty (relative values) of the reported concentrations is of the order of 5–10% for major and minor elements, but increase up to 20% for trace elements.

5. RESULTS AND DISCUSSIONS

Preliminary optical microscopy investigations showed signs of surface weathering for all bracelets fragments, as well as the existence of inner flaws. The glass pieces contain solid inclusions (≤ 0.05 mm) and many gas inclusions – spherical or oval bubbles – some of them noticeable even with the naked eye. Their presence is an indication for a faulty melting technique, *i.e.* loose melting. Transverse furrows, emphasized by the corrosion phenomena, can be noticed, on bracelets surfaces.

Fragment no. 1 (Stavropoleos), and all the fragments from Colțea (no. 3, no. 4 and no. 5) are partially covered by thin white-yellowish and brown layers, due to the existence of residual traces of calcite (from running waters) and of iron and manganese oxides and hydroxides. The explanation for this is the fact that the silica gel layers on the top of weathered glass surfaces can easily retain clay minerals like iron and manganese compounds, which are responsible for coloring of these layers.

Under the layer of corrosion products, a thin opal layer was noticed, with traces of chalcedony (anhydrous silicate) resulted from the crystallization of silica gel, a natural phenomenon occurring with time in archaeological glasses. This feature is present for glass bracelet fragments no. 1, 2, 3, 4, 5 and 6.

Recipes for common glass involve the presence of major constituents and additives. The particular constituents differ depending on the chosen manufacturing technique, the raw materials, the geographical area and/or the historical period. Different types of glass can be identified taking into account the balance of the main components, namely SiO_2, Na_2O, K_2O, CaO, MgO, and Al_2O_3.

In the case of the analyzed bracelet fragments, the following glass types could be distinguished – see Table 1 and Fig. 2:

- Fragments no. 1 and no. 2 (Stavropoleos) are of soda-lime-silica type;
- Fragments no. 3, 4, 5 (Colțea) and no. 6 (General Florescu Street) are of potash-lime-silica type;
- Fragment no. 7 (Udricani Church) is of soda-potash-silica type;
- Fragment no. 8 (Cărămidarii de Jos Church) is of potash-soda-silica type.

The presence of CaO and Al_2O_3 can be used as indicators for the origin of the sand, which is the main raw material for glass. For all bracelet fragments analyzed in this study, except for fragment no. 7, the concentrations of network modifiers and stabilizers indicate the likely use of calcareous sands.

The following components: MgO, Al_2O_3, TiO_2, Fe_2O_3, SnO_2 appear in the glass recipe as impurities of the raw materials. The same applies for P_2O_5 which, in these particular cases, given the low determined concentrations, could not be used as an indicator for the origin of the sands.

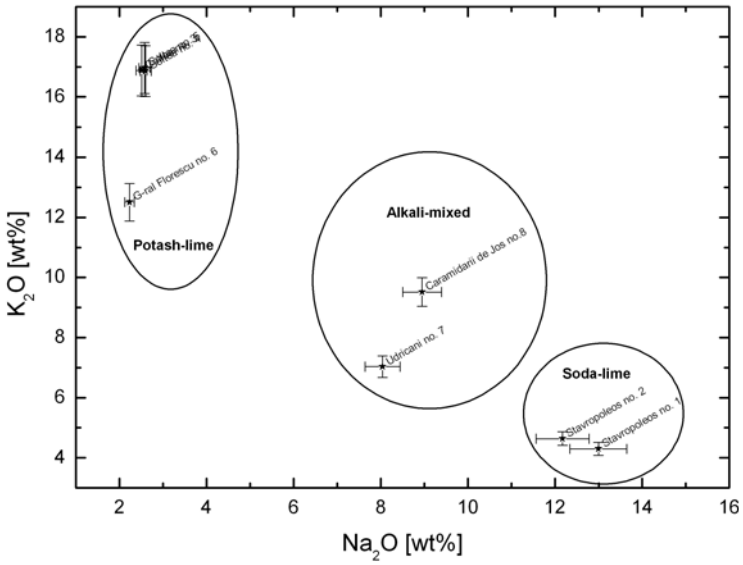

Fig. 2 – Alkali oxide diagram for all investigated glass bracelets fragments.

The IBA results point towards the conclusion that the blue color of all the analyzed bracelets, be it light or dark blue, derives in all cases from a Cu compound – namely cupric oxide (Cu^{2+}; oxidizing atmosphere). No Co traces were detected in any of the analyzed bracelets. There are differences in shades – for example, fragment no. 6 (General Florescu Street) has the darkest blue colour – see Fig. 1, finding in accordance with its high CuO content (6.13 wt%). Fragment no. 8 (Cărămidarii de Jos Church) has a greenish-blue color, probably as a result of the intentional addition of MnO, that oxidized Fe^{2+} to Fe^{3+}, giving a yellow shade to the glass.

In all samples, As is present in low concentrations; its presence in glass recipe can be explained by the existence of this element in trace amounts in the copper ore that was added as a colorant [25].

Bracelet no. 7 (Udricani Church) differs in composition from all others fragments, because of its low CaO content, which suggests the use of a feldspar or micaceous source of sand. On the other hand, the same bracelet has an elevated PbO content (13.94 wt%), pointing towards the use of a different recipe and, implicitly, to its production in a different workshop. The presence of lead as a network modifier could not be tested through the particularities this element normally triggers in glass properties, e.g. brilliance because of the weathering phenomena underwent by this glass fragment that was buried for a long period of time. The PbO concentration in this particular sample is too low to indicate a lead glass, taken into account the glass types and classification from reference [2].

6. CONCLUSIONS

In this paper, the bulk composition of eight fragments of glass bracelets excavated from different archaeological sites in Bucharest was determined using external IBA methods. The determined glass recipes turned out to be very different: some of the glass fragments are of soda-lime type (fragments no. 1 and 2 from Stavropoleos), other were of potash-lime type (the three fragments from Colței Street and General Florescu Street), while the fragments from Udricani Church and Cărămidarii de Jos Church belong to some mixed-alkali types of glass (soda-potash and potash-soda, respectively). For all glass fragments, the blue color was obtained through the intentional use of different amounts of cupric oxide. The different recipes found for the investigated glass bracelet fragments point towards their production in different workshops from different raw materials. An alternative to the hypothesis of different stable workshops could be the one of itinerant craftsmen that strolled through various districts, took orders for bracelets and manufactured them from different glass rods brought along with them. Once again, IBA approach proved to be an excellent tool for the compositional characterization of archaeological glasses. More analyses of this type are on-going; this kind of research is expected to bring about an increased knowledge about the history of glass manufacture on the nowadays Romanian territory.

Acknowledgments. Financial support by the Access to Research Infrastructures activity in the 7th Framework Programme of the EU CHARISMA Grant Agreement no. 228330 is gratefully acknowledged.

This work has been also supported by the European Community as an Integrating Activity "Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)" under EC contract no. 227012.

The contribution of Silke Merchel from HZDR in the realization of this project is gratefully acknowledged. Romy Aniol from HZDR is kindly thanked for her help in performing the polishing of glass samples.

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