



## Investigations of Byzantine glass bracelets from Nufăru, Romania using external PIXE–PIGE methods

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### ABSTRACT

The chemical composition of twenty glass bracelet fragments found in Nufăru, a Byzantine site from 10th–13th centuries A.D., nowadays located on Romania's territory, has been determined using Particle Induced X-ray Emission (PIXE) and Particle Induced Gamma-ray Emission (PIGE) in external beam mode. Most of the Byzantine bracelet fragments were identified as “mixed natron-plant ash” soda-lime-silica glasses. The obtained chemical compositions indicated that the manufacturing of these finery items was performed using similar raw materials and techniques, in most of the cases involving colored glass recycling. PIXE–PIGE results highlighted the glass chromophores (cobalt, manganese, copper and iron ions) and provided hints about the mineral pigments used to paint the external surface of some bracelets.

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### 1. Introduction

Chemical composition of historical glass artifacts can reveal information about the technology and raw materials used in their manufacturing. Chronological and geographical differentiations of ancient glass objects are reflected in distinct compositional categories (Craddock, 2009; Fiori and Vandini, 2004; Goffer, 1980).

Several authors have proposed classifications of ancient glass items according to their chemical composition. In most cases, the discrimination between types was related to differences in the concentrations of the main constituents (Freestone, 2005; Gratuze and Barrandon, 1990; Sayre and Smith, 1961).

Archaeometric studies of Byzantine glass artifacts were relatively scarcely published compared to studies of ancient glass from other historical periods (Palomar et al., 2009). A recent review of the status of Byzantine glass research, including studies of chemical composition, can be found in (Keller, 2010).

Throughout different epochs, glass bracelets have been a fashionable type of adornment. Remains of glass bracelets had been found in large number in many archaeological sites from different periods of times and geographical assignments (Boulogne

and Henderson, 2009; Köroğlu, 1998; Shindo, 2001; Spaer, 1992; Steiner, 2008). A recent study of Middle Byzantine glass bracelets is the one published by Lauwers and co-workers (Lauwers et al., 2010).

According to (Palomar et al., 2009), the most often employed analytical techniques used for the determination of the chemical composition of ancient glass objects are: Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX) (Aerts et al., 2003; Freestone et al., 2008), Scanning Electron Microscopy coupled with Wavelength-Dispersive Spectrometry (SEM-WDS) (SEM-WDS)/Electron Probe Micro-Analysis (EPMA) (Schibille et al., 2008; Shortland and Schroeder, 2009; Silvestri et al., 2008; Uboldi and Verità, 2003), X-Ray Fluorescence (XRF) (Silvestri et al., 2008; Wolf et al., 2005) and Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) (Foster and Jackson, 2009). Due to their excellent detection limits, Synchrotron Radiation induced X-Ray Fluorescence (SR-XRF) (Aerts et al., 2003) and/or Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (De Raedt et al., 2001; Wagner et al., 2008) are employed to complement SEM-EDX or SEM-WDS measurements on archaeological glass samples, to quantitatively determine the trace elements.

During recent years, ancient glass objects from different periods and provenances had their chemical composition determined using

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a combination of Ion Beam Analysis (IBA) techniques, namely Particle Induced X-ray Emission (PIXE) and Particle Induced Gamma-ray Emission (PIGE) (Cagno et al., 2012; Calligaro, 2008; Carmona et al., 2010; Climent-Font et al., 2008; Mäder and Neelmeijer, 2004; Sokaras et al., 2009; Šmit et al., 2012).

In this paper, the results of an external PIXE–PIGE experiment on some glass bracelet fragments discovered in archaeological contexts in Nufăru, Romania, and dated to the 10th–13th centuries A.D. are reported and discussed, in a trial to identify the raw materials and techniques employed for their manufacturing. In particular, twenty fragments of Byzantine glass bracelets were analyzed at the Ion Beam Center of the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) to determine their bulk glass chemical composition and the glass chromophores. The experimental data also provided information about the pigments used to paint the external surfaces of some bracelets.

## 2. Archaeological background and sample description

On the right bank of Danube, on Saint George Arm, 12 km downstream from Tulcea town, Romania, the archaeological investigations started in 1977 and continued until the present days evidenced the existence of a Byzantine site completely buried under Nufăru village (Damian et al., 2007–2008; Mănușcu-Adameșteanu, 1998, 2001).

An important urban settlement existed here during the 10th–13th centuries A.D., sheltered by the thick walls (~3 m) of a fortification built *a fundamentis* by the Byzantines in the last quarter of the 10th century A.D. This fortress was raised during the reigns of the emperors John I Tzimiskes (969–976) and Basil II (976–1025), strategically exploiting its location on a promontory nearby a Danube ford. The large size of inhabited area, the various archaeological findings and several cemeteries (300 graves investigated until present) suggested that a prosperous urban center flourished here during the 11th century. A serious crisis occurred in the evolution of the settlement in the middle of the 13th century: the Tartars attacked the fortress in 1242, burning and destroying the whole place to ground. After this cruel attack, the nearby zones continued to be inhabited – especially the Danube bank, but the settlement never recovered its previous thriving status (Damian et al., 2007–2008; Mănușcu-Adameșteanu, 1998, 2001).

The archaeologists localized here one of the most important Byzantine cities mentioned in the written sources – namely Prethlavitza, toponym found on several Byzantine seals (Iordanov, 1984; Oikonomides, 1983).

The development of Nufăru Byzantine settlement can be correlated to the rich archaeological deposits and the numerous dwellings and funerary inventories excavated in the 3 m thick archaeological strata. Apart from potteries, weapons, coins, metallic tools and adornments, a series of archaeological discoveries such as ceramic kilns, crucibles, molds, glass chunks and molten metal debris indicated that certain crafts were practiced here during the Byzantine period (Damian et al., 2007–2008; Mănușcu-Adameșteanu, 1998, 2001).

A large number of glass bracelets – most of them in fragmentary state – were found in the inhabited levels and in the funerary inventories from Nufăru (Damian et al., 2007–2008; Mănușcu-Adameșteanu and Poll, 1997). Such adornments were not discovered only in Nufăru, but also in other nearby Byzantine settlements situated on the Danube arms, in sites such as Păcuiul lui Soare, Dinogetia-Garvăn and Isaccea-Noviodunum-Vicina (Diaconu, 1965, 1976; Diaconu and Vâlceanu, 1972; Mănușcu-Adameșteanu and Poll, 2012; Ștefan et al., 1967).

Similar glass bracelets were found in Byzantine archaeological sites dated to the 10th–13th centuries A.D., located on nowadays

territory of Greece, Bulgaria, Serbia, Turkey and Russia (Antonaras, 2005, 2009; Cangova, 1961; Lauwers et al., 2010; Lightfoot, 2005; Neșeva, 1979; Philippe, 1970; Ristovska, 2009; Shtereva, 2000).

The glass bracelets discovered in Nufăru have different shapes (plain or twisted), variable dimensions (inner diameter and glass cane size), cross-sections (e.g. circular, flat or square), surface modeling (smooth, ribbed or with prunts) (Diaconu and Vâlceanu, 1972; Spaer, 1992; Ștefan et al., 1967). They have different colors: blue, green, violet, black, transparent white and red. Some bracelets were painted on their external surfaces with geometrical or vegetal motifs. In other cases red, yellow, golden or silver-gray colored thin glass threads (~several mm thick) were wound along a central glass cane. Most of the Nufăru bracelets were found as broken pieces. The majority of glass fragments are visibly corroded, being covered with iridescent exfoliating layers and showing a reduced transparency. However, some bracelets do not exhibit any apparent sign of glass weathering. Compared to the bracelets found in the inhabited levels, bracelets found in the funerary inventories have uneven facets, showing a rougher finishing.

Up to now, several types of Byzantine glass bracelets featuring different kind of decorations were identified, described and classified (Diaconu and Vâlceanu, 1972; Ștefan et al., 1967), but no strict connections between their typology and chronology have been established.

The most frequently encountered type of glass bracelet, found in all archaeological strata excavated in Nufăru, is the blue glass bracelet with circular cross-section and without any external decoration. The majority of such finds were dated to 11th–12th centuries A.D., period when the use of this kind of adornment seems to have been at its peak.

Bracelets with protuberances and deep creases – the so-called “pincer trails” decorations – appeared at the end of 11th century and were in use until the first half of the 13th century. This particular type of glass shaping was encountered not only in Byzantine glass objects, but also in Islamic glass artifacts from the same period (Klein and Lloyd, 2000).

According to Philippe (1970), bracelets with elaborated geometric and floral painted decors, as well as the ones made of red glass or by twisting red glass threads around glass rods of other colors were produced in the so-called imperial workshops (e.g. the ones active in Constantinople and/or Thessalonica).

Fig. 1 shows the photos of the twenty bracelets found in archaeological contexts in Nufăru investigated in this study.

All bracelet fragments were assigned to the 11th–12th centuries A.D., except for bracelet *Nufăru 1979/10*, which can be dated between the end of the 11th century and the first half of the 13th century A.D.

Prior to the PIXE–PIGE measurements, the glass bracelet fragments were examined with an optical microscope. The detailed description of the analyzed objects and the observations made using Optical Microscopy (OM) are presented in Table 1.

Concerning the typology of the objects under investigation, three main categories of glass bracelets were identified among the twenty fragments (Diaconu and Vâlceanu, 1972; Spaer, 1992; Ștefan et al., 1967):

- Undecorated/plain monochrome type (*Nufăru 1989/27* fragment);
- Twisted – with one (*Nufăru 1989/23*), two (*Nufăru 1989/28*) or three trails (*Nufăru 1981/37* and *Nufăru 1981/68*). These bracelets were made by winding thin glass threads of different colors around a central glass rod;
- Painted bracelets – with different shapes of the cross-section: flat (*Nufăru 1981/19*, *Nufăru 1981/58*, *Nufăru 1981/60*,

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