ANALYSIS OF HISTORIC GLASS BY ION-BEAM METHODS

TÖRTÉNELMI ÜVEGEK VIZSGÁLATA IONNYALÁB-ANALITIKAI MÓDSZEREKKEL

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Abstract

Analytical methods, based on irradiation of samples with MeV ion beams, notably particle induced X-ray (PIXE) and gamma ray (PIGE) emission analysis can be used to provide complete chemical analysis of glass objects in a non-destructive way. A review of applications is given that were performed at the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana, which involve glass of the first centuries BC, Roman and late Antique glass, as well early medieval and Venetian glass till the glass of the late 19th and early 20th centuries. Historical questions like the origin of raw materials and classification of glass compositional groups according to individual workshops are addressed.

Kivonat

Azok az analitikai módszerek, amelyek a minták MeV-es ionnyalábbal való besugárzásán alapulnak – nevezetesen a részecske-indukált röntgen-, ill. gammaemissziós (PIXE, ill. PIGE) módszerek –, alkalmasak üvegtárgyak kémiai (elem-) összetételének roncsolásmentes meghatározására. A cikkben áttekintjük a ljubljanai Jožef Stefan Intézet Tandetron gyorsítójánál, Kr. e. I. századi római és késő antik, valamint korai középkori, velencei és 19-20. századi üvegeken végzett vizsgálatokat. A kutatás során a megválaszolandó kérdések voltak: a nyersanyag eredetének meghatározása, összetétel szerinti csoportok felismerése és azonosítása az üveggyártó műhelyekkel.

KEYWORDS: PIXE, PIGE, GLASS ANALYSIS, ROMAN GLASS, EARLY MEDIEVAL GLASS, VENETIAN GLASS

KULCSSZAVAK: PIXE, PIGE, ÜVEGEK ANYAGVIZSGÁLATA, RÓMAI ÜVEG, KORAI KÖZÉPKORI ÜVEG, VELENCEI ÜVEG

Introduction

Chemical analysis by ion beam methods is based on excitation of characteristic X-rays and gamma rays. As quite many elements can be analyzed simultaneously, it is aptly used for the analysis of glass. Its main advantage is non-destructive way of measurements and simple handling of the investigated objects, provided their surface is not covered by a thick corrosion layer. Typical penetration depth of 3 MeV protons in glass is about 90 µm, and the main fraction of X-rays usually comes from about one third of this thickness. Representative measurements of the bulk composition can still be obtained if surface modification, like selective leaching of alkaline elements, reaches depths of 1-2 µm.

Glass is essentially made of silica whose melting point is lowered by flux; alkaline oxides are used for this purpose. Oxides of alkaline earths are added for chemical stability. As the agents encountered in nature are not chemically pure, small amounts of decolorants are added to the glass batch for obtaining clear transparent glass, or opacifiers and pigments for obtaining opaque or colored glass. It is the flux that exhibits largest variation through history. For the glass of Bronze Age Egypt and Mesopotamia, during the second millennium BC, alkalis were obtained from the ash of halophytic plants, harvested at sea shores and in deserts (Rehren 2008). The period between 800 BC and 800 AD is characterized by an extensive use of alkalis from the sediments of dry Egyptian lakes, known as natron (Sayre & Smith 1961). Glassmaking of natron-based raw glass then intensified in the eastern Mediterranean and dominated in Greek, Roman and Late Antiquity worlds. After the 6th c. AD several political disturbances in Egypt limited access to natron sources, and in the quest of alkalis the use of halophytic plants was resumed (Shortland et al. 2006). In the transition period between the 9th and 12th centuries, glass from the ash of halophytic plants gradually superseded natron-based glass that still participated in glassmaking as a recycling material. The new technology spread from the East, most likely Islamic or Byzantine world (Freestone 2005). After the 12th century, glassmaking in Northern Italy, notably in Venice directed the glass technology and glass trade (Verità & Zecchin

2009). Due to the high demand of the Venetian glassware, glassworks were formed also in other European towns that fabricated glass products in the Venetian style. In the 17th century, several improvements in treating raw material were introduced: purer silica sources and refined alkalis came into use, and arsenic started to be used as decolorant. In Northern and Central Europe, wood ash was used for making potash, which resulted in production of forest glass.

What are the open questions regarding production of historic glass? For Greek and Iron Age glass it is certainly the location of glassworks. This question is also important for Roman glass, although largely answered by strontium and neodymium isotope ratios measurements: in the Roman Imperial era, between the 1st and 4th c. AD, glass was produced in the Eastern and Western part of the Mediterranean, but production was concentrated in the Eastern part during Late Antiquity (Ganio et al. 2012). For Venetian and Venetian-like glassmaking, it is important to distinguish between the imported and locally produced objects (De Raedt et al. 2001). In the present review, we show measurements performed on Greek glass from Bulgaria, on Roman glass from several sites in the Eastern Balkans and Slovenia, on Venetian-type glass from Ljubljana and Slovenian castles, and on examples of modern glass. For each type of glass, compositional groups are determined by statistical methods and historical or provenance information for each group is sought.

Experimental methods

The measurements were performed at the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana, using in-air proton beam of 3 MeV nominal energy. The beam was extracted into air through a thin metal foil; aluminum of 8 μm thickness was used for PIXE, and tantalum of 2 μm for PIGE measurements. Different materials were used to avoid undesired background: no hard X-rays are induced in aluminum window during PIXE measurements, while aluminum gamma rays are undesirable for PIGE; using a high Z window (like tantalum) for PIGE results in low gamma energies, typically below 300 keV. Three spectra were taken in each measuring point: soft X-ray with a 5.7 cm air gap as the only absorber, hard X-ray with 0.1 mm Al as an additional absorber, and gamma spectrum. The beam current was a few tenths of nA for the first case and 1-3 nA for the latter two; typical X-ray spectra were measured for 5 minutes and gamma spectra for 20 minutes. The proton number was measured for PIGE only, using a thin wire mesh intersecting the beam in vacuum (Jezeršek et al. 2010). Some measurements were performed in a time-optimized way: tantalum exit window was used for all measurements, and hard X-ray and gamma spectra were measured simultaneously. The disadvantage of this type of measurement was the presence of Ta L X-rays in the spectra. The soft X-ray spectrum involved elements from silicon to iron, and the hard X-ray spectrum from iron till highest Z. The X-ray line intensities of the two spectra were recalculated into a single data set according to the iron line using calculated transmission of absorbers. For modern glasses, the content of iron was too low to enable reliable statistics. The hard X-ray spectra were then measured with an additional absorber of 700 μm kapton, and the two spectra were compared according to the calcium line. The size of air gaps between the exit foil and target and between target and detector were determined from the measurements of a few elemental and simple chemical compound targets. The elements Na, Mg and Al were determined from the gamma spectra using the lines excited by inelastic proton scattering: 440 keV for Na, 585 keV for Mg, and 844 and 1014 keV for Al (Hirvonen et al. 1995). The most critical measurement was that of Mg, as its line coincides with the line of 583 keV from natural background. Using a lead shielding around the gamma detector and a sufficient count rate of PIGE it was possible to achieve the lowest detection limit of 0.2 % MgO. The detection limits for other minor and trace elements obtained by PIXE are significantly better: about 100-50 μg/g for the elements between calcium and iron, and about 5 μg/g for iron and heavier elements in its vicinity. The detection limits then decrease with Z and are about 10 μg/g around Sr and Zr and about 100 μg/g around Sn and Sb. The detection limit of Pb that is determined according to its L-lines is about 5 μg/g. The interference of particular X-ray or escape lines reduces sensitivity for P (about 1%), Co (about 100 μg/g) and Ba (about the same level as the content of Ti).

The concentrations were calculated by an iterative method that considers matrix elements for X-ray and gamma ray spectra simultaneously. The method of independent atomic parameters was used for PIXE, while the PIGE values were normalized according to the values measured in glass standard NIST 620, using the surface approximation. The sum of metal oxides was normalized to unity, but for the control purposes it was also calculated independently using the argon line induced along the proton beam in air as an internal standard. The measurements with the sum differing much from unity were considered with caution. Glass standards NIST 620 and 621 were also measured periodically and treated as unknown targets. The accuracy of major elements was within ±5%; however, for trace elements and values close to detection limits it may deteriorate to 10-20%. An example of NIST 620 measurement is shown in (Marić Stojanović et al. 2015).

Results and discussion

Natron is a much purer agent than ash of halophytic plants, so the natron-made glass can easily be recognized according to its low contents of magnesium and potassium, typically below 1.6% MgO and 1% K_2O (Sayre & Smith 1961; Zucchiatti et al. 2007). Glass from the Greek colony Apollonia Pontica on the Black Sea coast in the present Bulgaria dated to the 5th and 4th c. BC undoubtedly contained natron (Ljubomirova et al. 2014). The glass composition is similar to that of other Greek cities, which points to a centralized glasswork. A location on the Rhodes Island is supposed, which is sufficiently close to the raw material sources in the Levantine area (*op.cit.*).

Roman glassworks produced raw glass in huge blocks weighting several tons, which were splintered in chunks and distributed commercially for reworking into objects. A glass chunk of this type was discovered close to Roman municipium Nauportus (today's Vrhnika near Ljubljana) as early as 1886; yet it was the recent chemical analysis that confirmed its manufacture with natron, and therefore its Roman origin (Istenič & Šmit 2012).

Roman glass was commonly recycled that may partly obscure its primary origin. Our principal knowledge of glass composition came form two shipwrecks, loaded with cargos of broken glass: Ouest Embiez close to Marseilles dated from the end of the 2nd till the beginning of the 3rd c. AD, and Iulia Felix close to Grado, dated to the first half of the 3rd c. AD. Statistical analysis of glass from south France identified 12 groups (Foy et al. 2003), two of them being Roman: glass of group 3 was used in a broad time interval between the 3rd c. BC and 9th c. AD; it was discolored by manganese oxide and its origin is Levantine. Glass of group 4 was used in a much narrower time period of the 2nd and 3rd c. AD; it was discolored by antimony oxide, while its origin is still unknown. Statistic analysis of glass from Iulia Felix produced two groups of colored and two groups of clear glass (Silvestri 2008; Silvestri et al. 2008); the colored glass agrees well with group 3, while one group of the clear glass agrees with group 4. The second group of clear glass from Iulia Felix embraces both group 4 and a large fraction of group 3.

The Roman glass of the Imperial period analyzed in the lab originated from Albania (1st-4th c. AD), Bulgaria (1st-7th c. AD) and Serbia (Marić Stojanović 2015; Šmit et al. 2013; Lesigyarski et al. 2013). The MgO-K_2O plots with low magnesium and potassium concentrations confirmed that the glass comprised natron; but it was for the Albanian glass that the plot revealed several groups (**Fig. 1a**).

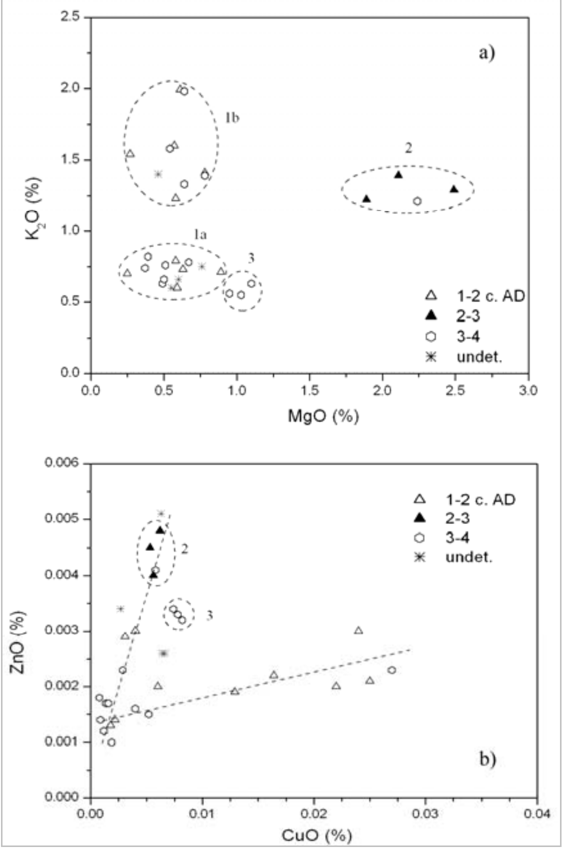

Fig. 1.: Roman glass from Albania shows individual features according to its MgO and K_2O contents (a), which may result due to different mineral impurities in the primary raw material, but may also be consequence of repeated recycling process, as shown in the distribution according to CuO and ZnO (b). Based on archaeological dating, the glasses were distributed into four groups: 1st-2nd c. AD, 2nd-3rd c. AD, 3rd-4th c. AD and undetermined (after Šmit et al. 2013).

1. ábra: Az Albániából származó római üvegek MgO és K_2O tartalmuk szerint jellegzetes összetételt mutatnak (a), ami lehet a felhasznált nyersanyag ásványi szennyező anyagainak következménye, de oka lehet ennek a többszöri újraolvasztás is, amint ezt a CuO és ZnO megoszlás mutatja (b). Régészeti kormeghatározás szerint az üvegek négy csoportba sorolhatók: i.sz. I-II. sz., i.sz. II-III. sz., i.sz. III-IV. sz. és ismeretlen korú üvegek (Šmit et al. 2013 nyomán).

Such groups may confirm that the minerals used for making raw glass came from different locations, which is consistent with the present model that production of raw glass during the Imperial period was dispersed (Ganio et al. 2012). However, such conclusions have to be made with caution, as specific mineral imprint can also be made during the recycling process and alloying with scrap glass. Copper and zinc are typical indicators of the recycling process (Freestone 2005), which is result of accidental mixing of colored and transparent glass in the recycled batch. **Fig. 1b** indeed shows the same groups as observed in the MgO-K_2O plot, which is a supporting argument of the glass differentiation in the secondary working process. The magnesium and potassium concentrations also increase with recycling on account of the impurity input, which results in the fact that the objects produced during recent centuries of the Roman era have higher concentrations of these two elements. It is tentative to use this effect for provisional dating: glass from the Kosmaj Mountain in Serbia lacks precise archaeological dating, but as its MgO and K_2O concentrations are below 1%, it can be dated to the first half of the Imperial period with high confidence. Recycling process also introduces elements that are related to mineral impurities, such as aluminum, titanium and iron. Higher levels of these elements are evident in the younger period glass from Bulgaria (Lesigyarski et al. 2013).

High levels of impurities, such as titanium, manganese and iron mark the new type of glass that appears in the fourth century AD and whose origin is yet unknown, though Egypt is strongly supposed as its production site (Freestone 2005). Known as the HIMT glass – an acronym indicating high iron, manganese and titanium, it is a wide-spread glass type in the Western Europe. Its occurrence in the eastern Mediterranean is modest, as the glass trade and production was still dominated by Levantine glassworks. The glass they produced was similar to the glass of group 3 from south France and is designated as Levantine I. In comparison with the Imperial period glass it contains slightly increased levels of calcium and aluminum oxides. Our measurements identified HIMT glass both among the 4th c. AD samples from Bulgaria and among the glass inventory of the Late Antique site Tonovcov grad from western Slovenia (Šmit et al. 2014). The site exhibits traces of all historic periods, the most prominent being a hilltop settlement with a complex of early Christian churches. Its population is divided into two phases, the older during the second half of the 4th and beginning of the 5th century, and the younger extending between the end of the 5th and the beginning of the 7th century. The majority of glass finds belongs to the younger period, though the glass inventory also contains a few examples of blue-green glass from the older period. The older glass contains smaller amount of MgO than the younger one. According to the origin of the sand component, glass of the younger period is of the type Levantine I, with a few examples of HIMT glass (**Fig. 2**). Some HIMT glasses have a lower amount of impurities, which suggests the glass was recycled with a certain amount of older glass.

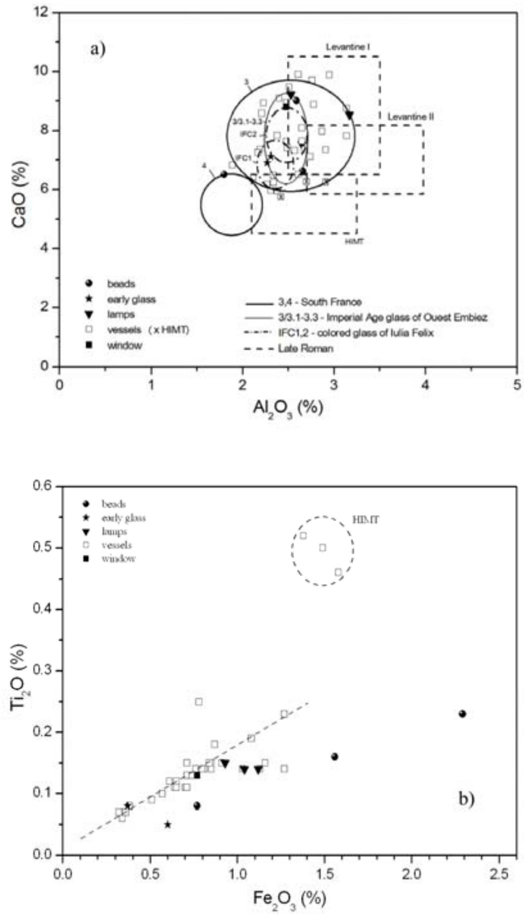

Fig. 2.: a) Distribution of glass from Tonovcov grad according to the sand composition reflected in $CaO–Al_2O_3$ plot (after Šmit et al. 2014). Lines show the accepted glass types. The group 3/3.1-3.3 represents Roman Imperial glass of south France and was obtained from Foy et al. 2003 subtracting the Late Roman groups 3.1 – 3.3 from the group 3. Data for colored glass of Iulia Felix are from Silvestri 2008 and for Levantine I and HIMT glass from Zucchiatti et al. 2007. (b) Only three examples of HIMT glass were found, which were well distinguishable according to their iron- and titanium content. (They are marked by × on Fig. 2(a)).

2. ábra: a) Tonovcov grad-ból származó üvegek megoszlása a homok összetétele szerint, $CaO–Al_2O_3$ diagramon (Šmit et al. 2014 nyomán). A vonalak az elkülönített üvegtípusokat mutatják. A 3/3.1-3.3 csoportok dél-francia római császárkori üvegeknek felelnek meg Foy et al. 2003 adatai alapján, kivonva a későrómai 3.1 – 3.3 csoportokat a 3. csoportból. A Iulia Felix-ből származó színes üvegek adatait Silvestri 2008 munkájából vette át a szerző, míg az I. levantei csoport és a HIMT üvegek adatai Zucchiatti et al. 2007. munkájából származnak. **b)** Összesen három HIMT üveget találtak, amelyek jól elkülönülnek vas- és titántartalmuk alapján (ezeket a 2(a) ábrán ×-szel jelöltük).

Glass inventory, containing Levantine I glass with a few examples of HIMT glass is characteristic also for some other sites in the Eastern Mediterranean (Arletti et al. 2010), which may be interpreted as an indicator of particular trade connections in the eastern part of the Empire.

Since the 6th c. AD there is a decline in the use of natron. There are several explanations – also climatic and political – for the diminished availability of natron sources. The latter seem most probable as several political disturbances inflicted Egypt between the 7th and 9th c. AD (Shortland et al. 2006). The shortage of natron was overcome with the ash of halophytic plants. The new technology spread from the Byzantine or Islamic East where it was practically never abandoned. The commercial items that are easy to disseminate are glass beads. Production of glass beads is well documented and certain types are historically well explored. For example, we know that beads with mosaic eyes, which are frequent finds in central and northern Europe, were produced in the Bagdad caliphate during the first third of 9th c. AD (Andrae 1973).

During our measurement of Late Antique glass from the hilltop settlement Gradišče nad Bašljem in northern Slovenia we also encountered beads made with the ash of halophytic plants (Šmit et al. 2009). The site was populated in Late Antiquity and during the Carolingian period. Archaeological finds show that its end was an abrupt military event – either related with a rebellion of Slavs against the Franks in 819 or connected with Hungarian incursions. There were numerous glass finds at the site – beads, pins and earrings with glass heads and also several ingots or cullet of raw glass. The majority of objects were made of natron glass. The cullet showed a more uniform composition than the objects, which excluded production of the objects at the site. Two glass beads were found to be made using plant ash, which is consistent with the dating of the second population phase into the Carolingian period. The small percentage of plant ash also demonstrates that glassmaking still relied on the supplies of the old glass from Antiquity, while influx of the new material was modest. One glass bead made of plant ash was also discovered at the site Tonovcov grad (Šmit et al. 2014).

As the composition of glass beads can be an important time indicator, a systematic study was performed for the glass beads discovered in early Slavic graves (Šmit et al. 2012). Their selection involved graves around Ptuj in eastern Slovenia and graves around the Bled Lake in the central part of the country – the two different locations lay along the axis of Slavic migrations, which spread from the east. The analysis showed that the beads formed two groups: beads made of natron-type glass and beads made of glass using ash of halophytic plants (**Fig. 3a**).

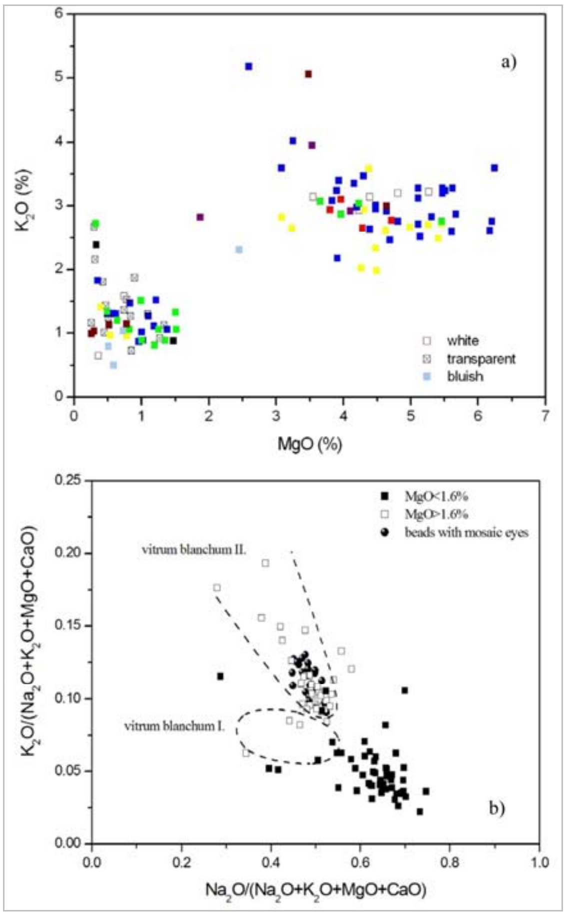

Fig. 3.: Beads from the early Slavic graves in Slovenia were made from the glass made of natron (low MgO and K_2O values) and from the glass made of the ash of halophytic plants (a). The latter group shows alkali composition similar to one group of Venetian glass (b) (after Šmit et al. 2012).

3. ábra: A szlovéniai korai szláv sírok gyöngyei a nátron típusú üvegből készültek (alacsony MgO és K_2O tartalmú alapanyag) és sótűrő növények hamujának felhasználásával készültek (a). A későbbi csoport gyöngyei a velencei üvegekhez hasonló alkália összetételt mutatnak (b) (Šmit et al. 2012 nyomán).

The latter groups also contained beads with mosaic eyes and knuckled beads, which were documented to be of Islamic origin. For dating the graves it can safely be assumed that the presence of beads made of halophytic plants assigns a date after 800 AD. Such beads appeared in the graves both from the central and eastern part of Slovenia, which has important consequences for dating of the Köttlach culture in Slovenia (Korošec 1979). The graves around Ptuj were dated to the end of the 8th and beginning of the 9th c. AD with respect to ceramics, which is consistent with the occurrence of glass beads. The difference occurs for the graves in the central and western Slovenia, which were traditionally dated to the 7th and 8th centuries, but are dated later, to the first half of the 9th c. by

European archaeologists (Giesler 1980). The identification of plant-ash glass beads in these graves provides strong arguments for the later dating.

Alkalis produced from the ash of halophytic plants are less pure than natron, so the contents of impurities can be used to identify their source. A useful indicator is the relative fraction of sodium and potassium oxides normalized to the sum of alkaline and earth-alkaline oxides (de Raedt 2001). The composition of glass beads made of ash of halophytic plants is similar to the glass produced in Iraq and around the Aral Sea (**Fig. 3b**), which confirms their oriental origin (Šmit et al. 2000). However, this type of glass is also common among the much later Venetian glass, which shows a very long exploitation of specific alkali sources. Scientific interpretations about this source are conflicting, which we learn on the example of Venetian glass.

The largest set of Venetian glass analyzed by IBA methods is from Ljubljana (Šmit et al. 2000; Šmit et al. 2002). There is documented glass industry in the city during the 16th century, including a detailed list of glass products, which is part of the last will of the glasswork lease holder Kristof Prunner (1564). There are also numerous glass finds from Ljubljana; 800 samples obtained from excavations are held in the National Museum of Slovenia (Kos 2007). The analysis using the combined PIXE-PIGE method involved more than 300 specimens. Beside the Venetian glass, several contemporaneous glass pieces from the castle ruins and examples of Roman and forest glass were analyzed for comparison and for checking the reliability of the statistical methods. Venetian-like glass from Ljubljana formed two distinct groups, which distinguished mainly due to the content of potassium oxide (Šmit et al. 2002).

We learned more about the Venetian glass when the measurements from Ljubljana were compared with the analytical results from Antwerp (Šmit et al. 2004). The city was a significant glassmaking center during the 16th and 17th centuries. Considering the relative fractions of sodium and potassium oxides, two groups of Venetian white glass (*vitrum blanchum*) were found (**Fig. 4a**). An independent group was formed by the more qualitative *cristallo* glass. The composition of *cristallo* manufactured in Venice and Antwerp found to be different: the Antwerp-made contained more potassium than sodium, so the two elements showed inverse correlation. Of the two groups of Venetian white glass, the one with more potassium also gives impression of inverse correlation. This fact inspired some researchers (Cagno et al. 2012) that only the group with low potassium content (v.b. I in **Fig. 4**) represents the true Venetian glass, while the high potassium group (v.b. II in **Fig. 4**) is glass made *à façon de Venise*.

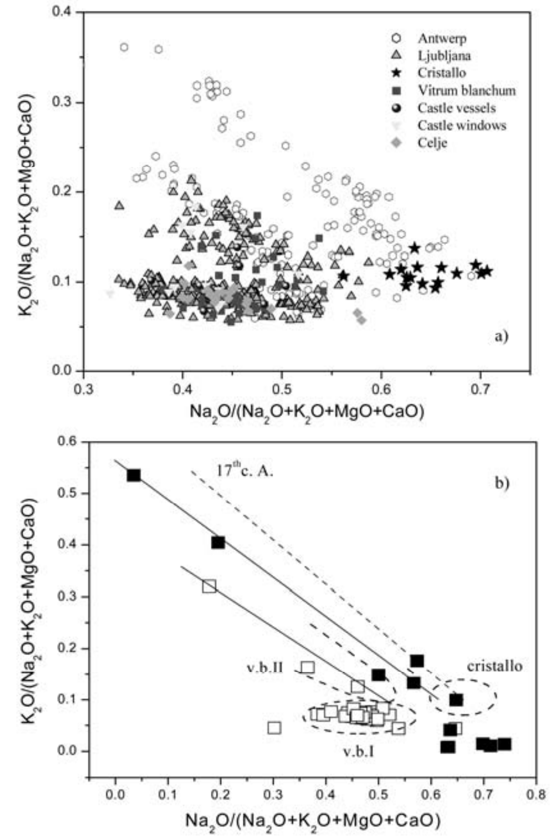

Fig. 4.: (a) Distribution of Venetian and *façon-de-Venise* glass from Slovenia (cities of Ljubljana and Celje and castle ruins) and Antwerp according to the composition of the flux (after Šmit et al. 2004). Two groups of Venetian white glass (*vitrum blanchum*, v.b. I and v.b. II) and a group of cristallo glass were found. (b) The same three groups also appear in the Albanian city of Lezha (after Šmit et al. 2009), indicating a technological step that was very likely adopted in the 17th century.

4. ábra: (a) Velencei és velencei típusú üvegek elterjedése, valamint antwerpeni típusú üvegek elterjedése Szlovéniában (Ljubljana és Celje városából, illetve várromokból), a folyósító anyag összetétele szerint (Šmit et al. 2004 nyomán). A velencei fehér üveg két csoportja (*vitrum blanchum*, v.b. I és v.b. II) valamint a *cristallo* üveg egy csoportját találták meg. (b) Ugyanez a három csoport jellemzi az albán Lezha város leleteit (Šmit et al. 2009 nyomán), ami arra utal, hogy a szükséges technológiai fogásokat a XVII. század folyamán sajátították el.

However, the latter groups also contain examples of original Venetian glass, so the two groups rather represent two different sources of alkalis that were used in Venice, but also in other glassmaking centers. It is tempting to identify the two groups with *alume catino*, harvested in the Levantine area, and barilla from Spain (Turner 1999). But if we consider again that the glass of the type v.b. II was also used for glass beads produced in Iraq and in the regions north of it, alkalis from v.b. II might rather be made of dessert-like plants, like *Kalidium caspicum*.

As the true Venetian and Venetian-like glass were made from the same type of alkalis, distinction between the home production and Venetian import is tedious. For Antwerp, home-produced glass contains more zirconium and hafnium impurities, as the silica used had a different geological background than in Venice (de Raedt et al. 2001). For Ljubljana, no distinction according to the two elements was found as both cities used silica from Alpine rivers (Šmit et al. 2005). The rare earth elements may also characterize the origin of silica.

It was the 17th century that brought a significant change of technology. The Albanian city of Lezha was under strong Venetian influence since the 15th century and excavations in the city revealed many pieces of Venetian glass. Its analysis showed three characteristic groups (Šmit et al. 2009). Two of them were the Venetian white glass, while the third group was different: its alkalis were of similar composition than the 17th c. glass from Antwerp and Netherlands (**Fig. 4b**). A rather pure silica source was used with low concentrations of iron, titanium and aluminum, and arsenic replaced manganese as decolorant. The glass then represents a new technological step following the Venetian glassmaking of the 15th and 16th century. This type of glass was not found in Ljubljana as its glassworks stopped operating before the early 17th century.

Forest glassworks that were active in the 18th and early 19th century used a rather uniform technology: abundance of wood was used for heating and producing ash that was precipitated into potash. Arsenic was used for discoloration. By the end of the 19th century new types of pigmentation were introduced. Our analysis included glass pigmented with uranium salts and glass colored red with colloidal particles. For both types of glass kept in the National Museum of Slovenia we identified three separate groups (Fajfar et al. 2013). One is very likely original production in the present Czech Republic, whereas two groups supposed to be local. One of them could possibly be located in the area of Pohorje in northern Slovenia where several forest glassworks were operating during the 19th century, and the other may represent products of the glasswork in Hrastnik in central Slovenia. The red-pigmented glass has a two-layered structure. The outer layer is typically engraved up to the transparent substrate. Pigmentation of the outer layer was achieved with copper; no gold according to the Egermann's technique was found.

Conclusion

Ion beam analytical methods can be successfully applied for the characterization of historic glass. In comparison with certain chemical methods they are surpassed in sensitivity that cannot reach below μg/g, which makes them incompetent for measuring the whole range of trace elements. They are also not able to provide isotopic information. However, these methods require sampling and pre-processing of samples with wet chemical methods. The main advantage of ion-beam analysis is non-destructive way of measurement in selected points of the integral glass objects. A wide range of elements can be measured simultaneously, which allow identification of the flux and determination of major impurities in the silica matrix, such as aluminum, titanium, iron, strontium and zirconium. The methods are also efficient for determination of decolorants, opacifiers and pigments. All this information is collected to give meaningful historic interpretation.

References

ANDRAE, R. (1973): Mosaikaugenperlen. Untersuchungen zur Verbreitung und Datierung karolingzeitlicher Millefioriglasperlen in Europa. *Acta Praehistorica et Archaeologica* **4** 101–198.

ARLETTI, R., GIACOBBE, C., QUARTIERI, S., SABATINO, G., TIGANO, G., TRISCARI, M., VEZZALINI, G. (2010): Archaeometrical investigation of Sicilian early Byzantine glass: chemical and spectroscopic data. *Archaeometry* **52** 99–114.

CAGNO, S., FAVARETTO, L., MENDERA, M., IZMER, A., VANHAECKE, F., JANSSENS, K. (2012): Evidence of early medieval soda ash glass in the archaeological site of San Genesio (Tuscany). *J. Arch. Sci.* **39** 1540–1552.

DE RAEDT, I. (2001): Composition of 16th-17th century façon-de-Venise glass excavated in Antwerp and neighbouring cities, *Ph.D. dissertation*, University of Antwerp. Antwerp, I. p. 23–24, II. p. 124–127.

DE RAEDT, I., JANSSENS, K., VEECKMAN, J., VINCZE, L., VEKEMANS, B., JEFFRIES, T.E. (2001): Trace analysis for distinguishing between Venetian and façon-de-Venise glass vessels of the 16th and 17th century. *J. Anal. At. Spectrom.* **16** 1012–1017.

FAJFAR, H., ŠMIT, Ž., KOS, M. (2013): PIXE-PIGE analysis of colored historic glass. *Glass Technol.: Eur. J. Glass Sci. Technol.* **A 54** 218–225.

FOY, D., PICON, M., VICHY, M., THIRION-MERLE, V. (2003): Caractérisation des verres de la fin de l'Antiquité en Méditerranée occidentale: l'emergence de nouveaux courants commerciaux. In: Foy, D. & Nenna M.-D., eds., *Échange et* *commerce du verre dans la monde antique. Actes du colloque de l'Association Française pour l'Archéologie du Verre, Aix-en-Provence et Marseille 2001,* Éditions Monique Mergoil, Montagnac, 41–85.

FREESTONE, I.C. (2005): The Provenance of Ancient Glass through Compositional Analysis. *Periodical of Material Research Society Symp. Proc*. **852** 1–14.

GANIO, M., BOYEN, S., BREMS, D., SCOTT, R., FOY, D., LATRUWE, K., MOLIN, G., SILVESTRI, A., VANHAECKE, F., DEGRYSE, P. (2012): Trade routes across the Mediterranean: a Sr/Nd isotopic investigation on Roman colourless glass. *Glass Technol.: Eur. J. Glass Sci. Technol.* **53** 217–224.

GIESLER, J. (1980): Zur Archäologie des Ostalpenraumes vom 8. bis 11. Jahrhundert. *Archäologisches Korrespondenzblatt* (Mainz) **10** 85–98.

HIRVONEN, J.-P. & LAPPALAINEN, R., (1995): Particle-Gamma Data. In: TESMER, J.R. & NASTASI M. eds., *Handbook of Modern Ion Beam Materials Analysis*, Materials Research Society, Pittsburgh, 573–613.

ISTENIČ, J. & ŠMIT, Ž. (2012): A raw glass chunk from the vicinity of Nauportus (Vrhnika). In: Lazar, I. & Županek B., eds., *Emona: between Aquileia and Pannonia,* Annales Mediterranei, Univerza na Primorskem, Koper 301–309.

JEZERŠEK, D., ŠMIT, Ž., PELICON, P. (2010): External beamline setup for plated target investigation. *Nucl. Instr. and Meth. B* **268** 2006–2009.

KOROŠEC, P. (1979): Zgodnjesrednjeveška arheološka slika karantanskih Slovanov / Archaeologisches Bild der karantanischen Slawen in fruhen Mittelalter, [Early medieval archaeological image of Karantanian Slavs]. (in Slovenian, German summary) *Dela / Slovenska akademija znanosti in umetnosti, Razred za zgodovinske in družbene vede [Works of the Slovenian Academy of Sciences]* **22**, Ljubljana, 1–248.

KOS, M. (2007): 15th and 16th Century Glass, *Collection of the National Museum of Slovenia*. National Museum of Slovenia, Ljubljana, 40–139.

LESIGYARSKI, D., ŠMIT, Ž., ZLATEVA-RANGELOVA, B., KOSEVA, K., KULEFF, I., (2013): Characterization of the chemical composition of archaeological glass finds from South-Eastern Bulgaria using PIXE, PIGE and ICP-AES. *J. Radioanal. Nucl. Chem*. **295** 1605–1619.

LJUBOMIROVA, V., ŠMIT, Ž., FAJFAR, H., KULEFF, I. (2014): Chemical composition of glass beads from the necropolis of Apollonia Pontica (5th-3rd century BC). *Archaeologia Bulgarica* **18** 1–17.

MARIĆ STOJANOVIĆ, M., ŠMIT, Ž., GLUMAC, M., MUTIĆ, J. (2015): PIXE-PIGE investigation of Roman Imperial vessel and window glass from Mt. Kosmaj, Serbia (Moesia Superior). *J. Arch. Sci.* **Reports 1** 53–63.

REHREN, Th. (2008): A review of factors affecting the composition of early Egyptian glasses and faience: alkali and alkali earth oxides. *J. Arch. Sci.* **35** 1345–1354.

SAYRE, E.V. & SMITH, R.W. (1961): Compositional categories of ancient glass. *Science* **133** 1824–1826.

SHORTLAND, A., SCHACHNER, L., FREESTONE, I., TITE, M. (2006): Natron as a flux in the early vitreous materials industry: sources, beginnings and reasons for decline, *J. Arch. Sci.* **33** 521–530.

SILVESTRI, A. (2008): The colored glass of Iulia Felix. *J. Arch. Sci* **35** 1489–1501.

SILVESTRI, A., MOLIN, G., SALVIULO, G. (2008): The colourless glass of Iulia Felix. *J. Arch. Sci.* **35** 331–341.

ŠMIT, Ž., PELICON, P., VIDMAR, G., ZORKO, B., BUDNAR, M., DEMORTIER, G., GRATUZE, B., ŠTURM, S., NEČEMER, M., KUMP P., KOS, M. (2000): Analysis of medieval glass by X-ray spectrometric methods, *Nucl. Instr. and Meth*. **B 161-163** 718–723.

ŠMIT, Ž., PELICON, P., HOLC, M., KOS, M. (2002): PIXE-PIGE characterization of medieval glass, *Nucl. Instr. Meth. Phys. Res*. **B 189** 344–349.

ŠMIT, Ž., JANSSENS, K., SCHALM, O., KOS, M. (2004): Spread of façon-de-Venise glassmaking through central and western Europe, *Nucl. Instr. Meth. Phys. Res*. **B 213** 717–722.

ŠMIT, Ž., JANSSENS, K., BULSKA, E., WAGNER, B., KOS, M., LAZAR, I. (2005): Trace element fingerprinting of façon-de-Venise glass, *Nucl. Instr. Meth. Phys. Res.* **B 239** 94.

ŠMIT, Ž., JEZERŠEK, D., KNIFIC, T., ISTENIČ, J. (2009): PIXE-PIGE analysis of Carolingian period glass from Slovenia, *Nucl. Instr. and Meth.* **B 267** 121–124.

ŠMIT, Ž., STAMATI, F., CIVICI, N., VEVECKA-PRIFTAJ, A., KOS, M., JEZERŠEK, D. (2009): Analysis of Venetian-type glass fragments from the ancient city of Lezha (Albania), *Nucl. Instr. Meth. Phys. Res.* **B 267** 2538–2544.

ŠMIT, Ž. KNIFIC, T. JEZERŠEK, D. ISTENIČ, J. (2012): Analysis of early medieval glass beads – Glass in the transition period. *Nucl. Instr. and Meth.* **B 278** 8–14.

ŠMIT, Ž., TARTARI, F., STAMATI, F., VEVECKA-PRIFTAJ, A., ISTENIČ, J., (2013): Analysis of Roman glass from Albania by PIXE-PIGE method. *Nucl. Instr. and Meth.* **B 296** 7–13.

ŠMIT, Ž., MILAVEC, T., FAJFAR, H., REHREN, TH., LANKTON, J.W., GRATUZE, B. (2014): Analysis of glass from the post-Roman settlement Tonovcov grad (Slovenia) by PIXE-PIGE and LA-ICP-MS. *Nucl. Instr. and Meth*. **B 311** 53–59.

TURNER, G. (1999): Allume Catina and the aesthetics of Venetian cristallo. *J. Design History* **12** 111–122.

VERITÀ, M. & ZECCHIN, S. (2009): Thousand years of Venetian glass: the evolution of chemical composition from the origins to the 18th century. In: JANSSENS, K. DEGRYSE, P. COSYNS, P. CAEN, J. VAN'T DACK L. eds., *Annales du 17e congrès de l'AIHV* (Antwerp 2006), University Press Antwerp, Antwerp, 602–613.

ZUCCHIATTI, A., CANONICA, L., PRATI, P., CAGNANA, A., ROASCIO, S., CLIMENT FONT, A. (2007): PIXE-analysis of V-XVI century glasses from the archaeological site of San Martino di Ovaro (Italy). *J. Cult. Herit.* **8** 307–314.