NON-DESTRUCTIVE ANALYSIS OF THE MOVABLE CULTURAL OBJECTS – STUDIES OF GLASS IN THE NATIONAL MUSEUM OF SLOVENIA

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1. Historical and art-historical context

Jožef Stefan Institute and National Museum of Slovenia performed several joint research projects dealing with non-destructive analysis of movable cultural heritage, for instance coins, arms, ceramics, and glass.

Interdisciplinary approach to the movable cultural heritage, especially from the view of the natural sciences, enables the confirmation of originality of the objects, the dating, establishing of the provenance and the manufacturer (or author), and spread of certain techniques or raw materials. For instance, the type of material and its stage of deterioration should imply the necessary conservation treatment. At the same time, it is one of the important elements of dating and establishment of the authorship. The major chemical composition may reveal the basic technological procedures used in the past. The trace elements may point to the origin of raw materials, which may be indicative further for trade routes and relations. The trace element fingerprinting also serve to identify fakes. In certain applications, the composition is characteristic for the age of production and may be used for dating (distinction between Roman, *façon de Venise* and 17th century glass).

Determination of Roman glass is difficult because of recycling and usage of pre-fabricated glass in the form of ingots. Nevertheless, the analysis of Slovenian Roman and Early mediaeval glass revealed that we can group the glasses from Bašelj in two groups: Late Roman and Carolingian.

At the end of the 15th century many of so called forest glassworks were operating in Europe. They produced a special kind of glass, using potash instead of natron. Towards the end of the 15th century the art of making glass in the Venetian manner started to became an important branch of Middle-European entrepreneurship. Also in Ljubljana, two leading merchants and entrepreneurs established the glassworks in 1520s. In 16th century two more glassworks started to produce glass in Ljubljana[1].

There are around 800 glass vessels and fragments in the glass collection of the National Museum of Slovenia, most of all supposed to come from Ljubljana glassworks. They were excavated at three locations in the city centre: at the location of the glassworks, at the glass shop, and at the former city dump place[2]. The most important question is whether the glasses were produced in Ljubljana or imported from Venice. In favor of the local production were the locations of excavations and the list of objects from an archival source, namely the inventory, made after death of glassworks lease holder, Christoph Prunner in 1564. But this is not enough to be certain. Venice is only 250 kilometers from Ljubljana (which is, on the other hand, situated only 100 km from the nearest port at the Adriatic Sea). So it is also possible that the glasses were imported either from Venice or elsewhere.

As a comparison we included in our project the objects that were acquired by the National Museum of Slovenia, not excavated, and we also added late antique objects. Among acquired objects were two stained glass plaques, which were possibly imported from South Germany.

Historical records and chemical analyses show that the same types of alkalis (obtained from halophytic plants) were used in Venice and in Ljubljana glassworks[3]. The glassware produced in Ljubljana was of the type of Venetian white glass (*vitrum blanchum*) and of the same quality (fig. 1). The only substantial difference was that the production of *vitrum blanchum* was introduced in Ljubljana approximately 70 years after the invention of *cristallo* (Angelo Barovier before 1460), thus being out of fashion (and production) in Venice.

Around the year of 1600 a great change happened in the glass production. The esthetics issues mostly concerning ornamentation schemes turned towards precious stones and rock crystal. Instead of elaborate fire-worked shapes that Muranese glaziers developed into perfection, the engraved ornaments became the most desirable. This new technique prevailed and caused the chemical changes in bulk mass and new glassmaking technologies. Venetian glassmaking lost its primate and declined. The most important glass centers became Bohemia and Silesia with the satellites all around Middle Europe.

The comparisons between late 16th and early 17th centuries *façon de Venise* glasses, and 17th century Middle-European glass show us the intermingling of both techniques, mutual influences, territorial increase and decrease of both, and other issues, important for glass history. Because of change of some ingredients in the glass mass, we can easily use the results for dating the glass objects. The time line before- and after the year of 1600 is clearly visible. After this period, very likely through the influence of glassmaking in Bohemia, the wood-ash based alkalis came into wide use at the glassworks of Slovenia.

The third part of the glass analysis dealt with the problem of the authorship. The problem was, whether the objects from the collection of the National Museum of Slovenia were produced at Loetz' Glassworks in Kláštersky Mlyn? This factory was an important plant, producing elaborate and expensive glass in Art Nouveau style at the end of 19th and early 20th centuries. Prices for their objects are as high as for those made by famous French Art Nouveau artists like Daum Frères or Emile Gallé. The results after the method, established by D. Jembrich *et alii*[4] revealed that there is a slight

Fig. 1. Examples of *façon de Venise* glass from Ljubljana.

difference in chemical structure of Loetz glass which enables the grouping and thus the confirmation of the authorship.

2. Experimental methods

The collaboration between the National Museum of Slovenia and Jožef Stefan Institute developed from a good starting position: The analytical methods available at the institute were based on the ionbeam analysis, which requires no sampling and is thus nearly non-destructive. The measurements were performed at the Tandetron accelerator of 2.2 MV nominal voltage. Irradiation with a proton beam of several MeV energy induce in target the characteristic X-rays, which form basis of the analytical method PIXE, and gamma rays of several light elements, which are exploited in the method of PIGE. Our measurements were carried out in the air, which strongly attenuated soft X-rays of the elements lighter than silicon. The elements sodium, magnesium and aluminum, which are essential components of glass, were then determined according to their characteristic gamma rays. For the calculation of concentrations, a special numerical code was developed which evaluates the concentrations iteratively from joint X-ray and gamma intensities, taking into account the matrix elements of the target. The procedure is facilitated by the fact that for glass all elements may be assumed in the oxide form. The technical problems that emerged with the development of the method involved normalization of the spectra. For gamma rays, the silicon line of the isotope Si-29 was used for most of the measurements, however, due to its low counting statistics, it was recently replaced by measurement of the proton current by a mesh made of thin platinum-rhodium wires. The X-ray spectra are normalized to the intensity of the argon line induced by protons in the air-gap between the exit window and target. Such measurement requires precise knowledge of the proton impact energy at the target and the distance between the target and X-ray detector, as the X-rays attenuate in the air. The calibration of geometrical quantities is done by a set of targets of known composition. The deconvolution of X-ray spectra is performed by the method of independent parameters, which employs published data of ionization cross sections, X-ray attenuation cross sections and stopping powers, while the treatment of the gamma spectra is done empirically using the glass standard NIST 620. At the end of the procedure, the sum of all metal oxides is normalized to 100%; the normalization factors are monitored as an indicator of reliability of particular measurements. The general accuracy of the method is 5% for major elements, about 10% for the elements of concentrations about 1%, and 10-20% for the trace elements. The sensitivity for the trace elements around zirconium may reach 10 µg/g by additional measurement of hard X-rays, applying an absorber of kapton foils totally 0.7 mm thick or a 0.1 mm aluminum foil. The only weak point of the method is determination of phosphorous. We can only detect its gamma line, but we do not dispose of a phosphorous-containing standard glass.

3. Studies of *façon de Venise* glass

Our initial and up to now the most comprehensive study involved about 400 glasses from Ljubljana, Slovenian castles and Late Roman sites[5]. The aim of the analysis was to find characteristic groups among them. Statistical treatment was based on the principal component analysis which involved all detected major and minor elements except silicon. As a result, the following principal groups were identified: *façon de Venise* glass, which involved the majority of glasses from Ljubljana and castles, Late Roman glass and forest glass[6]. Individual properties were also observed for a few examples of coloured glass plates that represent import to Ljubljana. The most important finding was that the façon de Venise glass splits into two groups (fig. 2).

From our measurements it was not possible to establish relation with the original Venetian glass. However, our measurements incited interest of Koen Janssens at the University of Antwerp. Collaboration was established, and our joint study continued on a much larger data base, which included also data on the glasses from Antwerp and Venetian white glass (*vitrum blanchum*)[7]. The study concentrated on particular glass components, i.e. siliceous matrix, alkali flux, alkaline-earth stabilizer, and decolourant.

Façon de Venise glass is split into two groups due to the use of alkali flux (fig. 3). Flux was

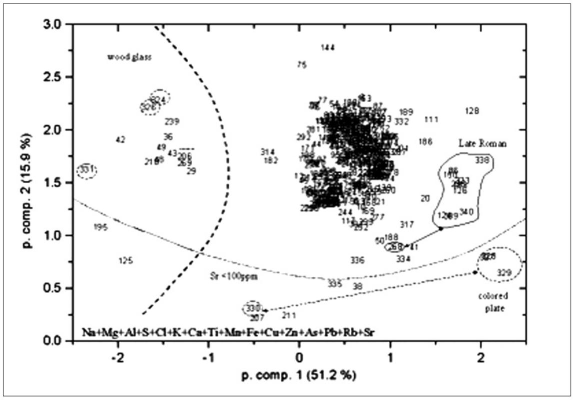

Fig. 2. Glasses from Ljubljana, Slovenian castles and Late Roman sites, and coloured plates sorted by the principal component analysis (ŠMIT et *alii* 2002).

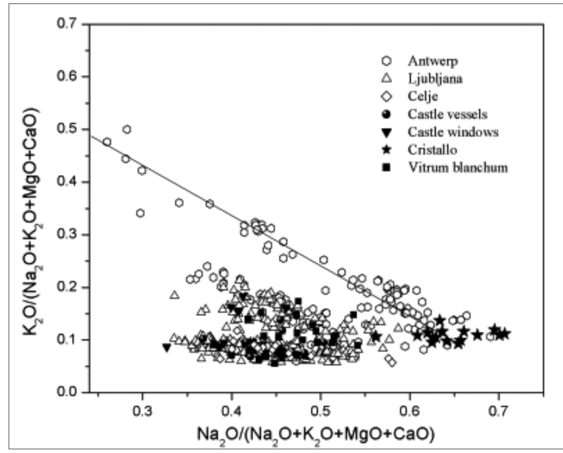

Fig. 3. Relative contents of sodium and potassium oxides in the total fraction of alkaline and alkaline-earth oxides (ŠMIT et *alii* 2004).

made from the ash of halophytic plants that were collected at the marshy coasts of Levant and Spain. The two groups are characterized by distinct fractions of sodium and potassium. In one group, the content of potassium is nearly constant; in the other it exhibits approximate inverse linear correlation, which may indicate combination of several flux types. It is significant that the two groups contain glasses from Antwerp, Slovenia (Ljubljana, Celje, individual castles), as well as original Venetian *vitrum blanchum*. This suggests that the flux produced in Venice was widely used in different regions of Europe. The glasses of Antwerp exhibit further another type of the flux, characterized by the inverse correlation between sodium and potassium and containing Venetian *cristallo*, which is finer and made of more refined materials than *vitrum blanchum*. It is interesting to note that *cristallo* was not encountered among the glasses of Slovenia.

As studies of the flux did not reveal differences between the imported, original Venetian glass and domestic products, the elements characteristic for the siliceous component may point to the local sources of silica. The concentrations of these elements are too low to be measured by ion beam methods, so a series of glasses was measured by LA ICP MS at the University of Warsaw[8]. Neither Hf-Zr correlations nor the rare earth elements pointed any significant differences between the glasses; it was only a Nd/Dy versus Zr plot that suggested a source of silica not used for the original Venetian glass. The small difference between silica sources may be explained by the use of pebbles from Alpine rivers, which are geologically similar.

The *façon de Venise* glass was discoloured by addition of manganese dioxide. It is already present in the ash of halophytic plants; some was probably added in a mineral form.

Within the cooperation program between Albania and Slovenia we were able to analyse a series of glasses from the city of Lezha, an important coastal town in northern Albania that was under the Venetian dominion. Brief characterization of the glasses from Lezha by the hierarchical clustering method and MgO/Al_2O_3 bivariate plot showed two distinct groups, which were studied further for the composition of the flux, purity of silica and decolorants used[9]. One glass group was made from the same type of the flux that we encountered in the glasses from Slovenia and Antwerp; it is characterized by a small content of potassium and denotes typical *façon de Venise* glass. We marked this group as v.b.I (fig. 4). Two glasses may belong to the other *vitrum blanchum* group (marked as v.b.II in fig.

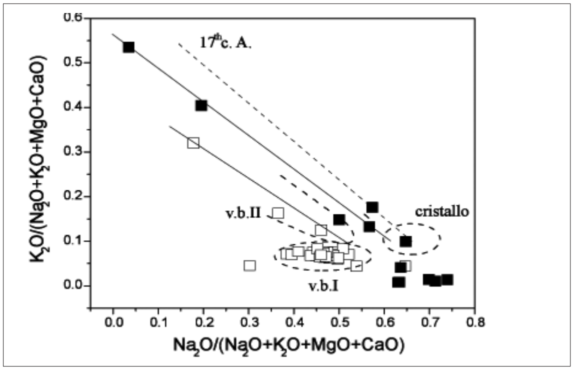

Fig. 4. Relative contents of sodium and potassium oxides for the glasses of Lezha (ŠMIT et *alii* 2009a).

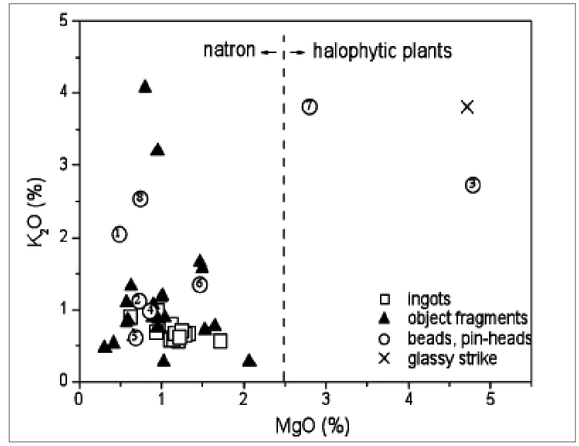

Fig. 5. Classification of the flux type in the Carolingian period glass from Bašelj according to the magnesium and potassium oxides (ŠMIT et *alii* 2009b).

4), but the flux of the second distinct group was made of entirely different flux, characterized by inverse correlation between sodium and potassium. Though this correlation line appears similar to the line for the Antwerp glass that contains *cristallo* and the locally produced glass dated to the 17th century, the two lines are not identical. Nevertheless we conclude that the two lines denote a similar technological procedure which produces a rather pure flux by the precipitation method (potash). This conclusion is corroborated by the concentrations of strontium, since its oxides are insoluble in water and are therefore removed from the precipitate. The contents of SrO are larger than 400 µg/g for the *façon de Venise* glass, but smaller than 100 µg/g for the glass of the second group. The second group further exhibits low contents of aluminium, iron and titanium oxides (typically below 0.1%), which indicates selection of rather pure silica as raw material. The third distinction parameter of the second group is discoloration by addition of arsenic oxide instead of manganese. All three features point to the second group to be made by a more advanced technology and is therefore more recent than the *façon de Venise* glass. The measurements on the glasses of Lezha therefore revealed two production phases, the typical façon de Venise glass and its later development.

4. Late Roman and early medieval glass

Glass in the Roman period was produced in gross quantities in a rather localized area of Egypt and Palestine, exploiting the natural sources of natron[10]. The raw glass was distributed to the secondary workshops in the form of ingots. The sources of natron became inaccessible through political disturbances since 8th c., so a new technology was developed in the Islamic or Byzantine world, which was based on the ash of halophytic plants. Our measurements involved a series of glasses from the site of Bašelj, where the majority of glass finds can be dated to the Carolingian period. The analysis showed that the glass fragments and several glass objects fragments were made of flux obtained from natron, and only two glass beads were made of flux obtained from ash[11]. This indicates that the glass made according to the Roman tradition circulated in the region of Eastern Alps well into the 9th century. The beads were very likely produced in the east and therefore reflect the new, eastern glassmaking technology. Our current work involves analysis of beads with mosaic eyes, which are common finds in western and central Europe and are dated to the first third of the 9th century[12]. As found by preliminary measurements, they were made from the ash of halophytic plants.

5. Conclusion

Important results were obtained on the *façon de Venise* glass produced in local glassworks throughout Europe. The used the same type of flux that was very likely produced in Venice and distributed commercially to the glassworks. As a very similar glass was identified in different regions, distinction between imported and local products can only be made tentatively, into small differences in the rare earth elements. In the case of Ljubljana, the local glassmaking is manifested in the technology that lags behind the contemporary procedures in Venice.

In the transition period between the Roman natron-based and medieval plant-ash glassmaking we identified well dated objects that belong to both technologies. This may clarify the intensity of the transition period and its appearance in particular regions.

NOTE

1 KOS, ŽVANUT 1994, pp. 19-23.
2 KOS 2007, pp. 12-14.
3 ŠMIT 2007, pp. 180-181.
4 JEMBRICH 2000.
5 ŠMIT *et alii* 2000; ŠMIT et alii 2002.
6 ŠMIT *et alii* 2002.
7 ŠMIT *et alii* 2004.
8 ŠMIT *et alii* 2005.
9 ŠMIT *et alii* 2009a.
10 FREESTONE 2005; SHORTLAND *et alii* 2006.
11 ŠMIT *et alii* 2009b.
12 ŠMIT *et alii* 2009c.

Abstract

A review is given about the application of ion beam analytical methods for the studies of glass kept in the National Museum of Slovenia. It is shown that the Venetian-type glass (*à la façon de Venise*) is distributed into two groups according to the flux. The analysis includes further the glass from the city of Lezha (Albania) which spans over two production periods: Venetian white glass and its later development phase. The flux type (natron or plant ash made) was identified in the early medieval glass from the site Bašelj near Preddvor.

Key words: medieval glass, ion beam analytical methods, Venetian-type glass, National Museum of Slovenia, Lezha (Albania).

Analisi non distruttiva degli oggetti mobili. Studio dei vetri conservati nel Museo nazionale di Lubiana

Si offre qui una rassegna dei metodi di analisi con l'applicazione del fascio di ioni per lo studio dei vetri conservati nel Museo Nazionale della Slovenia. In funzione del mutamento di tecnica produttiva si dimostra che il vetro di tipo veneziano (à la façon de Venise) è distinto in due gruppi. L'analisi comprende inoltre il vetro dalla città di Lezha (Albania) che si estende su due periodi di produzione: il vetro veneziano bianco e la sua fase successiva di sviluppo. La tecnica produttiva (mediante il natron o con ceneri di piante) è stata identificata nel vetro altomedievale da sito di Bašely presso Preddvor.

Parola chiave: vetro medievale, metodo di analisi con fascio di ioni, vetro veneziano, Museo nazionale della Slovenia, Lezha (Albania).

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