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GLASS MELTING EXPERIMENTS IN THE RECONSTRUCTION OF GLASS FURNACE FROM THE 9TH CENTURY

Abstrakt: The authors research and publish the results from a glass melting experiments conducted in a reconstruction of a historic wood-fired furnace from the 9th c. during the 2017–2019 period. The experiments focused on soda-lime glass and were implemented as pilot for the planned, long-term and annual experimentations in the Archeopark in Hanušovce nad Topľou. Experimental glass batches were weighed according to the composition of glass from archaeological samples from the 9th c., as well as according to the model soda ash glass. The aim was to obtain experimental data to verify archaeometric research of historical glass. The study focused on the possible use of a wood-fired furnace in the melting glass from glass batches, the effects of ash on the composition of glass, remelting of glass cullet, penetration of elements from crucible and flue gases into molten glass, causes of different quality of glass remelting or colouring with added CuO and MnO. Another aim of the study was to compare the results of the glass analyses from the SEM/EDS and XRF method, which we later interpret in historical contexts.

Keywords: Experimental melts, historical glass, furnace from the 9th c., SEM/EDS and XRF analysis

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1. INTRODUCTION¹

In the research of historical glass, it is rare to find records or knowledge of specific melting of glass batches in wood-fired furnaces. That's the reason why during the interpretation of the chemical composition of an ancient glass vessel or glass bead, for example, we use current knowledge of modern glass melting, the structure of glass and its properties. We concluded that facts, purposefully obtained and recorded from experimental melts carried out in a historical wood-fired furnace, could be useful to the interdisciplinary study of historical glass. For such a study, a furnace was built in 2017 in the Archeopark in Hanušovce nad Topľou, as a reconstruction of a glass furnace from the 9th c. (Fig. 1). Fragments of such a furnace were researched in Bratislava – Devínska Kobyla (Farkaš, Turčan 1998, pp. 31–32, Figs 4–6). The furnace is heated by beech wood and, in addition to the presentational function of the historical glass production for visitors of the Archeopark, we have also designed it for experimental melting of glass batches in order to obtain data on the course and results of such glass production². Experiments were performed from 2017 until 2019 and Authors present and discusses the data obtained by those experiments.

1.1. OBJECTIVES OF THE EXPERIMENTS

The experiments discussed in this paper, focused on soda-lime batches and their colouring. They were considered to be a pilot for the planned long-term experimentation ahead. In addition to the ash, we used laboratory raw materials for the preparation of glass batches in a composition that was based on a specific archaeological find of historical glass. We verified the results by subsequent melts of the same batch. The goal was not the melting of the same glass as the specific archaeological sample *per se*, but to verify and record the conditions under which the glass was melted during its production, the processes occurring during the melting, as well as the effect of contamination by other elements from flue gases and ceramic crucibles on molten glass. The study also focused on the comparison of the results of SEM/EDS and XRF analysis addressing the chemical composition of glass, which are missing in the professional literature records devoted to historical glass. All the performed steps, from the preparation and weighting of the batches, to the results of the analysis of the molten glass and related material, were recorded during the experiments.

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² Organizationally and professionally, this long-term project is covered by the Commission for Support of Interdisciplinary Glass Research at the Slovakia Archaeological Society in cooperation with the Slovak Glass Society, FunGlass of Alexander Dubček University of Trenčín in Trenčín, RONA Lednické Rovne, Kaštieľ and Archeopark in Hanušovce nad Topľou. The project has not been stably funded so far, only sponsored every year, always under different conditions.



Fig. 1. Hanušovce nad Topľou, district Vranov nad Topľou. Reconstruction of a glass furnace from the 9th c., a side view of the furnace picturing working openings and the opening of the cooling chamber.

Photo by D. Stašíková-Štukovská

This paper discusses basic information about the experiments and the interpretation of selected results that contain facts that do not appear often or have not been discussed in the multidisciplinary literature devoted to the archaeometric research of archaeological evidence of historical glass. The study adheres to the goal of providing professionals and the public with objective knowledge about the melting of sodium batches and cullet of glass in a wood-fired furnace and their interpretive contribution to the research of historical glass.

1.2. SODA-LIME GLASS AND ITS HISTORY

The soda-lime glass melted with natron (crystalline soda) occurs from prehistory to the Middle Ages throughout Europe, North Africa and the Middle East. Many researchers have been studying the soda-lime glass and its archaeological samples in their archaeometry research (e.g., Dekówna 1980, pp. 62–64; Dussubieux *et al.* 2010; Schibille 2011; Schibille, Freestone 2013).

In addition to the content of present oxides, trace elements are used to classify soda glass. Complex analytical methods determine the presence of those elements. This process makes it possible to recognize types and subtypes of historical soda-lime glass in time and location (e.g., Schibille *et al.* 2017). It is known from archaeological samples that the largest number of soda-lime glass or natron glass production centres existed in Roman times. The primary glass centres that produced the soda-lime-aluminium-silicate glass decolourized by MnO were identified in Egypt and throughout the north-eastern Mediterranean (Schibille *et al.* 2017). In the early Middle Ages³, glass melted with marine plant ash, which replaced natron, spread and gradually prevailed throughout Central Europe as well as in the Mediterranean (Barkoudah, Henderson 2006). However, archaeological samples in Europe still documented glass melted with natron or soda. The question of the origin of this glass in the 6th–10th centuries is the subject of various opinions and discussions, which relate mainly to the survival of glass smelters from the Roman period to the early Middle Ages as well as the source of mineral soda (Szóke *et al.* 2004, p. 97; Schibille, Freestone 2013, p. 12; Schibille *et al.* 2017). During the 8th–9th centuries, several types of beads and buttons, alongside other objects made of soda-lime or natron glass, appeared in the region of modern day Slovakia (Staššíková-Štukovská 2017). A glass furnace that was used to melt soda-lime glass was also studied in Bratislava-Devínska Kobyla. This glass workshop was extraordinary for the 9th c. in Central Europe because it was not located in the proximity to a church; the building was rather independent. Meanwhile, newer processing of yet unpublished architectural artefacts from the furnace construction proved glass melting in a tank with the capacity of 30L (Staššíková-Štukovská in the press). According to the archaeological samples of fragments from this tank furnace, a reconstruction in the Archeopark in Hanušovce nad Topľou was built where this study was carried out.

2. COMMON STEPS OF EXPERIMENTS

This chapter discusses the experimental steps of the study, in order to rationalize the scope of the text in the description of specific experiments. The melts were carried out once a year and the exact determination of the experiments in the following year was based on the results achieved in the previous year of the experiment. For example, the un-melted glass remains from 2017 were re-melted in 2018, *etc.* The procedures progressive followed each other. The study only considered the objectives from the pilot project of experimental melts focused on the soda-lime glass to be achieved in 2019⁴.

³ It is mainly in the 8th and 9th centuries in the area around the middle course of the Danube.

⁴ We plan to carry out experiments every year, and those interested in participating in the accompanying workshops will find information at <http://www.sas.sav.sk/komisie-sas/komisia-historia-skla/okomisii-hs/>.

2.1. HEATING TIME AND ACHIEVED TEMPERATURE

The consecutive experiments during the three years were conducted with slight time variations in the heating of the experimental furnace. The temperature of the furnace was recorded as accurately as possible; from the ignition of the fire to the last addition of wood to the stove. A pyrometer was used for measurements during all three years; however, Seger cones were also used in 2019 (900, 1100, 1200°C). The most accurate temperature measurement was performed electronically using the TESTO 175T3-Datalogger, the software for which is available at www.testo.com⁵. The temperatures were recorded with sensors located in the melting and cooling chambers. The recording interval of the temperature was initially set to 15 minutes; however, it progressed to 30 minutes after reaching 800°C. A brief record of the heating time and temperatures reached in the furnace during the experiments is given in Table 1. It should be noted that the temperatures in the melting chamber were not kept at the achieved value, but decreased and increased for a short time due to heat leakage caused by removing shutters from working holes during the demonstration of glass production to the public, removing ash from the firing chamber of the furnace or adding wood to the fire. Only one shutter of the furnace was opened; when pulling glass and producing objects for visitors of the Archeopark. The shutter to the experimental space was opened during the heating of the furnace only in 2018 while pulling glass rods of experimentally melted glass from the crucibles. On all other occasions, the working hole with the experiments remained closed during the melting process. The melting chamber, where the tank with glass for demonstrations was placed, was shared with the crucibles with experimental batches. Since the space was not dammed, the temperature drops did not only affect the part of the chamber presented to visitors, but also the area with experimental crucibles.

Table 1. Time required to heat the furnace and temperatures achieved during experiments in the years of 2017–2019

Day/month/ year/hour of setting the fire in the furnace	Temperature up to 500°C total number of hours	501–899°C total number of hours	900–1050°C total num- ber of hours	1051–1105°C total number of hours	Day/month/ year/hour/ of last feed to the fire in the furnace	Total number of hours to heat up wood-fired furnace
1	2	3	4	5	6	7
05/10/2017/ 08:00	10	20	19	8	07/10/2017/ 17:00	57
21/06/2018/ 08:00	8	20	20	8	23/06/2018/ 16:00	56
20/06/2019/ 11:00	2	9	33	10	22/06/2019/ 17:00	54

⁵ Many thanks to Stanislav Tkáčik from KAMIN Ltd. for lending electronic sensors.

The construction of the furnace was slightly modified in 2019, and the position of the ventilation openings was changed to increase the maximum temperature in the melting chamber and heat the cooling part of the furnace with flue gases. As a result of the change, the oxidizing atmosphere in the working and melting chamber changed the reducing atmosphere for a longer time than it was in the previous years 2017 and 2018.

2.2. EXPERIENCE WITH HEATING IN THE FURNACE

Throughout the experiments, the study gained some insights into the heating of a glass furnace. When melting glass, it is crucial to maintain the temperature throughout the melting process. In modern glass-work, the exact temperatures in the glass furnace can be set, controlled and regulated by a computer electronically. When heating a wood-fired furnace, there are less accurate controls available and the process is more dependent on the operators, their knowledge and experience with the furnace and, in no small extent, on the details of the construction of their glass furnace. For example, in the literature, we find records that beech wood is the most suitable for wood heating, but it is not recorded what dimensions the chopped logs should have and how should the fuel be correctly added to the hearth of the glass furnace. Members of KAMIN Ltd., namely Petr Havrila and Stanislav Tkáčik, provided the study with valuable advice and, using trial and error, the study was able to keep a glass furnace heated by beech wood at a temperature suitable for melting glass stems during all experiments. The study recorded that beech logs cut to a length of 80–92 cm, which are in a triangular cross-section with a length of one side of about 6–8 cm, proved to be optimal for heating the glass furnace in Hanušovce. Beech logs should be added obliquely upwards to the firing chamber of the furnace; there is a step at the interface of the firing chamber and the temperature channel for this purpose, exactly as it was found in the original archaeological find (Fig. 2a). The temperature in the furnace depends on the shape and size of the beech logs, as well as the method and amount of their insertion into the firing chamber. The removal of ash from the firing chamber without temperature loss in the melting chamber is equally essential. However, practical experience is most important factor; no amount of scientific instructions can substitute for experience. The study burned less wood in 2018 than in 2017 and even less in 2019 while reaching the same required temperature of 1100–1150°C. Being able to maintain the same temperature for several hours using less fuel than before confirms that

Fig. 2. Details of the reconstructed glass furnace from the 9th c. in Hanušovce nad Topľou
a – a view of the heating chamber, in the background there is a stand that separates the fire from the heat channel below melting chamber and serves to retain the ash; b – top view of the thermal opening and the shelf in the melting chamber with crucible imprints E1–E4 from the year 2017.

Photo by D. Staššíková-Štukovská (a), L. Krokker (b)



a

0 40 cm



b

such banal-looking factor as the method of adding wood to the furnace is crucial and needs experience and knowledge.

2.3. GLASS BATCH AND GLASS CULLET

The preparations of the glass batches were not accidental. First, the study chose a historic glass object⁶, the composition of which was to be achieved by preparing and melting a glass batch. The design and preparation of raw materials, as well as the expected chemical composition and weighing of the glass batches, were carried out by Alfonz Plško in the Laboratories of X-ray Fluorescence Spectrometry at the Alexander Dubček University of Trenčín in Trenčín. The specific batch was listed as a percentage by weight in 2017. In 2018, it was weighted to 100 grams, while in 2019 the specific batch was weighted to 200 grams of glass. The team used pure chemicals for the preparation of glass batches, except for glass sand with the content of SiO₂ 99.5% and ash.

The preparation of glass cullet was relatively easier. The glass cullet of barium glass for experimental melting of glass cullet, imitating a “return cullet”, were provided to the team by the company RONA, Lednické Rovne. The chemical composition is guaranteed by J. Sabošová, the main technologist responsible for refinement in this company.

The chemical composition of the glass cullet, expressed as a percentage by weight, was: 68.97% SiO₂, 9.84–11.26% Na₂O, 3.3–3.65% K₂O, 7.37–8.24% CaO, 5.4–6.29% BaO, 0.94–1.34% Al₂O₃, 0.95–1.20% ZnO. K₂O+BaO+ZnO = minimum 10%.

2.4. MARKING OF THE EXPERIMENTS

The study used different numbers of crucibles each year, and also repeatedly melted the glass in some of the already used ones. The team did not modify the melt in the crucibles which had been melted for the second time. The purpose was to protect them from secondary contamination in the deposits, where they were stored for about one year until the next melt. The experiments were marked in ascending order from 1 (the number is always preceded by the letter E). If the crucible was given a number, for example, in the year 2017 and was put in the furnace again in year 2018, the number received in 2017 stayed the same.

In addition to the glass melting, the study also experimented with archeo-faience, but the results for those experiments are not discussed in this paper.

In 2017, the team melted glass and batches in crucibles E1 to E4. In 2018, crucibles E3 and E4 were melted again and three new crucibles with batches E5, E6 and

⁶ We mainly used the chemical composition of glass beads because we have been dealing with them for a long time. Selected by D. Stašíšková-Štukovská.

E7 were added to the experiment. The experiments with archeo-faience marked as E8 (not the subject of the paper) also began in 2018. In 2019, glass batches in crucibles E9, E10, E11 and E13 were melted. Another experiment with archeo-faience was marked as E12, and was also continued to be experimented on with the production of archeo-faience E8 (the experiments are not included in the paper because they are not completed).

2.5. TYPES OF CRUCIBLES AND MANIPULATION WITH THEM BEFORE AND AFTER MELTS

The experiments used three types of crucibles for melting: one group consisted of flower pots purchased in Merkurie Market (from now on type A⁷). The second group consisted of crucibles hand-made for the experiments by the staff of Archeopark in Hanušovce nad Topľou from composite pottery white clay with the addition of fireclay for the year 2017 (from now on type B, assumed heat resistance 1100°C). The third group consisted of hand-made crucibles by Amália Holíková from composite clay Waller, Moravian earthenware with the addition of 10% fireclay from Hájske Hrnčiarstvo in Háj (www.hajskehrnciarstvo.sk). Holíková baked the crucibles at a temperature of 970°C (from now on type C). This crucible can withstand a temperature of 1250–1300°C. The data for the shape and dimensions of the crucibles according to the archaeological samples were supplied by D. Staššiková-Štukovská. The dimensions of the used crucibles are given separately for each experiment. The crucibles were filled with a glass batch or “return cullet” (cullet of glass) in the Archeopark in Hanušovce at the time of the experiment and immediately through the working opening no. 2 (intended for experiments) were inserted into the melting chamber of a glass furnace before its ignition (Fig. 2b).

They were removed from the furnace after its extinction and cool off. Crucibles with molten experimental glass were cut in half so that the team could better observe the molten glass from the profile. This process was led by Mr J. Skovajsa from Dvonta, a joint-stock company in Nové Mesto nad Váhom.

2.6. ANALYTICAL METHODS⁸

The chemical composition of the molten glass was analysed using a scanning electron microscope (SEM) with the EDS detector (from now on SEM/EDS, JEOL JSM 7600F), the analysis was led by D. Galusková, FunGlass-Centre for Functional and Surface Functionalised Glass in Trenčín. Significant inhomogeneities, bubbles

⁷ The flowerpots were of various sizes, the dimensions are given in a specific experiment, the verified heat resistance was 1050°C.

⁸ We took samples in two different ways. One sample was obtained from the glass that was cut of the crucible after melting, while the second one was cut from the glass rods pulled from viscous glass from the furnace at the time of melting.

visible to the naked eye, were present in the samples melted in 2018. Each glass sample from 2018 was cut and a part of it was embedded in polymer resin, while the surface of the sample in the section was polished to the required quality with a disc with a grain size of $\sim 0.5 \mu\text{m}$. To determine if the chemical composition of the selected glass part did not contain inhomogeneities (bubbles, unmelted SiO_2 grains), a layer of gold was deposited on the non-conductive surface of the glass sample. For each sample, 5 or 6 different sites (marked on SEM photographs) were selected and the point chemical EDS analysis was performed, together with scanned map of values. The term “point” refers to an analysis that measures data from a single point of a glass sample. The term “map” is used in cases where the beam scanned the qualitative distribution of the elemental composition on a selected area of the sample. Each detected element is displayed according to the intensity of its signal, i.e. increased concentration of content in a given phase on the scanned area is visible by colour contrast (each element is a different colour, explained by the legend of the elements in the image of the “map”). The map could be of an individual element or their overlap.

Samples melted in 2019 were not embedded in a polymer resin so it is possible to identify by-products from the crucible. The non-conductive surface of raw samples melted in 2019 was coated with a gold layer before SEM/EDS analysis.

Some glass samples were also analysed by quantitative (full-volume) analysis (from now on only XRF or bulk analysis by XRF method), performed by A. Plško. The term “bulk analysis” is intended to emphasize that it is an analysis of chemical composition made of a larger piece of glass sample, the results of which are representative of the whole sample volume for the preparation method used. Sample preparation for XRF analysis was as follows. The required amount of sample crushed into pieces with a maximum size of up to about 6.3 mm was ground in a tungsten carbide planetary ball mill for 10 minutes at 300 rpm. The ground sample was sieved on a sieve with a mesh size of 0.045 mm. The following sample preparation procedure was used to determine the minor components in the sample: from the extruded portion of below 0.045 mm, the required sample was weighed, wax of 0.1 times the sample weight was added, and the mixture was homogenized in a planetary ball mill for 10 minutes at 180 rpm. From the homogenized mixture, the tablets were compressed in an aluminium container for 60 seconds with a force of 200 kN. The following sample preparation procedure by melting was used to determine the major components in the sample: Lithium Tetraborate weighing about 16 times the sample was weighed into a crucible (PtAu5), and a weighed sample of the fraction below 0.045 mm was added. The mixture was mixed thoroughly. A standard melting procedure with pouring the glass into a mould (PtAu5) and cooling were used to prepare the molten “bead” of the sample. The measurement was performed on an S8 TIGER X-ray fluorescence wave-dispersive spectrometer in the X-ray fluorescence spectrometry laboratory.

Both workstations, where analysis of glass samples from experiments in Hanušovce were performed, are part of Fun GLASS – the Alexander Dubček University of Trenčín in Trenčín.

2.7. ANALYSIS

The study conducted a visual analysis of the structure, homogeneity, colour, and other details of the melt or glass in the crucible with the naked eye or using magnifying glasses before and after cutting after each melt. After cutting the samples, the team took samples of glass cullet from one half of the crucible where they documented the glass and its homogeneity in detail with the help of an electronic magnifying glass with a photographic recording at different magnifications. If the glass was removed from the crucible during the melting, they proceeded in the same way as when dealt with the glass in the crucible. The team recorded a description of the whole drawn rod, and then took a sample and observed it at different magnifications. If necessary, for example, to assess the re-melting of the glass and its homogeneity, these optical observations were supplemented by the results of microstructure analysis recorded in SEM photographs. The key information from these optical analytical procedures is summarized in the descriptions of the results of each experiment.

3. EXPERIMENTS NOS 1-7, 9-11, 13, DETAILS OF IMPLEMENTATION AND RESULTS

In this section, we pay attention to the facts we have gained from specific experiments. As already mentioned, each experiment has its number, by which we denote not only the crucible but also its content, sample, molten glass or other experiments related to the experiment. We signify the experiments by Arabic numbers, which are at the same time the label of the respective container-crucible. The same number is given in the results of analyzes, photographs or other documentation relating to a specific experiment. The number is preceded by the letter E.

3.1. EXPERIMENT E1

The study used the shape of crucible type A with the following dimensions: height 50 mm, bottom diameter 32 mm, bottom internal diameter 28 mm, rim diameter 51 mm, rim internal diameter 47 mm, wall thickness 2 mm, bottom wall thickness 2 mm and the wall thickness of the roughened edge 4 mm. The team painted the walls from the inside with a layer of separating clay (kaolin), which is used in the manual production of glass beads on a metal needle, the so-called windings so that they do not melt on the metal.

The filling of the crucible consisted of cullet of various shapes made of barium colourless transparent glass (chemical composition see above) with a size of 5 mm to 15 mm and a thickness of 1 mm to 2 mm, which was provided by RONA, joint-stock company, Lednické Rovne. The team filled the crucible with cullet to the edge, in the middle of the container a little extra.

Melting in 2017, the temperatures in the furnace are in Table 1: data for 2017. Results of the melt – visual analysis: The fragments in the crucible were melted on a clear glass which formed a layer above the bottom to a height of 21–25 mm. After cutting the crucible in half, the glass was completely and without effortlessly separated from the wall in both halves of the crucible (Fig. 3a). In other words, the glass did not melt to the surface of the crucible and did not form a thin glaze coating on the walls either. The glass was transparent, colourless with a slight shade of green, and numerous bubbles were visible when magnified under a microscope (Fig. 3b). In the surface layer of the molten glass, we observed dark dots after the flue gases, and the glass around it had a soft green colour.

Analysis of chemical composition: We did not perform analyses due to their low evidence for our purposes and also the financial aspect.

3.2. EXPERIMENT E2

The study used the shape of a type A crucible with the same dimensions as E1. The team painted the walls on the inside with a layer of separating clay (kaolin), as with E1.

The contents of the crucible: cullet of various forms made of barium colourless, transparent glass, 5 mm to 15 mm in size and 1 mm to 2 mm in thickness, provided by RONA, joint-stock company, Lednické Rovne. The team filled the crucible with cullet to the edge and a little extra. Among the colourless glass, the team mixed a coffee spoon of orange glass in the size of cullet of about 1 mm to 2 mm, which is commonly used for glazing ceramics and is distributed in the sales network of QUARTRO Považská Bystrica under the name “frita”. Thus, imitating the situation when there are coloured cullet of glass in a cluster of colourless glass. The team wanted to know the extent to which colourless glass can be coloured with this coloured glass.

Melting happened in 2017, and temperatures are in Table 1: data for 2017. Results of the melt – visual analysis: The glass fragments (cullet) in the crucible were melted into a compact layer of clear colourless glass 21 mm to 25 mm high above the bottom, as observed in the profile of half of the crucible after cutting in half (Fig. 3c). Sporadically small carbons were found in the glass, especially in the surface layer and melted orange-coloured lines over the molten coloured glass. The glass, which was out of colour, was transparent, with a slight green tinge. The glass was not welded to the walls of the crucible, and it could be removed effortlessly, as in experiment E1 (Fig. 3d). The orange pieces of glass possibly melted only in the place where they were located between the cullet of transparent glass, numerous bubbles in the glass structure and local colouring caused by molten orange cullet were visible under the microscope (Fig. 3e). The natural source of bubbles is the decomposition and reaction of raw materials; bubbles are formed by chemical reactions in the melt. They can also be formed mechanically, i.e. in all operations connected with the homogenisation and moulding of glass. The temperature in the furnace was not high enough to re-melt the cullet. Due to

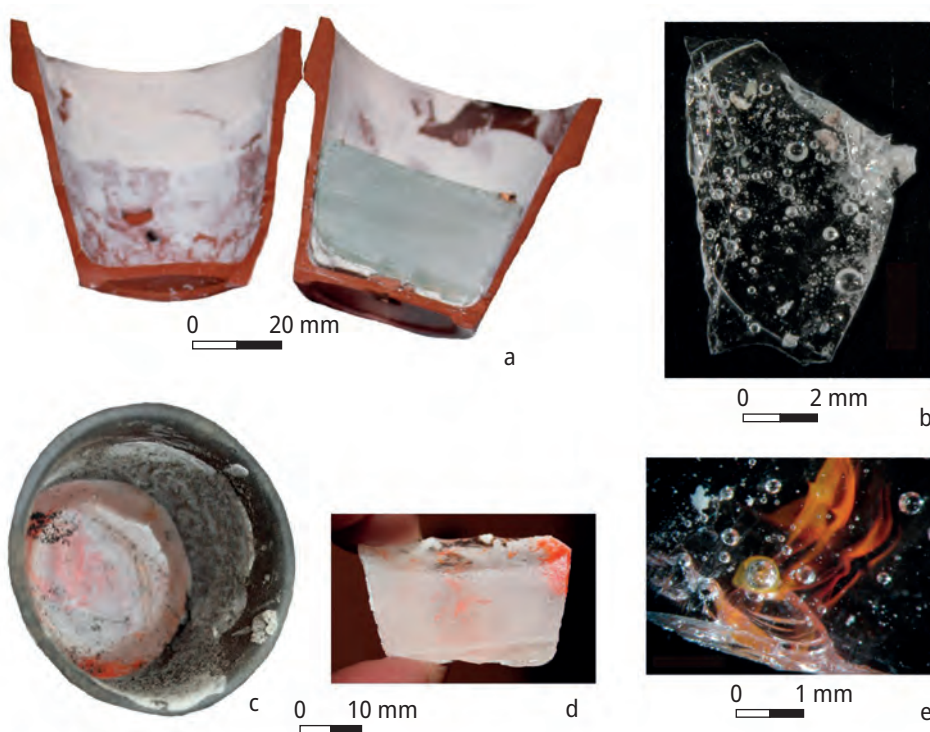


Fig. 3. Experiments E1 and E2

a – a view of the profile of the crucible E1, the left one shows the half without molten glass, which has separated without problems, the right one is the half with molten glass. The white layer on the inner walls of the crucible is the remaining separation mixture we used to paint the walls before melting; b – the structure of E1 glass magnified under a microscope; c – the glass in the crucible E2 stained with orange glass; d – separated E2 glass, separated due to the presence of a kaolin layer on the walls of the crucible. The orange coloured spots can be seen in the structure of the glass at the place where the orange cullets melted; e – a structure of E2 glass at the place of molten orange frit, magnified by microscope.

Photo by D. Staššiková-Štukovská (a, c, d) and D. Staššiková-Štukovská, J. Mihályiová (b, e)

their different sizes, bubbles could be trapped in the melt volume during melting. Their initial elimination could possibly be achieved by crushing and then grinding the cullet into smaller particles. Coloured glass or an appropriate oxide (dye) with a similar particle size would then be homogeneously mixed with the fines thus prepared from the cullet or the glass batch. In the case of using cullet from Lednické Rovne, it is necessary to achieve higher melting temperatures, which, however, is probably not possible from the technical point of view of the construction and heating of a replica of a glass furnace.

Analysis of chemical composition: The team did not perform analysis of the E2 sample due to their low evidence, data output and financial restrictions.

3.3. EXPERIMENT E3

The study used the shape of a crucible type B with the following dimensions: height 65 mm, bottom diameter 62 mm, bottom internal diameter 50 mm, rim diameter 109 mm, rim internal diameter 92 mm, the wall thickness at the edge 4 mm to 9 mm, wall thickness 4 mm and bottom thickness 5 mm. Modification of interior walls was not implemented.

The filling-content of the crucible formed a glass batch. The required composition was determined according to group A1 from the classification proposed and used in the Czech Republic (Černá *et al.* 2001, pp. 71–73) and the findings of soda glass beads from Slovakia. The team needed to melt a glass batch composed only of CaO, Na₂O and SiO₂. A ratio of 70% SiO₂ was weighed, 20% Na₂O and 10% CaO were filled in the crucible to the brim with a glass batch of this composition.

The melting was done in 2017 (furnace temperatures are in Table 1: data for 2017) as well as in 2018 (furnace temperatures are in Table 1: data for 2018).⁹

Results of the melt in 2017 – visual analysis: In the crucible, the foamed mass was hardened approximately 15 mm from the edge with the content of un-melted SiO₂ grains and several large or smaller bubbles and dimples (Fig. 4a). As the crucible was not cut yet in 2017, the team could only observe the top layer of molten fabric below the edge, to a depth of about 1 cm. It was clear that below the surface and highly probable to the bottom of the pot, the experimental glass batch E3 did not melt completely into the glass, as was the case with the E1 and E2 cullet. Therefore, it was decided to re-melt the glass once again in further experiments in 2018.

Melt in 2018: Crucible E3, with the content of the melt from 2017, was again placed in the melting chamber in the experimental furnace of the Archeopark in Hanušovce before the furnace was ignited. The sample was left in there until the furnace cooled down, i.e. until June 24, 2018, when the temperature in the furnace was only around 40°C. During melting, the team pulled a glass rod out of the crucible with the help of a blowpipe. After being transported from Hanušovce, the team had the crucible cut in two halves in the company Dvonta.

Visual analysis in 2018: The cross-section of the crucible E3 allowed for the optical description of the molten glass in the entire volume of the crucible to be recorded. Transparent glass with a shade of green, with numerous round bubbles

⁹ For more details on melting temperatures and times, see above for 2017 as well as for 2018.

Fig. 4. Experiment E3 and E4

a – a top view of the melt in the crucible E3 after the first melting in 2017; b – a profile view of the glass E3 in the crucible after the second melting in 2018; c – glass E3 magnified under a microscope; d – top view of the melt in the crucible E4 after the first melting in 2017; e – a profile view at the glass in the crucible E4 after the second melting in 2018; f – glass E4 magnified under a microscope; g – a glass rod that we pulled from crucible E4 during melting in 2018.

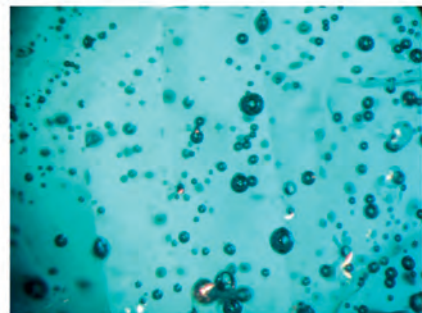
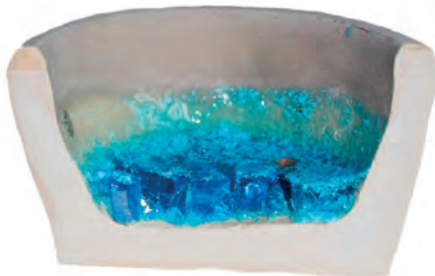
Photo by D. Staššíková-Štukovská (a, b, d, e, g) and D. Staššíková-Štukovská, J. Mihályiová (c, f)



0 a, b, d, e 50 mm



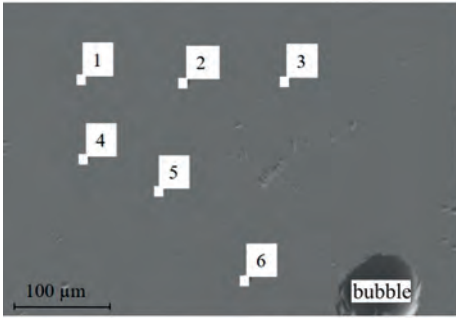
0 2 mm



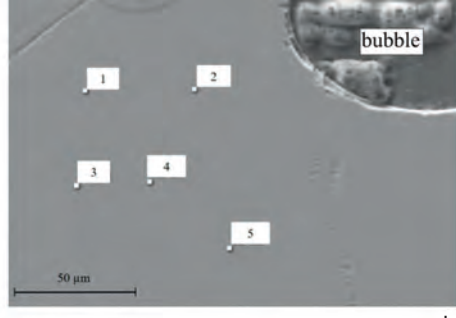
0 0,5 mm



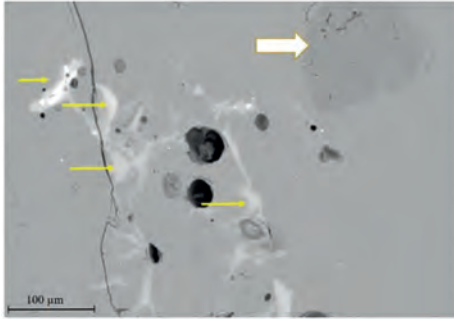
0 50 mm



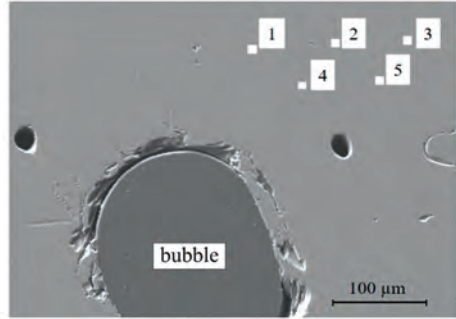
a



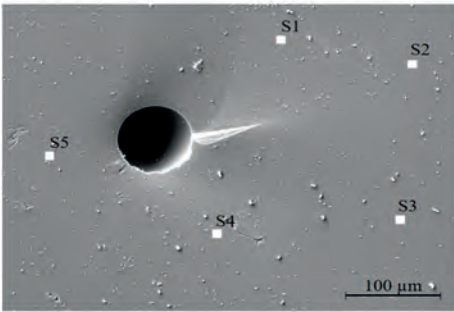
b



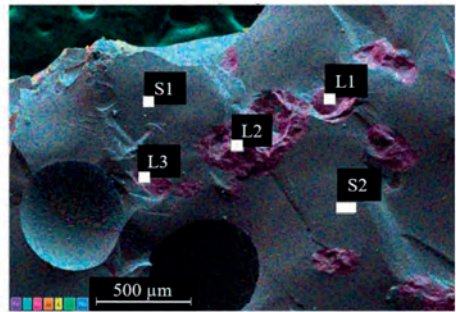
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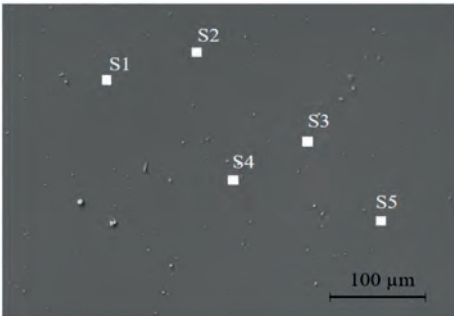
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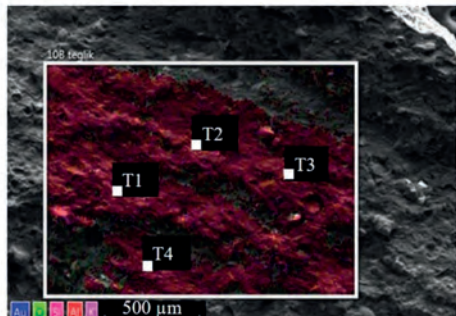
e



f



g



h

Fig. 5. SEM photo with marked points of the analysis of experiments E3–E7 and E9–E10
 a – E3, points 1–6; b – E4, points 1–5; c – E4, marked places with incompletely remelted grains of quartz (white arrows) and increased iron content (yellow arrows). The image depicts the centre of the cut of the drawn with a blowpipe; d – E7, points 1–5; e – E9, points S1–S5; f – E10A, a foam layer, measuring points S1, S2. Points L1, L2, L3 – unknown possibly crystalline phase (SiO_2) with a content in the range of 98–100 wt %; g – E10B, glass with measuring points S1–S5; h – E10C, ceramics of the crucible, measuring points T1–T4. Based on the chemical analysis, SiO_2 and Al_2O_3 will be the majority phases likely represented in the crucible.

Photo by D. Galusková

of small dimensions, formed a continuous layer 20 mm thick settled on the bottom and cracked (probably a secondary consequence of sawing the crucible). Above this glass mass, on the inner walls of the crucible, there was a layer of glass up to a height of 4 mm to 10 mm from the edge of 1 mm to 2 mm in places with impurities and black residues of flue gases (Fig. 4b) and round bubbles (Fig. 4c). Although the glass in the crucible appeared coloured green (Fig. 4b), it appeared colourless in a thin shard and in the lumen under the microscope (Fig. 4c). Proper re-melting of the glass without recorded un-melted inhomogeneities was also confirmed by SEM photographs of the microstructure (Fig. 5a).

Point analysis by SEM/EDS (in weight percent): Six points were measured (Fig. 5a). In addition to Na_2O , SiO_2 and CaO , the presence of MgO was detected in the glass at two points, in one Al_2O_3 , and in three K_2O (Table 2: E3 points 1–6). However, we did not add these elements to the glass batch.

The glass was also analysed by XRF (results determined from two parallels, which were measured three times): in addition to SiO_2 , Na_2O and CaO , we also found the presence of Fe_2O_3 , TiO_2 , Al_2O_3 , MgO , K_2O by this method (Table 3: E3 and E3 error). Due to the team's prior understanding of the raw materials that made up our glass batch T3, we were able to conclude that these oxides got into the glass secondarily during melting in the furnace (flue gas or diffusion of ions released from crucible due to corrosion in glass melt), because the original experimental glass batch did not contain them.

3.4. EXPERIMENT E4

The study used the shape of a crucible type B with the following dimensions: height 57 mm, bottom diameter 82 mm, bottom internal diameter 60 mm, rim diameter 97 mm, rim internal diameter 75 mm, the wall thickness at the edge of 4 mm to 9 mm, wall thickness of 11 mm to 17 mm and bottom thickness 14 mm to 17 mm. Crucible filling: glass batch which was a mixture of 70% SiO_2 ; 20% Na_2O ; 9% CaO ; 1% CuO weighed to 100 g. Substrate for batch – same as above for batch A3 with the addition of colouring oxide CuO . The sample was melted in 2017 (furnace temperatures Table 1: data for 2017) and repeated in 2018 (furnace temperatures, Table 1: data for 2018).

Table 2. SEM/EDS point analysis for the samples E3-E11 and E13. The analysis was done by D. Galusková

Sample number	Method of analysis	Point/Fig.	Oxides (wt %)									
			SiO ₂	Al ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K ₂ O	MnO	CuO	TiO ₂
E3	EDS	1/Fig. 5a	77.9	<	<	10.30	<	11.60	0.19	<	<	<
E3	EDS	2/Fig. 5a	81.0	<	<	8.60	0.27	9.90	0.20	<	<	<
E3	EDS	3/Fig. 5a	83.6	<	<	7.60	<	8.90	<	<	<	<
E3	EDS	4/Fig. 5a	78.3	0.48	<	9.80	0.29	10.90	0.19	<	<	<
E3	EDS	5/Fig. 5a	77.6	<	<	10.80	<	11.60	<	<	<	<
E3	EDS	6/Fig. 5a	82.3	<	<	8.50	<	9.30	<	<	<	<
E4	EDS	1/Fig. 5b	76.6	<	<	10.80	<	10.90	0.33	<	1.45	<
E4	EDS	2/Fig. 5b	76.7	<	<	10.20	0.41	10.90	0.36	<	1.34	<
E4	EDS	3/Fig. 5b	76.4	<	<	10.50	<	11.20	0.33	<	1.58	<
E4	EDS	4/Fig. 5b	76.5	<	<	10.70	<	11.20	0.35	<	1.26	<
E4	EDS	5/Fig. 5b	77.5	<	<	10.30	<	10.80	0.26	<	1.10	<
E7	EDS	1/Fig. 5d	78.3	0.87	<	9.02	0.54	10.50	0.74	<	<	<
E7	EDS	2/Fig. 5d	77.3	1.10	<	8.92	0.72	11.30	0.77	<	<	<
E7	EDS	3/Fig. 5d	80.1	0.56	<	7.68	0.51	10.30	0.82	<	<	<
E7	EDS	4/Fig. 5d	79.6	0.84	<	7.88	0.74	10.20	0.70	<	<	<
E7	EDS	5/Fig. 5d	77.8	1.00	0.45	8.35	0.70	10.90	0.74	<	<	<
E9	EDS	S1/Fig. 5e	68.7	1.84	0.85	7.17	5.30	10.30	2.80	3.01	<	<
E9	EDS	S2/Fig. 5e	68.7	1.98	0.86	7.49	5.60	12.10	2.90	2.82	<	<
E9	EDS	S3/Fig. 5e	66.5	2.03	1.06	7.70	5.70	11.50	2.80	2.77	<	<
E9	EDS	S4/Fig. 5e	68.3	1.80	0.91	7.26	5.50	10.90	2.70	2.68	<	<
E9	EDS	S5/Fig. 5e	67.2	2.04	0.79	7.33	5.40	11.70	2.90	2.65	<	<
E10A	EDS	S1/Fig. 5f	74.9	2.18	2.28	7.60	0.30	11.70	1.04	<	<	<
E10A	EDS	S2/Fig. 5f	75.5	1.98	2.09	7.94	0.42	11.10	0.93	<	<	<
E10B	EDS	S1/Fig. 5g	73.1	2.44	2.61	9.78	0.37	10.60	1.08	<	<	<
E10B	EDS	S2/Fig. 5g	73.0	2.60	2.36	9.79	0.34	10.70	1.13	<	<	<

Sample number	Method of analysis	Point/Fig.	Oxides (wt %)										
			SiO ₂	Al ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K ₂ O	MnO	CuO	TiO ₂	
E10B	EDS	S3/Fig. 5g	74.5	2.16	2.35	9.07	0.38	10.40	1.15	<	<	<	
E10B	EDS	S4/Fig. 5g	73.3	2.65	2.63	9.22	0.31	10.7	1.16	<	<	<	
E10B	EDS	S5/Fig. 5g	74.3	2.37	2.70	9.12	<	10.3	1.15	<	<	<	
E10C	EDS	T1/Fig. 5h	54.6	37.80	1.81	0.33	0.44	1.66	2.41	<	<	1.06	
E10C	EDS	T2/Fig. 5h	54.8	37.70	1.57	0.28	0.34	1.59	2.31	<	<	1.50	
E10C	EDS	T3/Fig. 5h	57.6	34.20	1.96	0.42	0.43	1.56	2.35	<	<	1.45	
E10C	EDS	T4/Fig. 5h	64.7	31.60	1.67	0.28	0.23	1.31	2.34	<	<	0.92	
E11A	EDS	S1/Fig. 11a	70.8	1.37	<	7.66	0.68	18.8	0.67	<	<	<	
E11A	EDS	S2/Fig. 11a	70.9	1.33	<	7.49	0.73	18.9	0.64	<	<	<	
E11A	EDS	S3/Fig. 11a	71.0	1.31	<	7.33	0.74	19.0	0.59	<	<	<	
E11A	EDS	S4/Fig. 11a	70.7	2.36	<	7.16	0.68	18.4	0.64	<	<	<	
E11A	EDS	S5/Fig. 11a	70.9	1.36	<	7.50	0.82	18.8	0.64	<	<	<	
E11B	EDS	E11B-S1/Fig. 11b	63.6	10.00	0.35	3.48	0.48	21.3	0.78	<	<	<	
E11B	EDS	E11B-S2/Fig. 11b	65.7	7.68	0.46	4.37	0.52	20.2	0.72	<	<	0.32	
E11B	EDS	E11B-S3/Fig. 11b	68.3	2.93	0.43	6.83	0.91	20.0	0.60	<	<	<	
E13	EDS	Ty1/Fig. 11c	70.6	<	<	8.06	0.37	18.0	0.31	<	<	2.7	
E13	EDS	Ty2/Fig. 11c	71.2	<	<	8.10	<	17.9	0.36	<	<	2.6	
E13	EDS	Ty3/Fig. 11c	70.7	<	<	8.09	<	18.1	0.43	<	<	2.7	
E13	EDS	Ty4/Fig. 11c	70.9	<	<	8.13	<	18.0	<	<	<	2.9	
E13	EDS	Ty5/Fig. 11c	71.8	<	<	8.32	<	17.4	0.32	<	<	2.2	
E13	EDS	Ty6/Fig. 11c	71.7	<	<	8.42	<	17.3	0.39	<	<	2.2	
E13	EDS	T1/Fig. 11d	67.5	0.63	<	10.40	0.38	18.8	0.25	<	<	2.1	
E13	EDS	T2/Fig. 11d	68.2	0.47	<	10.10	0.31	18.5	<	<	<	2.4	
E13	EDS	T3/Fig. 11d	68.7	<	<	10.30	<	18.2	0.28	<	<	2.5	
E13	EDS	T4/Fig. 11d	69.4	<	<	10.30	<	17.8	0.23	<	<	2.2	
E13	EDS	T5/Fig. 11d	68.2	<	<	10.20	<	18.8	0.28	<	<	2.5	

Note: < below level of detection.

Table 3. Chemical composition of glass E3-E7 and ash used for the experiments. The analysis was performed by the XRF technique and done by A. Piško

Oxides (wt.%)	E3	E3 error	E4	E4 error	E5	E5 error	E6	E6 error	E7	E7 error	Ash
SiO ₂	73.350	0.160	70.480	0.130	67.35	0.15	77.74	0.17	70.900	0.080	4.07
Al ₂ O ₃	1.012	0.003	0.256	0.002	2.00	0.70	1.98	0.70	0.221	0.001	2.74
Fe ₂ O ₃	0.220	0.002	0.090	0.002	0.57	0.42	1.90	0.17	0.079	0.002	0.483
CaO	7.000	0.020	9.300	0.030	5.84	0.20	7.10	0.18	9.230	0.010	45.15
MgO	0.680	0.010	0.256	0.003	4.60	0.52	0.35	1.03	0.248	0.004	2.15
Na ₂ O	16.930	0.030	18.210	0.050	14.87	0.17	10.02	0.19	19.020	0.060	0.17
K ₂ O	0.730	0.002	0.311	0.002	2.91	0.27	0.90	0.51	0.266	0.001	2.904
MnO	<	<	<	<	1.87	0.50	<	<	<	<	0.197
CuO	<	<	1.060	0.010	<	<	<	<	<	<	0.0268
TiO ₂	<	<	0.035	0.001	<	<	<	<	0.034	<	0.109
P ₂ O ₅	<	<	<	<	<	<	<	<	<	<	2.28
SO ₃	<	<	<	<	<	<	<	<	<	<	0.393
BaO	<	<	<	<	<	<	<	<	<	<	0.248
Cl	<	<	<	<	<	<	<	<	<	<	0.164
SrO	<	<	<	<	<	<	<	<	<	<	0.1486
ZnO	<	<	<	<	<	<	<	<	<	<	0.0745
NiO	<	<	<	<	<	<	<	<	<	<	0.006
Rb ₂ O	<	<	<	<	<	<	<	<	<	<	0.0045
As ₂ O ₃	<	<	<	<	<	<	<	<	<	<	0.003

Note: < – below level of detection.

Results of the melt in 2017 – visual analysis: A foamed porous mass containing un-melted Si grains was hardened in the crucible (Fig. 4d). It is the same porous, hardened melt-like foam that we described in experiment E3, only in experiment E4 the colour was turquoise.

Results of the melt in 2018 – visual analysis: Thin layer (1–2 mm) covered the walls to a height of 16 mm to 18 mm from the edge and in a continuous layer, 13 mm thick was also at the bottom of the vessel (Fig. 4e). It was cracked, which may also be a consequence of cutting the crucible. On the surface of the continuous mass of glass, there were 1 mm to 2 mm thick and discontinuous remnants of foam, a similar layer occurs between the wall and the glass and it is well observable in cross-section. The glass is transparent, beautiful turquoise colour (Fig. 4e), in the structure, there are small bubbles (Fig. 4f). With the naked eye, even when magnified under a magnifying glass, no impurities other than sporadically black flue gases are observed in the glass structure except for bubbles. Inhomogeneity was recorded by SEM photo as sites with increased content of Fe_2O_3 and SiO_2 also manifested visually (Fig. 5b). However, it is not limited to un-melted grain or stones. In 2018, a sample of glass rod pulled out of the crucible (Fig. 4g).

Point and map analysis by SEM/EDS method (Table 2: E4 points 1–5) based on the chemical composition of the molten glass. As expected, it belongs to the group of sodium-calcium-silicate glasses (Table 2: E4 points 1–5; SEM photo) with the marking of the measured places as in Fig. 5b. The blue colour is caused by the presence of copper. The presence of un-melted quartz grains and places with an increased occurrence of iron were recorded in the glass (Fig. 5c). Of the elements that was not added to the glass batch, K and Mg appear here.

The bulk analysis by XRF of the chemical composition (Table 3: E4) were also expected to confirm sodium-calcium-silicate glass with CuO colouring oxide. Of the elements that were not added to the glass batch, the presence of Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , K_2O , which entered the glass secondarily, was detected by XRF method. They were not introduced to the batch with the raw materials, because the chemicals of high purity were used and accurate measurements applied to match the theoretical composition of glass before melting.

3.5. EXPERIMENT E5

The team used the shape of a type A crucible with the following dimensions: height 82 mm, rim diameter 80 mm, rim internal diameter 72 mm, bottom diameter 46 mm, bottom internal diameter 38 mm, wall thickness 4 mm and bottom thickness of 3.5 mm to 5 mm.

The crucible was filled with a glass batch weighed to 100 g of glass: 65.9 g of SiO_2 , 27.4 g Na_2CO_3 , 4.1 g K_2CO_3 , 10.7 g CaCO_3 , 10.7 g MgCO_3 , 2.3 g MnO_2 , 1.7 g Al_2O_3 , 6 g Fe_2O_3 .

The sum of the listed values was 128.8 g. The crucible was filled to the brim with this glass batch.

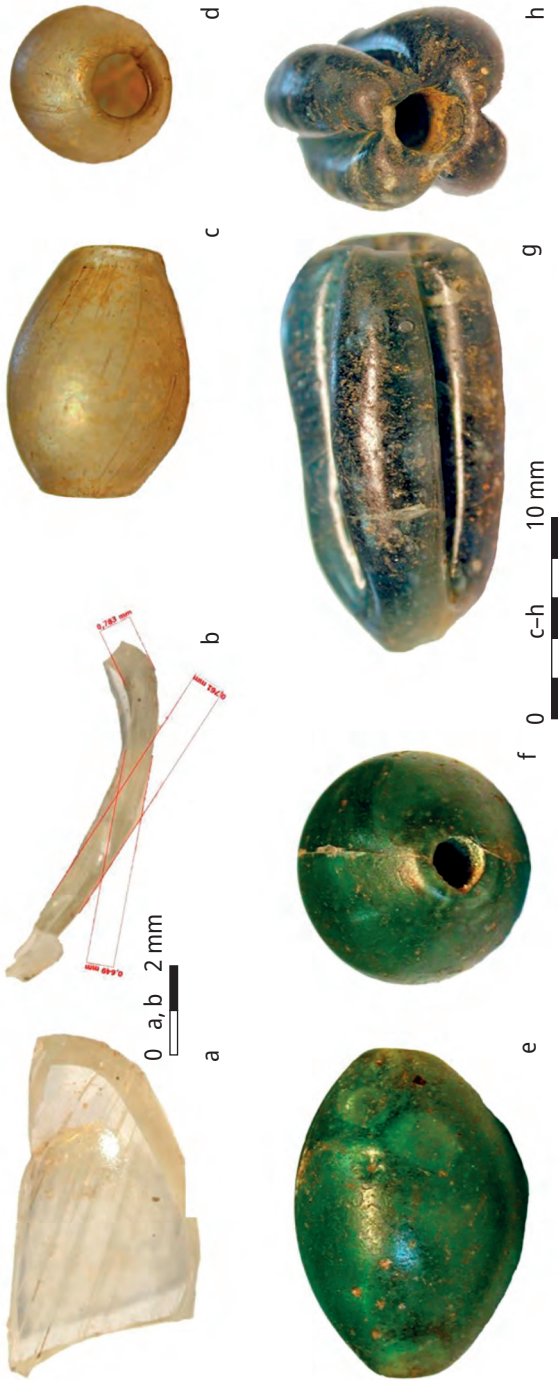


Fig. 6. Beads from the 9th c. according to which soda-lime and soda-ash batches were prepared

a, b – Skalica, plant-ash glass; fragments of a glass bead made by blowing glass, a view into the inner part of the bead and the profile view of the wall; c, d – Dolní Věstonice, soda-lime glass, blown bead; e, f – Dolní Věstonice, smooth olive-bead; g, h – Dolní Věstonice, longitudinally divided olive-bead.

Photo by Staščíková-Štukovská (a, b), Š. Ungerma (c-h)

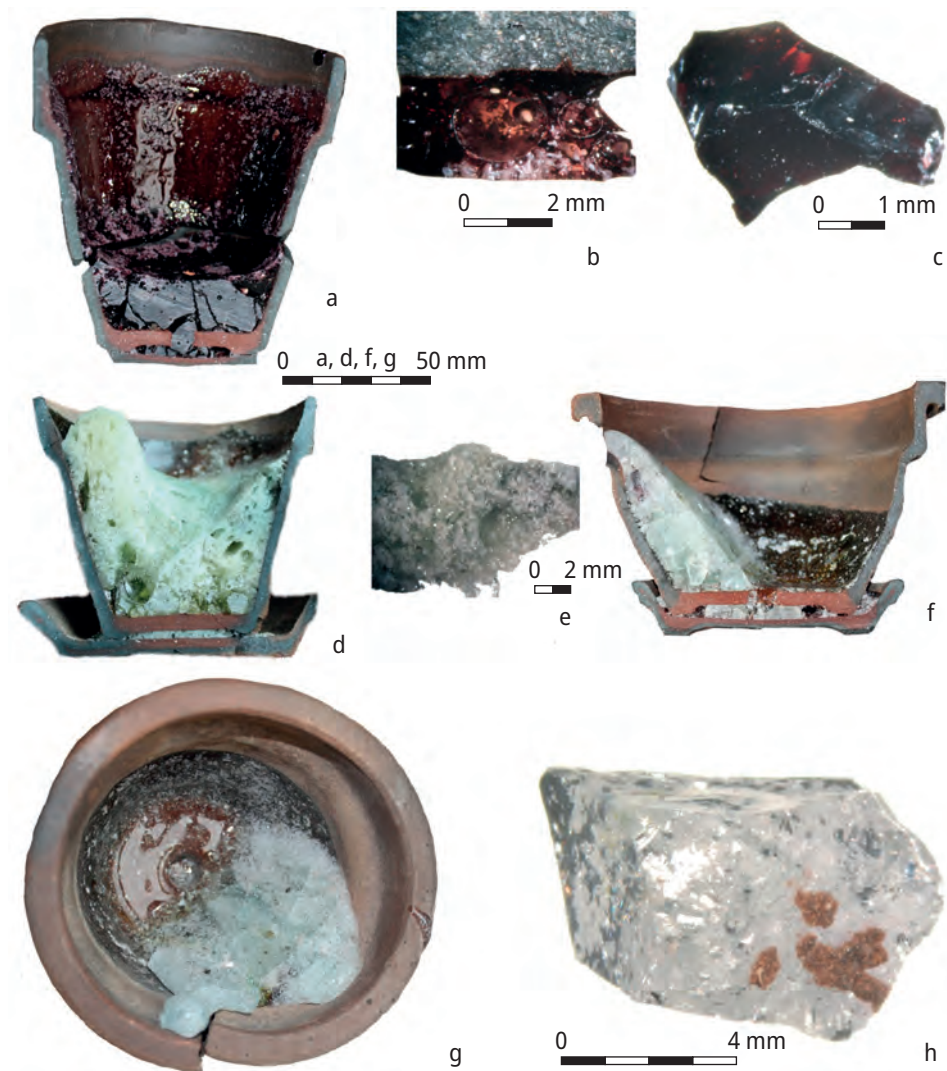


Fig. 7. Experiments E5, E6 and E7

a – a profile view of the crucible E5 with the molten glass; b – a detailed view at the fragment of the glass fused to the wall of the crucible E5; c – a bigger mass of the glass E5 appears dark or black, the burgundy colour is visible at the thinner edges; d – a profile view of the crucible E6 with the glass melt and a hole after the glass whistle; e – cullet of the melt E6; f – a profile view of the glass in the crucible E7; g – a view at the crucible E7 before cutting it; h – cullet of glass E7 with the remnants of the attached wall from the crucible.

Photo by D. Stašíková-Štukovská (a, b, d, f, g) and D. Stašíková-Štukovská, J. Mihályiová (c, e, h)

The batch was calculated based on the required glass composition (in weight percent): 16% Na₂O, 65.94% SiO₂, 1.7% Al₂O₃, 5.1% MgO, 2.8% K₂O, 6% CaO, 0.56% Fe₂O₃, 1.9% MnO. The glass of this chemical composition belongs to an archaeological sample of a bead from the 9th c. (culture of Great Moravia). It was made by blowing glass and comes from an archaeological site in Skalica (Slovak Republic). The glass of the bead is well melted with sporadic bubbles after gas leakage, transparent with a fine honey shade, walls thinner than 1 mm (Fig. 6a, b)¹⁰. The actual type of bead is considered to be an import from the Mediterranean advanced glass environment in the territory of Great Moravia. Soda-plant ash glass is widespread in finds in Central and Northern Europe in the 9th c. Beads made by blowing glass are rare, the relatively most numerous finds in Central Europe are in the 9th c. in Moravia, Slovakia and Lower Austria.

The sample was only melted in 2018 (furnace temperatures Table 1: data for 2018).

Results of the melt – visual analysis: The glass formed a continuous 15 mm thick layer at the bottom of the crucible, which was cracked. Above this layer, the inner walls were covered with a 1 mm to 2 mm thick layer of glassy coating with un-melted particles and secondary impurities up to a height of 10 mm to 15 mm from the edge (Fig. 7a). The glass is transparent, burgundy coloured, well re-melted with more bubbles (Fig. 7b). In a larger layer, the glass appears dark, on the translucent at the edges of the culet, it has a nice even burgundy or brown-red colour (Fig. 7c). The historical glass, according to which we prepared the glass batch, was colourless (Fig. 6a, b), the burgundy colouring of the E5 glass is the result of different conditions and the technology with which we melted it, compared to the historical one.

Bulk analysis by XRF (Table 3: E5 and E5 error). Only elements that were weighed into the glass batch appeared in the composition of the glass. Of the colouring oxides, FeO is present, which colours the glass in green and blue tones, but also MnO, which colours the glass in shades of purple. It is also used as a decolourizer against unwanted iron colouring. In the case of experiment E5 and with the contribution of melting conditions, the glass was certainly coloured with the presence of MnO. MnO served as a decolourizer when melting glass for historical blown glass beads.

3.6. EXPERIMENT E6

The study used the shape of a type A crucible with the following dimensions: height 53 mm, rim diameter 80 mm, rim internal diameter 59 mm, bottom diameter 40 mm, bottom internal diameter 34 mm, wall thickness 3 mm at the edge and bottom 4 mm.

Crucible was filled with glass batch weighed to 100 g of glass: 72.6 g of SiO₂, 23.6 g of Na₂CO₃, 1.4 g of K₂CO₃, 14.9 g of CaCO₃, 0.3 g of MgCO₃, 2.1 g of Al₂O₃ and 2.0 g of Fe₂O₃. The sum of the listed values was 116.9 g.

¹⁰ How the whole bead made by blowing looks like, see Fig. 6c, d.

Required glass composition (percentage by weight): 13.81% of Na₂O, 0.93% of K₂O, 8.33% of CaO, 0.16% of MgO, 2.03% of Fe₂O₃, 2.11% of Al₂O₃, 0.04% of CuO and 72.6% of SiO₂.

The glass for experiment E6 was selected according to an archaeological sample from an olive-shaped smooth bead (Fig. 6e, f) from Dolní Věstonice (glass Na₂O–CaO–Al₂O₃–SiO₂), which is dated to the 9th c. A similar composition of glass also has a bead from Borovce, which we included in our original classification in group C, i.e. sodium-calcium-silicate glass (Staššíková–Štukovská, Plško 1997, Table 7). Smooth as well as longitudinally divided olive beads (Fig. 6g, h) in the early Middle Ages (mainly in the 8th to 10th centuries) are known in archaeological finds not only from Slovakia and the Czech Republic but also from Thuringia, Brandenburg, Moravia and Polish Silesia (for more on the distribution of these beads, see Staššíková–Štukovská, Ungerman 2009, pp. 41–42; Tomková 2007). Objects were produced from Na₂O–CaO–Al₂O₃–SiO₂ type glass in the 9th c. in the glass furnace in Bratislava–Devínská Kobyla (Surovec 1998, p. 44), and as mentioned above, according to this furnace, the study carried out the reconstruction of the glass furnace in Hanušovce so far known facts about the origin of olive beads and glass type Na₂O–CaO–Al₂O₃–SiO₂, it is seen that this type of beads and glass is the successor of older glass production in Bohemia developed in Slovakia and Moravia in the 9th c.

The sample was melted in 2018, furnace temperatures are in Table 1: data for 2018.

Results of the melt – visual analysis: The product in a crucible cannot be classified as glass, but rather a melt containing a glassy and crystalline phase of greenish colour with whitish islets (Fig. 7d). Thus, the glass batch did not melt completely into the glass. When tried to remove the test glass from this crucible E6 during melting, traces of the whistle were preserved in the flesh in the form of a large hole approximately in the middle of the crucible (Fig. 7d). There are numerous and variously large pits in the melt after the gas leak, and in some places more continuous islands of homogeneously looking transparent, green glass also appear (Fig. 7e). The melt at the walls fills the pot in places up to the edge, a millimetre layer of glass covers the inner wall up to a height of 9 mm to 12 mm from the edge (Fig. 7d).

Bulk analysis by XRF (Table 3: E6 and E6 error) demonstrated the expected presence of all elements that we weighed into the glass batch. No other oxides were detected here. The measured values of the experimental melt are approximately similar to the original glass of the historical bead, with small insignificant differences.

3.7. EXPERIMENT E7

We used the crucible type A with the following dimensions: height – 65 mm, bottom diameter 60 mm, bottom internal diameter – 50 mm, rim diameter 109 mm, rim internal diameter 92 mm, the wall thickness at the rim 4–9 mm, wall thickness – 4 mm, bottom wall thickness – 5 mm.

Content of the crucible: glass batch with ash. We have weighed it to 100 g of glass: 69.1 g SiO_2 , 34.1 g Na_2CO_3 , 22.1 g ash. We used ash from deciduous trees growing wild in the White Carpathians, without any treatment (chemical composition is in the Table 3: Ash). We obtained it by burning these trees in our own fireplace in the winter of 2018, in preparation for our experiments in Hanušovce.

Melted only in 2018, see temperatures in Table 1: data for 2018.

Results of the melt – visual analysis. During the melting in the furnace, we pulled a glass rod from the crucible. The pulled-out glass rod had a diameter of 10 mm. The fact that we reached into the molten mass with a blow-pipe might be a reason of the asymmetricly hardened molten glass in the crucible after the melting. The molten glass is located in a thicker layer only on one side of the crucible E7 and occupies about 1/4 of the container up to a height of 20 mm from the edge, in an unequal thickness of 6–18 mm (Fig. 7f, g). The glass has many holes from the gas leak, there are black and green dots – impurities. The glass was transparent; it has a slight shade of blue, however we do not register that colour if we observe a smaller piece of glass (Fig. 7h). White inhomogeneities occur in the glass structure. The walls of the crucible are “glazed” on the inside with a continuous 1–2 mm thick layer of glass up to a height of 21–23 mm from the edge. In the SEM picture (Fig. 5d) there are clearly visible oval and round wells of larger and smaller dimensions. The glass was not well clarified, respectively, we did not intentionally blacken it during the melting which is also reflected in its structure.

Point analysis by SEM/EDS (Table 2: E7 points 1–5). The composition of the glass contained CaO in the amount of 7.68–9.02%, which could have been introduced to the glass with ash, as we did not artificially weigh it into the glass batch and there is no other option to get it into the glass. Among the other elements, we also found Al_2O_3 which also got into the glass from the ash or from the wall of the crucible. The contents of MgO and K_2O are surprisingly low – they do not even reach 1%. If we did not know that ash was added to the batch, we would not consider this glass to be melted with ash.

Bulk analysis by XRF (Table 3: E7 and E7 error): We found the content of CaO up to 9.23%, K_2O was only 0.27% and MgO 0.25%, i.e. less than they were found by SEM/EDS analysis. Also, a small content belonged to Al_2O_3 , only 0.22%. The only element that was not previously detected by SEM/EDS analysis was TiO_2 in the amount of 0.03%. Even considering the XRF analysis, we would not be able to say that ash was added to the batch as the content of MgO and K_2O is less than 1%. However, in the historical glassmaking, only glass containing more than 2% of MgO and 4% of K_2O can be considered as ash glass.

3.8. EXPERIMENT E9

We used the crucible type C with the following dimensions: height – 65 mm, bottom diameter – 65 mm, bottom internal diameter – approx. 40 mm, rim diam-

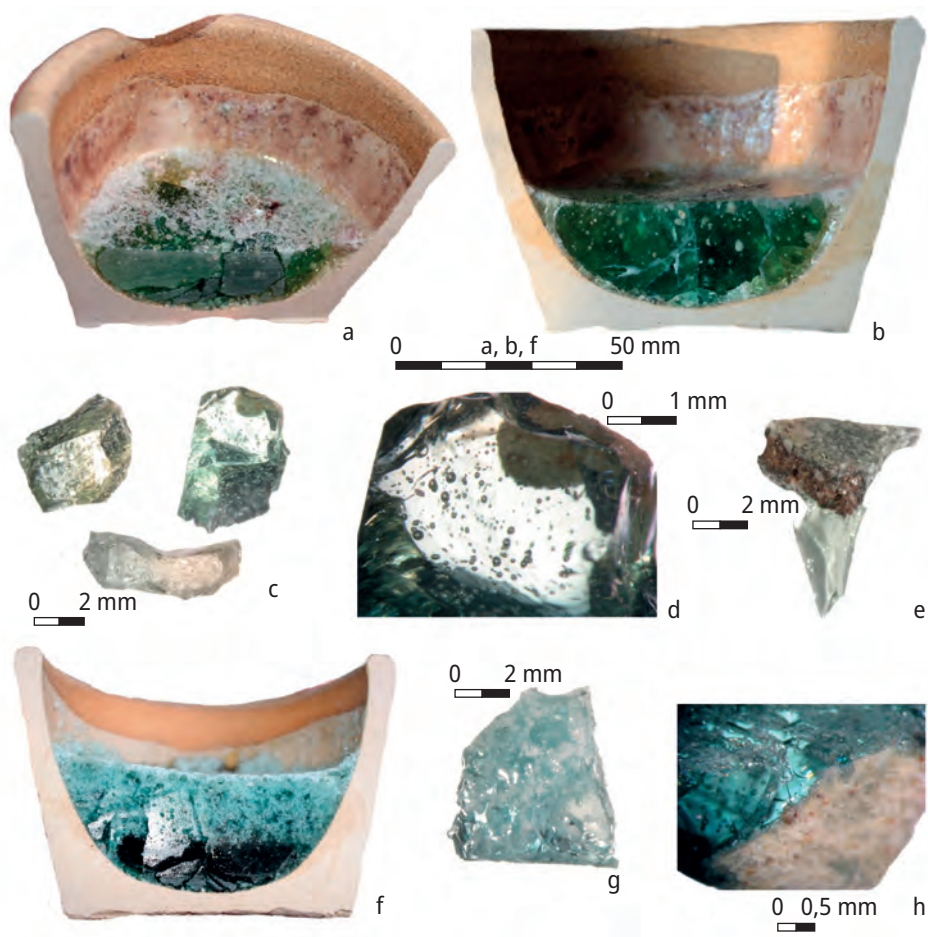


Fig. 8. Experiments E9 and E10

a – a view at the top foam layer in the crucible E9; b – a profile view of the molten glass in the crucible E9; c – cullet of green glass E9 appear to be different in colour; d – detail of glass E9, many bubbles visible; e – a fragment of a crucible E9 with adhered molten glass; f – a profile view of crucible E10; g – well-remelted glass E10A with a layer of glass and layer of partially molten glass E10B; h – well remelted glass with a piece of crucible wall E10C.

Photo by D. Staššíková-Štukovská (a, b, c, e, f, g) and D. Staššíková-Štukovská, J. Mihályiová (d, h)

eter – 92 mm, rim internal diameter – 79 mm, wall thickness – 5 mm, wall thickness at the bottom – 15 mm, bottom thickness – 4 mm.

We put a glass batch in the crucible. The basis for the required composition were plant-ash glass beads from Skalica (Fig. 6a, b), which we melted as experiment E5 in 2018 (the detailed required composition of glass as well as historical glass and the finding above in experiment E5).

The E9 glass batch was weighed to 200 g in the following amounts: 131.9 g SiO₂, 54.7 g Na₂CO₃, 8.2 g K₂CO₃, 21.4 g CaCO₃, 21.3 g MgCO₃, 4.7 g MnO₂, 3.4 g Al₂O₃, 1.1 g Fe₂O₃. The sum of the listed values was 246.7 g.

Melted in 2019, furnace temperatures see Table 1: data for 2019.

Results of the melt – visual analysis: The melted glass formed a layer of transparent glass of green colour 21 mm thick at the bottom of the crucible, the flesh of glass was cracked (Fig. 8a, b). There were numerous bubbles of different sizes in the structure of the glass (Fig. 8c, d). The relative homogeneity of the molten glass can be seen in the SEM photographs (Fig. 5e). There is a discontinuous layer of hardened foam (1–1.5 mm thick), which consists of white inhomogeneities and pits on the surface of this continuous, relatively well-melted mass of glass. The walls of the crucible, above the continuous mass of molten glass, are covered with a thin (approx. 1 mm thick) glassy layer with brown inhomogeneities up to a height of 12–15 mm from the edge. The colour of the glass in the crucible appears as grass green, it has all different shades of green, brown-pink or transparent colour in the cullet, depending on its thickness, or from which place in the crucible it was peeled off and how light falls on it (Fig. 8c, d, e). The colouration is therefore uneven, but the glass is transparent.

Point analysis by SEM/EDS: A sample of the molten glass was taken and analyzed at five locations on the glass (Table 2: E9 points S1–S5). The results correspond to the elements from the glass batch, the model of which was a glass bead from Skalica. Slight differences between the melted experimental and original historical glass are in the determined values of weight percentages of oxides present. However, MnO was an exception, there was significantly more of it in E9 glass (2.65–3.01%) than in the historical one.

3.9. EXPERIMENT E10

We used the crucible type D with the following dimensions: height 62 mm, bottom diameter – 64 mm, bottom internal diameter – 40 mm, rim diameter 89 mm, rim internal diameter – 74 mm, wall thickness – 5 mm, wall thickness at the bottom – 15 mm, bottom wall thickness – 4 mm, bottom wall thickness at the wall – 10 mm.

A glass batch was inserted into the crucible. We repeated the composition of an olive-shaped bead from Dolní Věstonice (Fig. 6e, f), which we melted as E6 (the composition of the glass of the archaeological find is also given here).

The glass batch was weighed to 200 g of glass: 145.3 g of SiO₂, 47.2 g Na₂CO₃, 2.7 g K₂CO₃, 29.7 g CaCO₃, 0.7 g MgCO₃, 4.2 g Al₂O₃, 4.1 g Fe₂O₃. The sum of the listed values was 233.9 g.

It was melted in 2019, the temperatures in the furnace are shown in Table 1 of the data for 2019.

Results of the melt – visual analysis (Fig. 8f, g, h). The glass batch did not melt evenly; it consists of two different layers of glass with different

homogeneity and quality of glass. The best remelted is a layer of transparent green to turquoise glass at the bottom of the crucible (5–11 mm thick), above which is a porous light-turquoise foam layer (16–23 mm thick) with numerous wells (size 1–5 mm) after gas leakage and unmelted, crystalline phases probably from partially melted quartz grains. Untreated quartz were also confirmed by SEM/EDS analysis (Fig. 5f points L1, L2, L3). The glass, or rather the opaque glossy layer of the foam structure, is a thin 1–1.5 mm layer that also covers the inner walls above the continuous melt up to a height of 10–12 mm from the edge of the pot (Fig. 8f). When observing the fragments that we removed from the foam layer, it can be stated that this layer of the glass batch was also partially melted (Fig. 8g) and with prolonged heating, it would probably melt completely, exactly as it happened with the content above the crucible (Fig. 8f). The glass was glued to the wall of the crucible, we did not observe any colour or qualitative changes of the glass at the transition of glass and ceramic material (Fig. 8h), although we know that some elements pass from the material of the crucible into the glass, e.g. FeO, Al₂O₃.

Point analysis by SEM/EDS. We analyzed well-melted glass (Table 2: E10B, measuring points S1–S5; Fig. 5g), a foam layer (Table 2: E10A, glass S1–S2, and the unknown crystalline phase with measuring points L1, L2, L3; Fig. 5f) and also ceramics from the crucible (Table 2: E10C, measuring points T1–T4; Fig. 5h: T1–T4). The chemical composition of the foam layer as well as of the well-remelted glass did not differ significantly from the content of the elements. It can be seen in the SEM photo that the quartz in the melt was already in the dissolving phase; it no longer had the shape of beads (Fig. 5f, measurement points L1–L3). This is confirmed by optical observations with a magnifying glass, the foam layer already consists of a greater extent of the glass phase. The colour of the glass does not resemble the original; it is more blue, we would call it turquoise.

The ceramic crucible (Table 2: E10C, T1–T4; Fig. 5h: T1–T4) contains the same elements as glass with the exception of TiO₂ (in the amount of 0.92–1.5%), the presence of which was not confirmed in the glass by analysis, nor we artificially added it. The major oxides in the crucible are SiO₂ and Al₂O₃ (31.6–37.8%). In the ceramics of the crucible, there is a higher proportion of K₂O than in glass, less Fe₂O₃ compared to glass, but approximately same amount of MgO (0.23–0.42%). We also found the presence of Na₂O (1.31–1.66%) and CaO (0.28–0.42%) in ceramics, but they are much less prevalent in the glass.

3.10. EXPERIMENT E11

We used the crucible type C with dimensions: height 62 mm, bottom diameter – 63 mm, bottom internal diameter – about 40 mm, rim diameter – 85 mm, rim internal diameter – 74 mm, wall thickness 5 mm, wall thickness at the bottom – 12 mm, bottom thickness – 7 mm, bottom wall thickness – 12 mm.

The content of the crucible was a glass batch. We repeated the composition of soda-lime-silicate glass with the addition of ash, which we melted as experiment

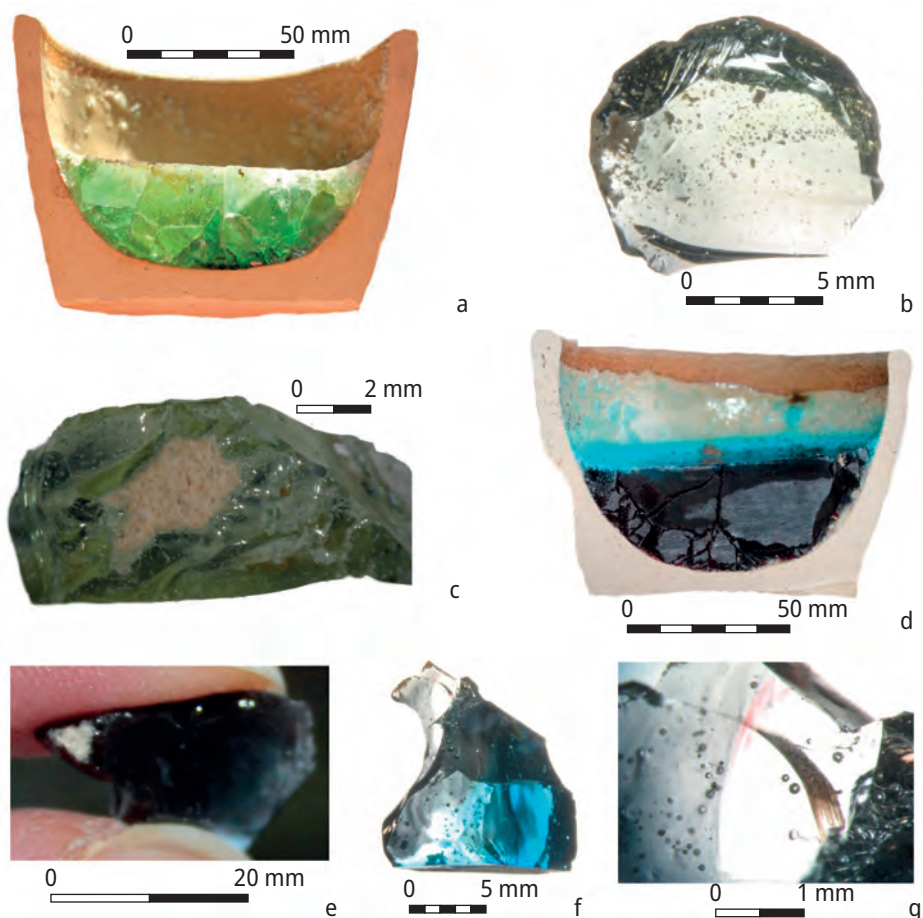


Fig. 9. Experiment E11 and E13

a – a profile view of the molten glass in the crucible E11; b – the glass cullet E11 appears colourless, many bubbles are visible in the structure; c – glass cullet with a piece of wall from a crucible E11; d – a profile view at the crucible E13 with a partially melted layer of glass; e – cullets of glass E13 coloured to gray-black colour; f – glass cullets E13 at the interface of turquoise and gray-black colour; g – pink-colored spots also appeared in the dark glass E13 at high magnification as a result of the play of light.

Photo by D. Stašíková-Štukovská (a, d) and D. Stašíková-Štukovská, J. Mihályiová (b, c, e, f, g)

E7 in 2018 (here is the composition of ash). Weighed to 200 g of glass: ash 44.3 g; SiO_2 138.2 g, Na_2CO_3 68,3 g. The sum of the listed values was 250.8 g.

Assumed final composition (in weight percent): 68.3% SiO_2 , 19.5% Na_2O , 0.6% K_2O , 9.8% CaO , 0.5% MgO , 0.1% BaO , 0.6% Al_2O_3 , 0.1% Fe_2O_3 , 0.5% P_2O_5 , 0.1% SO_3 .

Melted in 2019, furnace temperatures are in Table 1: Data for 2019.

Results of the melt – visual analysis: The glass batch was melted into transparent green glass that formed a 22 mm thick layer at the bottom

of the crucible while it was also secondarily cracked (Fig. 9a). Numerous small bubbles are recognizable in the structure of the glass; unmelt inhomogeneities are not observed (Fig. 9b). On the surface of the molten glass, there is a layer of approx. 1–2 mm thick white foam with many holes after gas leakage and unmelted inhomogeneities. The glass glaze also covers the inner walls of the crucible up to its edge (Fig. 9a). It is shiny and contains islands of unmelted grains glued to the walls of the crucible. After breaking the cullet of molten glass, the glass appears colourless in the lumen (Fig. 9b), while the glass is transparent and green under different lighting conditions and in a larger layer of the glass (Fig. 9c).

Point analysis by SEM/EDS: Was performed on a sample of E11A glass, as well as on a sample with a piece of E11B ceramics, where we focused on determining the Al_2O_3 contents as possible penetrations from ceramics (Fig. 9c). As expected, the glass of sample E11A was the type Na_2O – CaO – SiO_2 with higher Al_2O_3 content. The glass measured near the ceramic residues from the crucible (analysis E11B) showed a significantly higher content of Al_2O_3 (7.68–10.00%), which decreased with the distance from the ceramic (2.93%; see Fig. 11b measurement points E11BS1– E11BS3). TiO_2 and Fe_2O_3 (0.35–0.46%), which were not measured in the glass, also appeared near the ceramics. The ash also contained Al_2O_3 , but not in such significant amounts as ceramics. The contents of K_2O (0.59–0.67%), as well as MgO (0.68–0.82%), would not indicate the presence of ash in the glass batch using current methods for the classification of soda glass. CaO contained in the glass (7.16–7.66%) is related to the addition of ash, as we did not add CaO to the glass batch.

3.11. EXPERIMENT E13

We used the crucible type D with the following dimensions: height 60 mm, bottom diameter – 61 mm, bottom internal diameter – 40 mm, rim diameter – 90 mm, rim internal diameter – 76 mm, wall thickness – 4–5 mm, bottom thickness of the wall – 13 mm.

The crucible was filled with a glass batch, weighed to 200g as follows: 138.0 g SiO_2 , 68.4 g Na_2CO_3 , 35.7 g CaCO_3 , 2.0 g CuO . The sum of the listed values was 244.1 g.

We repeated the composition of soda-lime glass coloured with CuO as in E4, which we melted in 2017 and 2018, and resulted in a beautiful turquoise glass (Fig. 4f, g). Such colour of glass occurs on the penetrated beads with foil, which are characteristic for the second half of the 8th and the beginning of the 9th c. at the sites of Avar Kaganat as well as they were found in the oldest Great Moravian tombs (Fig. 10a, b).

Assumed glass composition expressed as a percentage by weight: 20% Na_2O , 69% SiO_2 , 9% CaO and 1% CuO .

We melted the glass batch only in 2019, the temperatures of the furnace can be seen in Table 1: data for 2019.



Fig. 10. Segmented multilayered beads made of two different quality glass
a – Borovce, district Piešťany; b – Dolní Věstonice, a profile of the glass bead.

Photo by D. Staššíková-Štukovská (a), Š. Ungerman (b)

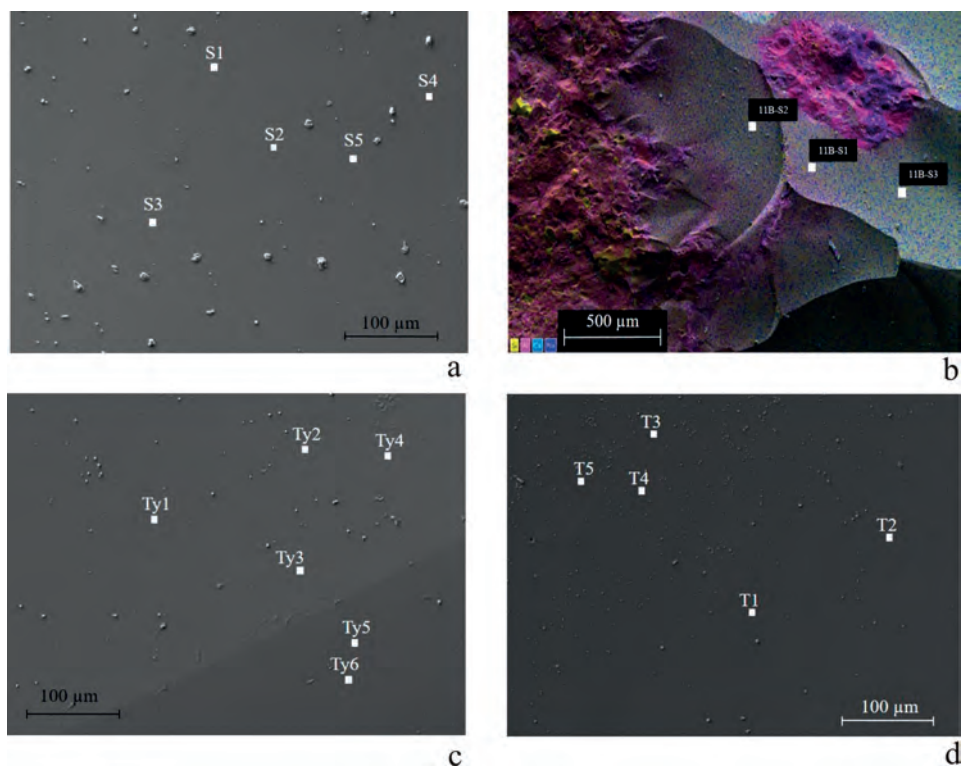


Fig. 11. SEM photo with the marked points of analysis E11 and E13
a – E11, points S1–S5; b – E11, map, glass with the part of the crucible and points S1 and S3; c – E13, turquoise glass points Ty1–Ty6; d – E13 dark glass, points T1–T5.

Photo by D. Galusková

Results of the melt – visual analysis: The glass batch was melted into the glass in a 25–30 mm thick layer deposited at the bottom of the crucible (Fig. 9d). On the surface of this glass, there is a thin layer of turquoise-coloured porous melt, possibly hardened foam. The inner walls above it are covered almost to the edge with a creamy white glossy opaque melt with a turquoise-coloured transparent layer of glass. The expected turquoise colour of the glass, in addition to the foam layer, is also in the glass by the wall of the crucible. From the wall inward, however, the colour changes from turquoise to grey-black (Fig. 9f). In a larger layer, the colour of the glass appears black (Fig. 9d, e). The glass is transparent; the unmelted parts of the batch are invisible even at higher magnification; it contains numerous bubbles (Fig. 9f, g). The inhomogeneity of the colour is also evidenced by the places with a pink tint, which, however, is visible when enlarged and examined in more detail (Fig. 9g).

Point and map analysis by SEM/EDS were performed on a turquoise coloured (Table 2: E13, measuring points Ty1–Ty6; Fig. 11c) as well as on grey-black glass (Table 2: E13, measuring points T1–T5; Fig. 11d). CuO was present in equal amounts in both glasses. Al₂O₃ (0.47–0.63%) and also MgO (0.31–0.38%), which were not in turquoise glass, were captured in two places in the dark glass. Both glasses lacked Fe₂O₃ and the turquoise glass contained less CaO than the black glass. The contents of Na₂O and SiO₂ were more or less the same in both glasses.

4. INTERPRETATION

We mainly focused on those results that have brought new facts and information to the issues already discussed in the literature about the historical glass. When discussing or generalizing these results, we keep in mind that they relate to our experiments where we have documented melting from the first ignition of the furnace, through the material of crucibles, the chemical composition of glass batches to the heating method, etc. Through our interpretations, we want to show how the data we have collected should be approached in interdisciplinary research of the historical glass. We do not pay attention to the well-known facts, such as that glass cullet melt more easily than glass batches made of raw materials, or that soda glass is melted from soda glass batches.

4.1. DIFFERENT QUALITY OF MELTED GLASS

As the first indisputable fact, we should mention that we melted glass from the glass batch in all experiments where we used the batch, some of them immediately the first time we tried it (E5, E7, E9, E11, E13). The reached temperature never exceeded 1150°C. Today's glassmakers would probably turn their noses at the quality of our glass due to the several issues, such as the number of bubbles, the presence of incompletely melted quartz, the presence of flue gases or the contamination by

the elements found in the crucible wall. However, such issues with the glass quality are well known for the glass made in the 9th c. or older. This mainly applies to beads and other glass jewellery. Compared to some historical inhomogeneous glass, our glass is of excellent quality. At the same time, we draw attention to the frequent misunderstandings between archaeologists and experts in the field of today's glass-making¹¹. The main issue between those two disciplines is the definition of glass. The definition of glass is understood differently in the area of historical glass compared to today's glassmaking. The issue also relates to the transfer of terms from today's glassmaking to the historical one¹².

A few of the glass batches had to be melted twice because the glass batch did not wholly melt due to the technology we used during the first melting. We obtained a "foam" melt by appearance and structure (experiments E3 and E4). In that case, repeated or longer melting with higher temperature would make a proper glass as we proved with experiments E3 and E4 that were melted in 2017 and 2018 (compare the foam in Figs 4a and 4d with the glass in Figs 4b and 4e). The glass batch could also melt partially, as we see in the experiment E10 (Fig. 8f). Here, the melting resulted in the glass and foam melt at the same time during one melt. Therefore, the argument that soda-lime glass could never melt in a wood-fired furnace while showing the required quality in a single melt should not be used in the literature and research. Those arguments are usually shared by experts accustomed to the results of advanced glass melting technology and with no experience with glass melting in a wood-fired glass furnace.

Our experiments have shown that various factors influence the quality of the remelting of the glass batch. Even in the historic wood-fired furnace, attention immediately turns to the atmosphere in the melting chamber. During the melting in 2018, we melted three crucibles filled with glass batch (E5, E6, E7) only once. The raw materials from experiment E6 did not melt properly and created a foam (Fig. 7d), but glass batches E5 (Fig. 7a, b) and E7 melted entirely to create the glass (Fig. 7f, h). The crucibles stood side by side at the same place in the melting chamber, so there is no possibility of being exposed to dramatically different atmospheres or temperatures. However, the crucibles had different dimensions and thickness of walls also differentiate. This means that there was a different level of transferred heat. On the other hand, we did not find a connection between the different quality of our glass and the metric values of the crucibles. We suspect that in the experiments,

¹¹ These are mainly specialists from natural or technical disciplines who devote themselves to historical glass without the necessary compromises with the history required by this interdisciplinary research. However, it is true that even an archaeologist is not always clear what we call glass in historical glassmaking.

¹² We mean, for example, the problem of introducing today's glass terminology, without the support of the results of archival studies, of naming materials, glass tools, parts of glass furnaces or parts up to several hundred or thousand years older archaeological finds associated with glass and glassmaking. As a shining example of such an unfortunate transfer of current terms to archaeology, we can mention the term "faience", firmly established mainly in the Early Bronze Age, where it refers to the findings of beads with a fine glassy coating on the surface.

these metric differences of the melting crucibles were not a decisive factor that caused the uneven melting of the glass. We achieved a similar result in the melting of E10 in 2019. This time we were already heating the furnace without unnecessary energy losses and yet the batch melted only partially into the glass, most of it was hardened foam melt that was not completely melted (Fig. 8f). All the mentioned glass batches (E3, E4, E6, E10), which were not melted into a glass in the first melt, belonged to soda recipes and were weighed according to the glass of olive-shaped beads (Fig. 6e–h) or soda glass. Thus, it is a recipe of soda glass that was massively widespread, especially in Roman times or even ancient ones, as some researchers call it. The glass batches, which melted into the glass completely during the first trial, were weighed either according to plant-ash glass with chemically raw materials (E5 and E9) or soda glass, weighed with raw materials with the addition of ash (E7 and E11). For the last two batches, we did not add CaCO_3 (except for ash). These batches were melted in 2018 and 2019. They were melted in the melting chamber together with natron batches which did not melt well. As mentioned above, the crucibles stood side by side in the melting chamber (Fig. 2b) and were subject to the same heating or temperature loss conditions. We want to point out the fact that those details today's glassmaking must take into consideration when melting glass (wall thickness, crucible size, proximity to the chamber wall, and so forth) may not always be as important for the research in historical glassmaking. The apparent reason for the poorly molten batch in the experiments seems to be their composition. The natron batch is more demanding to melting conditions and temperatures compared to the ash batch or the soda batch with the addition of ash. This fact contributes to an interesting historical interpretation. Historically, we have proven that ancient soda batches are replaced in the early Middle Ages (8th–9th centuries) by glass “ash” batches, which significantly dominate in the early medieval Central Europe. Thus, the development of glass production in Central Europe goes from harder fusible batches to less heat demanding ash batches. It proves our observations from the analysis of beads from Borovce (Staššíková-Štukovská, Plško 1997).

The fact that in the early Middle Ages object made of glass, especially jewellery, are popular in a broad mass of the population, appears to play a role in the choice to switch to easier-melting glass.

People started to make glass beads locally (e.g. olive-shaped smooth beads, melon-seed-shaped beads) which would often contain various elements that do not occur in glasses originating from advanced Levantine glassworks. Could this mean that there was significant experimentation with glass in Central Europe? In Roman times, soda glass was melted in glass centres; however, we have more evidence of the production of vessels than the production of glass beads or other jewellery. In Byzantine culture, the production of plant-ash glass was expanding as the glass beads in Central Europe grew more popular. We have found thousands of glass beads from the 8th–11th centuries in the area of the middle Danube. The glass that would melt easier did not have the same demands on pyrotechnic equipment as soda natron glass. It simplified the production of glass outside glass centres and made experimentation with the production of glass jewellery easier.

4.1.1. Poor quality glass in multi-layered beads

A porous, foam-like, melt (glass batch not melted completely) appeared in the experiment E10 in one crucible. There was a thicker layer of foam melt together with a more adhesive layer of well-remelted glass (Fig. 8f). This discovery draws our attention to the archaeological finds of segmented multi-layered beads decorated by a layer of glass with different quality (Fig. 10a, b). The thickest layer is formed by the inner body, which is made of porous inhomogeneous glass. On top of that, the silver foil can be applied, which is covered with a thin layer of well-melted glass (Fig. 10a, b). Such beads appear in the early Middle Ages in the 8th and the beginning of the 9th c., especially around the Middle Danube region in Slovakia, Hungary and Austria. They are also known from today's Germany and Poland. The origin of porous glass or melt, from which the body of these technologically unusual beads is made, remains an open question. In the professional literature, the possible source of such porous glass is considered to be many times remelted and air-enriched glass, which is formed at the bottom of crucibles or glass pans in the advanced glassmaking (Siegmann 2006, pp. 954–955). From our experiments (mainly E10) we see that foam-like poor quality glass melts even with imperfect remelting. We made a glass rod out of this type of glass during our experiments (Fig. 4g). This makes us aware of the possibility that it is actually possible to create simple shapes such as glass rods out of the foam melt.

As such, we can further research question whether the inhomogeneous glass with many wells after gas leaks does not actually come from foam melts, similar to that we achieved during our experiments. It is also necessary to point out that the foam, or porous glass, forms during every melting of the glass. When the glass is well melted, the millimeter layers of foam still remains at the walls or on the surface of the glass in the crucible. For the issue of historical beads layered from two types of different quality glass, it is important to know the fact that one crucible can contain a layer of foam as well as a layer of well-melted glass, as we saw in the experiment E10 (Fig. 8f). This type of glass production does not have to tie to the most advanced glass environment; on the contrary, it can somewhat be expected from lower quality glass production. It should also be emphasized that during our experiments, we only got two types of different quality glass from the glass batch; this did not happen when we melted cullet of actual glass.

4.2. EFFECT OF FLUE GAS (SMOKE)¹³ IN THE MELTING CHAMBER ON THE MELTING GLASS

When filling the crucibles with either cullet or a glass batch, we paid attention to cleanliness, i.e. the contents of the crucibles were not contaminated with dust, and we recorded the chemical elements from which we weighed the glass batch. This

¹³ The flue gases, popularly called smoke, also contain unburned wood residues, so they are basically pieces of ash.

fact allowed us to observe and find out the secondary elements in the melted glass, for example, elements from the flue gases during melting. We best visually observed the flue gases in experiments E1 and E2, where we melted glass cullet. Surprisingly, although we used colourless cullet, the glass had a slight green tint and green, or dark impurities appeared on the surface (Fig. 3a, c, d). Dark particles from flue gas were also observed in crucibles E3 and E4 when the batch was remelted into foam (Fig. 4a, d). During the experiments in 2018, we observed that fewer flue gases appeared in the glass, they showed mostly on the surface of the crucible and at the parts where glass became green-tinted (Fig. 4b, e). Flue gases were also observed in the glass that was not appropriately melted that covered the inner walls of the crucible as a glassy layer (e.g. Fig. 8a). The flue gases, essentially ash, that fell into the molten glass were able to secondarily enrich the glass with several other elements, in addition to carbon, that were not in the original glass batch. According to the results of the glass analysis for experiments E3 and E4 glass, the following oxides were present: Fe_2O_3 , TiO_2 , Al_2O_3 , MgO , K_2O . Basically, oxides that contained ash (Table 3, Ash). However, when it comes to Al_2O_3 and Fe_2O_3 , we cannot exclude the possibility of penetration from the crucible ceramic (see next chapter).

4.3. ELEMENTS THAT TRANSFERED INTO GLASS FROM CERAMIC CRUCIBLES

In the professional literature, the possible introduction of Al_2O_3 from crucible ceramics into a molten glass is pointed out relatively often. The fact that we exactly know what elements we weighed into the glass batch allowed us to focus on the issue of diffusion of Al_2O_3 from the ceramic walls of the crucible into the glass. As expected, analysis of the ceramic composition of the crucible E10 showed following results: in addition to SiO_2 , the Al_2O_3 is also present (31.6–37.76%) together with TiO_2 (Table 2: E10C, T1–T4; Figs 8g; 5h). We did not put these elements into the glass batch; however, the molten glass still contained them. For example, Al_2O_3 was present in the amount around 1.75–2.65%, which is a content that would already affect the properties of glass. In experiment E11, we focused our attention on the Al_2O_3 content, as it probably diffused to the glass from ceramic crucible. Higher content of Al_2O_3 (7.67–9.98%) was detected in the vicinity of the ceramic residues. However, the content of Al_2O_3 decreased (to 2.93%) when there was a higher distance from the ceramic particles (see Fig. 11b points E11B, S1–S3, Table 2: E11B, S1–S3). TiO_2 was also found in the glass in the vicinity of the crucible ceramics. This element could diffuse into the glass from the crucible ceramics, in addition to the flue gases. Based on the comparison of the chemical composition of the ceramic with the original composition of the glass in E10 and E11, we are certain that the elements Ti and Al found in the glass come from the crucible and not from the glass batch.

Other oxides determined in the ceramic crucible were either present in the glass batch or found in the ash (Na_2O , MgO , K_2O , Fe_2O_3). There is a high probability that they also diffused into the glass and thus influenced the amount that we found by a point or bulk chemical analysis. Therefore, when it comes to the historical glass-

making, one has to be very careful when classifying glass groups according to the content of individual oxides (for more see Dekówna, Olczak eds 2002, pp. 189–192).

4.4. GREEN-TINTED GLASS

In the professional literature devoted to the historical glass, the unwanted colouring of glass in shades of green by the influence of Fe_2O_3 from the glass batch or, as proved in our experiments, by penetration from ceramic pottery or flue gases is one of the well-known facts. We intentionally introduced Fe_2O_3 into the glass



Fig. 12. Olive shaped and blown-beads from Borovce
Uneven green and blue colouring of the glass between the individual beads and within their bodies.
Photo by D. Stašíková-Štukovská

batch in the experiments E6, E9, E10. In experiments E5 and E11 Fe_2O_3 was introduced into the glass batch with ash. As we know, iron based oxides colour glass into yellow-brown colour (Fe^{3+}), green colour (Fe^{2+} and Fe^{3+}) or blue colour (Fe^{2+}), depending on oxidation or reduction conditions in the melting chamber. During our experiments, we melted either under reduction or oxidation conditions.¹⁴ With

¹⁴ We did not exactly specify this fact.

a minor correction of the furnace in 2019¹⁵ we changed the melting atmosphere in the furnace to be more reducing and less oxidizing. We also did not affect the melts from the glass batches by mixing them to homogenize the glass by reducing the number of bubbles and its colour. The result of our experiments is therefore appropriate to the methodology we use. Our glass, in addition to numerous bubbles, has different shades of green not only among itself but also in the molten glass in crucible, which contains different shades of green or blue-green in its body (compare Figs 4b; 7f; 8b, c; 9a, c). It also agrees with the colour of the historical beads, for example, when it comes to olive-shaped beads made of transparent glass (8th–10th centuries). The randomness of colouring is visible; this occurs mainly due to the unfamiliarity of glassmakers with iron contamination or their constant fight with the furnace atmosphere. Each bead has a different colour, and various shades are also in the body of one single bead (Fig. 12). In this context, we may ask ourselves whether these types of imperfectly coloured glass beads are the actual products of glass masters from the advanced glass environment? On the other hand, this might be evidence of production in the local environment and thus the proof of the adoption of technology from the advanced glass environment by local masters. With the involvement of other facts available to archaeological research on the subject, while the results of archaeometric study richly published by the natural sciences and little-used social sciences taking into account, we can find compelling answers to the development and spread of glassmaking in Europe. We can specify the knowledge about the quality level of glass production in specific localities.

4.4.1. Glass colour in the experiments E5 and E13

Colouring of the glass belongs to the most technologically complex activities in glassmaking. If we colour glass with metal oxides, the resulting colour can be affected by the atmosphere in the melting chamber in the furnace. For example, copper colours in two oxidation states. The colour is caused by Cu^{2+} ions to the blue and green-blue shades, while an oxidizing atmosphere is required. Monovalent Cu^+ turns bright red with a hint of grey in a sharply reducing environment. Copper is one of the most common oxides, used to colour glass in the early Middle Ages, which is a reason we chose it for experiments E4 and E13. During the experiment E4, after the second melting in 2018, we obtained beautiful turquoise coloured glass (Fig. 4d–g). During the experiment E13, we repeated the melting of the same composition of the soda (natron) batch with colouring oxide CuO in 2019, but the turquoise colour was given only to the foam edges and glass at the surface of the molten mass and the walls of the crucible. Most of the glass was stained black or grey-black (Fig. 9d–g). In the thin part of the cullet, the glass appeared to be transparent with a slight grey tint (Fig. 9g). The divalent Cu did not have a sufficient oxidizing atmosphere to colour the glass. Monovalent copper, which is colour-

¹⁵ This reconstruction of the furnace was focused on the flue gas discharge. In 2019 flue gases returned to the melting chamber and then went to the cooling chamber.

less, can show a grey or red colour in the reducing environment. The unexpected result of the colouring in the experiment E13 (where we coloured the glass grey to black without changing the content of the experimental glass batch or the colouring oxide CuO) was interpreted as a consequence of the atmosphere in the furnace. As mentioned above, in 2019, we made slight changes to the hot airflow in the melting chamber, which probably resulted in a more frequent reducing atmosphere than in previous years. Although we did not get a bright red glass, a colour produced by monovalent Cu in a reducing environment (we were missing iron oxides and protective colloids for that), we coloured the glass grey or black, which is not a well-known fact to historical glass. The important thing is that we did not colour the glass black intentionally; it was an accident. We can assume that during the early Middle Ages, technological coincidences were the reason for oddly coloured glass and other peculiarities, especially in the production of beads and jewellery, as we have seen many times in our research of glass beads. These technological „coincidences“ can contribute to uncovering the originality of early medieval glass in Central Europe. We have already pointed out several technologies unusual for the classic glassmaking for this area such as hair effect, glass granulation or inhomogeneous green-olive-shaped beads.

4.4.2. Another discussion about the unexpected colours

The experiment E5 resulted in an unexpected burgundy colour as we did not plan to achieve it. Initially, we wanted to get a clear colourless glass with a subtle honey tint, similar to the glass of a bead from Skalica, according to which we weighed the glass batch E5. After melting, all the elements we prepared for the glass batch were present, but the glass had a burgundy colour instead of the expected transparent one (Fig. 7a–c). How did it happen that the experiment resulted in the burgundy colour? The following colouring oxides were present: Fe₂O₃ (colours the glass in green and blue tones) but also MnO (colours the glass in purple shades). In low concentrations, MnO is used as a decolourizer, eliminating unwanted iron colouring, which is probably the reason why it was found in the transparent Skalica beads. The contribution of melting conditions during E5 resulted in the glass being coloured by the presence of MnO to the burgundy, almost violet-burgundy colour. It is clear that MnO acted as a colouring oxide instead of a decolourizer.

The experiment E2 also introduced a few interesting points to the question of the complexity of colouring glass as we introduced fragments of orange glass between the transparent cullet. It turned out that the coloured glass melted, but resulted glass in the crucible was not full-colour. It was not possible to colour the glass with coloured glass by simply putting it among the colourless cullet in the crucible, especially when one does not have any experience with colouring. Even here, the empirical experience of who produced the glass and coloured the glass was significantly important. Knowledge of the right glass colouring procedures provides us with interesting facts that we can use in archaeological finds of glass when interpreting the production environment of the artefacts. For example, we could

point out at the melon-seed shaped beads from the 8th c. known in the context of the Avar Kaganat. These beads are supposed to be made locally from recycled glass, which does not require a special glass furnace; one only needs a glass hearth to melt a small amount of glass. However, it is not particularly easy to colour transparent glass into a dark colour that was extremely popular with melon-seed shaped beads in the 8th c. Archaeological finds of the Avar Kaganat culture showcase glass beads that are made of a transparent, slightly greenish glass with a thin layer of black colour on the surface (we do not know the origin of the black colour).

The most likely interpretation of the bead with two-layers seems to be the manufacturers' efforts to create a black-coloured glass bead while the manufacture lacked experience and knowledge to achieve desired results. The compromise, in this case, could have been the discovery of an unknown technology that applied a black layer to clear glass which resulted in the black glass beads. We could find more examples in the archaeological finds in Slovakia and Moravia that appear to be a manifestation of glassmakers who could not colour glass. Secondly, we can see this as evidence of the actual glass production in the local environment. However, this topic does not receive any attention, and as such, it is waiting for further research.

Only experienced masters had a proper knowledge of how to colour glass correctly. It required empirical experience with weighing raw materials for glass batch, together with the necessary glass furnace (with the required reducing or oxidizing atmosphere), as well as additional knowledge essential to melt the glass and its colour. If the transparency and homogeneity of colour are not deemed essential, it is still possible to melt the glass; however, the colour would be a surprise. Thus, unfamiliarity with the glass colouring can be a potential indication of production in the actual cultural environment outside of advanced glass centres.

4.5. DIFFERENCES BETWEEN BULK XRF AND POINT SEM/EDS ANALYSIS OF CHEMICAL COMPOSITION OF GLASS

In the research of the historical glass, the results of chemical composition of glass of the archaeological finds have undeniable importance. They provide basic data for the interpretation of the chemical type of glass of an archaeological find. These facts are further used to study historical glass technologies, the origin of discoveries or dating of those discoveries. They are useful for learning about the history of cultural and trade contacts of archaeological cultures or the history of glass production. It is not always easy to interpret the chemical composition of glass only from the measured contents of elemental oxides, without the knowledge of the raw materials used for the glass batch. Unlike glassmakers using a current glass production technology, historians and archaeologists do not have an exact source to determine what percentage of a given oxide measured in the analyzed glass is the result of conscious technology or, on the other hand, is not essential to take into the account. Interdisciplinary research has yielded results in the form of various classifications of historical glass according to chemical composition as well as proposals for unify-

ing quantified criteria for element oxides and their importance in melting analyzed glass (review Dekówna, Olczak eds 2002, pp. 189–190, 196). From the above, it is clear how important is the accuracy of the outputs of chemical analyzes towards the whole glass and not just its parts. In archaeology or the research of the historical glass, the first requirement for the choice of the method of analysis is a possibility of having a non-destructive method of measurement or the required minimum sample size. That is also the reason why SEM/EDS point analysis is massively used for historical objects and archaeological finds of glass in interdisciplinary research. It is gentle and non-destructive to rare historical artefacts. It is well known that SEM/EDS analysis is less accurate when compared to bulk analysis XRF; however, it should also be emphasized that it is less effective in terms of quantification of the chemical composition of the entire glass of the analyzed object.

On the other hand, the bulk XRF analysis does not take into account the presence of inhomogeneities, while point SEM/EDS analysis, data collection is carried out from the area that does not contain inhomogeneities (at least unmelted grains of raw materials can be identified and excluded). However, there are scarce data in the literature on the historical glass that would more accurately record the differences between the results of point SEM/EDS analysis and bulk XRF analysis regarding the glass from a wood-heated historic glass furnace. Therefore, we took the opportunity and during our experiments E3, E4, and E7, we performed both types of analysis of the same experimentally melted glass. By comparing the results of measurements (Tables 2–3), we obtained exactly documented values of the differences between these two, in the sample size requirements, different methods of analysis. If we compare the results of the chemical composition obtained by point SEM/EDS and bulk XRF analysis of glass (for example, E3 and E4), there are actual differences between them in the values of measured weight percentages and the detected elements. For example, in the glass E3, XRF analysis detected the presence of 0.22% Fe_2O_3 while the SEM/EDS didn't capture the element. Also, according to the XRF analysis, Al_2O_3 is present in the amount of 1%, the SEM/EDS detected it only in one point (No. 4) of the measured area of glass E3 in the amount of 0.48%, meaning it was below the level of analytical possibilities (Table 2: E3 point 4; Fig. 5a). The differences between the detected elements by SEM/EDS and XRF analysis in our experimental glasses E3 and E4 are both for K_2O ¹⁶ and MgO ¹⁷. The situation is slightly different in E7, the XRF analysis measured 0.22% Al_2O_3 and the SEM/EDS analysis recorded the presence of Al_2O_3 in all five points in the amount of 0.56–1.1%, meaning it was a significantly larger amount that can be assumed for the whole glass. All the mentioned differences relate to trace amounts of elements and are in quantities of up to 1%.

However, we also found more substantial differences in the measurement results. In E3, the XRF analysis measured 16.93% of Na_2O , while the SEM/EDS analysis

¹⁶ The XRF analysis indicates the amount of 0.73 K_2O and SEM/EDS analysis found it in only three of the measured points in the value of 0.19–0.2% (compare the data in Tables 2–3).

¹⁷ The XRF analysis found about 0.68% of MgO , SEM/EDS analysis found it in only three of the measured points in the value of 0.27–0.29% (compare data in Tables 2–3).

measure only 8.9–11.6% of the element at six places. According to the XRF analysis the same oxide was present in E4 in the amount of 18.21% while the SEM/EDS analysis showed only 10.2–11.2%. In E7, there was about 19.02% of Na₂O according to the XRF analysis, while SEM/EDS analysis showed only 10.2–11.3%. The differences are about 8–9%. This may affect the interpretations in those classifications of historical glass that take the amount of Na₂O into account. The differences between the results of the analysis concern all measured elements as we did not find a match in any of the cases.

It should be emphasized that the differences found in the quantities and the presence of elements between the SEM/EDS and XRF analysis do not question the accuracy of the instrument's measurements. Our experimental glass, as well as the historical ones, is inhomogeneous. Point SEM/EDS analysis refers to the chemical composition of the glass at the exact point it measures, while the bulk analysis XRF a more massive amount of glass as a whole, so the results are closer to the overall composition of the glass from which the sample comes.

Our results for the differences between point SEM/EDS and bulk XRF analysis relate to our experiments. They should not be generalized; however, they can not be rejected either. They provide exact data on the differences in the results of measurements of the chemical composition of historical glass by SEM/EDS and XRF analysis. At the same time, they indirectly confirm the reliability of the design of uniform quantification criteria for alkalis, colouring oxides and other elements that influenced the properties of glass and that must be taken into consideration to determine the elemental chemical composition of the historical glass (Dekówna, Olczak eds 2002, pp. 189–260).

4.6. SODA ASH GLASS AND THE QUESTION OF MgO AND K₂O CONTAIN

In the classification of historical glasses according to their chemical composition, the MgO and K₂O contents, expressed as a percentage by mass, are used to distinguish between soda glass and plant-ash glass. It is generally accepted that the ash raw material contains a high rate of MgO and K₂O that enters the molten glass and their weight percentages can be used to determine the presence or absence of ash in the glass batch.¹⁸ The ash that we added to our experimental glass batches E7 and E11 contained 2.90% of K₂O and 2.15% of MgO (Table 3: Ash). The glass of E7 (melted in 2018) is translucent colourless almost without shade while E11 (melted in 2019) is translucent green colour. Both were fully melted during the first melt. However, both SEM/EDS and XRF analysis found surprisingly low content of MgO and K₂O, which were less than 0.54%, respectively less than 0.74% (see Tables 2: E7 and E11; 3: E7). If we took into account only these results concerning MgO and K₂O, we would not know that ash was added to the batch, and we would certainly

¹⁸ Content of K₂O higher than 4% and MgO higher than 2% means that ash was used as alkali in soda glass.

not consider the glass to be melted with ash. CaO showed in the maximum volume of up to 7.68–9.02% an ash-introduced oxide (exactly measured amount depending on the method of analysis and, in the case of point analysis, also the measured site). Ash, as a source of CaO, is nothing new to the research of historical glassmaking. But in the previous research of the historical glass, especially in Central Europe and in the findings of the early Middle Ages, researchers have focused more on the presence of MgO and K₂O as evidence of the presence or absence of ash compared to CaO actually may originate from the ash.

5. CONCLUSION

The concept of the experiments was modelled so that we could accurately document the selected facts. At the same time, we imitated a possible scenario of glass melting by inexperienced glassmakers, who gain knowledge from advanced glass centres, but lack the necessary empirical experience, for example with colouring or blackening glass. We attribute this the fact that we had melted a different glass colour or quality of glass in each of the experimental crucibles, even when the glass batch remained the same. On the other hand, we were able to base our interpretations of unexpected results on exact facts.

Our experimental melts have proved that it is possible to melt glass from a glass batch during the first melt in the quality comparable to the quality glass of historical beads.

In one crucible of E10, the melted glass of two qualities that formed either foam or glass (Fig. 8f) drew attention to the research into the origin of the technology of beads made from two types of different quality glass that occurred in the 8th–9th c. So far, we have been looking for an answer in a quality glass environment.

Significant for archaeometric research of the historical glass are the results that show the degree of enrichment of the glass composition by elements introduced by flue gases or diffusion from the walls of the crucible. In addition to trace amounts of elements, this may be a content that affects the properties of the molten glass, for example in E11, the element Al₂O₃ penetrated into the glass in an amount of more than 2%. Other elements that can affect the total composition of the glass or glass stem include SiO₂ and Al₂O₃ as well as Na₂O, MgO, K₂O, Fe₂O₃ and TiO₂.

Another factor that affects the composition of glass and introduces other oxides is flue gases. Fe₂O₃, TiO₂, Al₂O₃, MgO, K₂O got into the glass through the flue gases. The visible consequence of the flue gas is the green colour of the glass.

The addition of ash to the glass batch introduces CaO into the glass, and therefore ash is considered an important source of CaO, in addition to limestone (CaCO₃), dolomite (CaCO₃MgCO₃) or silica-calcium sand. Our experiments have shown that ash introduces up to 9% of CaO into the glass. The glass melts well and is of good quality and transparency.

The addition of ash to the glass did not result in an increased content of MgO or K₂O during our experiments.

The experiments showed that natron batches are more difficult to melt than the ash ones. Historically, we know that natron or soda-lime glass, which prevailed in Roman times, in the early Middle Ages (especially in the 8th–9th centuries) was replaced by ash. This fact supports the interpretation that the development of jewellery glass or glassmaking since Roman times in Central Europe goes from harder fusible natron glass to more fusible ash glass.

While interpreting the results of experiments, we realized how necessary is the refinement of knowledge what in a given time and space was high-quality glass and what is produced by unplanned coincidence. It is mainly about the colouring of glass as we obtained a different colour than the planned colour in two cases and in all cases at least different shades of the same colouring. In addition to that, we found out that copper added to glass batch as CuO will turn our glass to grey-black colour under the right conditions. This way, we have also inadvertently documented in detail the process during which new glass technologies are discovered. No one doubts the importance of the empirical knowledge of a glassmaker that either coloured or discoloured glass to the desired colour. Without this knowledge, it is possible to colour the glass only randomly; the result is not always what we want to achieve. To understand the details of the spread of glass technologies, we consider inhomogeneous colours of glass to be an indication of lower quality glass production. We must pay attention to this fact before reviewing it with the general accuse that glassmakers could not colour glass well at the time.

The production or melting of glass by inexperienced glass masters also reflects in the remelting of glass cullet, which could not be coloured by simply throwing a randomly selected coloured cullet into the recycled glass.

Our experimental melts, the results of which we have briefly presented in the paper, have brought various facts to the melting of glass in wood-fired glass furnaces. Our experiments aimed to obtain evidence-based results that were needed in the interdisciplinary research of historical glass. Model experiments with melting in the new electric laboratory furnaces would not yield them.

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BIBLIOGRAPHY OF WORKS CITED

- Barkoudah Y., Henderson J. 2006, *Plant ashes from Syria and the manufacture of Ancient glass: Ethnographic and scientific aspects*, „Journal of Glass Studies”, 48, pp. 297–321.
- Černá E., Hulínský V., Gedeon O. 2001, *Výpověď mikroanalýz vzorků skel z raného středověku*, Sum.: *Microprobe analyses results of early medieval glass specimens*, „Archeologické rozhledy”, 53, pp. 59–89.
- Dekówna M. 1980, *Szkło w Europie wczesnośredniowiecznej*, Sum.: *Glass in early medieval Europe*, Wrocław–Warszawa–Kraków–Gdańsk.
- Dekówna M., Olczak J. eds 2002, *Principes de description des verres anciens depuis les temps les plus reculés jusqu'au XIIIe siècle de n.è. (D'après l'analyse du matériel archéologique du Centre, de l'Est et du Sud-Est de l'Europe et de la Transcaucasie)*, Warszawa–Toruń.
- Dussubieux L., Gratuze B., Blet-Lemarquand M. 2010, *Mineral soda alumina glass: occurrence and meaning*, „Journal of Archaeological Science”, 37, pp. 1646–1655.
- Farkaš Z., Turčan V. 1998, *Věsnostredoveká sklárská pec v Bratislave na Devínskej Kobyle*, Sum.: *Frühmittelalterlicher Glasofen in Bratislava auf Devínska Kobyla*, „Slovenská archeológia”, 46/1, pp. 31–54.
- Schibille N., 2011, *Late byzantine mineral soda high alumina glasses from Asia Minor: A new primary glass production group*, „PLoS ONE”, 6(4): e18970, doi:10.1371/journal.pone.0018970.
- Schibille N., Freestone I.C. 2013, *Composition, production and procurement of glass at San Vincenzo al Volturno: An early medieval monastic complex in southern Italy*, „PLoS ONE”, 8(10): e6479, doi:10.1371/journal.pone.0076479.
- Schibille N., Sterrett-Krause A., Freestone I.C. 2017, *Glass groups, glass supply and recycling in Late Roman Carthage*, „Archaeological and Anthropological Sciences”, 9/6, pp. 1223–1241.
- Siegmann M. 2006, *Bunte Pracht – die Perlen der frühmittelalterlichen Gräberfelder von Liebenau, Kreis Nienbrug/Weser, und Dörverden, Kreis Verden/Aller. Chronologie der Gräber, Entwicklung und Trageweise des Perlenschmucks, Technik der Perlen*, 5, Beiträge zur Ur- und Frühgeschichte Mitteleuropas, 28. Beier.
- Staššíková-Štukovská D. 2017, *Natron and Plant-Ash Glasses in the middle Danube region during the Early Middle Ages*, [in:] *Annales du 20e Congrès de l'Association Internationale pour l'Histoire du Verrre, Fribourg/Romont 7–11 septembre 2015*, Romont, pp. 366–373.
- Staššíková-Štukovská D. in the press, *Bola v bratislavskej sklárskej peci panva, pernica alebo sklárská vaňa?*, Sum.: *Did the Bratislava glassmaking furnace contain a melting pot, „pernica“ or melting tank?*, [in:] *Krajinou archeologie, krajinou skla, Studie věnované PhDr. Evě Černé, K. Tomkové, N. Venclové eds*, Most–Praha.
- Staššíková-Štukovská D., Pliško A. 1997, *Typologische und technologische Aspekte der Perlen von Borovce*, [in:] *Perlen. Archäologie, Artikel, Analysen*, U. von Freeden, A. Wiczorek eds, Bonn, pp. 259–278.
- Staššíková-Štukovská D., Ungerman Š. 2009, *„Olivovitě“ koráliky – terminologické poznámky a makroskopické pozorovania nálezov z pohrebiska v Dolných Věstonicích*, Zusamm.: *Olivenförmige Perlen – terminologische Anmerkungen und makroskopische Beobachtungen von Funden aus dem Gräberfeld in Dolní Věstonice*, *Študijné zvesti*, 45, pp. 39–57.

- Surovec J. 1998, *Posúdenie sklárskej pece z technologického hľadiska*, „Slovenská archeológia”, 46/1, pp. 43–44
- Szőke B.M., Wedepohl K.H., Kronz A. 2004, *Silver-stained windows at Carolingian Zalavár, Mosaburg (southwestern Hungary)*, „Journal of Glass Studies”, 46, pp. 85–104.
- Tomková K. 2007, *Olivovité korálky v Čechách z pohledu dějin jejich studia*, *Zusamm.: Olivenförmige Perlen in Böhmen aus forschungsgeschichtlicher Sicht*, „Archeologie ve Středních Čechách”, 11, pp. 531–548.