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Beata Miazga

WHAT IS HIDDEN UNDERNEATH THE BLACK AND BROWN ON SILESIAN GLASSWARE? ABOUT THE ARCHAEOMETRIC CHALLENGE IN THE STUDY OF PAINTED DECORATIONS ON LATE-MEDIEVAL AND POST-MEDIEVAL FINDS FROM WROCŁAW, SW OF POLAND

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At the end of the Middle Ages and the beginning of the post-medieval period, painted glass vessels were not uncommon and are found during archaeological excavations, especially in urban sites. In the first quarter of the 21st century in Wrocław, a considerable collection of painted glassware was obtained during excavations: some of these artefacts were characterised by multicoloured painted decorations, while others seemed to be made using a modest colour palette, mainly brown and black. It was decided to take a closer look at the latter vessels and establish the cause of such differences. For this purpose, non-destructive and minimally invasive analytical tools were employed, commonly used to study archaeological artefacts, such as microscopic observations in visible light (OM), X-ray fluorescence spectrometry (XRF) or scanning electron microscopy coupled with an energy-dispersive spectrometer (SEM-EDS). In the course of archaeometric research, the results confirmed the assumptions about the significant contamination of painted decorations by mineral substances, especially iron and sulphur. The deposition of these elements on the surface of paint caused a permanent change in the colour of decorations on glass vessels.

Beata Miazga, Institute of Archaeology, University of Wrocław, 48 Szewska Street, 50-139 Wrocław, Poland; beata.miazga@uwr.edu.pl

Introduction

Glass belongs to the category of luxury items which became increasingly available and were used in the Middle Ages and the post-medieval period (Siemianowska 2015, 261). Glass vessels are not only the furnishing of manors and rich houses, but are also included in the inventories of burgher houses (Gluziński 1987, 67; Wyrobisz 1987, 56–57). Due to the increasing number of glass products, a natural process is the need to make them more attractive in the form of various types of decorations. Such decorations made on the glass are diverse and quite closely related to the chronology of the glass itself. When looking at medieval glass, different types of decorations are perceptible (Biszkont 2005; Twardosz 2017, 107–118) than those found in the Renaissance or Baroque periods (Gołębiewski 2004; Cymbalak et al. 2020). For this reason, the study of decorations on glass is important from the point of view of conducting research not only on crafts and glassworking, but also on the broadly understood heritage of material culture. Particularly valuable are the studies of glass from archaeological excavations, in which a lot of new information about our ancestors is obtained (e.g. the fashions in decoration, the degree of advancement of craftsmen, the raw materials used). However, the very process of examination of archaeological glass is also a source of new analytical challenges which have not been encountered when studying well-preserved glass from museum collections. One of these problems is the progressive corrosion processes of glass and painted decorations, leading to significant damage to some ornaments caused by their reduced durability and also frequent change of decoration colour due to deposition in soil layers (Miazga 2017). While considering this problem, non-invasive archaeometric tools with a low degree of interference in the archaeological structure will be used.

Research method

In the study of decorated glass vessels from Wrocław, non-destructive and minimally invasive archaeometric tools were used. Studies began with light optical microscopic observation, which is a standard procedure in the case of artefacts (Tite 2004, 370; Davison 2006, 233–241). Examination was done with the Olympus SZX9 microscope, which allows for magnification in the range of 6.3x–63x. After the microscopic studies were performed, spectroscopic analyses were carried out based on various analytical radiation excitation systems and detection systems. The X-ray fluorescence spectrometers Spectro Midex and the EDS spectrometer by Oxford Instruments, coupled with the Hitachi TM 4000 scanning electron microscope, were used.[1] The use of such tools is a common practice in the analysis of glass products (Milazzo 2004, 243–249; Constantinescu et al. 2005; Samek et al. 2007; Verma 2007;

[1] For XRF measurements, Spectro Midex energy-dispersive spectrometer with an X-ray tube with molybdenum anode and a Peltier-cooled, semiconductor Di Drift Detector (SDD) was used. It operated with a voltage of 46 kV and an amperage of 0.4 mA. The measuring spots were in a range of 0.2–4.0 mm. SEM-EDS analysis was made with Hitachi TM4000plus scanning electron microscope. The microscope was joined with the AztecOne EDS spectrometer (Oxford Instruments) equipped with the Silicon Drift Detector (detection area is 30 mm^2). The analyses were performed with energy resolution of 158 eV (Cu-Kα, equivalent to 129 eV with MnKα), acceleration voltage was 5 kV and charge-up reduction mode was used (this mode offers easy observation of the non-conductive materials, without pre-treatment).

Cílová & Woitsch 2012; Pankiewicz et al. 2017; Kunicki-Goldfinger et al. 2018). The artefacts which were examined were in various states of preservation, some were corroded and some were subjected to preliminary cleaning and preservation of painted decorations with Paraloid B72. Spectral studies were carried out without any special preparation of glass fragments, only for scanning electron microscopy coupled with an energy-dispersive spectrometer (SEM-EDS) examinations, the Paraloid coating was removed with acetone, and only in fragments, so as not to expose the decorations and glass to further deterioration changes. In studying the colour change, small areas of size of a few mm^2 were additionally cleaned mechanically.

Research results and discussion

Painted decorations on glass

Decorating glass products was a fairly frequent phenomenon, involving various raw materials and technologies, as well as strongly associated with different periods in the history of civilisation. Objects made of glass were decorated with glass supplements of the same or different colour. In the Middle Ages, thread decorations and knobs in various shapes, e.g. drops, etc., were created on glass (Biszkont 2005). Glass was also decorated with various tools, including diamond tools that could cut and polish the surface of glassware (Siemianowska 2015). Glass paintings belong to the younger type of decorations. Chronologically, this technique is commonly associated with the post-medieval glass and the 16th–17th century (Buczkowski 1987; Ciepiela 1987; Siembora 2017; Cymbalak et al. 2020), although Silesian finds of painted glassware with an earlier, medieval chronology are known (Lech Marek, personal communication). The goal of painting glass objects was not only to decorate the finished products, but also to hide the imperfections of the glass raw material itself, i.e. mainly bubbles visible in the glass even to the naked eye (Fig. 1). Therefore, painted decorations very often occupy a very large surface of a glass product, especially glasses, which are decorated practically from the base to the rim, with large patterns of varying nature: there are representations of human figures (Fig. 2), animals, as well as heraldic symbols.

The state of preservation of glass and decorations

Archaeological glass is rarely in perfect condition. It is a consequence of physical damage, accumulation of deposits of extraneous substances on the glass surface (including minerals), and also of chemical processes (Davison 2006). In addition to significant defragmentation, which occurs as a result of both material imperfections and impacts, damage caused by thermal shock, often occurring in the archaeological environment, is observed, along with corrosion changes resulting from the chemical properties of glass components and their interaction with water.

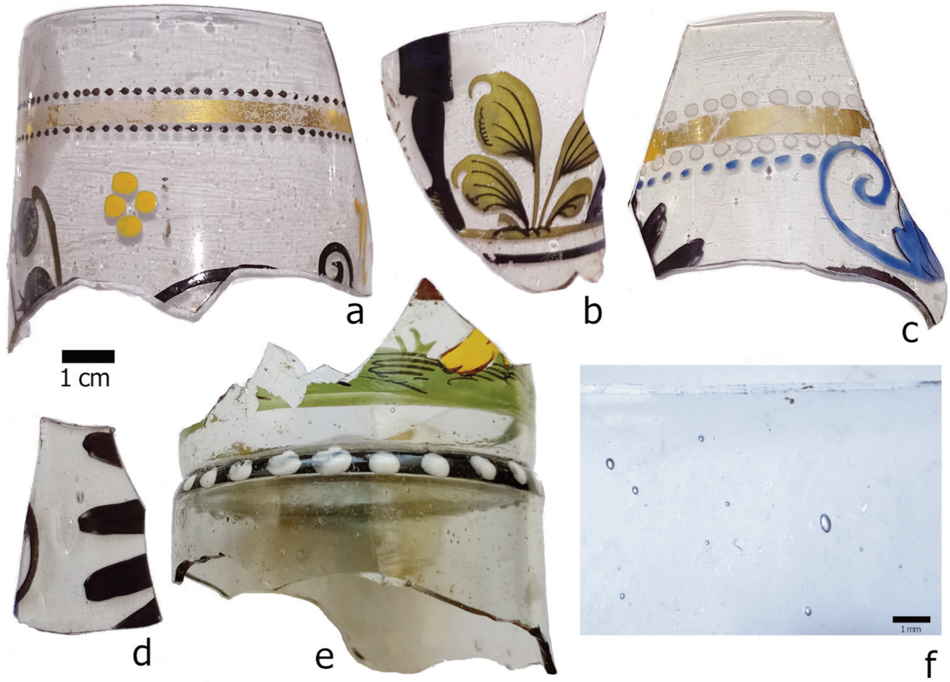


Fig. 1. Selected fragments of painted vessels from Wrocław. Visible imperfections in the glass, photo by B. Miazga.

The alkali leaching processes or the dissolution of the silicon glass structure then proceeds. As a result of these processes, the glass undergoes not only the process of weathering, but also the phenomena of weeping and crizzling[2], which can result in cracking of the glass surface and furthermore, its complete structural disintegration. The deterioration changes of glass are also accompanied by the destruction of decorations which were painted on the glass. These are often abrasions of decorations, detachment of entire decorated areas and changes in the colour of decorations due to the deposition of extraneous substances on the decoration. Such a phenomenon was also recognised in the case of Silesian finds of painted vessels, which often have a significantly darkened colour of the painting, sometimes to the point of appearing black or brown.

Nowosielska (2004, 57), describing a glass from Wrocław, reports that painted decorations which we can now find on glass artefacts are sometimes brown. The author presents the object with a bell-shaped bowl and three volute ears as made of fairly pure light green glass, decorated with a representation of a woman and a man.

[2] Weathering of glass is a decay dependent on the environment, where the moisture is the main influencing factor. After this process, 'the weathering crust' appears (Cronyn 1990, 130). Weeping is connected with the hydrolytic attack of atmospheric water on the glass and in consequence the slippery surface films or droplets are visible. Crizzling is a process in which the surface of the glass is becoming less transparent due to very fine surface crazing (Brill 1975, 121).

Fig. 2. Selected fragments of painted glasses from Wrocław (St. Catherine (św. Katarzyny), St. Vit (św. Wita), Jodłowa, St. Nicolaus (św. Mikołaja), Kiełbaśnicza-Ruska and Rzeźnicza streets) with representations of woman and man. Visible browning or blackening of paintings, photo by B. Miazga.

Both human figures are described as painted with enamels which, according to Nowosielska, retained their 'vivid colours'. The woman's face and hands are painted with light brown paint and she is wearing a white shirt and a brown sleeveless dress with a yellow hem. A scarf/sash without the specified colour is placed in the woman's hand. The figure of the man is less well preserved, but also here in the description of the preserved representation, there are references to a white shirt and brown trousers. Hence, in Nowosielska's description, we see the dominance of brown over other colours. The situation is similar in the case of decorated glasses found in Głogów and described by Pogorzelski and Szajt (2016). One of them is presented as decorated with gilt, optical ornament and enamel. The colours of the artefact shown by the authors in a figure refer to the palette of yellows and browns (Pogorzelski & Szajt 2016, fig. 10a). The second painted object is a glass with a representation of a couple: a woman holding a wreath in her hand and a man holding a chalice. The decoration, as shown in photograph and figure, is currently brown, both in the part of human figures and in the accompanying floral (lily of the valley), geometric (dots) or inscriptions motifs (Pogorzelski & Szajt 2016, fig. 11 and 12a). Similar glasses with representations of a couple come from the archaeological excavations carried out in Nysa and recently again in Wrocław, where, during the research on two Old Town sites, several glasses containing the same representation were obtained. Interestingly, despite the similarities in the manner of presenting the figures of woman and man, there are significant differences in colours of the decorations. The glass from Nysa is very colourful: the woman has a blue sleeveless dress, a red apron and a white shirt. Similar to one of the glasses from Wrocław, from St. Catherine (św. Katarzyny)–St. Vit (św. Wita) Streets, the woman wears a blue sleeveless dress, a white shirt, a yellowish brown coat and a white headdress (Fig. 2: c). On another glass from this site, the female figure wears very dark clothes (an almost black dress and a tawny apron, Fig. 2: d). In turn, in Jodłowa Street in Wrocław, one glass was discovered where the figures of the woman and the man are currently almost completely black, apart from the man's face, hands, hair and collar, and green floral motifs (Fig. 2: a; Miazga 2017). During the archaeological excavations carried out at the end of the 1990s, in the quarter of Wrocław Old Town streets of St. Nicolaus (św. Mikołaja), Kiełbaśnicza, Ruska and Rzeźnicza, also glasses with figures of a woman with wreath and a man with a chalice were discovered. One of the glasses is quite colourful: woman's dark blue skirt, black top, vest and shirt, and white collar. Similarly, the man wears black hat and clothes with white collar and dark blue stockings (Fig. 2: e). In turn, two other representations of women have completely different colours. One of the figures wears brown dress and apron (Fig. 2: f), while the other wears brown dress, yellow apron and white shirt's sleeve (Fig. 2: d). The occurrence of such different colours in similar representations on Silesian vessels is extremely interesting and has contributed to the archaeometric research that could describe this phenomenon.

Intentionally made black painted decorations

Considerations concerning the problem of black paintings should begin with the study of those paintings which were originally black. Among the finds of glass vessels from Wrocław, black decorations are not very common. In the collection in question, these are elements of human figures depicted on vessels. Men's hairdos, beards and clothes were painted with black paint. Only in two cases, bird representations were depicted with black enamel. In the assemblage of analysed glasses, floral decorations and geometric patterns in black were also recognised (Fig. 3). Microscopic observation of these representations indicates their fairly good durability, resulting from the thermal fixation of the enamel (Fig. 4). Chemical analysis of black decorations confirms that in the analysed collection, black decorations were made with paints containing iron compounds, accompanied by a variable amount of manganese, cobalt, copper and arsenic (Fig. 5: a). This is consistent with literature reports on iron-containing mineral raw materials (Pollard & Heron 2008, 164; Eftekhari et al. 2018, 105–106). In the studied assemblage of decorated glass vessels from Wrocław, iron was indicated as the colouring agent in black paintings. It was also found that black decorations are most often opaque, which is a consequence of a considerable amount of tin appearing as an opacifier (Fig. 5). In the two examined fragments of glasses from St. Nicolaus (św. Mikołaja) Street (inv. no. 336/99), the tin content was determined in the course of semi-quantitative EDS analysis, and it ranged from 5.1 to 10.7 wt% in terms of tin oxide SnO_2. In the studied group of glasses, an example of black painting was also found in which the determined level of tin was not high, practically impossible to determine semi-quantitatively. This is a glass from St. Nicolaus (św. Mikołaja) Street with a representation of woman and man dressed in black costumes. The tin

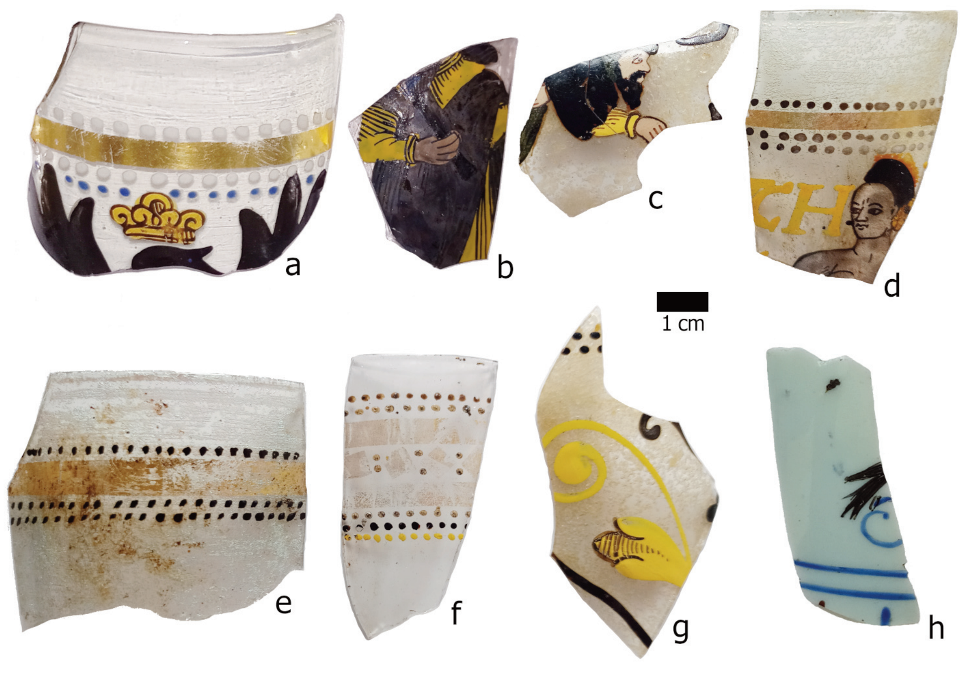


Fig. 3. Examples of intentional black painted decorations on glassware from Wrocław, photo by B. Miazga.

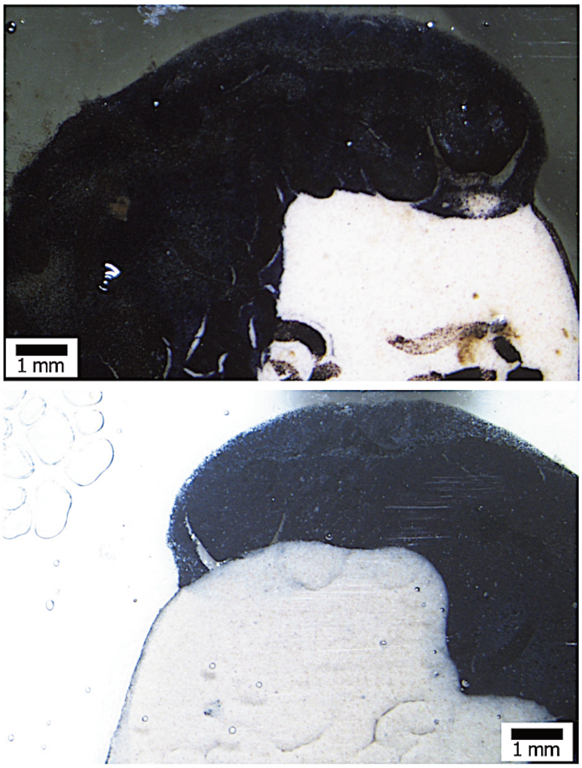


Fig. 4. Microscopic image of a black decoration, showing its opacity and good state of preservation, photo by B. Miazga.

level determined for the black dress of the woman, the black hat and the jacket of the man was very low and quantitatively did not exceed 0.5% by weight (Fig. 6).

Painted decorations unintentionally black – darkening of multicoloured paint layers

The study on the nature of the colour change (both blackening and browning) began for the originally white painting decorations, which are the base. The reason is fairly simple chemical composition of the white enamel (Henderson 2000, 36; Molera & Vendrell-Saz 2001; Robinet & Eremin 2012, 274). Due to the fact that it is a lead glass clouded with tin, the reference base is simple, and it should not be difficult to capture the decoration change due to the deposition of various minerals while the glass was embedded in the soil layers. Deposition on white paints of mineral layers and possible corrosion changes caused by unfavourable environment should be reflected in the results of chemical examination. The objects suitable for such a research were selected thanks to microscopic observations. Analysis of the

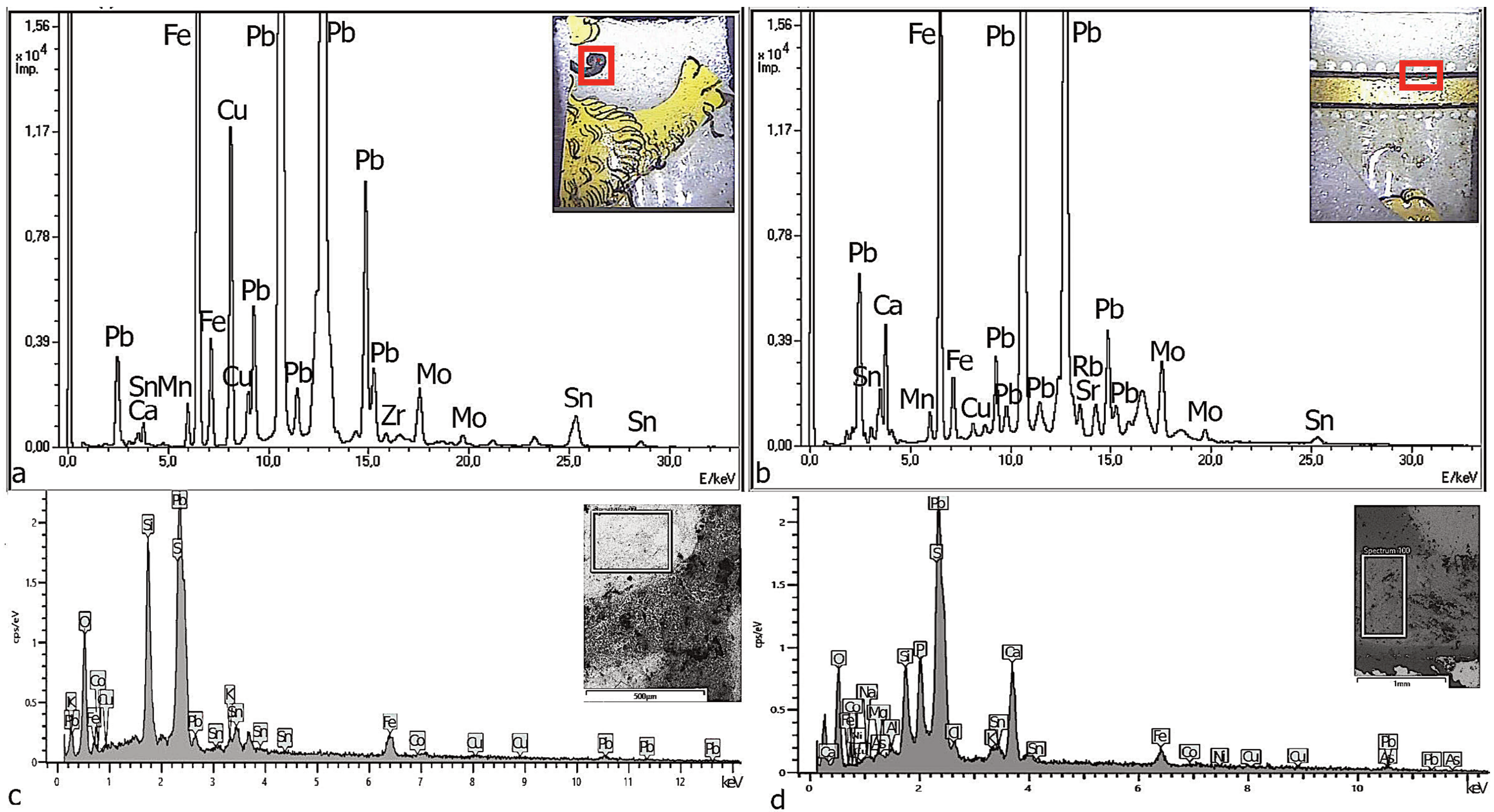


Fig. 5. XRF and EDS spectra of black decoration on fragments of glasses from St. Nicolaus (św. Mikołaja) Street in Wrocław. The glass with the animal decoration: XRF spectrum (a) and EDS spectrum (c). The glass with the golden decoration, white dots and black line: XRF (b) and EDS spectrum (d), edited by B. Miazga.

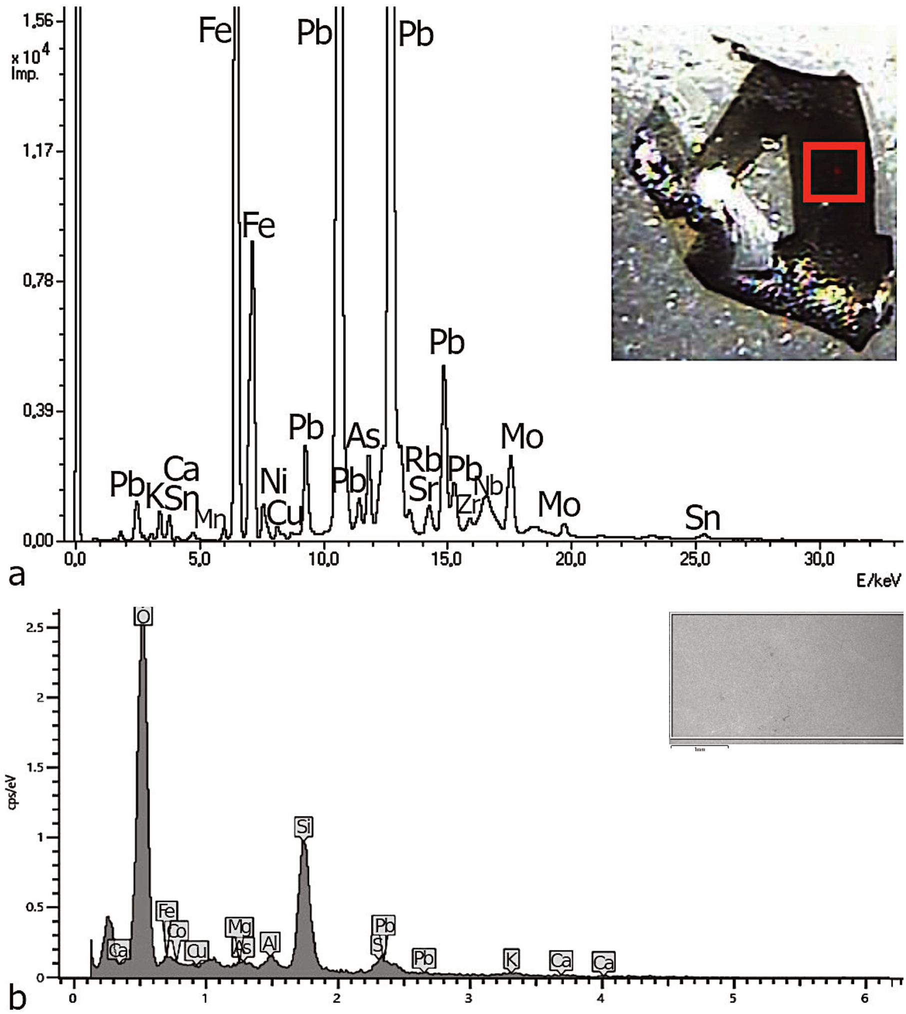


Fig. 6. XRF (a) and EDS (b) spectra for black decorations from St. Nicolaus (św. Mikołaja) Street in Wrocław. Visible strong iron signals and variable tin intensity, edited by B. Miazga.

top and bottom sides of glass vessels from St. Nicolaus (św. Mikołaja) and Kiełbaśnicza street allowed to indicate which decorations were originally white. Figure 7 presents a few examples of pearl decorations which were white and currently are either light brown or completely black. Additionally, in order to confirm the legitimacy of this choice, some of the decorations were spot cleaned, thanks to which the whiteness of these decorations was revealed (Fig. 8). The artefacts selected for research were preliminarily analysed by X-ray fluorescence (XRF). For the fragment of glass shown in Fig. 8, a comprehensive study of the decoration initially uncleaned and then cleaned was carried out. For this purpose, a

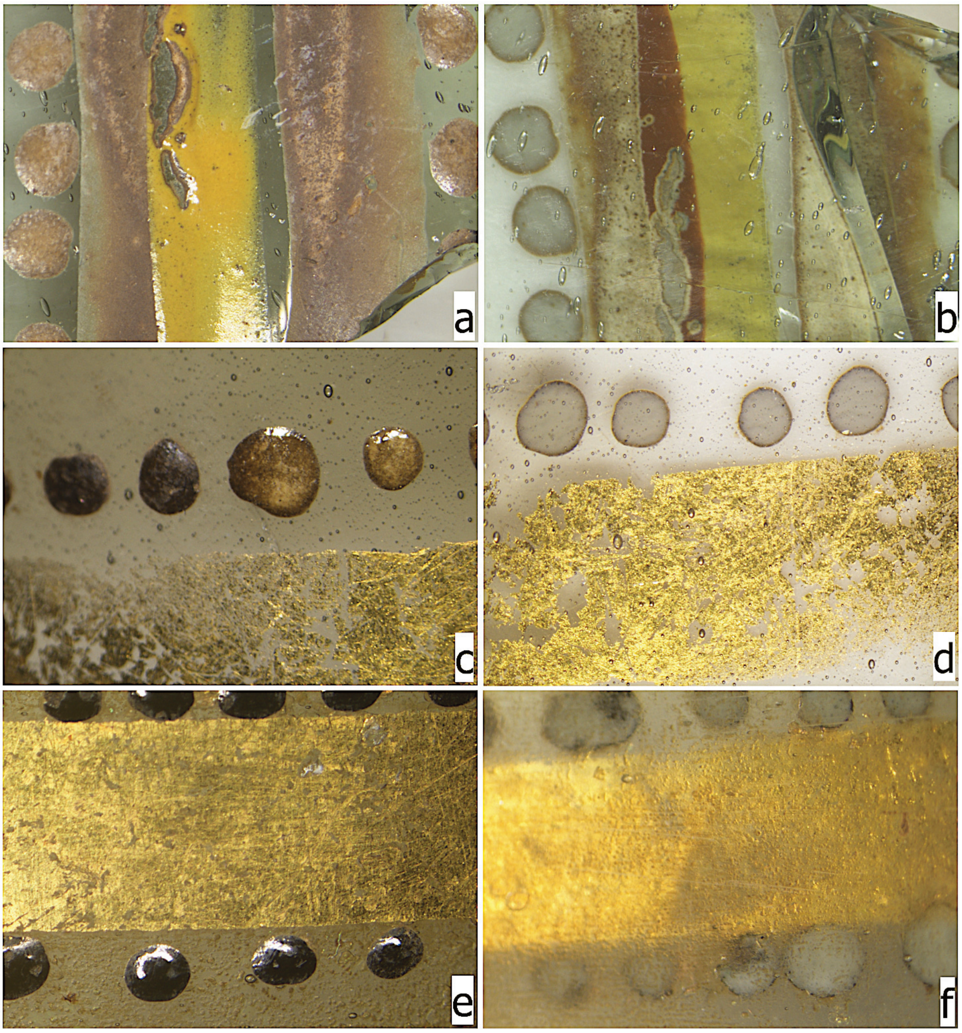


Fig. 7. Selected examples of pearl ornaments on glasses from Wrocław, which were originally white but currently are brown or black (light microscopy, magnification 6.3x), photo by B. Miazga.

dozen or so point XRF analyses were performed in various areas of the vessel fragment. The collected data from the study of uncleaned, currently black, decorations indicate that the strongest analytical signals belong to tin and lead, quantitatively about 30% Sn and 60% Pb. The next element which was determined in the XRF examination was iron in the amount of about 2–6% Fe (Fig. 9). By subjecting this fragment to the microscopic spectral analysis, SEM-EDS data were also obtained on the content of light elements. Comparing the collected data, both qualitative and semi-quantitative, one can observe differences in the content of iron, sulphur, chlorine and phosphorus in the flower decoration, examining it before and after

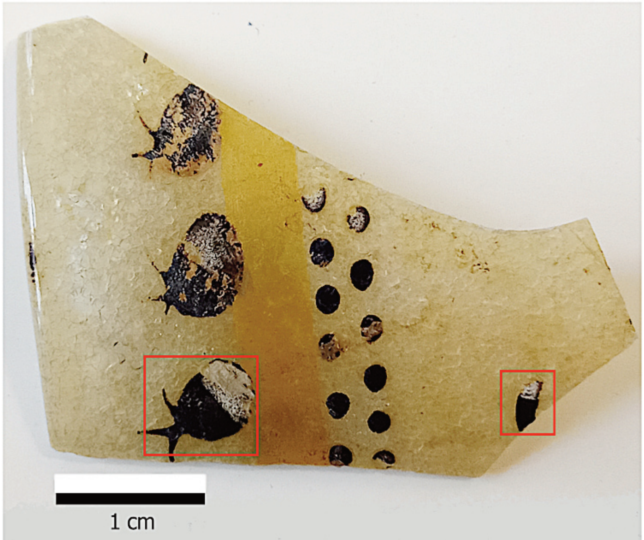


Fig. 8. Fragment of glass rim from Wrocław (St. Catherine (św. Katarzyny)–St. Vit (św. Wita) Streets, inv. no. 10/17), photo by B. Miazga.

cleaning. Phosphorus is a typical element present in a soil, which is related to human activity and is a natural consequence of deposition in ground layers. Therefore, the level of a few per cent calculated as phosphorus oxide P_2O_5 should be associated with the context of finding the glass. In the cleaned decoration, the phosphorus content is practically immeasurable. It is similar to chlorine. The situation is different with iron and sulphur, which are also common soil pollutants, and occurs in the studied decoration both before and after its cleaning. The determined sulphur level reaches even several per cent (up to 20% calculated as SO_3) when the dark part of the lily of the valley was examined, and a few per cent (about 2% SO_3) when the white part of the flower was analysed. The iron content determined for the studied decoration was similarly significantly different: from a level of a few per cent (about 4–6% FeO) before the cleaning to less than 1% FeO when the decoration was restored to white colour. Quantitatively, the difference is even six to eight times. When analysing the obtained data for several dozen other samples of currently black – formerly white decorations from Wrocław, exactly the same relationships can be perceived. White lead-tin decorations currently contain a few per cent phosphorus, much more (even several weight per cent) sulphur and a similar amount of iron. Interestingly, when the decoration was originally white, arsenic is not found in it. In this manner, it can be determined whether the decoration was originally black or white.

Following the hypothesis of linking the darkening of decorations with mineral deposits, mainly the level of iron and sulphur, other currently black decorations were examined, the original colours of which were once green, blue, yellow, brown and red. A very rare case is a change in the colour of yellow decorations, which was noted

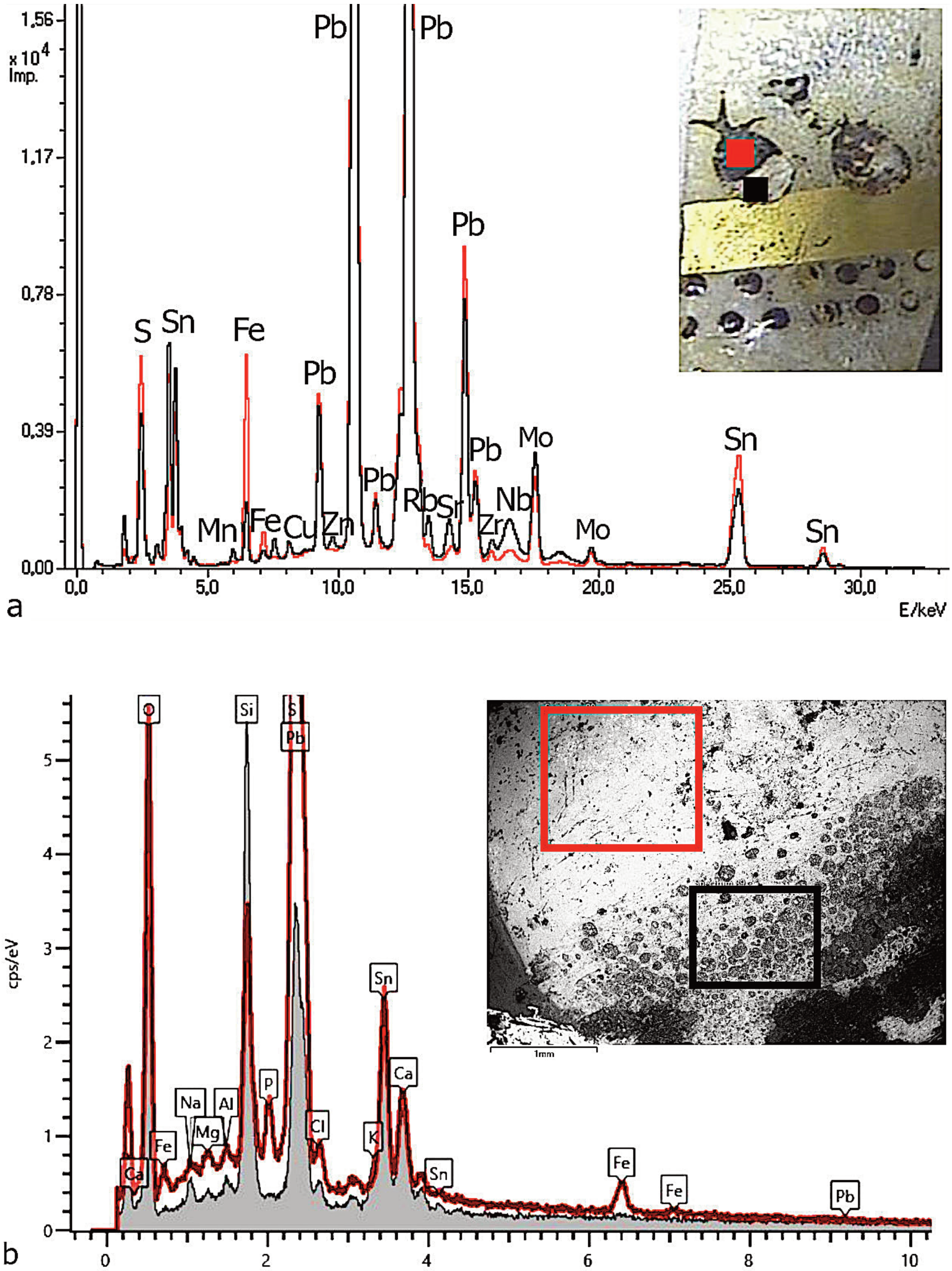


Fig. 9. XRF (a) and EDS (b) spectra for a fragment of decoration on a glass rim (St. Catherine (św. Katarzyny)–St. Vit (św. Wita) Streets, inv. no. 10/17). Red line marks the results of examination of uncleaned places, and the black line marks the mechanically cleaned area, which is recognised as original white colour of decorations, edited by B. Miazga.

for several individual cases, when studying several hundred pieces of decorated glass. However, it is also worth to pay closer attention to this phenomenon, because yellowish decorations also have a fairly strictly defined chemical composition. In the group of glass artefacts from Wrocław, they were made with the use of tin-lead-antimony material. As a result of secondary firing of the yellow paint on the glass, lead pyroantimonate was obtained (Henderson 2000, 27, 35–38; Clark 2002, 16; Robinet & Eremin 2012, 273; Holakooei 2013). Yellow paintings on vessels from Wrocław have a perfectly glassy form, and therefore, other substances do not often deposit on them (as is the case with more porous paintings). However, an exception to the above-described situation can be noticed in Fig. 10, and the analysis of the

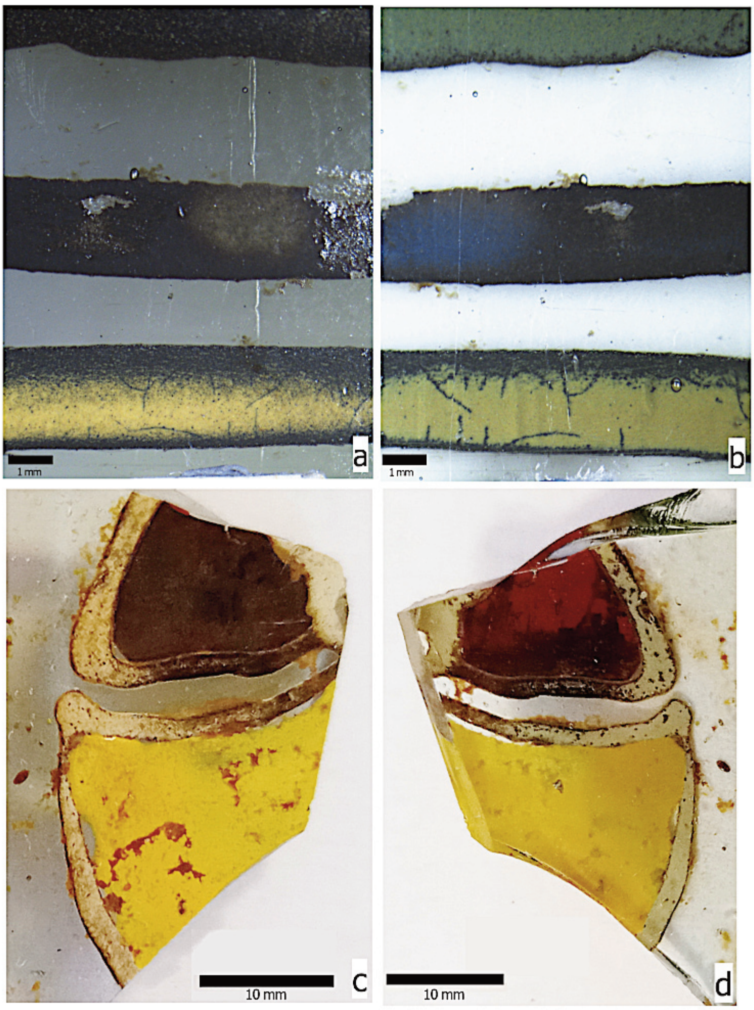


Fig. 10. Microscopic image of the top (a, c) and bottom (b, d) side of a glass fragment from Wrocław (St. Catherine (św. Katarzyny)–St. Vit (św. Wita) Streets, inv. no. 5503/17 (a, b) and St. Nicolaus (św. Mikołaja) Street, inv. No. 56/97 (c,d), photo by B. Miazga.

microscopic image of the decoration showed a colour change not only of the blue and green decoration but also a partial darkening of the yellow band. Comparison of the XRF and EDS spectra (Fig. 11: a, b) shows that when we study the yellow area of decoration, very strong signals of lead, antimony, tin and iron are obtained and much weaker signals of other elements (manganese, copper). However, the appearance of a dark deposit on the yellow decoration results in change of the elements' content; the content of iron and sulphur may be significantly higher (sulphur is two times and iron is about 1.5 times more). The phosphorus level has not been established for this glass fragment. The studied glass fragment was also analysed in the areas of blue and green decorations, visible in Fig. 10. Study of the discolouration of the blue band indicated that it contained the elements that usually create blue enamel paints (Henderson 2000, 30–34; Roldán et al. 2006; Pollard & Heron 2008, 162–163). Apart from lead and tin, iron, cobalt, copper and arsenic were identified in the XRF examination (Fig. 11: c). The EDS analysis confirmed this result and additionally indicated the presence of significant amount of sulphur (Fig. 11: d). For the uncleaned blue paint, the level of sulphur expressed as SO_3 was 20%, and after cleaning the band fragment, it was two times smaller. The iron content has thus also decreased, but significantly less by about one-fifth. Cleaning the band improved the ability to measure cobalt, the level of which increased significantly (even two times considering the results of the semi-quantitative XRF and EDS analysis). However, cleaning did not change the determination of arsenic.

At the inspection of the green decoration on this fragment of the glass revealed the use of an interesting material. Green enamel paint, as shown by XRF examination, contains both copper (directly responsible for the green colour) and a small amount of a mixture of cobalt and antimony compounds, i.e. blue and yellow carriers. The copper content, determined in the XRF examination, is about 0.3–0.4%, similar to that of cobalt, while antimony is about 3% (Fig. 11: e–h). In green paint, lead and tin, as well as iron and arsenic, which are carriers of pigments, were also recognised. This indicates the use of two sources of green colour in the enamel in question. This is consistent with literature reports dealing with the subject of green paint composition (Hahn et al. 2009; Holakooei 2013; Hložek & Trojek 2015). In turn, when considering the change from green to practically black, differences in the content of iron and sulphur were observed, which are respectively two times and three times higher in the black parts of the once green painting. The sulphur level is above 20% SO_3, and in a slightly cleaned place, it drops to about 7% SO_3; for iron, the FeO level was about 6%, and when green was exposed, the content was about 3.5% FeO.

While studying the phenomenon of changes on brown or red colours, the situation becomes much more complicated. The reason is the very chemical composition of such paints and the presence of iron compounds. Therefore, it becomes more difficult to describe the qualitative and quantitative reasons for the darkening of these paintings, as capturing the original iron level is not easy without significant interference and the risk of destroying these paintings during its preparation by mechanical cleaning. The analysis of brown decorations on the described glass from

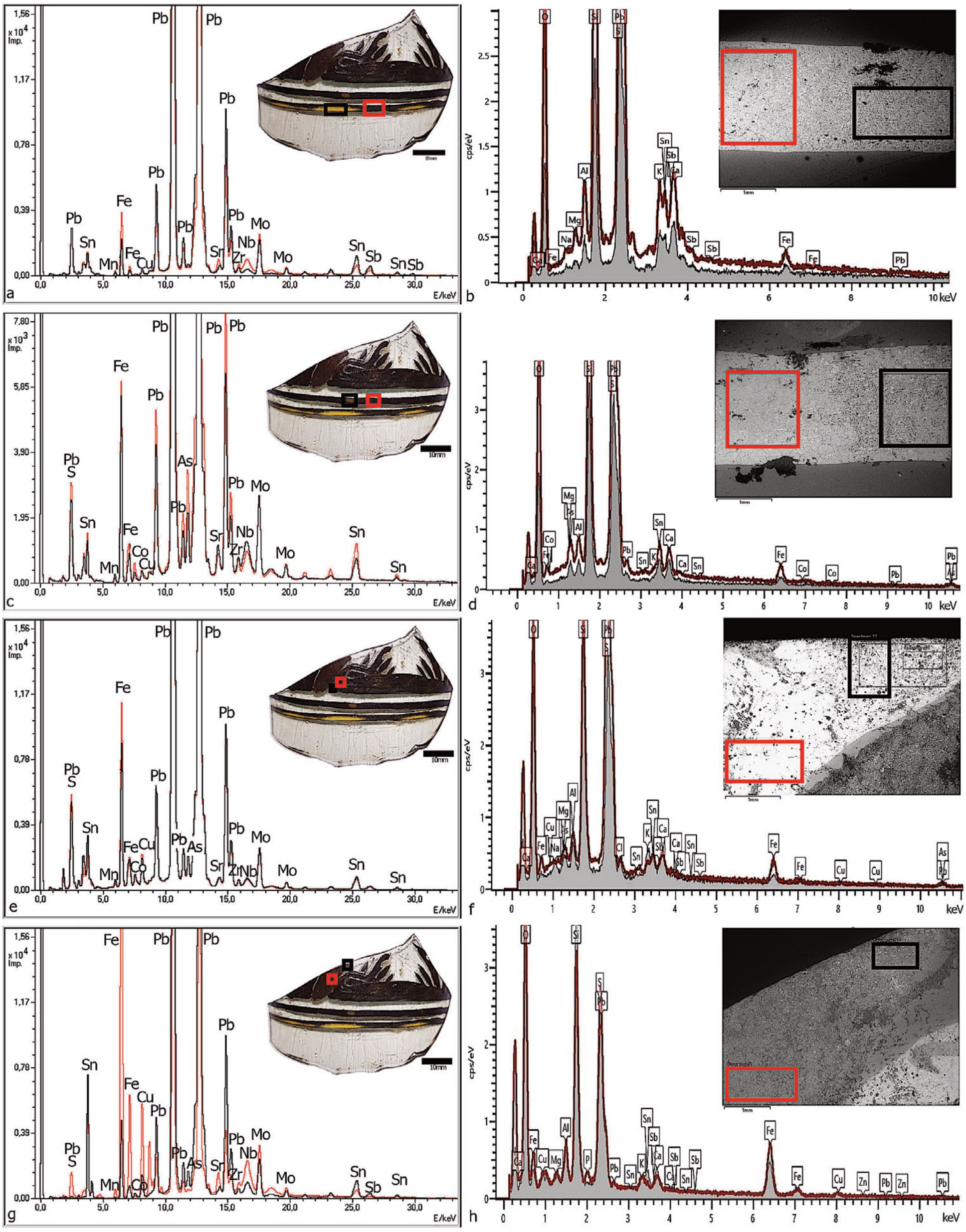


Fig. 11. XRF (a, c, e, g) and EDS spectra (b, d, f, h) for fragment of yellow decoration (a, b); blue (c, d); green (e, f) and brown (g, h) on a glass rim (St. Catherine (św. Katarzyny)–St. Vit (św. Wita) Streets, inv. no. 5503/17). Red line marks the results of examination of uncleaned places, black line marks the original colour of decorations, edited by B. Miazga.

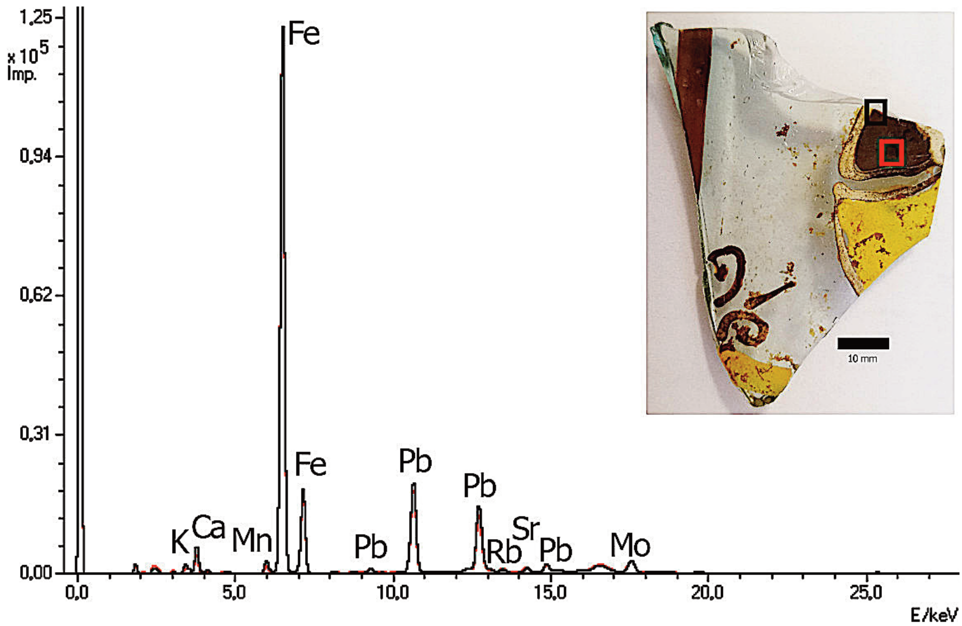
Wrocław showed that the surface study of the brown area gave information about a very high content of silicon, iron, sulphur and lead (25% SiO_2, 22% FeO, SO_3 and 15% PbO, respectively) with a much lower proportion of aluminium, copper, zinc, calcium, phosphorus, magnesium and potassium (Fig. 11: g, h). Cleaning this decoration results in changes of mutual proportions of its components, increasing the proportion of silica, lead and tin at the expense of a decrease in sulphur and iron levels. After abrasion operations, the level of FeO and SO_3 was 14%. Due to the possibility of destroying the decorations, no further cleaning activities were carried out, establishing iron and sulphur as responsible for the significant blackening of the original brown painting on the glass. The study concerning red colours will be discussed for another fragment of the glass vessel from St. Nicolaus (św. Mikołaja) Street (inv. no. 56/97). Also in this case, the microscopic analysis showed that the red colour hides under the brown of the floral decoration (Fig. 10: c–d). The spectroscopic confirmation of this hypothesis however, was not easy. In the XRF analysis, almost the same spectral image was obtained for both cleaned and uncleaned decorations (Fig. 12: a). The use of SEM-EDS as a tool giving greater possibilities of sample enlargement and more precise selection of the study areas gave slightly better results (Fig. 12: b). The analysis of the elements' signals indicates the presence of glass-forming components in the decoration (such as Si, K, Ca), but also slight differences in the intensity of the signals of iron, sulphur and phosphorus can be observed.

Simultaneously with the SEM-EDS studies of the decorations, unpainted glass near the ornaments was analysed. The analysis produced over one hundred results. The obtained data indicated that most of it had significant amounts of calcium oxide, potassium oxide and sometimes lead oxide (from a few to several weight per cent, see Table 1). It also contains relatively low impurity levels of magnesia (MgO),

Table 1. SEM-EDS analyses (in wt% of oxides) of glass raw material for selected fragments of decorated items excavated on St. Nicolaus (św. Mikołaja) Street

Sample (inv. no.)		SiO_2	Na_2O	CaO	K_2O	MgO	Al_2O_3	FeO	MnO	PbO	As_2O_3
336/99	1	57.0	0.4	8.8	7.5	2.9	1.4	–	–	21.9	–
	2	62.4	1.4	14.0	7.0	2.5	1.0	1.7	–	9.9	–
	3	18.3	2.9	12.1	1.1	0.7	1.1	3.1	–	59.8	0.9
	4	63.4	0.7	19.3	12.9	2.8	0.8	–	–	0.1	–
	5	83.7	0.8	5.8	1.5	1.4	5.5	–	–	1.4	–
	6	76.4	–	–	10.9	1.8	6.9	–	1.8	–	2.2
	7	63.9	1.3	21.2	9.4	2.8	1.3	0.1	–	–	–
	8	63.0	1.4	19.3	9.1	2.2	1.8	0.5	1.7	0.5	0.5
	9	38.7	4.2	38.4	2.2	3.7	6.9	–	–	–	5.9
	10	55.5	1.0	24.5	12.2	1.9	1.8	–	–	2.6	0.5
	11	65.0	0.8	10.9	11.2	3.3	1.4	3.1	3.2	1.0	–
335/99	1	76.6	1.0	4.8	5.4	2.0	1.9	1.9	4.3	2.0	–

(a)



(b)

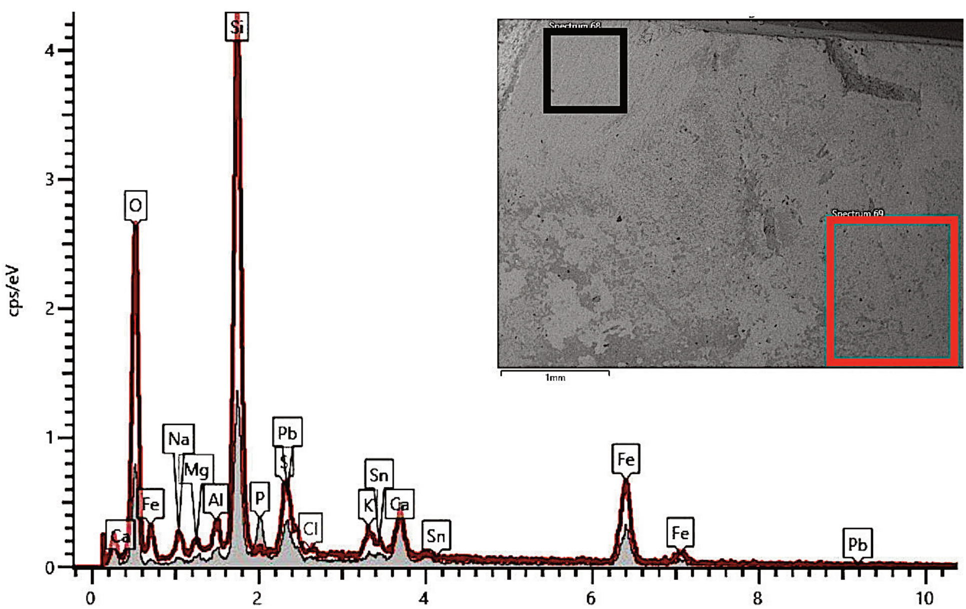


Fig. 12. XRF (a) and EDS (b) spectra for fragment of red decoration on a glass rim (St. Nicolaus (św. Mikołaja) Street, inv. no. 56/97). Red line marks the test results of examination of uncleaned places, black line marks the original colour of decorations, edited by B. Miazga.

aluminia (Al_2O_3), iron oxide or manganese oxide. This suggests that most of the painted glasses from Wrocław were probably a local product rather than an import.

Conclusions

Archaeological glass constitutes a considerable analytical challenge, not only in terms of the significant degree of corrosion of the research material, but also due to the numerous deposits of mineral substances which, while depositing on the glass surface and decorations, make archaeometric studies much more difficult. Various mineral compounds present in the soil adsorb to the glass and enamel paints used to decorate a vessel, which can cause permanent colour changes in painted decorations. This can be observed in case of enamels of different colours, both thermally fixated and resin paints. On the former, due to the glassy surface and chemical composition of the enamel paint, the colour does not always change radically. An example of such paints is yellow enamels containing lead pyroantimonate, which only sometimes darken (Fig. 11: a). Most often their colours remain unchanged, as shown on the fragments of vessels presented in Figs 5: a, b, 7: a, 10: a, b or 12: a. Decorations of other colours are not as resistant to colour change, and often browning or blackening is observed. Non-destructive chemical analysis shows that such changes are caused by a variable content of several elements, including an increased concentration of iron and, most often, sulphur. In some samples of dark decorations, an increase in the intensity of phosphorus and chlorine signals was also observed. After their point, gentle cleaning (mechanical abrasive action), a decrease in the content of these elements is noted. Analysing collected spectroscopic data for several dozen samples, it can be proposed that the significant darkening of painting decorations on glass products is caused not only by iron-containing substances, but also by sulphur, phosphorus and chlorine. The increased presence of iron and its compounds in these decorations is not surprising due to the fact that this element is widespread in the environment and the fact that it is the fifth element in the order of its occurrence in the Earth's crust (Bielański 1976, 590). Considering its high chemical activity, it is not surprising that its compounds are contaminants of glass vessels which were deposited in soil layers for several hundred years. Phosphorus and chlorine, in turn, are directly related to human activity, and it is obvious that for glass obtained from cesspits, as well as marketplaces, the level of P or Cl is not low (Majorek 2017, 193; Kittel & Tołoczko 2019, 69–73). When studying technological issues related to painting decorations on glass artefacts, it is worth conducting integrated microscopic analyses and the chemical composition examination. The results of these studies are very often complementary, and the initially conducted microscopic study in visible light allows for formulating hypotheses considering the possible colour of the decoration. However, without physicochemical studies, it is impossible to confirm/exclude the proposed colour of painting. A particular difficulty is the fact that the paints used to decorate glass vessels rarely have a simple chemical composition, and most often they are mixtures of various substances, and iron compounds as a common mineral pigment are popular enamel components.

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Beata Miazga

MIS ON PEIDUS SILEESIA KLAASI MUSTA JA PRUUNI VÄRVI ALL? WROCŁAWI HILISKESKAEGSETE JA VARAUUSAEGSETE KLAASILEIDUDE MAALITUD KAUNISTUSTE ARHEOMEETRILISE UURIMISE PROBLEEMIDEST

Resümee

Nii arheoloogilistel väljakaevamistel leitud kui ka teiste säilinud vanade klaasesemete uurimine annab mineviku kohta suure hulga olulist infot. Valdkonnad, mida käsitletakse, on klaasitöös kasutatud tehnoloogia areng ja nõuvormide ning nõude kaunistuselementide populaarsus. Keskaegsete ja varauusaegsete klaasesemete põhjal saab samuti välja tuua nõude mitmekesisust. Sel perioodil on klaas sedavõrd tavaline, et neid ei kasutata pelgalt mõisate ja jõukamate majapidamiste sisustuses, vaid neid leidub ka linnakodanike varaloendites, sh ka Sileesias. Lihtsakujuliste klaasnõude kõrval muutuvad üha arvukamaks ka kaunistatud klaasesemed. Selleaegsete klaasnõude mitmekesised kaunistused on valmistatud erinevat toorainet ja mitmeid tehnoloogilisi lahendusi kasutades, mille esinemine on seotud klaasesemete kronoloogiaga. Klaasnõud võivad olla kaunistatud sama või eri värvi aplikatsioonidega, millest keskajal olid levinumad klaasniit, erikujulised nupud, tilgad jne. Samuti kasutati mitmeid kaunistusvõtteid, mis ulatuvad teemantgraveeringust kuni sisselõigete ja pinna poleerimiseni. Maalingud kuuluvad hilisemate kaunistusviiside hulka, mida ajaliselt võib enamasti seostada varauusajaga (16.–17. saj). Klaasimaalingu ülesanne polnud üksnes valmistoodangu kaunistamine, vaid ka klaasis olevate vigade, peaasjalikult palja silmaga nähtavate õhumullide varjamine. Seepärast kaunistab maaling sageli suurt osa klaastoote pinnast, nt on joogiklaasid tihti maalitud peaaegu servast servani.

Käesoleva sajandi esimestel kümnenditel Wrocławis toimunud väljakaevamistel tuli päevavalgele märkimisväärne hulk maalitud klaasnõusid. Neist mõned olid kaetud mitmevärvilise maalinguga, teiste puhul oli värvivalik tagasihoidlikum ning koosnes peamiselt pruunidest ja mustadest toonidest. Viimaseid otsustati lähemalt uurida, et selgitada, mis on sellise olukorra põhjus. Selleks valiti mittelõhkuvad või klaasi minimaalselt kahjustavad arheomeetrilise analüüsi meetodid. Esmalt uuriti esemeid valgusmikroskoobiga, mis on üks klaasesemete uurimise standardsetest meetoditest. Järgnesid spektroskoopilised uuringud, milleks kasutati röntgenfluorestsents-spektromeetrit ja energiadispersiivset spektromeetrit koos skaneeriva elektronmikroskoobiga. Uuringutulemused lubasid maalingute värvimuutuste osas

määrata polükroomsete emailvärvide koostist sõltumata sellest, kas algsed värvid olid silmaga näha. Tulemuseni võisid viia nii makroskoopilised kui ka mikroskoopilised vaatlused või ainult keemilised analüüsid. Selgus, et rohelise, sinise, valge, punase ja pruuni värvi muutumist põhjustab nende oluline saastumine mineraalsete ainetega, eelkõige raua ja väävliga. Raua ja selle ühendite suurem esinemine kaunistustes ei ole üllatav, sest seda elementi leidub keskkonnas palju ning on leviku poolest maakoores viiendal kohal. Arvestades, et raua keemiline aktiivsus on kõrge, on mõistetav, et rauaühendid põhjustavad klaasnõude värvikihtide saastumist, sest uuritud klaasnõud on pinnasekihtides olnud aastasadu. Fosfor ja kloor on seevastu otseselt inimtegevuse tulemusel tekkivad elemendid ning seetõttu leidub neid enam klaasnõudel, mis pärinevad jäätmekastidest, aga ka nt turuplatsidelt. Uuringu tulemusel õnnestus ka selgitada, et kasutatud värv ei pea alati oluliselt teisenema. Näiteks kollane email säilib enamasti muutumatuna. Klaasnõudel asuvate maalingute tehnoloogiliste küsimuste uurimisel tasub kasutada üheskoos nii mikroskoobiuuringuid kui ka keemilise koostise uuringuid, sest tulemused täiendavad sageli teineteist ja esmalt valgusmikroskoobi abil tehtu võimaldab püstitada hüpoteese kaunistuse algse värvi kohta. Ilma füüsikalis-keemiliste uuringuteta pole siiski võimalik kinnitada või välistada hüpoteetiliselt pakutud värvi tegelikku olemasolu. Enim raskusi põhjustab asjaolu, et klaasi kaunistamisel kasutatud värvained on enamasti keeruka koostisega ja sisaldavad paljusid mineraalaineid, sealhulgas ka mitmeid rauaühendeid.