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A study of eighteenth century glass vessels from central Europe by x-ray fluorescence analysis

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Radioisotope x-ray fluorescence (XRF) analysis was employed in provenance and technological studies of luxury colourless glass vessels originating from 18th century glasshouses in central Europe. The results refer to Polish, Brandenburg and Saxon glassware. A number of discriminating elements were selected and certain correlations between some of these elements, characteristic for the specific recipes and glasshouses, were found. The content of lead in crystal glass is discussed, and also that of some trace elements constituting characteristic contamination of raw materials. Multivariate statistical analysis, such as cluster and principal component analysis, allowed the grouping of the examined vessels. Certain limitations of energy-dispersive XRF for the analysis of historical glass vessels are also presented.

INTRODUCTION

Glass history has already acquired a considerable place in the field of the history of art. Recognizing technological aspects of glass constitutes a very valuable complement to stylistic, iconographic and archival studies of both artistic and utilitarian glass artefacts. The determination of chemical composition plays an important role in this process.

Physico-chemical studies of historical glass vessels should be conducted with the use of completely non-destructive and non-sampling methods which do not deface the examined objects in any way.[1] Methods that need sampling, including those that require very minute samples which have been developed in recent years,[2] are not widely applied to the examination of valuable and well preserved glass vessels in museum displays. Moreover, in the case of an examination of a single sample, the question remains of how representative this sample is with respect to the whole of the investigated object.[3]

X-ray fluorescence (XRF) phenomena have been used in various analytical techniques that are well established in studies of historical glass.[1,4–9] Numerous specific aspects of XRF and microprobe analysis of historical glass have been reported.[10–12] However, there have been only a few studies dealing with the non-destructive examination of historical glass vessels by the use of XRF analysis.[13,14]

Here, by the use of radioisotope excited XRF, we attempted to find, among numerous chemical constituents of glass, features that would be characteristic or specific for different Central European glass centres of the 18th century and for the glass objects that were manufactured at that time. We hoped to find these features among data on the concentrations of trace and minor elements. It was assumed that these elements could be characteristic of specific recipes and of specific contamination of raw materials from different sources. The results presented concern 227 objects manufactured in Saxony (Dresden), Brandenburg (Potsdam, Zechlin) and the Polish–Lithuanian Commonwealth (mostly in Naliboki and Urzecze, plus a limited group originating from Lubaczów) in the 18th century. Some of them possess unquestioned attributes that were taken as a basis for the grouping of the remaining items. The examined collection contained mostly engraved colourless glassware, mainly goblets with and without covers, flutes, beakers and other types of vessels. This paper presents the results of the characterization of the glass composition and the attribution of the objects, with special emphasis on the possibility of distinguishing 'crystal glass objects', that previously has only been outlined in preliminary reports[15,16] [the term 'crystal glass' has been used mainly for lead crystal glass; another meaning covers also other historical high-quality glass, e.g. non-leaded 'Bohemian crystal' (potash–lime glass)].

EXPERIMENTAL

Energy-dispersive x-ray fluorescence (EDXRF) analysis was used. X-ray spectra were collected using an 80 mm^2 Si(Li) detector (EG&G ORTEC) with 180 eV resolution for Mn Kα. The ^{109}Cd radioisotope annular source ($\sim$200 MBq) was applied to excite the elements in glass. The live-time of the measurements was 1000 s. The spectra were collected by a multi-channel analyser and computed using the Analysis of X-ray Spectra by Interactive

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Least-squares Fitting (AXIL) software.[17] The examined vessels were placed directly at the source shield with the help of a movable tabletop with a central hole for the detector. The whole measurement layout has been shown in a preliminary report.[15] The area of glass analysed was ~ 2 cm^2.

To correct for differences in matrix absorption and for measurement geometry, the coherently and incoherently scattered peaks were taken into account. The following equation was used:[18]

$$S_{ij} = \frac{N_{ij}}{N_{j(\mathrm{coh})} + N_{j(\mathrm{incoh})}} \quad (1)$$

where N_{ij} denotes the intensity of x-rays characteristic of element i and for an object j and $N_{j(\mathrm{coh})}$ and $N_{j(\mathrm{incoh})}$ denote the intensities of coherently and incoherently scattered peaks for an object j, respectively. The results obtained for S_{ij} were used as a basis for chemical classification and for further comparative studies.

For the results discussed in this work, 12 primary variables were taken into account, namely the intensities of the Kα lines of K, Ca, Mn, Fe, Cu, Zn, As, Rb, Zr, Sr and Y and the Lα line of Pb. No quantitative chemical analysis was carried out. Only PbO contents were determined. The evaluation of results was done using STATISTICA software.

The glass surfaces for EDXRF analysis were carefully selected in order to have a surface that is flat and free from any kind of scratches, roughness and glass decoration (engraving, enamels, etc.). Some objects were examined several times in several places on their surfaces under slightly different measurement geometries. The results obtained, with the application Eqn (1), showed of good reproducibility. Before the analyses, the vessels without crizzling (a specific kind of corrosion) were locally washed using 50% ethanol. Crizzled glasses were analysed without any washing procedures.

Since the glass surface layers were not removed, the depth of EDXRF analysis had to be taken into account during the interpretation of the results. For the described layout (^{109}Cd source) and for the simplified formula of glass (70% SiO_2, 20% K_2O, 10% CaO), the depth of potassium analysis, for instance, is about 80 μm. With a PbO concentration of 5%, the depth of potassium analysis decreases to about 65 μm. On the other hand, for some heavier elements, if the Kα lines are taken into account, the thickness of the glass must also be considered; this concerns Rb, Sr, Zr and Y. This problem could arise in a only few cases, and we did not observe any significant aberrations of the results.

RESULTS AND DISCUSSION

Continental crystal glass in the 18th century contains lead as one of the constituents intentionally introduced into the glass batch. However, lead, in smaller amounts, could also be introduced into other types of glass batches. Therefore, in order to distinguish crystal glass, a knowledge of the concentrations and ratios of some other elements is helpful.[15] This is connected with different and more purified raw materials rather than those applied to the manufacture of more ordinary vessels.

Figure 1 shows a double scatter plot, where Y is placed on the horizontal axis, Rb on the left vertical axis and Pb on the right vertical axis. For each glass that is characterized by Y concentration on the horizontal axis, there are two points. The first (black circles) is concerned with the scatter plot for Y against Rb and the second (open squares) with the scatter plot for Y against Pb. All elements concentrations are expressed in arbitrary units. We can simultaneously follow the Rb and Pb variations as the Y concentration increases in the examined glass vessels. In Fig. 1, points are shown for all examined vessels, irrespective of their glass composition. At first sight, several groups can be seen. The first, on the left side of the scatter plot, is situated between lines S and Z, without points on the left vertical axis. The lack of Pb or the presence of only trace amounts of Pb and the positive linear correlation between Y and Rb are characteristic for the group. It consists only of vessels not made of crystal glass (these are mainly so-called 'ordinary' or 'white' glasses). On the left vertical axis, the second group

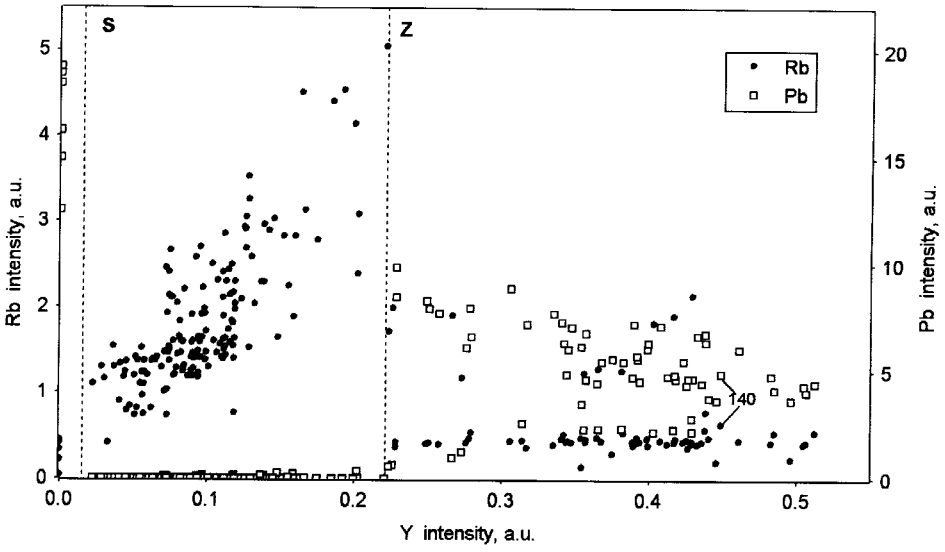

Figure 1. Double scatter plot of Y against Rb and Pb.

of points refer only to Saxon crystal glass. These are characterized by high a Pb content with a total absence of Y and a low level of Rb. On the right side of line Z we can distinguish two groups of vessels. One shows a negative linear correlation between Y and Pb and a low and stable level of Rb. In this group there are 10 vessels with higher Rb and lower Pb concentration with no correlation between Y and Pb or between Y and Rb. These 10 vessels belong to the intermediate collection and refer to the third main type of glass composition manufactured during that time in this part of central Europe. However, the group is too small and seems not to be homogeneous enough for any definitive conclusions.[16] It must be stressed that the vessels in this group may also contain lead introduced intentionally. Nevertheless, the composition and the raw materials used are different from those applied for crystal glass.

Figure 2 presents the same scatter plot as Fig. 1, showing the same points but with the 10 vessels of the intermediate group removed. A positive correlation between Y and Rb for objects not made of crystal glass on the left side of the plot and a negative correlation between Y and Pb for all crystal glass items are evident. It can also be seen that the Rb content in all crystal glass batches is almost constant. It is also interesting that, in contrast to vessels in Fig. 1 between lines S and Z, all the remaining items (and also those of the intermediate group) show blue fluorescence under short-wave ultraviolet radiation.[15]

The results obtained allowed us to define some features characteristic of glass recipes and in certain cases also of the glass production centres.

Crystal glass compositions

These compositions are characterized by a high concentration of Pb and As (Fig. 3). However, an equally high As content was also found in a few vessels not made of crystal glass. What follows is that the As content is not a specific feature of crystal glass composition. Both lead and arsenic were introduced into glass batches independently, with different raw materials. Therefore, the correlation between them is of a technological nature. On the other hand, the crystal glass objects are well defined on a scatter plot for Ca and As (Fig. 4). This feature (Ca/As ratio) is also of a technological nature. The vessels with these recipes also exhibit a positive correlation between Ca and Sr (Fig. 5), which probably represents contamination of raw material. Other features characteristic of this kind of object are a negative correlation between Y and Pb that still needs to be explained and also a low and stable level of Rb (Fig. 2).

There is a possibility of distinguishing between vessels from different glass centres among these crystal glass objects, as can be seen, for example, on the scatter plots for Pb and Ca (Fig. 6), for Ca and As (Fig. 4), for Zr and Fe and for Mn and Fe.

The Saxon crystal glass exhibits an absolute absence of Y, the highest contents of Pb, As and Ca and a low concentration of Zr. The Brandenburg crystal glass is characterized by the highest Zr concentration and the lowest contents of Ca, Sr and Fe. The Naliboki (Polish) crystal glass shows higher Ca and similar Pb contents compared with the Brandenburg glass and higher Zr and Mn contents and a similar level of Fe compared with the Saxon glass.

The crystal glass objects from these three centres can also be distinguished on a scatter plot for Ca–K (Fig. 7), but this requires a more comprehensive explanation. Some of the examined vessels show on their surfaces a specific kind of corrosion, crizzling, that is characteristic of so-called 'unstable glass.' For EDXRF, the concentrations of light elements obtained by surface measurements have lower values than those for the bulk of the glass. This is due to both the depth of EDXRF measurements and the corrosion phenomena. In the case of a crizzled surface the depletion of K is much greater than that for a non-crizzled surface and has an edge nature when observed as an alkali profile on the cross-section of the glass. Therefore, the EDXRF analysis of crizzled glass exhibits a much smaller value of K content. In Fig. 7, all crizzled vessels are marked by arrows. We can move them to the right side, towards the higher K concentrations, and then three areas of crystal glass objects, that correspond to three glass centres, are revealed. Moreover, a crystal glass composition is generally characterized by a lower

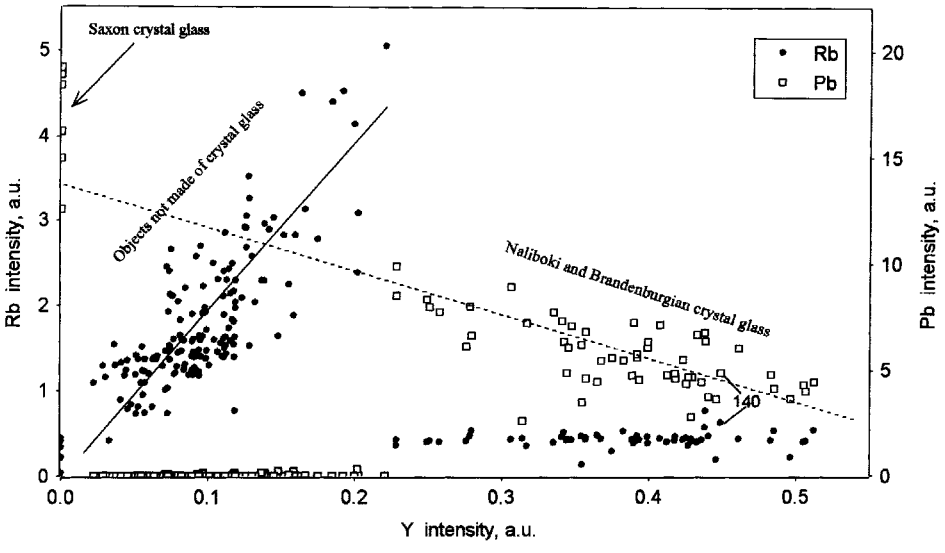

Figure 2. Double scatter plot of Y against Rb and Pb, as in Fig. 1 but after removal of 10 vessels of the intermediate group.

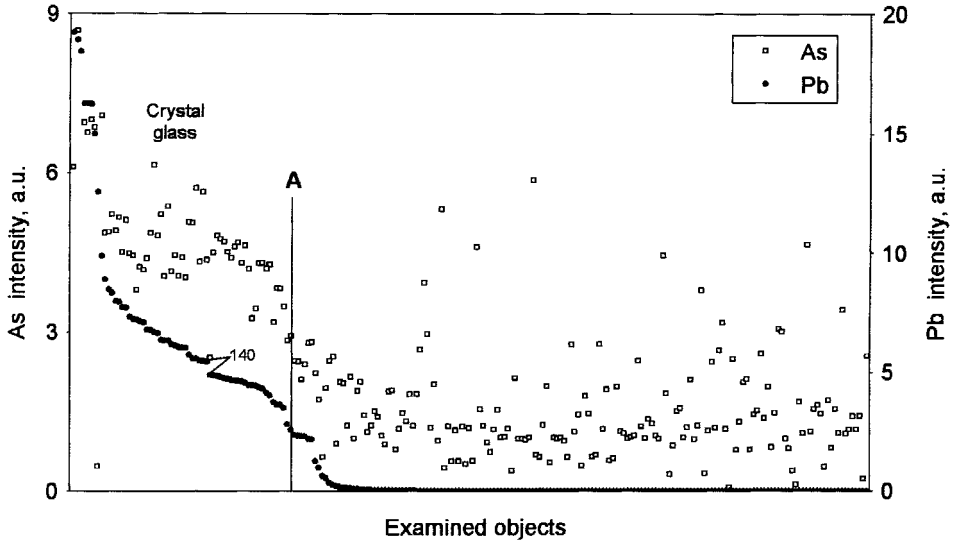

Figure 3. Double dots diagram for Pb and As. The vessels are placed on the horizontal axis in order from the item of highest Pb content on the left side. Line A divides items between vessels made of crystal glass on the left side (with one exception, No. 140) and remaining ones on the right side.

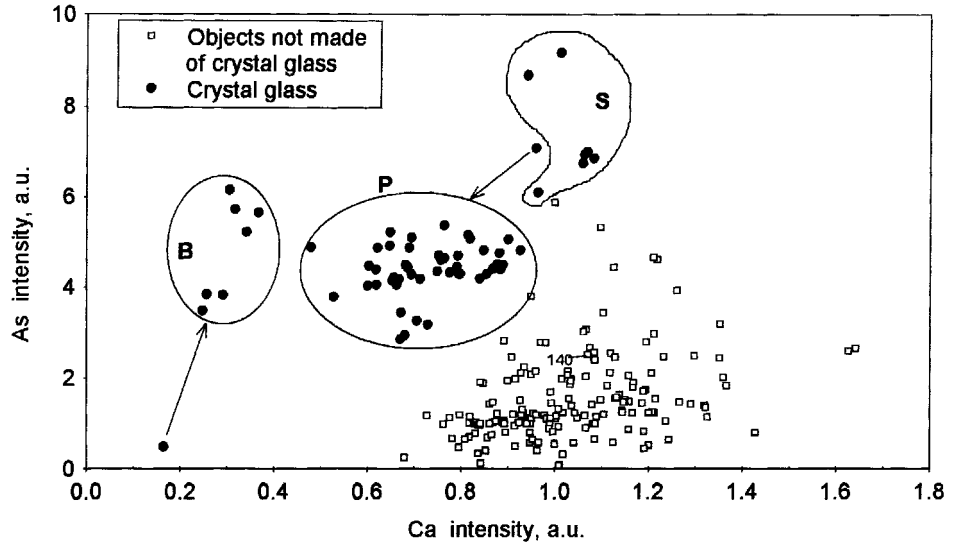

Figure 4. Scatter plot of Ca and As. S-Dresden (Saxon); B-Potsdam/Zechlin (Brandenburg); P-Naliboki (Polish).

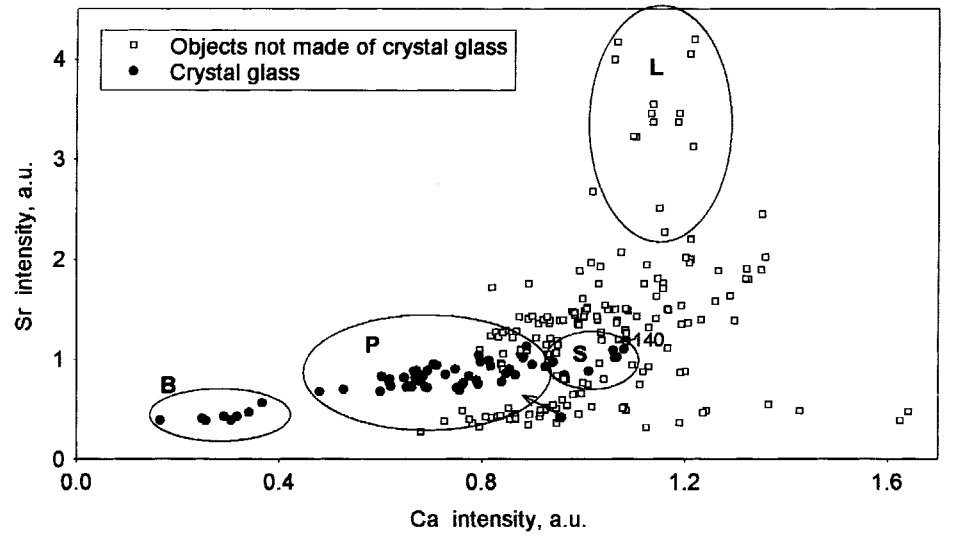

Figure 5. Scatter plot of Ca and Sr. S, Dresden (Saxony); B, Potsdam/Zechlin (Brandenburg); P, Naliboki (Polish); L, Lubaczów (Polish).

Ca/K ratio in comparison with other compositions. This may be one of the possible explanations of the crizzling phenomenon. In the present work we found crizzled items only among vessels of crystal glass composition.

Remaining glass objects (not made of crystal glass)

It must be stressed that only Polish and Saxon vessels with these recipes were examined. All examined vessels from Brandenburg appeared to be crystal glass, as shown by the EDXRF results. Before the measurements it was impossible to distinguish the vessels with these different recipes.

The examined vessels not made of crystal glass were characterized by a lower Pb content or even by the absence of Pb. Those with no Pb also exhibit a positive correlation between Y and Rb (Figs 1 and 2) and between Zr and Fe. These features are most likely connected with the contamination of raw materials. The positive correlation between Mn and Fe is a result of using manganese as a decolorizer. Among these objects, Lubaczów vessels could be distinguished on the basis of Zr–Rb–Sr–Y concentrations,[15] but a high Sr content alone is also very characteristic of them (Fig. 5). It is also possible to distinguish the vessels of the intermediate group (Figs 1 and 2).

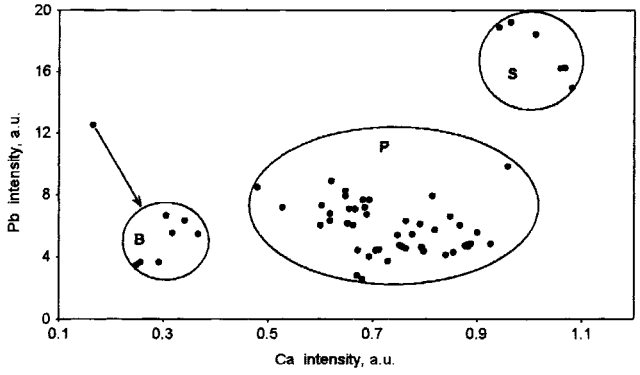

Figure 6. Scatter plot of Ca and Pb for crystal glass objects. S, Dresden (Saxony); B, Potsdam/Zechlin (Brandenburg); P, Naliboki (Polish).

Multivariate analysis

Cluster analysis was applied to all the examined Saxon, Brandenburg and Polish vessels (Fig. 8). Ten variables were taken into account. Results concerning K and Zn were eliminated, K because of the above-described crizzling phenomenon and Zn because of the possibility of detecting surface contamination of some vessels by traces of white zinc that was sometimes used for lettering and labelling of museum objects. Even a very accurate cleaning process of the historical glass surface may not be able to remove these traces. During this project, such cases were actually found. Cluster analysis gave interesting results and good agreement with data obtained by the use of other methods. First, all vessels were divided into two main groups: crystal and non-crystal glass objects. Moreover, crystal glass vessels from different centres are linked in groups. Objects not made of crystal glass were divided into two further groups. These are connected with, among others, the Ca/Sr ratio. It seems to be one of the more important features of differentiation and can be used for further interpretation process (see also Fig. 5). On the left branch (Fig. 8), are situated among others, all Naliboki vessels of unquestioned attribution and the vessels of intermediate groups (with only one exception). These glass vessels have similar Ca/Sr ratios. The remaining objects are placed on the right branch of a 'non-crystal' vessel system and, among them, Lubaczów vessels can be seen. The Ca/Sr ratio for the glass from this branch is either lower or higher than that for the left branch. It should be also stressed that in several cases cluster analysis allowed us to characterize table services and it was possible to establish the vessels that were made of glass from different batches.

Principal component analysis, conducted for all the objects placed on the left side of line A in Fig. 3, i.e. for all the items of higher Pb content, gave very interesting results (Fig. 9). The same 10 variables were taken into account. On a scatter plot of the first and second principal components, that have over 72% of cumulative variability, three groups of crystal glass objects were separated and also one vessel, marked 140, which does

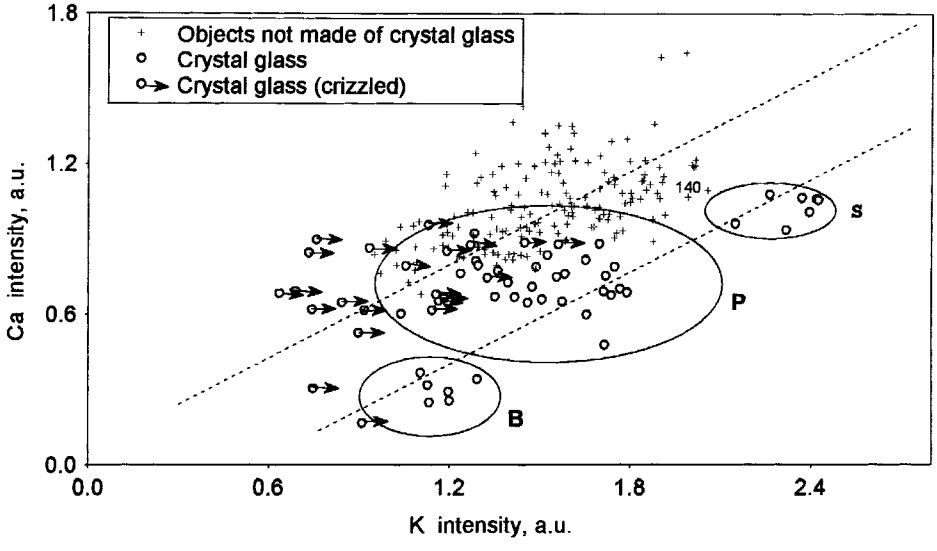

Figure 7. Scatter plot of K and Ca. S, Dresden (Saxony); B, Potsdam/Zechlin (Brandenburg); P, Naliboki (Polish).

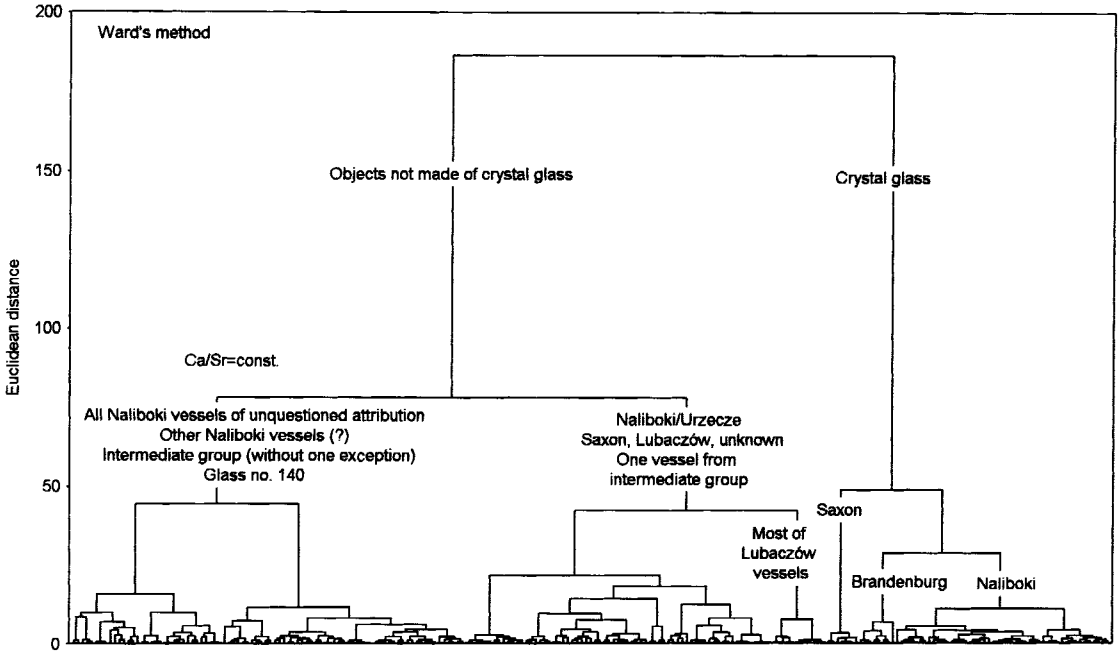

Figure 8. Cluster analysis: dendrogram for vessels of all glass compositions and glass centres.

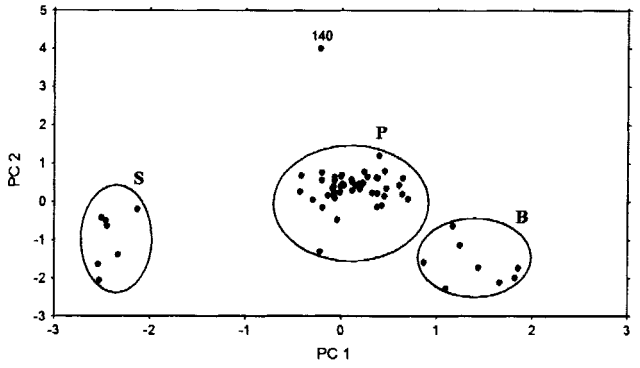

Figure 9. Scatter plot of PC1 and PC2 for the vessels containing significant amounts of lead (that are placed on the left side of line A in Fig. 3). Objects made of crystal glass: S, Dresden (Saxony); B, Potsdam/Zechlin (Brandenburg); P, Naliboki (Polish). Item No. 140 is not made of crystal glass.

not belong to the class of items made of crystal glass. It was possible to differentiate this vessel, in spite of its significant Pb content. This piece constitutes the eleventh vessel belonging to the aforementioned intermediate group (see the vessel marked in Figs 1–5, 7 and 8).

On the basis of this EDXRF study, following the unquestioned attribution of certain glass examples examined, it was possible either to confirm or to change the previous attribution of several vessels. Additional information concerning the glass composition seems to be a new and very valuable feature, helpful in glass attribution studies that, until now, has very rarely been taken into account.

CONCLUSIONS

One of the most important conclusions drawn from the reported results is that provenance studies of historical glass vessels represent a much more complicated task than it appeared at the beginning of the project. Both differences in the chemical compositions of glass made in numerous glass centres and differences between different glass batches possibly manufactured in one place at the same time must be taken into account. Glass vessels from different places made from similar batches by the use of similar or the same raw materials, often imported from one source, in several cases can reveal more similarities of their chemical compositions than glass vessels made in one glasshouse by the use of different recipes. It must be stressed that in most cases differentiating luxury vessels made from different glass batches is impossible without using very sophisticated analytical techniques such as EDXRF.

The EDXRF technique seems to be a very valuable, non-destructive tool for the examination of colourless historical glass vessels. It permits the examination of large numbers of objects from museum collections without moving them to the laboratory. The method as described here allowed us to differentiate of 18th century central European glass vessels and to discriminate several glass compositions. The objects made of crystal glass from different factories could be distinguished from each other, and also some other objects, e.g. manufactured in the Lubaczów glasshouse.

Many variables have been found (element concentrations and ratios between them) that could be essential for the confirmation of the attribution process of 18th century glass vessels from central Europe. Characteristic and specific features for each examined glass composition and for most of glass centres were defined. The results obtained indicate that the knowledge of the PbO content is not sufficient to differentiate the applied recipes. Lead could also be added to the batches of non-crystal glass (see the example of the examined glass No. 140), but often in such small amounts that no technological explanation could be given other than, for example, it was a result of habits or a technological experiment. It could also enter the glass with badly sorted cullet.

Cluster and principal component analysis allowed us to differentiate glass vessels from different centres made of different kinds of glass. It was also possible to find items that constituted exceptions. On the other hand, it has to be stressed that grouping by multivariate statistical analysis gave results the same as or very similar to those obtained on numerous scatter plots. Cluster analysis also gave good results in the study of table glass services.

During the interpretation of the EDXRF results obtained by the measurements through the outer leached layer, both the depth of XRF analysis for each element and corrosion processes (e.g. the depletion of several elements in corroded layers) have to be taken into account. This especially concerns crizzled surfaces, because in those cases the alkali depletion process is much stronger. Some difficulties may also arise when traces of removed outer paint layers (e.g. inventory numbers) remain on the glass surface. These limitations must always be taken into account during the interpretation of EDXRF results.

The amount of data collected within this project is large and many further aspects of these data are still being elaborated (e.g. Cu content and Ca/Sr ratio). In the future, it would also be interesting to study the concentrations of Ba, Sb and the yttrium earths in the discussed vessels.

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