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Of time and shapes: Compositional variation in post-medieval glass from the Netherlands

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ABSTRACT

The compositional variation in a reference collection of glass tableware and bottles from the Netherlands, spanning the period 1500 – 1900 AD was analyzed using hand-held XRF. Variations in the alkalis are reflected in the relationships between CaO, K_2O, Rb and Sr.

Timelines show major changes in glass composition c.1680. This time period saw the introduction of transparent lead glass and the start of a trend towards cleaner raw materials, mostly for tableware. It also saw the separate emergence of (green) bottle glass, characterized by high contents of Fe_2O_3.

KEYWORDS

Alkali, bottles, hand-held XRF, post medieval glass, tableware, The Netherlands.

Introduction

Glass commonly occurs in post-medieval urban archaeological sites. Cess pits from several cities in the Netherlands have yielded a range of glass objects. Based on such finds, a clearly defined typo-chronological sequence is available. Such a sequence, however, does not provide much information on the raw materials used and how they varied through time.

Raw materials and techniques for the production of glass are known to have changed several times since c.1500 AD. In the UK, there are clear chronological changes in the composition of window glass (Jones 2011; Dungworth 2011, 2012a), bottles (Dungworth 2012b in press) and crystal glass drinking vessels (Dungworth and Brain 2009). The study of raw materials provides insight into production methods, provenance and the use of glass products. These are important aspects of the study on trade connections, artisanal production and the cultural influence of glass during the post mediaeval period.

We investigated to what extent changes in the elemental composition of glass could be detected in glass objects from the Netherlands. We analyzed c.300 glass objects that form the basis of the glass National Reference Collection (NRC). They originate from four different cities in the Netherlands (Nijmegen, Tiel, Dordrecht, Deventer) and range in age from the 15th to the 19th century (Bartels & Kottman 1999). Dating is based on typology and considered accurate to within 15 / 80 years. The objects are mainly bottles and various types of drinking glasses, but some other types of objects (e.g. salt dishes) are also present. Fig. 1 illustrates some of the object types that are included in this collection.

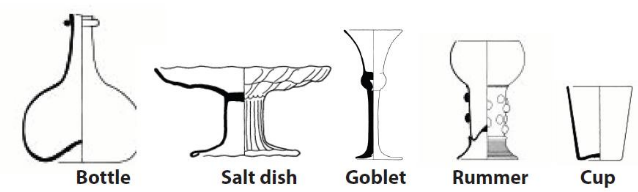

Fig. 1. Examples of the types of objects that were analysed.

Methods

Since destructive analyses were not allowed, which is often the case with museum and other collections, the chemical composition of the glass objects was determined using a Niton hand-held XRF Xlt 3 equipped with a large area silicon drift detector. The lightest element that can be analyzed with this ED-XRF is Mg. It is therefore not possible to determine the sodium concentration. Concentrations are calculated from peak intensities by the built-in fundamental parameters program. In addition, external linear calibration factors were determined by analyzing several geological samples and one glass standard (BAM S005 B). The resulting dataset contains 662 analyses. Since measurements were done on potentially leached surfaces, values for K_2O and, to a lesser extent, CaO and MgO may be affected by leaching. Other elements, including Rb and Sr, are probably less affected (Dungworth 2012a).

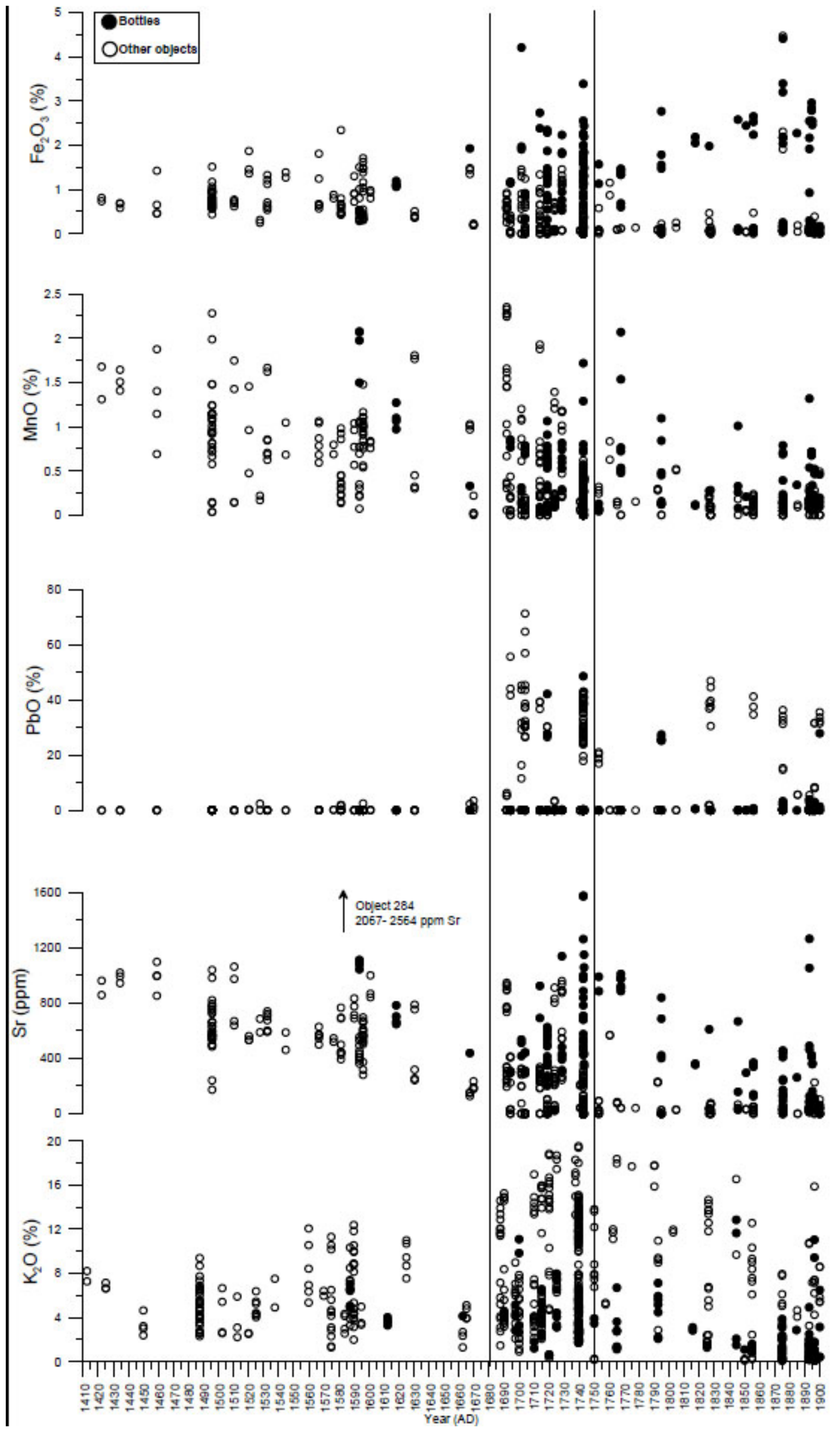

Fig. 2. Diagrams showing composition of the analyzed objects through time for selected elements. Bottles are indicated separately. Dates are +/- 40 years or better.

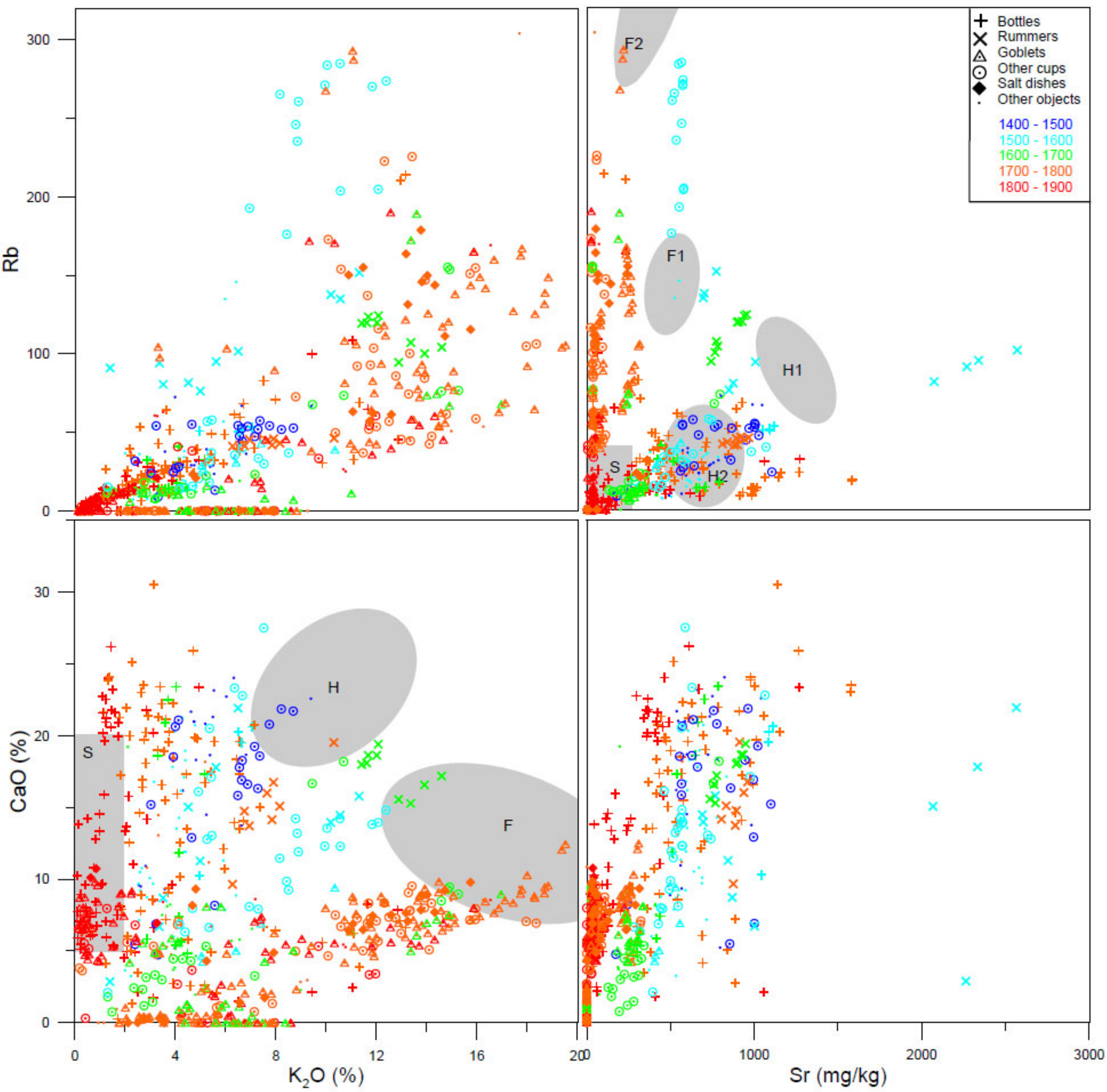

Fig. 3. Scatterplot of Ca, K_2O, Rb and Sr. Lead glass is left out. Colour indicates age, symbol refers to the type of object. Grey blocks mark compositional groups identified by Dungworth (2012a) for English window glass; H = High Lime Low Alkali (HLLA), F = forest glass, S = glass made with synthetic soda.

Results and discussion

Changes through time

The plots in fig. 2 show how some key elements changed through time:

The content of Fe_2O_3 is fairly constant before 1680, but shows higher values and more variation after that. Moreover, after 1680 bottle glass becomes distinctively richer in Fe than the rest. In later periods, especially after 1750, this distinction becomes more prominent because the Fe_2O_3 content in other glass types drops, whereas it seems to increase in bottles. An explanation for this difference is that bottles that were used as containers for wine, beer, etc. and needed to have a dark colour in order to enhance the preservation of the contents. Tableware on the other hand, was, in general, expected to be transparent and colourless. The lower Fe_2O_3-contents of non-bottle glass after c.1750 may indicate a switch to a cleaner sand source that made production of colourless glass easier. A drop in the contents of the MnO decolourizer around the same time corroborates this. Low contents of MnO in bottle glass demonstrates that no attempt was made to decolorize these objects.

The introduction of lead glass, the invention of which is usually dated 1674 (Dungworth and Brain 2009), results in a sudden occurrence of high lead values after 1680.

Sr contents, an alkali earth Ca substituent, seem to show a steady decline from 1500 to c.1680 AD. After that, bottles show increased Sr contents that are maintained until the end of the time series. Tableware shows a continuing decline. The higher Sr contents in bottle glass may be attributed to Sr that is associated with iron oxides (cf. Huisman et al. 1997), or the use of a different lime component (shells or other carbonates versus woodash). The decline of Sr contents in tableware mirrors the trend in English bottle glass (Dungworth 2012b) and may be attributed to the selection of cleaner raw materials in order to produce clearer glass.

Potassium (K_2O) contents show more variation and have the highest values after c.1680, but not in bottle glass.

Variations in alkali and lime

Changes in alkali and lime for glass production is apparent from the time plots in fig. 2, especially from the trends in Sr and K_2O. More information can be gleaned from scatter plots of components that are associated with these raw materials. Fig. 3 combines scatter plots of CaO, K_2O, Rb and Sr for all objects except lead glass. Age is indicated by colour and the type of object with a choice of symbol. Grey areas indicate groups identified by Dungworth (2012) in a dataset of British window glass. From the complex looking fig. 3 it can be learned that:

The Rb-K_2O scatter plot shows a more or less consistent positive correlation between the two elements. Different potential sources for potassium (e.g. several types of ash, potash and silicate minerals) are likely to have different Rb/K_2O ratios which will be reflected in the glass. Groups of 16th century cups and some of the 18th and 19th century objects show higher Rb/K_2O ratios than the rest. Overall, it seems that the source of K_2O in which Rb occurs as an impurity has not changed significantly.

The Sr-CaO scatterplot, however, shows some systematic changes in its composition. As mentioned earlier, Sr can substitute for Ca in glass. Sr/Ca ratios are likely to differ between the various potential sources of Ca, which include shells, limestone and the various types of ash used in glass manufacture. In general, there is a trend of decreasing Sr/CaO ratios, with absolute Sr contents approaching zero in the majority of the 18th and 19th century material. However, a subgroup consisting of 18th century rummer cups and 18th/19th century bottles does not show such a trend.

The K_2O-CaO scatter plot shows distinct groups with different K_2O-CaO ratios. Following the window glass groups defined by Dungworth (2012a), we can identify some of the groups:

- A large part of group of 18th/19th century low Sr/CaO forms a group of high K_2O - low CaO, approaching the forest glass group (F) of Dungworth (2012a). This group consists almost exclusively of drinking vessels and a tight group of salt dishes. Their lower K_2O/CaO ratio may indicate the use of potash instead of plant ash.
- Most 18th/19th century bottles fall in or close to Dungworth's range of low-K_2O glasses, probably made using synthetic soda.
- The rest of the dataset seems to contain many groups that are difficult to separate. Each group seems to have a specific K_2O/CaO ratio. The overall picture is that of a fan shaped group, which in general would fall into the High-Lime, Low-Alkali (HLLA) group of Dungworth (2012).

However, the match with Dungworth´s groups is not very good. Our Rb-Sr plot clearly shows a fan like pattern formed by separated groups with distinct Rb/Sr ratios. Comparison with the Rb/Sr groups of Dungworth shows hardly any matches. Only his synthetic soda-based glass matches some of our 19th century objects. The other groups (two different types of forest glass, and two different types of HLLA glass) only partly overlap.

The problematic match of the Dutch glass composition with the English glass of Dungworth (2012a) may be explained by stronger leaching during burial in the Dutch glass. Unexpectedly, the Rb-Sr plot indicates a worse match between the British window glass and our dataset. This is surprising since Rb and Sr are less sensitive to leaching. Another explanation may be that differences existed between the production methods for window glass and tableware. It is more likely that the glass industries in the UK and the Low Countries, were using different raw materials or recipes. More research is needed to resolve this issue.

Conclusions

Analyses of the composition of a group of representative Dutch glass bottles and tableware from the 15th to the 19th

century shows clear trends in time, type and place. Major changes in glass composition occurred c.1680 – 1750. This included the introduction of lead glass and the use of purified raw materials (mainly sand) in tableware. From this time, bottle glass seems to have been made with different raw materials to the other glass types and remains a separate compositional group until the 19th century.

Through time, the system CaO - K_2O -Sr - Rb is highly variable, representing variations in alkalis and calcium sources used as raw material. However, more research is needed to elucidate these variations and to identify, delineate and compare compositional groups.

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