

MODERN ANALYTICAL METHODS FOR HISTORICAL GLASS ARTEFACTS ANALYSIS

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Abstract

Antique glasses can be generally found as one of the architectural components in several heritage places from Europe and not only. Glassmaking has been as industrial activity for more than four thousand years. The medieval stained glass constitute a part of our cultural heritage that has been exposed to environmental damage over centuries. The main purpose of this paper is to provide new insights into the composition and deterioration sources of stained glass. To analyse the ancient glass, have been used small pieces of broken glass without any possibility to be included in other pieces. Different coloured glass (brown, green, uncoloured) were quantitatively analysed by EDXRF. Assuming that each kind of glass can be characterized by a specific composition of major, minor and trace elements, the selection of appropriate analytical methods is essential. In this work, ICP-AES was used complementary to EDXRF which gives an overall view of the samples' composition. By applying ICP-AES, it was possible to determine a number of elements which are present below the detection limit of EDXRF and to evaluate the homogeneity of investigated material. It was possible to determine new elements which could not be determined by others techniques.

Key words: ancient glass, EDXRF, ICP-AES

1.Introduction

There have been significant and impressive new advances in instrumentation over the past decade that allow for more sophisticated analyses of artefacts than ever before. The best choice of instrumentation is only part of the equation. It is necessary to decide what information is needed, then choose the right method, and then correctly interpret the information. In many cases more than one method is used on an ingot or coin to arrive at a correct interpretation. Throwing an ingot or coin into an analytical instrument and expecting a print-out to confirm authenticity is not likely to be successful. The "black box" approach doesn't work.

Data interpretation is every bit as important as the performance of the tasks themselves. Technical instruments demand a thorough understanding of their procedures in order to deliver quality data. In this regard, a researcher should consider using analysts that are trained in the fields under consideration, particularly persons who perform these tasks daily.

Glassmaking is an industrial activity for more than four thousand years. Glass is made up of few components: network formers, network modifiers and coloring elements. The main network former of medieval of medieval stained glass is silica, whose concentration determines the physical and chemical behaviour and the glass stability. The network modifiers, flux being one of them, can decrease the temperature at which the mixture melts (silica) and is made up of alkaline elements. After some reports, in medieval times, a flux was introduced into the mixture as vegetal ash. Also, as

network modifiers, too, the stabilizers (lime, magnezia) make the glass strong and more water resistant. Phosphorus is a common component of medieval glass and can act as a network former. Also, some metals (Cu, Co, Mn, Fe) were used for glass colouring.

The process for glass production in northwestern Europe in the period 800–1700 AD was based on melting a siliceous constituent (e.g., quartz sand, crushed quartz pebbles) with a fluxing agent (e.g., potassium- or sodium- rich vegetable ashes) while sometimes an additional calcium-rich material (such as limestone, seashells [1] or marble) was used. In a number of cases, also a lead source and small amounts of colorant, opacifier or decolorant materials were added to the melt. Fig. 1 provides an overview of the most important periods in the history of glassmaking in northwestern Europe. In the Antique to the post-Roman period, glass was made with Natron as fluxing agent, a mixture of NaHCO_3 , Na_2CO_3 and other Na-salts, found in Wadi Natrun (Egypt). This resulted in a durable Na-rich glass which could be worked into a variety of shapes. In view of its relatively low Fe content, it could easily be rendered colorless by addition of oxidizing products such as MnO_2 or Sb_2O_5 [2,3]. After the breakdown of the Roman Empire and roughly until 1000 AD, knowledge on glass making was no longer available in northwestern Europe while also some of the raw materials were no longer available. During the wood and plant ash period (800–1800 AD), the dominant fusing agent for glassmaking in northwestern Europe was ashes from wood and terrestrial plants. With this agent, a calco-potassic glass (having SiO_2 , K_2O and CaO as major constituents) was made. According to Wedepohl [4], in Germany, within the wood and plant ash period, a subperiod between 1000 and 1400 AD can be distinguished where glass was made from sand and wood ash and a second period between 1400 and 1800 where glass was made with sand, wood ash and lime. The first glass type is known as potassic glass, the second as calcic glass. Both glass types have a typical greenish-yellow color and are collectively known as forest glass or Waldglas. Wood ash is calcium- and magnesium-rich, but potassium-poor. In the northern half of France, wood ash was also used for the production of potassic and calcic glass, but additionally fern ash was used for the production of potassic glass. Ferns contain significant quantities of potassium and much less calcium and magnesium. The production of sodic glass (having Na_2O , SiO_2 and CaO as major constituents, similar to modern soda-lime glass) in northwestern Europe started with the arrival of Italian glassmakers during the 16th century in the urban centres. They produced glass in the Venetian style with locally available raw materials [5]. This glass has a slightly different composition than the genuine Venetian glass, which was available in two varieties: (1) Vitrum Blanchum that was in use from the 14th century onward, and (2) Cristallo that was produced since around 1450 [6]. The most prominent feature of both these types is that they are colorless, transparent glass with a specific composition [6]; however, the more common Vitrum Blanchum was made with less pure raw materials than the top quality Cristallo.

The main purpose of this paper is to evaluate the composition and degradation cause (sources) of stained glass.

The analysed samples have been provided by Regional History Museum from Brasov and belong to XVII- XVIII centuries. They were broken small pieces not useful and without any possibility to be included into other large pieces. For analysis has been used energy dispersed X-ray fluorescence (EDXRF).

2. Experimental part

2.1. Aparatus and methods

X-ray fluorescence analysis was performed with an energy dispersive instrument, type Minipal, with a Si(Li)-detector of 150 eV resolution at 5.89 keV (Mn-Ka-line). An Rh-tube with an acceleration voltage of 30 kV was used for excitation. Due to varying surface structures and inhomogeneities in the surface composition of the samples analysis was performed on both sides of the objects and a mean

value was calculated. The area of X-ray irradiation had a circular shape with a diameter of approximately 10mm.

An energy dispersive X-ray fluorescence (EDXRF) spectrometer EDXRF PW4025 – MiniPal – Panalytical, has been used for all the measurements [7-12].

Inductively Couple Plasma Atomic Emission Mass Spectrometry (ICP-AES) was used for major elements and some trace elements. Detection limit for major elements is 0.01%. The analytical precision calculated from replicate analysis of one sample is better than $\pm 1\%$. A Varian Liberty 110 Series spectrometer was used for the ICP-AES analysis. Multielement, matrix matched standards were used for the quantitative determinations.

Microwave assisted digestions were performed in a Berghof microwave oven with the use of high-pressure closed Teflon PFA vessels and online pressure and temperature control. In particular, 0,1g of each sample was placed in the Teflon PFA digestion vessels and a mixture of 5 ml HF 40 % and 5 ml HNO₃ 69.5 % was added.

2.2. Archaeological materials

For analysis we must take into account some restrictions:

- Reduced number of availability samples;
- High alkali content;
- Significant presence of certain volatile elements (chlorine from the vegetal ash used as raw material);
- The presence of some elements (metals) used as colouring agents can be useful not only for the color determination, but also as potential weathering agents.



3. Results and discussion

- After potassium or sodium concentration, the glass can be divided into few categories:
- Glass produced between 12th and 15th century which is a potassic in composition (SiO₂, CaO and K₂O);
- Sodium composition (SiO₂, CaO and Na₂O);
- Carbonated glass (SiO₂, CaO and sodium carbonate (Na₂CO₃)).

A chemical composition of glass is an important source of information about the provenance of a single object and it can also support knowledge about technological history of glassmaking obtained from historical documents from archives and libraries.

Elemental analysis plays an important role in the scientific classification of archaeological samples. In this field, nondestructive analysis is preferable because samples are invaluable and not allowed to be damaged. The term "nondestructive" commonly used in chemical analysis is, however, often not acceptable in archaeology since the sample should be generally powdered due to the limitation of the sample size to be analyzed. Although there are some special analytical methods such as X-ray fluorescence analysis and particle induced X-ray emission analysis that can be applied for elemental analysis of large samples, they fundamentally give information only about the surface of the sample.

A chemical composition of glass is an important source of information about the provenance of a single object and it can also support knowledge about technological history of glassmaking obtained from the technical literature and other historical documents available in archives and libraries [1–6; 13–15]. The elemental analysis of glass is also investigated in order to distinguish originals from forgeries and to support conservation with respect to understanding corrosion phenomena and degradation of archaeological glass [15–19]. Although the knowledge about the elemental composition of glass does not provide sufficient information for a full characterisation of an examined glass object it is often used for this purpose. Also, the chemical composition is reputed to be relatively easy for examination and interpretation. Depending on the concentration and accompanying minor or trace constituents, certain group of elements (e.g. Si, Ca, Na, K, Pb, Mn, As, B and Sb) usually reflects main composition of raw materials used for the glass production together with the information about the methods of the preparation and sources of raw materials. Various elements and their concentration levels are often recognised to be specific for particular periods, areas, and technological traditions. Therefore, when these elements are found in the object, it can be stated that the glass examined fits into the already known glass group. In some cases, we have to create new subgroups or describe glass as a single object that does not fit to any of the already well known groups. Usually a combination of several analytical techniques is needed for collecting complete information about major, minor and trace elements of the sample [1, 20, and 21]. The preferences are made to these analytical techniques, which allow fast analysis on a routine basis, because revealing relations between chemical composition of historical glass and its provenance demands collecting large databases of compositions of well described samples. Due to historical and very often also high material value of investigated objects preferences to non-destructive methods are given [21].

Among various analytical techniques ICP-AES seems to be a good choice for glass analysis: the method offers very low detection limits for the most of elements, together with isotopic information and possibility to inspect a distribution of analysed elements over the investigated area [22–25]. Several non-destructive methods like: synchrotron radiation X-ray fluorescence (SRXRF), neutron activation analysis (NAA) or particle induced X-ray emission (PIXE) allows achievement of similar detection limits for many elements, but ICP-AES is much more accessible than the others.

Therefore homogeneity of analyzed samples can be evaluated on the basis of the obtained results. This method has already been applied for glass analysis. Micro-destructiveness is a big advantage of this method for historical objects analysis and allows limiting sample consumption to the absolute minimum [14].

Assuming that each kind of glass can be characterized by a specific composition of major, minor and trace elements, the selection of appropriate analytical methods is essential. In this work, ICP-AES was used complementary to EDXRF which gives an overall view of the samples' composition.

All results were recalculated into the concentration (wt.%) of respective oxides (Na_2O , CaO , SiO_2 , K_2O , Al_2O_3 , MnO , MgO , As_2O_3 , Fe_2O_3 , BaO , PbO) and the results are presented in Table 1.

Sample color	Brown	Green	White
Na ₂ O	3	5.2	5.4
MgO	0.8	1.6	1.6
Al ₂ O ₃	3.8	6	3.5
SiO ₂	69.4	72.3	59.1
P ₂ O ₅	9.12	0.56	0.93
SO ₃	1	0.71	0.2
Cl	1.73	1.95	2.7
K ₂ O	2.15	0.47	10.5
CaO	7.37	10.4	12.8
MnO	1	0.028	0.563
Fe ₂ O ₃	0.708	0.579	0.816
CuO	-	-	0.035
PbO	-	-	1.8
TiO ₂	0.12	0.11	0.12
ZnO	0.03	-	-

Table 1. Chemical composition of medieval glass by EDXRF

In Europe, numerous investigations of the 17th and 18th century glasshouses and glass waste have been achieved [13, 14].

The study on the chemistry of late 16th century and early 17th century green container glass, similar to the materials in this study, documents the wide use of high-calcium glasses (CaO 17.9-28.5%) during this period [15].

Analysis of the major and minor oxides indicated a high concentration of calcium as a result of manufacturing preferences that used wood ash as a component in the glass recipe. Due to the potash (which could contains small amounts of Fe₂O₃, the glass could exhibit a pale green colour, or yellow-green colour, such glass being known as Waldglass (forest glass) [16].

In addition to lead compounds and wood ash (potassium carbonate) (potash), two common ingredients like potassium tartrate (HOOC-CHOH-CHOH-COO-K⁺), Salpetre (KNO₃), sea salt (NaCl) and borax (Na₂B₄O₇·10H₂O) were used.

The presence of phosphorus oxide indicated the use of wood ash (including from bone ash). This composition is typical for the glass production in Western Europe from the tenth to seventeenth century [17]. The presence of German glass makers from the centre of Europe in the Transylvanian manufacturies could explains the types of models and techniques from the Transylvanian manufacturies.

The exact amount of alkali would be difficult to determine precisely during glass manufacture, since the concentration of alkali within the ash varies between, and even within, tree species [18].

Consequently, the final chemistry of a glass will vary in oxide proportions and will effect its interaction with water.

Sample color	Brown	Green	White
Ag	14.4	4.6	4.85
Ti	2032.77	665.21	462.78
Pd	211.15	363.76	211.15
Zr	10636.96	4314.55	2189.27
Tl	231.19	3.09	60.27
Al	125819.13	23423.52	12776.03
Sr	2114.02	434.6	402.00
Ca	28938.4	30448.44	54332.28
Ba	10117.96	6321.9	6084.12
Si	2195281.78	591180.23	745005.26
Mn	2638.27	78.4	3617.25
Fe	8716.91	2385.49	3232.39
Cr	33.08	367.6	
Mg	2782.44	6119.51	8889.59
Na	114809.96	41979.12	31819.14
Sn	31.26	16.51	343.95
Zn	312.58	34.21	181.18
Cu	92.31	23.65	58.03
Li	233.29	21.3	10.07
Re	263.17	1187.69	287.07
K	3361.73	5307.31	3563.62
P	9686.76		6343.85

Table 2. Chemical composition of medieval glass by ICP-AES (in mg/kg)

The Na-rich glasses typically show greater silica content (around 60% ranging from approximatively 55-65%) [19]. Cu, homogeneously added to white glass can produce a pale green color. The glass body contains several elements such as Pb, Si, Al, Na, Fe for yellow, Cu for dark green and Co for dark blue colors.

The most interesting aspect of the glass production is the CaO/MgO ratio, and the concentration of calcar, dolomite and magnezia, especially.

It is noticed that for transparent glass the concentration of K₂O is similar with CaO, his being a first proof for the venetian receipt of glass bleaching, by glass treating with MnO, being known as Manganesi [20], this being one of the most superior glass type. After that period, the new type Kreyde-Kristallglas (chalk crystal) glass is almost everywhere in the glass manufacturing. Also, are used: salpêtre (KNO₃), braunstein (manganese minereum), and salt (sodium sulphate) in order to clarify and bleach the glass melting.

The leaching experiments are extremely interesting. The K₂O-CaO-SiO₂ glasses are preferentially leached out over calcium. As calcium increased above 10%, uniform leaching of the oxide components was observed. When the glass is exposed to the atmosphere over long time period (1-6 years) revealed that potassium is preferentially leached out over calcium by as much as 10%. This is attributed to the higher bond strength of the bivalent calcium ion to the non-bridging oxygen sites in the glass. It is evident that under different conditions, sodium and potassium are more mobile than calcium and are depleted preferentially to calcium [21].

The ratio of major oxides concentrations: Na₂O/SiO₂ and CaO/SiO₂ characterizing matrix composition of the glasses have been calculated and compared with average values of Na₂O/SiO₂ and CaO/SiO₂ in the investigated samples. The information about respective oxides concentrations in the historical glass samples was obtained by means of SEM and EDS.

4. Conclusions

To analyse the ancient glass, we have used small pieces of broken glass without any possibility to be included in other pieces. Different coloured glass (brown, green, uncoloured) were quantitatively analysed by EDXRF.

Assuming that each kind of glass can be characterized by a specific composition of major, minor and trace elements, the selection of appropriate analytical methods is essential. In this work, ICP-AES was used complementary to EDXRF which gives an overall view of the samples' composition. By applying ICP-AES, it was possible to determine a number of elements which are present below the detection limit of EDXRF and to evaluate the homogeneity of investigated material.

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