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APPLICATIONS OF X-RAY MICROANALYSIS TO THE STUDY AND CONSERVATION OF ANCIENT GLASSES

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Abstract

X-ray microanalysis can be successfully applied to the study of the chemical composition and weathering processes of ancient glass. The problems concerned with this kind of application are considered. A verification is conducted of the accuracy and sensitivity of this technique, which are sufficient to obtain useful information on technologies and raw materials used and consequently on the origin and dating of ancient glasses.

This analytical method also discloses meaningful data for the optimization of restoration and the choice of appropriate conservation operations.

Introduction

The investigations of the history and technology of glassmaking and of the chemical composition of ancient glasses carried out by several authors (2, 10, 20) have shed considerable light on these topics and sufficient information is available at least about certain manufacturing centers and historical periods.

We can say that the great majority of the glass produced in early times up to the end of the Middle Ages was obtained by melting together only two or three natural raw materials, namely a siliceous constituent, a fluxing agent and sometimes one or more colorant (or decolorant) elements. The siliceous constituent was feldspathic or quartz sand, or quartz pebbles reduced to a finely ground powder suitable for melting. The fluxing agent was natural soda like natron coming from salt lakes in Egypt, or vegetable ashes whose main component was sodium carbonate (coastal plant ash) or potassium carbonate (inland plant ash). A number of minerals were used for coloring and decoloring, mainly manganese, iron, copper and cobalt. Other additives such as antimony, tin, lead, boron, etc. were also used for particular applications (for instance, the opacification of glass, ceramic glazings, etc.); their use was known only in certain periods and manufacturing places.

The raw materials used by early glassmakers were natural ones, of relatively low purity; therefore, it should not come as a surprise that glasses obtained by melting together only two or three components will actually contain more than twenty different elements. Because of the complex composition of ancient glasses, chemical analysis of glass remains can give abundant meaningful information from both the historical and the archaeological point of view.

For instance, the composition of a glass will allow identification of its age, if a compositional classification has been previously established with a significant number of well-authenticated glasses

KEY WORDS: X-ray microanalysis, ancient glass, restoration, conservation, dating.

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made in certain manufacturing centers or during certain historical periods (4,11,15,18). Similarly, chemical analysis will help the expert to discover spurious pieces or copies of ancient glasses produced in later centuries.

The restoration departments of museums will use chemical analyses of the glasses and their weathered layers to choose the most appropriate restoration procedures and conservation conditions (3).

However, the analytical procedure to determine the composition of ancient glasses is rather complicated, in that a large number of elements must be analysed, most of which are trace elements. Beside insufficient knowledge of glassmaking and the lack of preliminary qualitative analyses, such difficulty is one of the reasons why many scientific publications give incomplete compositions restricted to the analysis of major components, neglecting other elements whose determination may often be decisive to the correct authentication of the glasses.

Other problems in the analysis of ancient glasses are caused by the weathering products which often cover them; these are of entirely different composition and therefore need to be analysed separately (1), or in cases in which the glass is associated with other materials, for instance ceramic glazings, cullet pieces, etc.

A last and most important problem is the need for non-destructive analysis of valuable glasses; since this is not feasible at present, a technique that requires only microscopic samples is of utmost interest.

The impossibility of giving an adequate solution to these problems by conventional chemical analysis spurred in the past two decades the study and application of other analytical techniques, such as X-ray microanalysis; though considered in the early sixties only a qualitative complement to chemical analysis (5), this technique allows the above problems to be effectively solved today.

#### Sample Preparation and Analysis

Samples to be examined by X-ray microanalysis are usually cut from the glass object or fragment by means of a very thin diamond wheel and are prepared by the same procedures as minerals or metal samples. Since carbon is not a constituent of glass, a vacuum evaporate conductive film is applied on the sample surface. This film has the advantage of being very transparent to the X-rays emitted during the analysis and consequently the thickness of the carbon film is not critical. Therefore, the problems encountered in X-ray microanalysis applied to the study of ancient glass are very similar to those faced in studying modern industrial glass (9,19,22).

A first problem originates from the mobility peculiar to the sodium ion in the glass network, and to a lesser extent the potassium ions. Owing mainly to the heat produced by the electron beam, these elements gradually leave the region being analysed, thus inducing a decay in the X-ray emitted. This phenomenon is more remarkable in Wavelength Dispersive Spectroscopy (WDS), in which the beam current is much higher than in Energy Dispersive Spectroscopy (EDS), where this problem is practically negligible (12). For a WDS detector the decay of sodium  $K_{\alpha}$  characteristic X-ray is of 50% in 10 seconds with the operating conditions of 15 kV, 15 nA and an electron beam spot of about one micron diameter. The solutions proposed to this problem (6,8) suggest that during a counting time of 10-20 seconds the electron beam is kept scanning a surface of about one hundred square microns, that sodium is analysed as first element in the acquisition program and a glass is used as standard, so that the eventual modest decay of the counts will be similar in the sample and in the standard, without altering the results of the analysis.

A second problem concerns the analysis of weathered glass layers. Knowing the composition of these layers is essential to the understanding of the alteration mechanisms of the glass and to decide the most suitable restoration operations; indeed, the weathered layer may sometimes have a protective effect on the glass, whereas it must be completely removed in other cases in which it would facilitate spreading of the alteration. The weathered glass layers are not a homogeneous material but consist instead of discontinuous flakes of a substance similar to silica gel, with a density lower than that of the original glass. Because of the porous structure of the material, the coating film of carbon is insufficient to discharge all the electron beam current; the resulting charge accumulation causes a considerable, discontinuous variation of the absorbed current, so that only semi-quantitative determinations of the composition of weathered layers are usually feasible.

In order to verify the precision, accuracy and sensitivity limits of X-ray microanalysis with WDS detectors applied to ancient glasses, the analysis was performed on a fragment of a Venetian glass of the 16th century. This sample had been previously analysed by conventional methods, i.e., by solving the glass in hydrofluoric acid and subsequent determination of the composition by volumetric, colorimetric and atomic absorption techniques. The instrument used was a CAMEBAX microprobe produced in 1978 by CAMECA (France) equipped with two vertical and one inclined spectrometers (PET-TAP-LiF crystals); automation and data processing was ensured by an on-line Digital PDP 11 computer. The detectors were argon-CH<sub>4</sub> 10% gas flow-counters

adjusted to a fixed voltage (a compromise between the ideal voltage of the elements being analysed). A ZAF program of CAMECA was used for the correction for quantitative analysis. Glasses were used as standards, such as the reproductions of ancient glasses called B and D made by Corning, and glasses controlled by the chemical laboratory of the Stazione Sperimentale del Vetro and by other European glass laboratories. The analytical conditions were as follows: 15 kV, 15 nA and 10 sec. of counting time for the main elements and 20 kV, 60 nA and 10 sec. of counting time for the trace elements. The results for precision and accuracy are reported in Table 1. Among the factors affecting precision are the stability of the device used and the impossibility of adopting optimal analytical conditions for each element; a considerable improvement seems possible with more recent, microprocessor-controlled instruments. As concerns sensitivity, it was found to vary between a minimum detection limit of 100 ppm for cobalt and iron oxides, 200 ppm for manganese, copper and tin oxides up to 500-600 ppm for heavier oxides, i.e., barium and lead oxides.

TABLE 1

Chemical composition expressed in %wt oxides of a Venetian glass of the XVIth century, determined by conventional chemical analysis and by X-ray microprobe using a WDS detection system.

	chemical analysis	WDS analysis	
		average	deviation
SiO <sub>2</sub>	67.8	67.5	± 0.60
Al <sub>2</sub> O <sub>3</sub>	2.03	2.10	± 0.15
Na <sub>2</sub> O	12.35	12.5	± 0.30
K <sub>2</sub> O	2.50	2.50	± 0.15
CaO	10.10	10.0	± 0.20
MgO	3.30	3.20	± 0.15
Fe <sub>2</sub> O <sub>3</sub>	0.260	0.28	± 0.03
MnO	0.435	0.40	± 0.03
SO <sub>3</sub>	0.240	0.20	± 0.05
P <sub>2</sub> O <sub>5</sub>	0.260	0.25	± 0.03
Cl	0.80	0.80	± 0.05

By comparing these results, it can be concluded that the WDS X-ray microanalysis gives an accuracy very close to the one of the chemical methods, whereas its precision and sensitivity are lower. The results can be improved either by longer counting times or by increasing the number of the analyses performed on the same sample, which can

be easily done since the analysis time is of just a few minutes, or by increasing the electron beam energy. However, the results obtained up to now are sufficient to allow a good compositional classification of ancient glasses to be compiled, even neglecting the analysis of those elements whose concentration approximates their detection limits.

A similar investigation of microanalysis with the EDS system has not yet been published; a study carried out on silicate rocks (7) allows good results to be expected, though an experimental verification becomes necessary owing to the complexity of glass samples (over 20 elements to be analysed, many of which are trace elements).

The advantages and shortcomings of X-ray microanalysis as compared to conventional chemical methods for the study of ancient glasses can be exhaustively summarized as follows:

- a quick qualitative analysis of all the elements present in the glass can be carried out, which prevents omission of certain elements in the quantitative analysis, as is often observed in the analyses of ancient glasses published up to now;
- very small specimens can be analysed, so that samples can be taken even from valuable objects without inflicting significant damage;
- the analysed area measures only a few tens of square micrometers and so it is possible to analyse selectively the regions of interest. When the sample consists of different glasses (for instance, millefiori glass, milk glass threads on crystal glass, etc.), each glass can be analysed separately. Likewise, enamelled glasses, ceramic glazings, layers of glass mixed with refractory materials can all be analysed selectively. Moreover, weathered glass regions whose composition is different from the original glass can be excluded in the analysis;
- quantitative analysis takes a very short time as compared to conventional techniques.

The main limitations of X-ray microanalysis concern its low sensitivity to light elements such as lithium and boron, which may be present in ancient glasses (B<sub>2</sub>O<sub>3</sub> can be detected in glass to a concentration of about 2% with a WDS detector; values obtainable with a window-less EDS detector are not known); its low sensitivity appears to be insufficient for certain trace elements as well; last but not least, the cost of the instrument should not be overlooked.

Applications of Chemical Analysis

As mentioned above, chemical analysis of ancient glasses can be successfully applied to historical and archaeological studies, restoration

and dating of glass remains. It has also been observed that X-ray microanalysis can be a good substitute for conventional chemical analysis as a virtually non-destructive technique; moreover, it is the best technique available for other investigations such as:

- the analysis of composite glasses (millefiori, glasses decorated with enamels or opaque glass, etc.);
- the analysis of thin glass layers applied onto other materials (ceramics, refractory pots, etc.);
- the analysis of the glasses and their weathering products as a preparation to restoration (3,21).

An example in this last field concerns the analyses of medieval stained glass windows and a number of papers have been published reporting the use of X-ray microanalysis in these studies (14,16,17). Stained glass windows undergo several kinds of weathering such as surface corrosion and the consequent opacification, and the detachment of the grisaille. In the case of the 16th-century window of the Church of S.S. Giovanni e Paolo in Venice (14), two kinds of problems had to be solved before starting restoration:

- to understand why the 3-4% of the stained glasses were heavily corroded mainly at the outer surface, whereas the majority was in good condition;
- to establish the conditions of the original grisaille (the grisaille is a dark vitreous material based on iron oxide and low melting glass (silica, alkali and lead) which was used for shading, upward strokes, etc.).

The analysis with the X-ray microprobe of small specimens taken from corroded and non-corroded stained glasses gave the results shown in Table 2. It can be observed that all the panes showing corrosion were of potassium glass, a kind of glass probably imported in Venice from Germany (10), whereas all the panes without corrosion were of sodium glass, showing the typical composition of Venetian glass of that period. Apparently, in the case of sodium glasses the action of atmospheric agents favoured the formation of a protective layer of weathered glass (13), while in the case of potassium glasses the weathered layer decomposed progressively without protecting the glass below. In the case of the grisaille, which is not a homogeneous material (the vitreous phase bonds  $Fe_2O_3$  inclusions, sand, etc.), it was possible to concentrate the beam on the glass phase only and determine its average composition. Beside the average compositions of the grisaille and the glasses, Table 2 gives the theoretical thermal expansion coefficients calculated on the basis of chemical compositions. In this case, the difference in the expansion coefficients of the glass and the grisaille is negligible; consequently, the stresses at the interface between the two glasses are insignificant.

TABLE 2

Average chemical compositions expressed in %wt oxides of non-corroded and corroded stained glasses in the Church of S.S. Giovanni e Paolo in Venice, as determined by X-ray microanalysis. The analysed grisaille belongs to non-corroded glasses; due to the heterogeneity of the material, the reported composition is approximate and refers to the sole vitreous phase.

	Grisaille	Non-corroded glass	Corroded glass
$SiO_2$	40.0	68.5	63.3
$Al_2O_3$	1.50	1.00	1.50
$Na_2O$	1.50	13.6	0.30
$K_2O$	5.50	3.00	20.0
CaO	11.0	8.70	8.50
MgO	3.00	3.20	3.50
$Fe_2O_3$	10.0	0.33	0.30
MnO	-	0.32	0.40
$TiO_2$	0.20	0.07	0.05
$SO_3$	1.00	0.20	0.45
Cl	1.50	0.75	0.05
$P_2O_5$	0.20	0.25	0.80
PbO	23.0	-	0.60
CuO	0.70	-	0.30
BaO	-	-	0.30
Exp. coeff. $^{\circ}C^{-1} \times 10^{-7}$	99	95	101

A second example is the application of X-ray microanalysis to the study of the corporal preserved in the Orvieto cathedral, a precious medieval silver reliquary decorated with glass enamels. Several microfragments of enamel scaled from this object could be analysed and the subsequent calculation of the theoretical expansion coefficients revealed that the considerable difference between silver and enamel expansion values was responsible for microcracks formation and scaling of the enamel.

These two different examples are representative of how the information obtained by X-ray microanalysis applied to problems of glass conservation and restoration may help in taking correct operative decisions. In the case of the stained glass window the conservation operations concentrated on preventing glass corrosion; in the case of the reliquary, storage conditions with perfect thermal insulation of the object were required in order to

prevent the rising of stresses at the glass-metal interface due to temperature variations and consequent further deterioration of the glass enamel.

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#### Discussion with Reviewers

J.R.Millette: The minimum detection limit for manganese (atomic No. 25) is twice that of iron (atomic No. 26). How were the minimum detection limits determined? Why is there such a large difference between detection limits for elements with characteristic X-rays very close in energy?

Authors: The minimum detection limits were determined as  $3\sqrt{B}$ , where B is the counts per seconds measured on the background of the different elements. The difference between the m.d.l. of iron and manganese is due to the fact that the latter was determined with a PET crystal; it gives better results but cannot be used for the analysis of iron, for which a LiF crystal was employed.

G.W.Carriveau: How can the composition of glass be used as an authentication tool if a forger knows the correct composition and prepares the expected composition so that it matches with ancient recipes?

Authors: The chemical analysis of ancient glasses is a most useful tool for the expert for distinguishing an original glass from the imitation pieces. An exhaustive example is the production of perfect copies of XVI-XVIIth century glasses made in Venice in the XIXth century: the only difference is their chemical composition. Theoretically, it is possible that a forger prepares a composition exactly equal to the original one, even though it is rather complicated. However, glass counterfeiters have just imitated the shapes and outward features of glasses (colour, weathered surface layers, bubbles) up to now; the need for counterfeiting chemical compositions too will make their work far harder!

G.W. Carriveau: Isn't the small sample size limited to the homogeneity of the sample? How sensitive is this method to homogeneity and how does homogeneity compare with the area studied?

Authors: Glass is a highly homogeneous material; when several samples are taken and analysed for one glass, the resulting differences in composition are nearly always in the precision and accuracy limits of the method used.

G.W.Carriveau: Do you really need X-ray experiment to determine that enamel has a greatly different coefficient of expansion compared to silver alloy of reliquary?

What were the prescribed conservation treatments of the glass and reliquary and how did analysis assist in their choice?

Authors: In the case of the corporal preserved in the Orvieto cathedral the determination of the expansion coefficients of the enamels was not the only reason for X-ray microanalysis. Indeed, it was also necessary to identify corrosion products in order to understand the origins of this phenomenon and to establish the nature of the deposits in the microcracks of the enamel. On that occasion we also determined the chemical compositions and expansion coefficients of the different enamels, which we don't think can be determined otherwise. The results obtained suggested to protect the reliquary from temperature variations as far as possible; a washing procedure is also being set up to remove the salts deposits on the surface and in the microcracks.