Original Paper

Chemical composition of Medieval stained glasses from the Cathedral of León (Spain)

Francisco José Valle, Pilar Ortega and Luis Pascual
Instituto de Cerámica y Vidrio, CSIC, Arganda del Rey, Madrid (Spain)

Noemi Carmona and José Maria Fernández Navarro
Fundación Centro Nacional del Vidrio, San Ildefonso, Segovia (Spain)

Dedicated to Professor Oleg V. Mazurin on the occasion of his 75[th] birthday

A selection of glass samples from the stained glass windows of León Cathedral (Spain) dating from Medieval and Renaissance times has been chemically characterized. The techniques used for this characterization were X-ray diffraction, inductively coupled plasma, X-ray fluorescence and flame photometry. The analyses indicate that the samples are potash-lime glass, with the Medieval glass having a low alumina concentration. This fact has given rise to its deterioration throughout history due to environmental conditions.

1. Introduction

The chemical composition of Medieval stained glasses covers a huge range depending on its geographical origin and the time when it was manufactured. Glasses dating from the 13th and 14th centuries have suffered a more intense corrosion due to their low SiO_2 weight percentage and high content of K_2O. It is of great importance to know the chemical composition of the glass that makes up a stained glass window, in order to interpret the attack and deterioration processes that it might have suffered and also to adequately apply the suitable cleaning and protection techniques that may be necessary for its restoration.

The chemical analysis of stained glasses is usually carried out by nondestructive methods; among these methods, the electron probe microanalysis stands out [1 to 5]. Nuclear neutron activation has also been used in stained glass analyses [6], however less frequently.

Although more precise and exact than the aforementioned, the analytic techniques that require the sample to be destroyed (inductively coupled plasma [7], atomic absorption [8], or X-ray fluorescence [9]) are not widely used due to the fact that they require a higher amount of sample, which is not always easy to obtain.

The object of this work has been to determine the chemical composition of several pieces of glass from León Cathedral (Spain) dating from different periods and to relate it with their state of preservation and the time when they were manufactured. This characterization constitutes the preliminary phase of a wider research project aimed at studying the mechanisms of their chemical alteration and the possible restoration and protection processes.

Received 12 November 2001, revised manuscript 4 March 2002.

2. Experimental

2.1 Criteria for sample selection

Several glass fragments taken from the stained glass windows during the restoration process carried out at the turn of the 19th century, which had been stored ever since, have been available for this work. This fact has made it possible to have a sufficient amount of sample to carry out a complete analysis of the glasses by means of destructive methods.

Eleven samples were selected from the whole amount of available glass according to the following criteria: a) manufacturing period, b) type of surface alterations, c) degree of attack and d) colour.

2.2 Mineralogical analysis of corrosion crusts

The XRD spectra of the surface of the selected samples were recorded by putting the samples directly on the diffractometer sample holder. The XRD spectra were registered in a Siemens model D5000 diffractometer equipped with a Kristalloflex 710 generator. The radiation used was copper $K_{\alpha 1}$ radiation (λ = 0.15405 nm), with a nickel filter, a 0.1 mm detector collimator, at 50 KV and a 30 mA. Diffractograms of both the outward side and the one that had faced the interior of the cathedral were registered. Spectra of different fragments proceeding from the same sample have been registered in order to obtain the closest mineralogical composition of the glass surface.

2.3 Analysis of the glass samples

Altered layers on the sample surfaces were removed before analysis by polishing with 600 grit silicon carbide paper. The samples prepared in this way were quantitatively analysed by inductive coupled plasma (ICP) and flame photometry (FP). A Thermo Jarrell Ash Iris Advantage dual plasma spectrometer equipped with a solid state charge injection device detector (CID) was used in order to analyse the glasses. The minor and trace elements determination was tackled with axial measures and an integration time of 30 s; determination of the major elements was tackled with radial measures and an integration time of 5 s. The analysis of the alkaline elements was carried out with an atomic absorption spectrometer Perkin-Elmer model 2100, using acetylene as combustible.

When the available amount of sample was enough (> 1 g), a weight of 0.5000 g of each sample was melted with anhydrous sodium carbonate following the process described by Bennet [10] or attacked with a mixture of concentrated H_2SO_4 and concentrated HF. Silica was gravimetrically determined while the alkaline elements were analysed by FP following the process described by Voinovitch [11]. The other elements besides the alkaline ones were analysed by ICP.

When only a little amount of sample was available (< 1 g), the lithium metaborate flux process, as described by Ingamells [12], or attack with a mixture of HF and HNO_3, as proposed by Bernas [7], were used to put the samples in solution.

3. Results and discussion

3.1 Study of corrosion crusts by XRD

The chemical composition of the glass and the environmental conditions to which it has been exposed for many centuries determine, in essence, the formation of both the gel layers and the corrosion crusts [13]. While the gel layer formed on the glass surface is homogeneous and can be considered as a continuation of the vitreous structure but more open, the corrosion crusts are inhomogeneous and are made up of different crystalline and amorphous phases whose composition varies depending on the depth and the surface analysed [13 to 18].

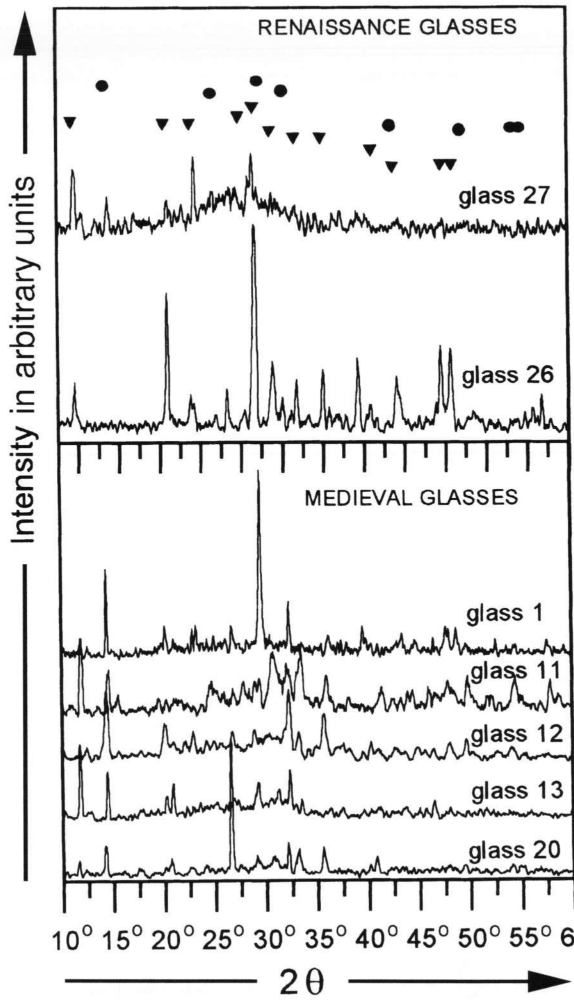

Figure 1. Diffraction spectra of the corrosion product crust on the surface of some Medieval and Renaissance window glasses; ▼: gypsum ($CaSO_4 \cdot 2H_2O$); ●: bassanite ($CaSO_4 \cdot 0.5H_2O$).

Figure 1 shows some diffraction spectra of the surface of the selected Medieval and Renaissance glass panes. The analyses reveal the presence of gypsum ($CaSO_4 \cdot 2H_2O$), bassanite ($CaSO_4 \cdot 0.5H_2O$), or a mixture of both, as major crystalline phases, both on the outward side and on the side that faced the interior of the cathedral. The corrosion crusts of the interior side show a lower degree of crystallization and in some cases they are amorphous. No evidence of the existence of syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) has been found. According to Pérez y Jorba [16] syngenite is formed, together with gypsum, in Medieval glasses with a total content of alkali greater than 16 wt%, that is to say, there are other factors, apart from composition, that influence the nature of the crystalline phases which form the corrosion crust.

Table 1. Quantitative analysis of selected Medieval glasses (composition in wt%) from León Cathedral as obtained by ICP and FP

	sample no.						
	1	10	11	12	13	20	23
SiO_2	46.2	50.1	53.4	50.9	49.5	53.2	48.2
Al_2O_3	1.30	0.75	0.83	0.60	1.82	0.93	1.21
BaO	0.27	0.14	0.082	0.16	0.40	0.066	0.2
CaO	22.9	13.0	13.6	14.1	19.7	14.4	20.3
CoO	0.010	0.28	0.005	0.010	0.002	0.003	0.004
Cr_2O_3	0.008	–	–	0.003	0.007	0.006	0.004
CuO	0.035	0.24	0.005	0.050	0.028	0.027	0.032
Fe_2O_3	0.50	0.82	0.52	0.43	0.35	0.55	0.44
K_2O	22.0	17.2	16.3	17.2	20.8	16.8	23.3
MgO	2.71	7.10	7.12	6.80	3.10	5.90	2.20
MnO	0.58	1.46	0.84	1.55	0.56	0.80	0.95
Na_2O	0.31	2.65	2.90	3.16	0.16	2.50	0.26
NiO	0.020	–	0.001	0.001	0.002	0.002	0.002
P_2O_5	1.48	4.30	3.70	3.70	1.15	3.45	1.19
PbO	0.36	0.25	–	0.001	0.85	0.003	0.26
Rb_2O	0.10	0.080	0.050	0.070	0.17	0.057	0.18
SO_3	0.34	0.38	0.20	0.29	0.38	0.15	0.22
SrO	0.13	0.040	0.050	0.045	0.10	0.060	0.090
TiO_2	0.096	0.11	0.095	0.052	0.085	0.10	0.096
ZnO	0.051	0.50	0.044	0.033	0.037	0.038	0.035

3.2 Quantitative analyses

3.2.1 Medieval glass

Table 1 shows the results of the analyses of the seven Medieval glass panes selected. These pieces are characterized by their low silica and alumina content which, along with the high potash concentrations, make them very easy to be attacked. These panes of glass were, at first, classified as Medieval due to their aspect and the decoration strokes. Among them, two groups can be clearly recognized according to the concentration of the major components:

a) group made up of samples numbers 10, 11, 12 and 20 (group M1);

b) group made up of samples numbers 1, 13 and 23 (group M2).

Group M1 is characterized by having silica concentrations higher than 50 %, moderate to high concentrations of CaO and K_2O, unusually high MgO concentrations and P_2O_5 and Na_2O concentrations higher than those of the Renaissance glass. Group M2 has, with regard to M1 group, slightly lower silica concentrations, very high CaO and K_2O concentrations and low contents of Na_2O and P_2O_5.

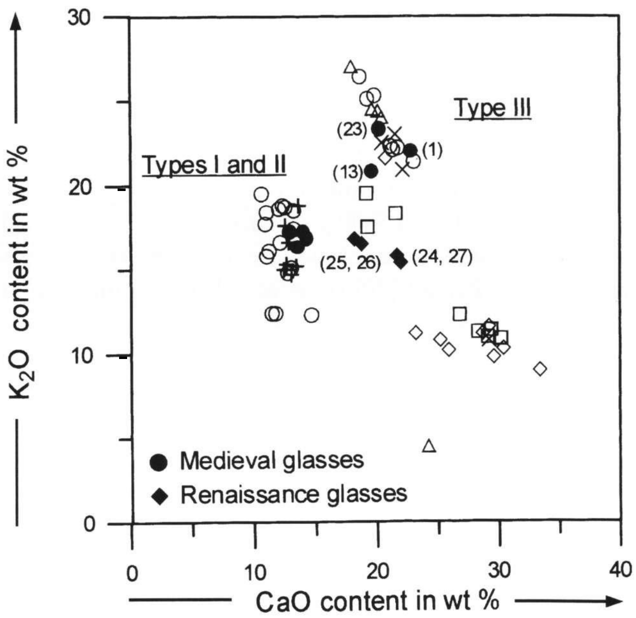

Figure 2. CaO versus K_2O content (in wt%) in Medieval and Renaissance glasses from León Cathedral, compared with Medieval stained glasses from different sites. □: Cologne Cathedral; ◇, ×: St. Catherine Church Oppenheim; ○: clerestory in León Cathedral; △: Erfurt Cathedral; +: St. Gatien Cathedral Tours.

The existence of two groups of Medieval glass, as well as the differences existing between them, becomes evident when the relations between concentrations in wt% of the major oxides that become part of their composition are represented (figures 2 to 5). R. H. Brill [19] has classified the Medieval glass, as regards its composition, in three different types. Glass of types I and II have a similar composition, although not identical. These glasses are characterized by having a high K_2O concentration, 12 to 20 wt%; a moderate to high percentage of CaO, 10 to 15 wt%; and a high MgO content, 5 to 10 wt%, along with high concentrations of P_2O_5, 2 to 6 wt%. The difference between glass of types I and II is not very clear; perhaps, the biggest difference is related

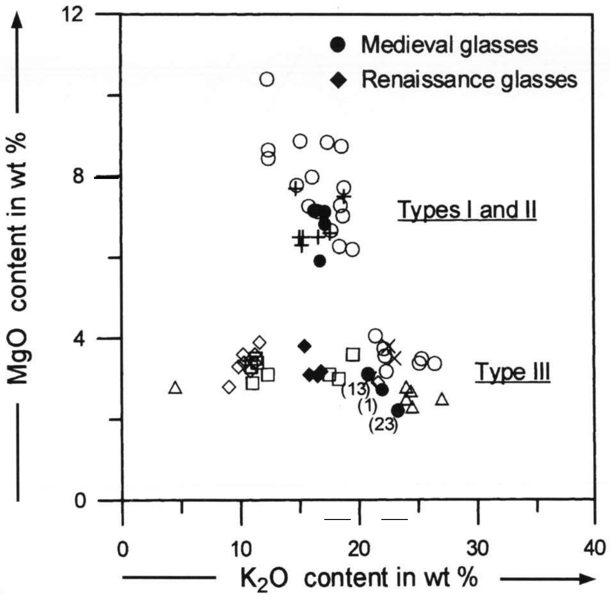

Figure 3. MgO versus K_2O content (in wt%) in Medieval and Renaissance glasses from León Cathedral, compared with Medieval stained glasses from different sites. □: Cologne Cathedral; ◇, ×: St. Catherine Church Oppenheim; ○: clerestory in León Cathedral; △: Erfurt Cathedral; +: St. Gatien Cathedral Tours.

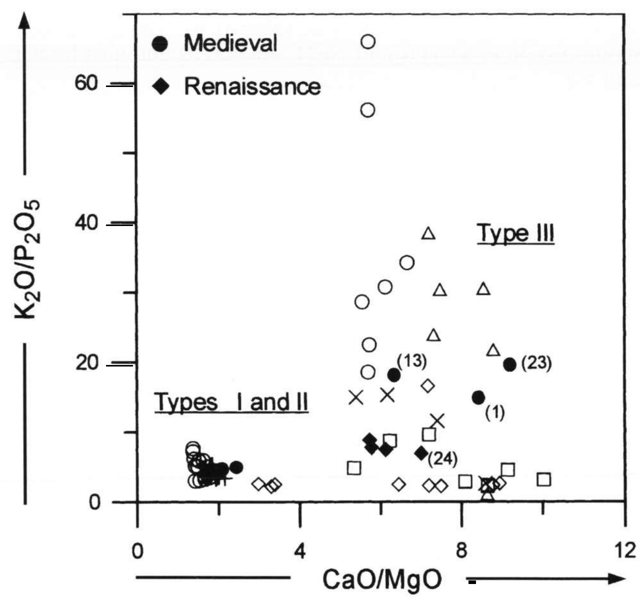

Figure 5. K_2O/P_2O_5 versus CaO/MgO in Medieval and Renaissance glasses from León Cathedral, emphasizing differences by using different plant ash sources. □: Cologne Cathedral; ◇, ×: St. Catherine Church Oppenheim; ○: clerestory in León Cathedral; △: Erfurt Cathedral; +: St. Gatien Cathedral Tours.

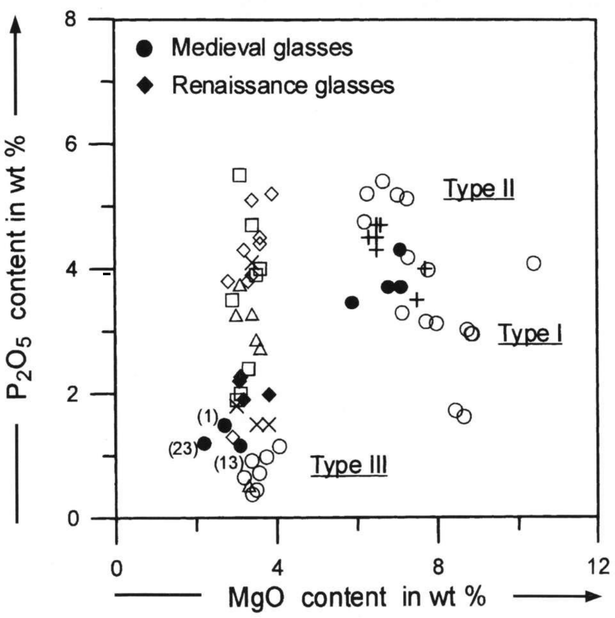

Figure 4. P_2O_5 versus MgO content (in wt%) in Medieval and Renaissance glasses from León Cathedral, compared with Medieval stained glasses from different sites. □: Cologne Cathedral; ◇, ×: St. Catherine Church Oppenheim; ○: clerestory in León Cathedral; △: Erfurt Cathedral; +: St. Gatien Cathedral Tours.

to the P_2O_5 concentration which is higher in glass of type II, around 4 to 5 %, in contrast with glass of type I which has a 2 to 3 % concentration. This difference can be indicative of the different origin of the ashes used to manufacture the two types of glasses. Glasses of type III are characterized by having a low silica content (often lower than 50 wt%), a very high content of K_2O (20 to 27 wt%) and CaO (19 to 24 wt%), along with moderated percentages of MgO (≈ 4 wt%) and a low P_2O_5 concentration (≈ 1 wt%).

The analyses of the Medieval glass which have been carried out in this work coincide with those made by R.H. Brill [19] in the clerestory glass from León Cathedral, and confirm that in the stained glass windows of this cathedral there are glasses manufactured in different periods and/or places. According to R.H. Brill, the glasses of types I and II were manufactured between the 13th and 14th centuries, while the glasses of type III belong to the 16th century. The fact that there is a great variety in the compositions and in the different periods of manufacture of the glass is a consequence of the multiple transformations that the stained glass windows of León Cathedral have suffered during both their manufacture and the following conservation and restoration interventions to which they were subjected throughout their history [20], Brill [19] considers that the high concentrations of MgO (> 6 %) and K_2O found on the glass of types I and II are unusually high for glass dating from this period. He has taken this fact as an indication that the glass panes of León Cathedral dating from the 14th century were manufactured in the region. Nevertheless, these compositions are also found in other contemporary churches and cathedrals in Europe. It is also frequent to find Medieval glass with a high MgO concentration (> 6 %) along with K_2O concentrations of 17 to 20 wt% [21 and 22]. In spite of the similarities between these compositions, the possibility that the glasses from León Cathedral were melted in glassworks in Burgos or León is not ruled out.

Table 2. Quantitative analysis of selected Renaissance glasses (composition in wt%) from León Cathedral as obtained by ICP and FP

	sample no.			
	24	25	26	27
SiO_2	46.3	47.8	49.2	47.2
Al_2O_3	4.59	4.69	3.90	4.20
K_2O	15.8	16.8	16.5	15.4
Na_2O	1.83	1.87	1.68	1.98
Rb_2O	0.006	0.010	0.008	0.01
CaO	21.7	18.2	18.8	22.0
MgO	3.10	3.18	3.07	3.81
SrO	0.085	0.10	0.075	0.056
BaO	0.15	0.21	0.20	0.70
MnO	0.66	0.84	0.68	0.37
ZnO	0.028	0.38	0.27	0.011
PbO	0.032	0.077	0.050	0.018
NiO	0.085	0.026	0.017	0.010
P_2O_5	2.27	1.90	2.20	1.98
TiO_2	0.25	0.21	0.20	0.25
CoO	0.97	0.11	0.084	0.043
CuO	0.026	1.87	1.34	0.12
Cr_2O_3	0.004	0.003	0.0008	0.003
Bi_2O_3	0.16	–	–	0.020
As_2O_3	0.20	0.10	0.080	0.020
Fe_2O_3	1.02	0.84	0.82	1.05
Ag_2O	–	–	–	0.020
SO_3	0.21	0.32	0.20	0.19

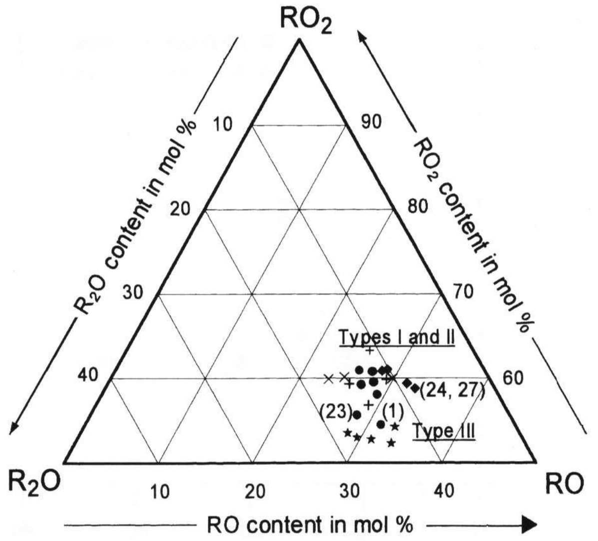

Figure 6. Triangular representation of glass compositions (in mol%) of samples from León Cathedral. ●, ◆: Medieval and Renaissance glasses (this work); +, ×, ★: types I, II and III Medieval glasses from León Cathedral [5].

3.2.2 Renaissance glass

Table 2 shows the results of the analyses of four pieces of Renaissance glass. Renaissance glass compositions are more complex and constant than Medieval glass ones. However, if only the CaO/K_2O relation is taken into account, two subgroups formed by samples 24 and 27 and by samples 25 and 26 can be established (figure 2). Even though it may be considered that the composition of Renaissance glasses is similar to that of type III defined by R. H. Brill, the lower content of K_2O and, especially, the high concentration of alumina (of the order of 4 wt%) clearly distinguish them from Medieval glasses that have the same silica proportion. The presence of alumina in low proportions stabilizes the glass due to the formation of tetrahedric groups $[AlO_4]$.

Among the minor oxides that form part of the Renaissance glass composition, it is worth pointing out the presence of Ag_2O (sample 27) and of Bi_2O_3 (samples 24 and 27) in relatively high concentrations. Both oxides probably come from impurities of the source materials used for the batch preparation. Silver is a common impurity of sands and quartzites, where it can be found in concentrations of the order of 10^{-3} wt%, whereas bismuth oxide is incorporated through both ashes and source materials which furnish silica [5]. Bismuth oxide forms part of the composition of Medieval glass, except for English glass, in concentrations of 1 to $5 \cdot 10^{-3}$ wt%. Curiously, this oxide is not present in the compositions of the Medieval glass in León Cathedral that had been analysed by R. H. Brill [5 and 19].

3.2.3 Iliffe-Newton diagram

The representation of the compositions of the eleven Medieval and Renaissance glass samples in an Iliffe-Newton diagram (figure 6) [23] highlights some affirmations previously made. The compositions of the clerestory glass in León Cathedral that had been analysed by R. H. Brill [5] have been represented in the same figure. In both cases, the existence of two composition groups for the Medieval glass, types I–II and type III, is confirmed and the existence of two glass groups for the Renaissance glass is also revealed.

4. Conclusions

The possibility of having a sufficient number of Medieval and Renaissance glass samples from León Cathedral has allowed chemical analysis of the glass by means of techniques that require the samples to be destroyed and which provide a high reliability.

The silica content has not been a defining factor in order to distinguish Medieval and Renaissance glass. Nevertheless, the proportion of major oxides and the relations between them allow the glass from both periods to be clearly distinguished. This relationship establishes the existence, within the Medieval glass, of two groups manufactured in different places or periods.

Renaissance glasses are more complex and have a greater constancy in their composition than Medieval glass. The greater chemical stability of these glasses is, above all, due to their high content of alumina.

The corrosion crusts formed on the surface of the panes of glass correspond to the chemical composition of the glass and to its degree of attack caused by atmospheric agents in the course of time. The XRD spectra of the surface of the panes of glass reveal the presence of gypsum and bassanite as main crystalline phases.

*

The authors wish to thank the CE-FEDER-CICYT (2FD 97-0418) project for financial support.

5. References

[1] Schreiner, M.: Secondary ion mass spectrometer analysis of potash-lime-silica glasses leached in hydrocloric and sulfuric acids. J. Am. Ceram. Soc. **72** (1989) n. 9, p. 1713–1715.

[2] Schreiner, M.; Grasserbauer, M.: Microanalysis of art objects: objetives, methods and results. Fresenius Z. Anal. Chem. **322** (1985) p. 181–193.

[3] Schreiner, M.; Stingeder, G.; Grasserbauer, M.: Quantitative characterization of surface layers on corroded Medieval window glass with SIMS. Fresenius Z. Anal. Chem. **19** (1984) p. 600–605.

[4] Pérez y Jorba, M.; Dallas, J. P.; Collongues, R. et al.: Etude de l'alteration des vitraux anciens par microscopic électronique à balayage et microsonde. Silic. Ind. **43** (1978) p. 89–99.

[5] Brill, R. H.: Chemical analyses of early glasses. Vol. 1+2. Corning, NY: Corning Museum of Glass, 1999.

[6] Olin, J. E.; Sayre, E. R. W.: Neutron activation and electron beam microprobe study of a fourteenth century austrian stained glass panel. In: Proc. International Conference on the Application of Nuclear Methods in the Field of Works of Art, Rome – Venice, 1973.

[7] Bernas, B.: A new method for decomposition and comprehensive analysis of silicate by atomic absorption spectrometry. Anal. Chem. **40** (1968) p. 1682–1686.

[8] Bock, R.: Handbook of decomposition methods in analytical chemistry. Glasgow: Blackie, 1979. p. 444ff.

[9] Lahanier, Ch.: Analyses de verres de vitreaux par spectrometrie de fluorescence X. In: Proc. IX International Congress on Glass, Versailles 1971. Paris: Institut du Verre, 1971. p. 201–224.

[10] Bennet, H.; Reed, R. A.: Chemical methods of silicate analysis. British Ceramic Research Association. London et al.: Academic Press, 1972.

[11] Voinovitch, I. A.; Debras-Guedon, J.; Louvrier, J.: L'analyse des silicates. Paris: Ed. Hermann, 1962.

[12] Ingamells, C. O.: Lithium metaborate in silicate analysis. Anal. Chim. Acta. **52** (1970) p. 323–334.

[13] Müller, W.; Corrosion phenomena of Medieval stained glasses. In: Proc. XVI International Congress on Glass, Madrid 1992. Bol. Soc. Esp. Ceram. Vidr. **31-C** (1992) no. 1, p. 219–239.

[14] Collonges, R.; Perez y Jorba, M.; Tilloca, G.: Nouveaux aspects du phénomène de corrosion des vitraux anciens des églises françaises. Verres Refract. **30** (1976) p. 43–55.

[15] Newton, R. G.; Fuchs, D.: Chemical compositions and weathering of some Medieval glasses from York Munster. Pt. 1. Glass Technol. **29** (1988) p. 43–48.

[16] Pérez y Jorba, M.; Tilloca, G.; Michel, D., Dallas, J. P.: Quelques aspects du phénomène de corrosion des vitraux anciens des églises français. Verres Réfract. **29** (1975) p. 53–63.

[17] Gillies, K. J. S.; Cox, A.: Decay of Medieval stained glass. Pt. 2. Relationship between the composition of the glass, its durability and the weathering products. Glastech. Ber. **61** (1988) p. 101–107.

[18] Pérez y Jorba, M.; Dallas, J. P.; Bauer, C.: Deterioration of stained glass by atmospheric corrosion and microorganisms. J. Mater. Sci. **15** (1980) p. 1640–1647.

[19] Brill, R. H.: Chemical analysis of some stained glass windows in León cathedral. In: Proc. XVI International Congress on Glass, Madrid 1992. Bol. Soc. Esp. Ceram. Vidr. **31-C** (1992) no. 7, p. 143–148.

[20] Gómez Rascón, M.: Catedral de León. Las vidrieras. El simbolismo de la luz. León: Edit. Edilesa, 2000. p. 149–151.

[21] Vassas, C. D.: Etude chimique, thermographique et physique de verrres de vitraux du moyenage. In: Proc. IX International Congress on Glass. Versailles, 1971. Paris: Institut du Verre, 1971. p. 241–266.

[22] Müller, W.; Torge, M.; Adam, K.: Ratio of CaO/K2O > 2 as evidence of a special Rhenish type of Medieval stained glass. Glastech. Ber. Glass Sci. Technol. **67** (1994) p. 45–48.

[23] Iliffe, C. J.; Newton, R. G.: Using triangular diagrams to understand the behaviour of Medieval glasses. Verr. Refract. **30** (1976) p. 30–34.

E302P005

Contact:

Dr. L. Pascual
Instituto de Ceramica y Vidrio
Ctra. de Valencia, Km. 24,300
28500 Arganda del Rey, Madrid
Spain
E-mail: Lpascual@icv.csic.es