Original Paper

Ratio of $CaO/K_2O > 2$ as evidence of a special Rhenish type of medieval stained glass

Wolfgang Müller, Manfred Torge and Karin Adam

Bundesanstalt für Materialforschung und -prüfung, Berlin (Germany)

The chemical compositions of more than 300 medieval stained glass samples of different local origin have been published so far. Regarding their characteristic components they can be classified into five types. About 80 % of all investigated samples proved to be potash-lime-silica glasses with roughly equal concentration of CaO and K_2O (type 1). But a small group of little more than 20 samples gave a ratio of $CaO/K_2O > 2$ (type 2), all but three of which had been taken from two churches of the Rhine region (St. Catherine Church Oppenheim and Cologne Cathedral). Hence, it seems likely that a corresponding recipe was used there, which was nearly unknown elsewhere in Europe. Investigation of further objects of this region might be of interest for the history of technology.

Das Verhältnis von $CaO/K_2O > 2$ als Hinweis auf einen besonderen Rheinlandtyp mittelalterlichen Farbglases

Die heute von mehr als 300 mittelalterlichen farbigen Flachglasproben unterschiedlichster lokaler Herkunft bekannten chemischen Zusammensetzungen lassen eine Einteilung in fünf verschiedene Typen zu. Etwa 80 % aller untersuchten Proben haben sich als Pottasche-Kalksilicatgläser mit einem ausgeglichenen CaO/K_2O-Verhältnis (Typ 1) erwiesen. Eine kleine Gruppe von etwas über 20 Glasproben zeigte dagegen erheblich geringere K_2O-Konzentrationen bei gleichzeitig sehr hohen CaO-Werten, so daß ein prozentuales Masse-Verhältnis von $CaO/K_2O > 2$ vorlag (Typ 2). Von drei Ausnahmen abgesehen stammten alle Proben dieses Typs aus zwei Glasmalereibeständen von Kirchen im Rheinland (Katharinenkirche Oppenheim, Kölner Dom). Das Ergebnis läßt darauf schließen, daß in einer rheinischen Hütte nach einem Rezept gearbeitet wurde, das sonst im Mittelalter kaum bekannt war. Die Untersuchung weiterer Glasproben aus der Region wäre von technikgeschichtlichem Interesse.

1. Composition of medieval window glasses

Medieval stained glass windows owe their brilliance in part to the glowing colours of potash–lime–silica glasses. The little of information on recipes for the glass production of that period is not satisfactory. It makes reference only to sand and plant ashes [1 and 2]; but at least lime, lead oxide and some colouring agents must have been applied as well. Analysis data of meanwhile more than 300 samples of different European provenance indicate this fact. Distinctions in the weathering behaviour gave rise to a systematization of medieval glasses according to their chemical composition. These attempts have been partially successful [3]. The great majority of all examined glass samples proved to be type $K_2O-CaO-SiO_2$ with a broad variation of component quantities, which may be likewise due to the concealment of recipes and to local differences in raw material compositions. To find clear evidence of regularities requires more reliable data, and application of statistics might be useful only then.

Nevertheless, a classification has been attempted on the base of analysis data of altogether 343 different samples, which had been investigated in six laboratories [4 to 9]. It should be mentioned here that typifications have been made so far only with respect to special objects, as e.g., by Brill [10] regarding the stained glass windows in Leon cathedral (Spain). However, a general scheme, comprehending results of locally spread provenance, is still outstanding.

Table 1 shows that distinct differences between five glass types have been found, considering only the type-specific components. The rest of them, such as MgO, Al_2O_3, MnO, FeO etc., is less than 10 wt% in sum and without type specificity. Moreover, small amounts in the range from 0.1 to 1 wt% of BaO, TiO_2, Cl, SO_3 etc. will be traceable in almost every medieval glass. Consequently, traces are also not sufficient for specification. Therefore, the types have been classified according to the main components only. Besides the common potash–lime–silica glasses (types 1 and 2) there are three more types: a blue soda–lime–silica glass, found in 12th century windows only (type 3), green glasses with high lead oxide content (type 4), and glasses with low concentration of both K_2O and Na_2O, becoming predominant in the renaissance period (type 5).

With the investigated 343 glasses the frequency of the different types is far from equally distributed. Almost 80 % of all samples have proved to be of type 1 composition (figure 1). It should be mentioned here that this figure does not reflect real frequency relations of all existing medieval glasses. The type 3 blue soda glass, for

Received June 24, 1993, revised manuscript October 18, 1993.

Table 1. Composition ranges (in wt%) of different medieval window glasses

glass type no.	SiO_2	CaO	K_2O	Na_2O	PbO	P_2O_5	colour
1	45 to 55	15 to 25	15 to 25	0 to 2	0 to 1	0 to 4	diverse
2	45 to 55	25 to 35	10 to 15	0 to 2	0 to 1	0 to 4	diverse
3	60 to 75	1 to 6	5 to 8	10 to 18	0 to 1	0 to 4	blue
4	30 to 40	5 to 20	5 to 20	0 to 1	10 to 50	0 to 10	green
5	55 to 70	10 to 20	2 to 8	2 to 8	0 to 1	3 to 10	diverse

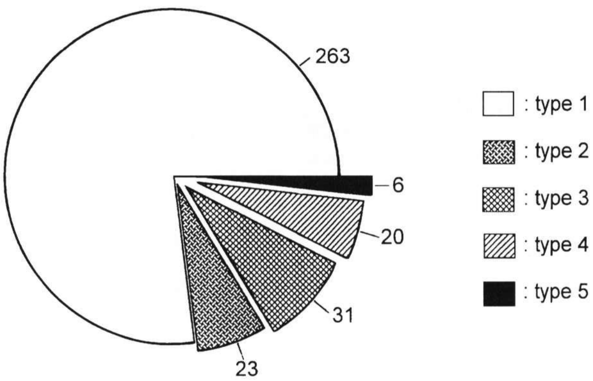

Figure 1. Frequency distribution of 5 main types of medieval window glasses (table 1) from 12th to 16th centuries.

instance, has been consciously selected for measurements because of its excellent conservation state. It is extremely rare and has been found so far only in six 12th century objects [4 and 9]. On the other hand, the majority of glass samples were investigated in the course of a project, which was to find out the relations between glass composition and surface corrosion stage [5]. Therefore, mainly samples with pitted and crusted surfaces were selected, whereas the more stable glasses of the late medieval and renaissance period were not considered. Type 5 glasses have been scarcely analyzed so far, but are certainly present in great number in 15th and 16th centuries objects.

At first sight, the discrimination of types 1 and 2 may appear arbitrary, for they only differ in the relation of CaO/K_2O. Nevertheless, recent investigations, which have been carried out within a German-French project on the medieval glass windows of St. Catherine Church Oppenheim (Germany) and Tours Cathedral (France) seem to justify the distinction of type 1 ($CaO/K_2O < 2$) and type 2 ($CaO/K_2O > 2$), as will be shown in section 3. of this work.

2. Sample selection and examination

The "German-French Research Programme for the Conservation of Historical Monuments" was founded in 1988. The project "glass damage", started in 1991, was to characterize the actual condition of the stained glass windows of St. Catherine Church Oppenheim and Tours Cathedral St. Gatien and to draw conclusions with respect to the impending restoration.

Analytical investigations have been made with representative glass samples by several research groups. The samples had been selected by workshop employees and passed on from one laboratory to the next. Finally, they were replaced into the panels of the windows.

In the author's laboratory microprobe analysis has been used to investigate 21 different glass samples from four windows of Oppenheim and 7 samples from one window of Tours. To get the composition of the bulk glass a small spot at the edge of any samples has been cut, polished with diamond paste and coated with carbon. With an electron microscope quantometer (SEMQ) with four spectrometers for the wavelength-dispersive systems (WDS) and with an energy-dispersive spectrometer (EDS) all elements with an atomic number $Z > 10$ could be detected. For WDS analysis the accelerating voltage of 15 kV, the beam current of 30 nA and the counting time of 4 s for the measurement of line-step profiles have been chosen. In the case of EDS quantitative analysis the working conditions were again 15 kV, but 1 to 2 nA and 50 to 100 s. A defocussed electron beam was used for the measurement of potassium and sodium, to diminish ion migration of these elements. Natural minerals and model glasses of known composition are necessary as standards. Quantitative electron microprobe analysis is based on the comparison of X-ray line intensities emitted from standard and sample, respectively. Data reduction was carried out with respect to ordinal number absorption and fluorescence.

3. Results

The 7 glass samples of Tours Cathedral showed little variation; they all were definitely type 1 (table 2). The contents of CaO slightly below and P_2O_5 in part slightly above the average ranges given in table 1 do not impair this conclusion. Thus, the glasses belong to the most common medieval type of potash–lime–silica glass with roughly equal concentration of both CaO and K_2O.

The compositions of the 21 samples of St. Catherine Church Oppenheim are less uniform. Surprisingly, two thirds of the glasses showed ratios of $CaO/K_2O > 2$. In particular, the glass samples of the window n IX proved all but one to be type 2 composition (table 3). Their representation in the Iliff-Newton diagram [11] makes the separation into two groups of glasses clearly visible (figure 2). The triangular coordinates have been calculated in mol% in the following way:

Table 2. Chemical composition (in wt%) of samples from the medieval stained glass window no. 213 of St. Gatien Cathedral, Tours (France). According to table 1 all glasses belong to type 1

sample no.	colour	SiO_2	CaO	K_2O	Na_2O	MgO	P_2O_5	MnO	FeO	Al_2O_3
1	yellow	52.0	13.7	18.8	1.8	7.5	3.5	0.4	0.3	0.8
2	blue	54.0	13.1	14.7	1.6	7.7	4.0	1.0	0.7	1.5
3	blue	53.5	13.5	15.2	2.1	6.3	4.5	1.0	0.8	1.8
4	white	52.2	12.6	17.6	2.2	6.6	4.7	0.8	0.3	1.8
5	red	54.3	12.7	15.3	1.9	6.5	4.3	0.8	0.5	1.9
6	purple	53.5	12.5	15.0	2.2	6.5	4.5	2.3	–	1.9
8	green	51.8	12.9	16.6	1.9	6.5	4.7	0.8	0.4	1.6

Table 3. Chemical composition (in wt%) of glasses of St. Catherine Church, Oppenheim (Germany)

sample no.	colour	window	SiO_2	CaO	K_2O	Na_2O	MgO	P_2O_5	MnO	FeO	Al_2O_3	type no. (see table 1)
1	white	n IX	51.6	23.2	11.2	–	3.6	4.5	0.7	0.8	3.8	2
3	white	n IX	46.0	33.4	9.0	–	2.8	2.8	0.7	0.5	3.9	2
4	white	n IX	44.8	31.6	8.5	0.4	3.1	4.3	0.8	0.6	3.8	2
5	white	n IX	46.9	30.4	10.3	0.3	3.4	3.9	0.7	0.6	3.0	2
7	yellow	n IX	49.7	25.9	10.2	0.4	3.6	4.4	0.6	0.7	4.0	2
9	yellow	n IX	43.5	29.2	11.6	0.4	3.9	5.2	0.8	0.8	3.6	2
13	green	n IX	48.3	20.8	21.6	0.1	2.9	1.3	0.4	2.1	2.2	1
15	blue	n IX	47.0	29.6	9.8	0.5	3.3	3.8	0.7	0.8	4.0	2
16	blue	n IX	45.4	30.0	9.2	0.6	3.6	4.7	0.7	0.6	3.5	2
17	blue	n IX	50.0	25.2	10.8	0.4	3.2	4.3	0.7	1.0	3.2	2
18	red	n IX	45.1	28.7	11.2	0.4	3.4	5.1	0.9	0.6	3.4	2
19	white	n IX	70.4	12.0	1.9	8.9	0.8	0.5	–	0.3	3.8	1)
23	red	s VIII	47.4	20.5	22.5	0.3	3.8	1.5	1.1	–	2.3	1
25	blue	s VIII	48.7	22.2	20.9	–	3.0	1.8	0.6	0.6	1.7	1
29	yellow	s VIII	46.6	29.2	10.8	0.6	3.4	4.1	0.8	0.4	3.3	2
30	purple	s VIII	46.7	21.6	23.9	–	3.5	1.5	1.1	–	1.9	1
49	green	I	50.8	20.2	19.6	0.3	3.1	3.2	0.5	0.4	1.6	1
50	blue	I	49.0	19.3	22.4	0.4	2.9	2.8	0.4	0.4	1.9	1
57	yellow	s II	49.1	26.9	10.7	0.4	3.8	2.6	0.9	0.4	3.7	2
58	purple	s II	53.7	17.1	15.7	0.5	4.0	4.7	0.9	0.7	1.6	1
59	red	s II	51.6	24.0	12.2	0.6	3.3	2.5	0.8	0.5	3.7	2

1) 19th century.

$$\text{"RO}_2\text{"} \equiv SiO_2 + 2Al_2O_3 + 2P_2O_5 + 2Fe_2O_3 \,,$$

$$\text{"RO"} = CaO + MgO + MnO \,,$$

$$\text{"R}_2\text{O"} \equiv K_2O + Na_2O - Al_2O_3 - Fe_2O_3 \,.$$

The compositions of the samples of both groups could easily be classified into types 1 and 2 with only negligible deviations in K_2O and P_2O_5 from the average ranges given in table 1. Glasses of other medieval types have not been found in both objects Oppenheim and Tours, respectively. Oppenheim sample no. 19 proved to be an exception; it is obviously a 19th century glass, and probably got into the panel by a former restoration.

4. Discussion

Although the analytical work has properly been made with the aim to give recommendations to restorers regarding cleaning and conservation, it may be of interest to consider historical relationships as well. The results of the measurements of Tours and Oppenheim glasses and likewise some compositions of medieval samples of Cologne Cathedral – determined in the authors' laboratory recently [12] – have already been included in the presentation of figure 1. At first sight, the predominance of type 1 glasses seems uncontested. However, considering the local distribution of the different types, remarkable tendencies can be observed.

Five out of 10 samples of Cologne Cathedral as well as 14 out of 21 of Oppenheim have turned out to belong to type 2. Consequently, 19 out of the overall number of 23 type 2 glasses originate from the two Rhineland objects, whereas among the almost fifty other places of provenance only little 4 samples of this type could be found.

This circumstance indicates a special Rhenish glass production according to recipes and technologies which other glass producers did not dispose of. It is quite possible that the material for the stained glass windows of

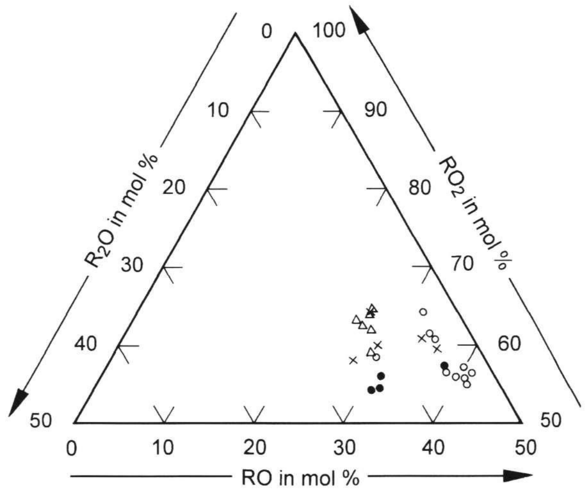

Figure 2. Triangular representation of glass compositions (mol%) of samples from St. Gatien Cathedral Tours and St. Catherine Church Oppenheim. △: Tours, window 213; ×: Oppenheim, windows I, s II; ○: Oppenheim, window n IX; ●: Oppenheim, window s VIII.

Cologne and Oppenheim came from only one workshop. The transport of glass panels on the river Rhine has been mentioned in literature [13]. The influence of Cologne Cathedral glaziers and glass painters on the work in Oppenheim may be assumed, not only because of local vicinity but also from iconographic similarities in some details of the painting.

Regrettably, there is no further written information from medieval time about glass production and workshops. It is only known for certain that the lime–potash–silica glasses have been produced in forest regions of west, north and central Europe. Rivers were predestined for the transport of as breakable goods as glass. Thus, the place of use need not necessarily be identical with that of production. But at least it can be concluded that in the 14th century the lime-rich type 2 glass was readily available in Cologne and Oppenheim, whereas it seems to have been nearly unknown elsewhere in Europe in the Middle Ages. It will be quite of interest to look for further test material from medieval stained glass windows of the Rhine region.

4. References

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