UNIVERSIDADE NOVA DE LISBOA

Faculdade de Ciências e Tecnologia

Núcleo do Departamento de Conservação e Restauro

Caracterização química de vidros *Millefiori* do século XVII provenientes do Mosteiro de Sta. Clara-a-Velha: comparação com a produção veneziana e *façon-de-Venise*

Chemical analysis of 17th century *Millefiori* glasses excavated in the Monastery of Sta. Clara-a-Velha: comparison with Venetian and *façon-de-Venise* production

Por

AUGUSTA RAQUEL FERREIRA MONIZ LIMA

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Orientador: Investigador Coordenador Jubilado António Pires de Matos

Co-orientador: Dr. Marco Verità

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Sumário

Dez fragmentos de vidro *Millefiori* datados do século XVII, provenientes do Mosteiro de Sta. Clara-a-Velha (Coimbra, Portugal), foram caracterizados através de microssonda electrónica, microscopia Raman e espectroscopia de absorção UV-Vis. Todos os vidros são silicatados sodo-cálcicos. A presença de cloro e de quantidades relativamente elevadas de MgO, K_2O and P_2O_5 sugere a utilização de cinzas de plantas costeiras. Verificou-se a presença de óxido de estanho ou antimoniato de cálcio nos vidros brancos, cobalto nos vidros azuis, cobre nos vidros turquesa, ferro nos vidros amarelados e esverdeados e ferro e cobre nos vidros vermelhos opacos e aventurina. Com base nos teores de alumina e sílica foram identificadas quatro fontes distintas de sílica, o que permitiu a classificação dos vidros nos seguintes grupos: alumina baixa (< 2 %), alumina baixa – *cristallo* (< 2 % e sílica > 70 %), alumina média (2 - 3 %), alumina elevada (3 - 6 %) e alumina muito elevada (> 6 %). Procedeu-se à comparação das composições obtidas com as publicadas de vidros venezianos e *façon-de-Venise* e concluiu-se que dois fragmentos são de produção veneziana, um fragmento de produção veneziana ou espanhola, e os restantes vidros são de origem desconhecida. Em dois fragmentos o vidro utilizado na decoração poderá ser de produção veneziana ou espanhola mas o vidro do corpo é de proveniência desconhecida.

Abstract

A set of ten *Millefiori* glass fragments dating from the 17th century, originated from archaeological excavations carried out at the Monastery of Sta. Clara-a-Velha (Coimbra, Portugal) were characterized by X-ray electron probe micro-analysis (EPMA), Raman microscopy and UV-Visible absorption spectroscopy. All glasses are of soda-lime-silica type. The use of coastal plant ash is suggested by the relatively high content of MgO, K_2O and P_2O_5, as well as by the presence of chlorine. Tin oxide or calcium antimonate were the opacifiers used in the white glasses, cobalt is present in the blue glasses, copper in the turquoise, iron in the yellow and greenish, and iron and copper were found in the opaque red and aventurine glasses. Based on the concentrations of alumina and silica four different sources of silica were identified, allowing the classification of the glasses in the following compositional groups: low alumina (< 2 wt%), low alumina – *cristallo* (< 2 wt% and SiO_2 > 70 wt%) medium alumina (2 - 3 wt%), high alumina (3 - 6 wt%) and very high alumina (> 6 wt%). Comparison with genuine Venetian and *façon-de-Venise* compositions showed that two fragments are of Venetian production, one of Venetian or Spanish production and the remaining are of unknown provenance. In two fragments the glass of the decoration is probably Venetian or Spanish but the glass used in the body is also of unknown provenance.

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1. Introduction

The glass fragments analyzed in this study originated from archaeological excavations carried out at the Monastery of Sta. Clara-a-Velha in Coimbra, Portugal. The Monastery is located on the left bank of the River Mondego and it was occupied by the Order of Poor Clares from 1317 until 1677, when it was abandoned due to frequent flooding. The archaeological excavations carried out by IPPAR, the Portuguese Institute for Architectural Heritage (now IGESPAR, IP), from 1995 to 2002, have yielded an important archaeological record. A preliminary study of the assemblages indicates that the finds derive mainly from the last 50 years of the Monastery's existence, that is, the second and third quarters of the 17th century. [1-2] A large number of glass fragments was collected, most of them very well preserved. Preliminary studies on the glass finds have already been published, and the chemical characterisation of a few glass fragments by micro-EDXRF was also performed. [3-4]

1.1 The analyzed glass fragments

The present work focus on a set of glass fragments from *Millefiori* blown glass objects decorated either by picking up scrap glass or slices of multicoloured rods, by rolling the parison on them on the marble. Strictly speaking, the term *Millefiori* refers exclusively to glass objects decorated with slices of rods, though, in this work, it also comprises the objects decorated with multicoloured scrap glass, as the technique and final effect are similar. A brief description of the analyzed glass fragments is given in **Table 1.1** and the corresponding images are presented in **Figure 1.1**.

Table 1.1: Catalogue number, typology and colour of the *Millefiori* glass fragments analyzed.

Fragment	Object typology	Colour
SCV 171	Small bottle	Turquoise blue body decorated with applied dots of opaque white and opaque red glass
SCV 173	Cup	Opaque bluish white body decorated with applied dots of blue glass and aventurine
SCV 174	Vessel	Opaque red body decorated with an applied opaque white trail on the rim, and applied *millefiori* rods sections in opaque white, blue and opaque red glass.
SCV 175	Vessel	Opaque red body decorated with applied *millefiori* rods sections in opaque white, blue and opaque red glass
SCV 176	Unknown	Opaque white body decorated with applied dots of opaque red, blue glass and aventurine
V 66	Small flask	Greyish green body, decorated with applied *millefiori* rods sections in opaque white, blue and opaque red glass
V 67	Small bottle	Greenish yellow body decorated with applied dots of red and light blue glass
V 68	Small jug	Light blue body decorated with applied *millefiori* rods sections in opaque white and opaque red glass
V 74	Small flask	Green body decorated with applied dots of opaque white, light blue and opaque red glass
V 108	Goblet?	Blue body decorated with applied *millefiori* rods sections in opaque white, opaque red and turquoise blue glass

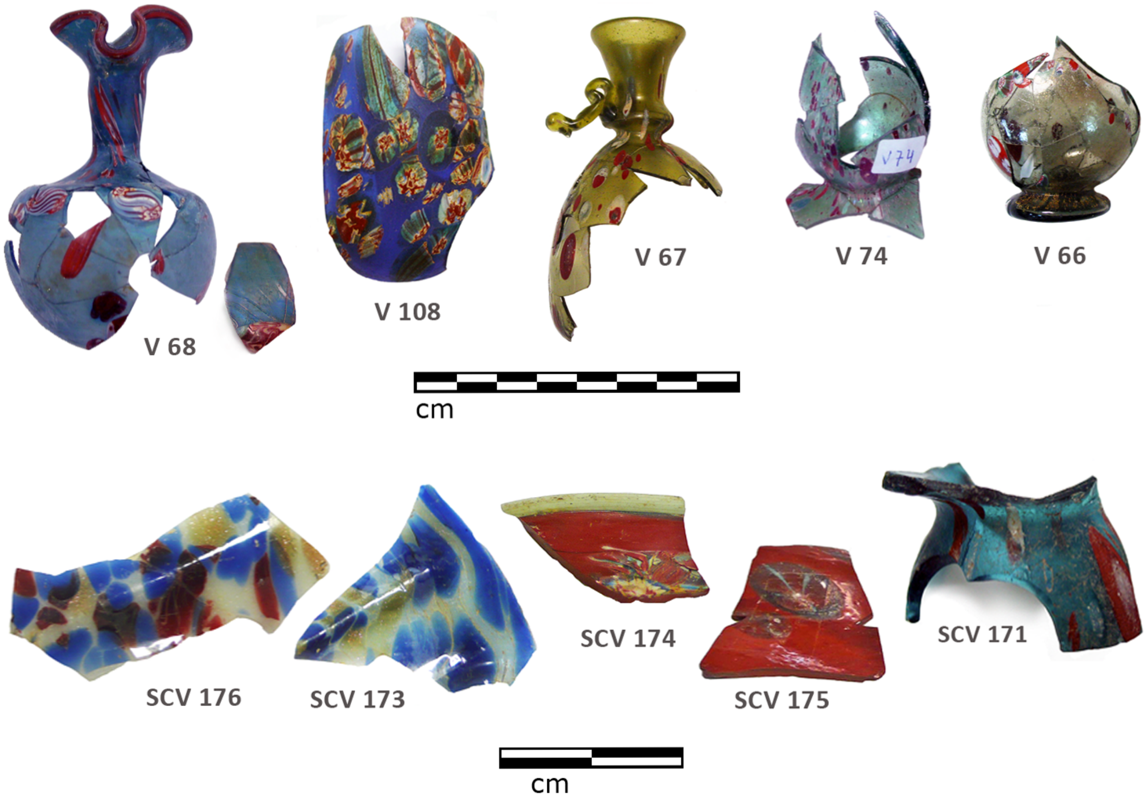

Figure 1.1: *Millefior*i glass fragments analyzed.

According to Teresa Medici[1], the fragments can be classified in three different groups based on their stylistic features. The first group includes fragments V 68, V 66, V 108, SCV 174 and SCV 175 decorated with multicoloured rods. This type of *Millefiori* glass is well known, primarily because there are many well preserved objects in museum collections. The majority of these objects are considered of Venetian production and dated between the end of the 15th and the beginning of the 17th century. [5] Others are supposed to be of Spanish origin, Catalan or Castilian as well. [6] Some archaeological information is available [7], showing not only the wide distribution of this latter category but also that during the 17th century *Millefiori* glass was produced in Amsterdam. [8]

The second group includes fragments SCV 176 and SCV 173 and consists of opaque glass vessels, decorated with dots of blue, red and aventurine glass. These fragments belong also to a well-known category of 17th century Venetian glass, including mainly cups, bowls and goblets. [9-11]

The third group comprises the fragments SCV 171, V 74 and V 67 and is related to objects that are abundant among the 17th century archaeological glass found in Portugal, showing some peculiar features: the body is usually made of coloured glass, in a range of yellows, greens or blues sometime with an intense tinge, and are decorated with opaque glass flecks of a limited palette of colours, mainly white, blue or red, arranged without a precise decorative scheme. This pick-up decorated

[1] Personal communication.

glass seems to be a simplified and coarser version of the previous groups. Apparently, there are no known examples comparable to these *Millefiori* glass vases. [7]

1.2 Research aims

In recent years, there was a growing interest on glasses originating from Portuguese excavations having in mind the provenance studies of the glass finds. A large variety of glass objects with different styles found in several locations has been investigated in order to distinguish imported glass from Portuguese glass.

The main objective of this work is to study the possible provenance of the *Millefiori glass* fragments originating from the Monastery of Sta. Clara-a-Velha based on the chemical composition of the various glasses. In a first step, the type of glass, as well as colourants and opacifiers added, used both in the body and decoration, will be identified. An attempt will also be made to distinguish compositional groups among the analyzed glasses and of establishing relations between the chemical compositions and the raw materials used. In a second part, the resulting compositions will be compared with those from Venetian and *façon-de-Venise* glasses in order to determine the possible manufacture locations for the *Millefiori* glasses.

With this work we expect to provide important evidence on production and circulation of glass in Portugal during the 17th century and to contribute to disclose the social habits of the Monastery of Sta. Clara-a-Velha.

1.3 The European post-medieval glass – glass centres, compositions and raw materials

In the 16th and 17th centuries, Venice was the most important European centre of glass production.

The style of Venetian glass, allied to its high quality and technique, was greatly admired all over Europe, becoming so successful that rapidly Venetian designs started to be widely imitated by other European glasshouses. The imitation of Venetian style started in the second half of the 16th century, when some glassmakers escaped from Murano to set up glasshouses in other countries, such as France, England, Low Countries (Belgium and Netherlands), Spain and Slovenia. [5][12-16]

Consequently, the same production methods, forms and decoration techniques were used in Venice and in these glasshouses and it is still difficult to distinguish with the naked eye genuine Venetian glass from the so called *façon-de-Venise* production. [10][14]

In Portugal, historical documents report the production of glass since the 15th century and in the 17th century several production centres were already active, including one in Coimbra. [17] Unfortunately, there is not yet archaeological evidence of these glasshouses.

Several studies have been made on Venetian and *façon-de-Venise* glasses, primarily with the aim of establishing the differences and similarities in chemical composition between the two productions and, in this way, to contribute to the provenance studies of glasses preserved in museums or found in archaeological contexts. [10][13-16][18-21]

The nature of the raw materials used (e.g. sand vs. quartz pebbles), the purification treatments to which some of these materials were subjected prior to use (e.g. of the plant ash) and the batch formulation are the main factors influencing the chemical composition. In some cases the compositions are so similar that the distinction of manufacture locations was possible only through the analysis of trace elements. [15-16]

The 17th century Venetian clear glass can be classified into three groups: *vetro comune* (ordinary glass, slightly coloured), *vitrum blanchum* (intermediate glass, colourless) and *cristallo*, all the three of soda-lime-silica type. *Cristallo* was the finest glass produced by the Muranese glassmakers; it was completely clear, free of defects and with high light transmittance, comparable to natural rock crystal. [10] In the making of *cristallo*, quartz pebbles of very high purity were used as silica source and purified plant ashes as the source of fluxing agents. The purification procedure reduced the amount of iron impurities but also the content of Ca and Mg leading to glasses particularly vulnerable to weathering. [10][22]

Concerning *façon-de-Venise* glass, some authors adopted the same classification as used for Venetian glass [14-15] while others classified the glasses according to the raw materials used. [19][21] Based on the published data on Venetian and *façon-de-Venise* glass [10][14][18][21] which average compositions are summarized in Table 1.2, some relevant conclusions for this work can be drawn. With respect to the silica source, the content of Al_2O_3 in Venetian glass is always below 2 wt% (usually, below 1 wt% for cristallo) and that of Fe_2O_3 is either below 0.5 wt%, in *cristallo* or *vitrum blanchum* glass, or below 1 wt% on common glass. The low amount of these oxides in *cristallo* or *vitrum blanchum* glass is related also with the use of high purity quartz pebbles. [10] Regarding *façon-de-Venise* glass, which designates here all non Venetian glasses, independently on the authors classification, the amount of Al_2O_3 is generally also below 2 wt%, except for the productions classified by Cagno *et al.* as "Tuscany Barilla" and "Tuscany Levantine". These *façon-de-Venise* glasses produced in the Italian region of Tuscany show amounts of Al_2O_3 varying from 4.1 - 4.6 wt% due, according to the author, to the use of local feldspathic silica sand. [21] The amount of iron is similar to that found on Venetian glasses. It was noted by Cagno *et al.* [21] that the K_2O content allows the identification of the origin of the ashes used: Levantine ash typically contributes to glasses with K_2O contents between 1.5 and 4 wt% whereas Barilla ash is usually related to glasses with K_2O levels above 5 wt%. This is a quite questionable interpretation, as there are other sources of K_2O indicated in medieval recipe books, such as tartar (a deposit of wine barrels, which after firing gives potassium carbonate) to be added to a soda-lime-silica batch. In a previous paper [14][19] the same authors considered that the Spanish II glasses, with an average content of K_2O of 3.48 ± 0.49 wt%, were produced with Barilla ash; however, these concentrations, accordingly with them, are in agreement with Levantine ash. Therefore, in this work, the classification of compositions having in mind the attribution of glass provenance will be made primarily based on the distinction of silica sources and not on the fluxes used.

The compositions of the French and Slovenian glasses were not included in this table. The former because it is not clear which glasses were imported from Venice and which were locally made and the later because as far as we know major compositions are not available (distinction between Venetian and Slovenian glasses was only possible through trace elements content).

It should be stressed out that the attribution of provenance based on chemical composition has some limitations. For instance, the use of different silica sources may lead to similar compositions, and the distinction of provenance is usually only possible when comparing trace elements analysed. [14] On the other hand, distinct locations could be using the same source of silica and manufacturing the same type of glass, and therefore the major composition of glass, and in this case also the trace elements are of no use for the attribution of provenance. [16]

Table 1.2: Average chemical compositions, and corresponding standard deviations, of Venetian and *façon-de-Venise* glasses, dating from the 16th-17th centuries, in weight percent of oxides.

Location	Classification	Type	Date	Nr. of samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	PbO	SnO_2
Venice [10]	*Cristallo*	Soda-lime-silica	16th-18th c.	*(n=16)*	17.17	1.81	0.68	70.49	0.15	0.3	1.00	2.93	4.88	0.03	0.32	0.24		
					1.49	0.38	0.14	1.34	0.04	0.07	0.11	0.41	0.69	<0.03	0.14	0.05		
	Vitrum Blanchum	Soda-lime-silica	16th-18th c.	*(n=33)*	13.64	3.35	1.03	66.9	0.31	0.24	0.86	2.97	9.76	0.05	0.47	0.37		
					1.36	0.73	0.37	1.71	0.12	0.08	0.12	1.20	1.18	0.02	0.20	0.08		
	Common	Soda-lime-silica	16th-18th c.	*(n=8)*	13.42	3.11	1.71	64.72	0.33	0.19	0.66	3.30	10.07	0.05	1.27	0.84	0.15	0.10
					0.92	0.25	0.15	0.66	0.09	0.04	0.07	0.59	0.57	0.01	0.32	0.08	0.07	0.06
Amsterdam [14]																		
Waterlooplein		Soda-lime-silica	17th c.	*(n=74)*	13.3	2.85	1.79	65.5	0.28	0.13	0.59	5.02	9.13		0.57	0.51		
					1.4	0.28	0.46	1.6	0.06	0.04	0.08	1.53	1.32		0.21	0.11		
Keizersgracht		Soda-lime-silica	17th c.	*(n=38)*	14.3	3.25	2.12	64.1	0.22	0.12	0.62	4.74	8.83		0.5	0.74		
					1.1	0.38	0.35	1.5	0.07	0.04	0.08	0.88	1.24		0.23	0.24		
Antwerp [14] *																		
	Façon-de-Venise	Soda-lime-silica	2nd half 16th c.		14.5	2.85	1.45	63.9	0.32	0.14	0.66	5.56	9.63		0.34	0.42		
					1.4	0.45	0.14	2.1	0.07	0.04	0.11	1.24	1.01		0.14	0.07		
	Cristallo	Soda-lime-silica	17th c.		15.02	1.68	1.64	69.7	0.35	0.19	0.67	4.51	4.85		0.51	0.32		
					0.94	0.24	0.47	1.93	0.77	0.07	0.14	0.83	0.76		0.16	0.07		
	MIxed Alkali	MIxed Alkali	17th c.		12.0	1.87	1.59	68.9	0.22	0.15	0.48	8.27	5.40		0.50	0.40		
					1.0	0.27	0.10	1.4	0.07	0.06	0.12	0.78	0.53		0.15	0.12		
London [14]																		
Old Broad Street		Soda-lime-silica	1st half 17th c.	*(n=32)*	13.1	3.14	1.76	64.7	0.33	0.20	0.57	5.05	9.62		0.68	0.55		
					1.3	0.36	0.21	0.9	0.07	0.04	0.11	1.50	0.56		0.30	0.14		
Aldgate		MIxed Alkali	1st half 17th c.	*(n=40)*	10.06	2.56	1.46	64.3	0.3	0.13	0.47	9.62	9.40		0.38	0.37		
			(probably 2nd quarter)		0.5	0.11	0.16	0.5	0.1	0.03	0.03	0.45	0.47		0.12	0.04		
Spain [18] **																		
	Spanish I	Soda-lime-silica	end 16th -17th c.		10.24	1.13	1.09	67.13	1.06	0.23		6.87	9.85		1.38	0.59	0.016	
					1.06	0.14	0.31	1.36	0.09	0.09		1.05	1.23		0.42	0.13	0.015	
	Spanish II	Soda-lime-silica	end 16th -17th c.		11.67	3.41	1.72	67.35	0.63	0.31		3.48	9.85		0.62	0.69	0.013	
					1.14	0.42	0.54	1.58	0.14	0.08		0.49	1.66		0.25	0.19	0.008	
Tuscany [21]																		
Gambassi	Tuscany Barilla	Soda-lime-silica	Mid 16th c.	*(n=8)*	14.2	3.4	4.6	59.2	0.4	0.1	0.5	5.7	9.5		1.3	0.7		
					1.0	0.3	0.3	0.5	0	0.1	0.1	0.6	0.4		0.4	0.2		
	Tuscany Levantine	Soda-lime-silica	Mid 16th c.	*(n=1)*	14.4	4.1	4.4	60.9	0.5	0.2	0.5	3.9	9.5		1.3	0.7		
San Giovanni Valdarno																		
	Tuscany Barilla	Soda-lime-silica	16th c.	*(n=11)*	14.4	3.1	4.3	59.3	0.4	0.1	0.6	6.0	9.8		1.0	0.6		
					1.5	0.4	0.3	1.6	0.1	0.0	0.1	0.8	1.2		0.3	0.1		
	Tuscany Levantine	Soda-lime-silica	16th c.	*(n=3)*	15.8	4.5	4.1	60.7	0.5	0.2	0.6	3.6	8.2		1.0	0.6		
					0.7	0.3	0.1	1.3	0.1	0.1	0.1	0.1	1.1		0.4	0.1		
	Pebbles Barilla	Soda-lime-silica	16th c.	*(n=1)*	10.3	3.4	1.7	62.7	0.4	0.1	0.5	8.8	10.7		0.7	0.5		
	Pebbles Levantine	Soda-lime-silica	16th c.	*(n=1)*	16	1.4	2.1	67.6	0.6	0.1	0.9	3.0	6.1		1.2	0.6		

***** A set of 132 glasses was analyzed but the exact number of glasses included in each group is not indicated by the authors. ** The number of glasses included in each group is not provided by the author.

2. Experimental

Small samples of few mm^2 were removed by dry cutting the fragments with a diamond file. The samples were embedded in cross-section in an acrylic resin and polished with abrasive papers and pastes down to 0.5 μm grain size. The chemical composition of glasses, of both body and decoration, was determined by X-ray electron probe micro-analysis (EPMA) using two different equipments: a Cameca SX-50 micro-analyzer equipped with three wavelength-dispersive spectrometers (PET, LiF and TAP crystals), from *Stazione Sperimentale del Vetro*, and a Jeol JXA-8500F micro-analyzer equipped with five wavelength-dispersive spectrometers (PET, LiF and TAP, LDE1 crystals) from *Laboratório Nacional de Engenharia e Geologia*. The operating conditions used in the first microprobe were: accelerating potential 15 kV, beam current 20 nA (major and minor components) or 100 nA (trace elements), respectively. A 40x50 μm scanning electron beam and limited counting time (10 s for major and minor elements, 20 to 30 s for traces) were employed to ensure that no significant alkali drift (ion migration) occurred during the irradiation. The net X-ray intensities (peak minus background) were quantified by means of a PAP correction program supplied by CAMECA. The operating conditions of the second microprobe were: accelerating potential 15 kV, beam current 10 nA (major and minor components). An 8-10 µm diameter electron beam and limited counting time (10 s for major and minor elements, 20 to 30 s for traces) was used.

At least two different areas were analyzed in each glass. The relative standard deviation for SiO_2, Na_2O, K_2O, CaO and MgO is below 1 % and for the remaining elements or oxides, Al_2O_3, SO_3, P_2O_5, Cl, Fe_2O_3, MnO, CuO, PbO, SnO_2, CoO, As_2O_5, ZnO and NiO, is below 5 %.

Two complementary techniques were also used in the study of colourants and opacifiers: UV-Visible absorption spectroscopy, to confirm the presence of the transition metal ions acting as colourants, and Raman microscopy, to aid in the identification of the crystalline phases, i.e. of the opacifying compounds. Raman microscopy was carried out using a Labram 300 Jobin Yvon spectrometer, equipped with an Nd:YAG laser 50 mW operating at 532 nm and a He-Ne laser 17 mW at 633 nm. Spectra were recorded as an extended scan. The laser beam was focused either with a 50 x or a 100 x Olympus objective lens. The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (optical densities 0.3, 0.6, 1 and 2).

The UV-Visible absorption spectra were measured with an Avantes AvaSpec-2048 fibre optic spectrometer. It is a fibre optic spectrometer with a 300 lines/mm grating. The operational range is 200 to 800 nm and the instrument has an FWHM resolution of 2.4 nm. The light transmitted was measured using a 200 μm transmission probe (Avantes FC-UV600-2).

3. Results and discussion

In this work, the interpretation of the obtained chemical compositions was performed in two ways: the study of colourants, decolourants and opacifiers was based in the compositions obtained directly from EPMA analysis, named hereafter as compositions of the “coloured glasses” (**Table 3.1**). The distinction of compositional groups among the analyzed fragments and the comparison of compositions with those from Venetian and *façon-de-Venise* productions, was carried out using the composition of the “base glass”. The majority of the analyzed Venetian and *façon-de-Venise* glasses is colourless or slightly coloured. In order to avoid variability of composition due to the presence of colourants and/or opacifiers, and thus an erroneous distinction of compositional groups, the composition of the base glass was obtained by subtracting to the composition of the “coloured glasses” the content of colourants, decolourants and opacifiers and then normalizing it to 100 wt% (**Table 3.2**). The concentration of the iron oxide in the blue and opaque red glasses was estimated having in mind the concentration of this oxide in the other glasses, in which iron is part of the base glass composition. However, these estimated values of the order of 1 % do not influence the final conclusions.

In this chapter, the nature of colourants, decolourants and opacifiers used in the *Millefiori* glasses (section 3.1) will be considered in first place, followed by a discussion on the raw materials used and the comparison of the base glass compositions with those from Venetian and *façon-de-Venise* production (section 3.2).

Table 3.1: Composition of the coloured glasses, in weight percent of oxides, obtained by EPMA.

Fragment	Colour		Analyzed area	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	SO3	P_2O_5	Cl	TiO_2	Fe_2O_3	MnO	Sb_2O_3	CuO	PbO	SnO_2	CoO	As_2O_3	ZnO	NiO
SCV 171	Turquoise blue	Transp.	Body	62.8	1.35	15.2	2.67	6.43	2.41	0.26	0.23	0.82		0.66	0.61		1.09	3.01	2.30				
SCV 171	Red	Op.	Decoration	58.1	1.26	13.3	2.28	8.26	3.19	0.19	0.28	0.73		3.19	0.52		0.92	5.14	3.18				
SCV 171	White	Op.	Decoration	55.5	0.69	11.8	1.93	6.51	2.80	0.11	0.24	0.79		0.39	0.23			11.3	7.75				
SCV 173	Bluish white	Op.	Body	65.1	1.27	14.3	3.30	8.45	3.06		0.25			1.01	0.33	2.67	0.22	0.23			0.09		
SCV 173	Aventurine	Transp.	Decoration	59.0	2.27	14.1	3.11	8.19	2.89		0.34			4.54	0.84	0.14	2.00	2.15	1.76			0.17	
SCV 173	Blue	Transp.	Decoration	65.4	1.61	12.6	2.66	3.32	1.13		0.06			1.84	0.75	0.25	1.09	5.59		0.65	2.84		0.18
SCV 174	Red	Op.	Body	58.5	4.59	15.9	2.47	7.18	4.02	0.13	0.40	0.87	0.19	4.04	0.15		1.11	0.49	0.41		0.13		
SCV 174	Blue	Transp.	Decoration	59.5	3.16	18.2	3.05	7.76	3.26	0.13	0.39	1.06	0.09	1.01	0.74		0.46			0.43	0.69		0.07
SCV 174	Red	Op.	Decoration	57.8	3.83	15.8	2.37	7.46	3.96	0.10	0.44	0.98	0.16	4.53	0.16		0.93	0.63	0.41				
SCV 174	White	Op.	Decoration	36.8	2.63	10.4	1.94	4.41	2.04		0.23	0.95		0.47	0.13		0.22	25.5	14.4				
SCV 174	White	Op.	Trail on rim	44.8	3.27	12.0	2.18	5.38	2.40	0.12	0.26	0.73	0.08	0.68	0.23		0.06	19.1	9.50				
SCV 175	Red	Op.	Body	58.1	5.33	14.1	5.39	8.20	2.81		0.37		0.29	4.34	0.44	0.16	1.12	0.20					
SCV 175	Red	Op.	Decoration	58.6	5.35	13.9	5.43	8.22	2.73		0.33		0.20	4.11	0.38	0.20	0.96						
SCV 175	White	Op.	Decoration	53.98	3.89	12.49	4.71	6.99	2.30	0.09	0.27	0.75	0.19	0.80	0.32		0.78	8.06	3.76		0.15		
SCV 176	White	Op.	Body	63.6	1.11	13.6	1.49	7.97	3.32	0.32	0.20	0.74		0.73	0.24	2.95		3.90				0.18	
SCV 176	Aventurine	Transp.	Decoration	59.4	2.38	13.6	1.80	8.71	3.19		0.30		0.09	3.17	1.23	0.18	1.82	2.50	1.90				
SCV 176	Blue	Transp.	Decoration	70.7	1.53	13.2	2.63	2.91	0.98	0.12	0.14	0.51		1.52	0.47	0.21	0.12	0.97		0.75	2.97		0.09
SCV 176	Red	Op.	Decoration	60.8	2.20	13.9	2.30	8.36	3.06		0.39		0.13	2.91	1.49	1.12	0.95	1.28	0.77		0.15		
V 66	Greyish-green	Transp.	Body	58.2	7.61	16.9	4.12	5.92	2.76	0.15	0.36	0.88	0.20	1.15	1.13								
V 66	Red	Op.	Decoration	60.3	6.27	13.4	3.42	8.78	3.69	0.11	0.36	0.64	0.21	1.68	0.92		1.25	0.48	0.22				
V 66	White	Op.	Decoration	42.1	5.36	10.9	3.01	2.61	1.30		0.46		0.19	0.63	0.18		0.22	29.20	3.00				
V 67	Greenish yellow	Transp.	Body	54.3	7.84	19.2	1.85	4.71	6.61	0.07	0.82	0.88	0.66	2.15	0.95								
V 67	Blue	Transp.	Decoration	66.6	1.22	14.9	2.24	8.42	3.46	0.36	0.33	0.87		0.89	0.10			0.18	0.10	0.11	0.28		0.04
V 67	Red	Op.	Decoration	56.0	1.23	13.2	2.22	8.81	3.06	0.22	0.28	0.63	0.10	3.17	0.70		1.15	5.22	3.16				
V 68	Light blue	Transp.	Body	58.4	3.81	13.2	5.72	11.14	2.97	0.09	0.36	0.46	0.29	1.66	1.34		0.03	0.13			0.15		
V 68	Red	Op.	Decoration	57.8	5.26	15.6	4.31	6.45	2.33	0.10	0.51	0.72	0.62	4.81	0.66		0.36	0.32	0.20				
V 68	White	Op.	Decoration	50.1	3.48	12.2	2.60	5.60	2.28		0.35		0.17	1.58	0.54		0.14	16.3	3.99				
V 74	Green	Transp.	Body	59.8	2.49	15.6	3.13	7.24	2.94	0.22	0.32	0.74		0.94	0.33		0.79	2.83	2.35				
V 74	Light blue	Transp.	Decoration	59.2	1.46	12.5	1.63	9.53	3.61		0.33		0.08	1.63	0.88		0.27	3.92	3.90		0.10		
V 74	Red	Op.	Decoration	58.0	1.34	12.1	1.76	9.23	3.48		0.33		0.09	3.90	0.82		0.69	4.21	4.03		0.14		
V 74	White	Op.	Decoration	51.3	0.83	11.6	1.66	6.00	2.72	0.13	0.26	0.59		0.50	0.72			11.9	11.2				
V 108	Blue	Transp.	Body	60.8	4.57	15.4	5.50	6.54	2.98	0.19	0.29	0.78	0.14	0.81	0.46			0.11	0.06				
V 108	Red	Op.	Decoration	57.0	4.18	14.3	5.18	6.89	3.45	0.19	0.30	0.61	0.15	6.10	0.46		0.53	0.33	0.37				
V 108	Turquoise blue	Transp.	Decoration	58.6	4.69	14.67	4.40	7.32	4.03		0.32		0.21	0.70	0.47	0.11	4.03	0.19	0.06				
V 108	White	Op.	Decoration	38.4	2.75	8.54	3.24	4.42	2.21	0.10	0.14	0.58	0.12	0.52	0.11		0.40	21.5	17.9				

Transp. = transparent; Op. = opaque.

Table 3.2: Calculated composition of the base glass of the coloured samples, in weight percent of oxides.

Fragment	Colour of glass		Area	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	SO_3	P_2O_5	Cl	TiO_2	Fe_2O_3
SCV 171	Turquoise blue	Transp.	Body	67.6	1.45	16.4	2.88	6.92	2.59	0.27	0.25	0.89		0.71
SCV 171	Red	Op.	Decoration	65.9	1.43	15.1	2.59	9.37	3.62	0.21	0.31	0.83		0.68
SCV 171	White	Op.	Decoration	68.5	0.85	14.6	2.39	8.04	3.46	0.13	0.30	0.97		0.74
SCV 173	Bluish white	Op.	Body	67.3	1.31	14.8	3.41	8.73	3.16		0.26			1.04
SCV 173	Aventurine	Transp.	Decoration	64.9	2.50	15.5	3.42	9.01	3.18		0.37			1.10
SCV 173	Blue	Transp.	Decoration	74.5	1.83	14.4	3.03	3.78	1.29		0.07			1.14
SCV 174	Red	Op.	Body	61.7	4.84	16.8	2.60	7.57	4.24	0.14	0.42	0.92	0.20	0.67
SCV 174	Blue	Transp.	Decoration	61.2	3.25	18.7	3.13	7.98	3.36	0.13	0.40	1.09	0.10	0.62
SCV 174	Red	Op.	Decoration	61.8	4.10	16.9	2.54	7.98	4.24	0.11	0.47	1.05	0.17	0.64
SCV 174	White	Op.	Decoration	61.6	4.39	17.3	3.25	7.38	3.41		0.39	1.58		0.67
SCV 174	White	Op.	Trail on rim	62.4	4.55	16.7	3.03	7.48	3.34	0.16	0.37	1.01	0.11	0.83
SCV 175	Red	Op.	Body	61.0	5.60	14.8	5.66	8.61	2.95		0.39		0.30	0.63
SCV 175	Red	Op.	Decoration	61.5	5.61	14.6	5.69	8.62	2.86		0.35		0.21	0.63
SCV 175	White	Op.	Decoration	62.4	4.50	14.4	5.44	8.08	2.66	0.12	0.31	0.87	0.22	0.97
SCV 176	White	Op.	Body	68.3	1.19	14.6	1.61	8.57	3.57	0.34	0.22	0.80		0.78
SCV 176	Aventurine	Transp.	Decoration	65.9	2.64	15.1	2.00	9.66	3.54		0.33		0.10	0.78
SCV 176	Blue	Transp.	Decoration	75.7	1.64	14.1	2.82	3.11	1.05	0.13	0.15	0.55		0.75
SCV 176	Red	Op.	Decoration	66.2	2.40	15.1	2.50	9.10	3.33		0.42		0.14	0.76
V 66	Greyish-green	Transp.	Body	59.2	7.75	17.2	4.19	6.02	2.81	0.16	0.37	0.90	0.20	1.17
V 66	Red	Op.	Decoration	61.5	6.39	13.7	3.49	8.95	3.76	0.11	0.37	0.65	0.21	0.95
V 66	White	Op.	Decoration	63.4	8.07	16.4	4.53	3.93	1.96		0.69		0.29	0.75
V 67	Greenish yellow	Transp.	Body	54.8	7.91	19.4	1.87	4.75	6.67	0.07	0.82	0.89	0.67	2.17
V 67	Blue	Transp.	Decoration	67.1	1.23	15.0	2.26	8.49	3.48	0.36	0.33	0.87		0.89
V 67	Red	Op.	Decoration	64.7	1.42	15.3	2.56	10.2	3.54	0.26	0.33	0.73	0.11	0.92
V 68	Light blue	Transp.	Body	60.0	3.92	13.5	5.88	11.4	3.05	0.09	0.37	0.47	0.30	0.92
V 68	Red	Op.	Decoration	61.1	5.56	16.5	4.56	6.82	2.46	0.11	0.54	0.77	0.65	0.95
V 68	White	Op.	Decoration	64.5	4.48	15.7	3.35	7.21	2.94		0.45		0.22	1.16
V 74	Green	Transp.	Body	64.0	2.66	16.7	3.36	7.75	3.15	0.23	0.35	0.79		1.01
V 74	Light blue	Transp.	Decoration	66.3	1.64	14.0	1.83	10.7	4.05		0.37		0.09	1.01
V 74	Red	Op.	Decoration	66.5	1.54	13.9	2.02	10.6	3.99		0.38		0.10	1.03
V 74	White	Op.	Decoration	67.9	1.10	15.3	2.20	7.94	3.60	0.17	0.35	0.79		0.66
V 108	Blue	Transp.	Body	62.1	4.67	15.7	5.61	6.67	3.05	0.19	0.29	0.79	0.14	0.83
V 108	Red	Op.	Decoration	61.3	4.50	15.4	5.57	7.41	3.71	0.21	0.32	0.66	0.17	0.75
V 108	Turquoise blue	Transp.	Decoration	61.7	4.94	15.4	4.63	7.71	4.24		0.34		0.22	0.74
V 108	White	Op.	Decoration	63.0	4.50	14.0	5.31	7.24	3.62	0.16	0.23	0.95	0.19	0.85

Transp. = transparent; Op. = opaque.

3.1 Colourants and opacifiers

In most glasses, the different colours were achieved through the addition of colourants and/or opacifiers to the base glass batch or directly into the melt. In a few cases, the colour is a consequence of using raw materials with a relatively high amount of iron impurities, combined with a partial decolouration process.

In the following paragraphs the different colours will be discussed individually, based on the composition obtained for the coloured glasses.

Opaque white glass

The colour and opacity of white glass is due to microcrystals dispersed in the glass matrix. For this reason, besides EPMA, Raman microscopy was also used in the study of these glasses to aid in the identification of crystalline phases. The analytical results revealed that, of the ten white glasses analyzed, cassiterite (SnO_2) was the colourant and opacifier used in eight glasses (**Figure 3.1**), while in the remaining two glasses (SCV 173 and 176), the white opacification can be attributed to crystals of calcium antimonate in its $Ca_2Sb_2O_7$ form (**Figure 3.2**).

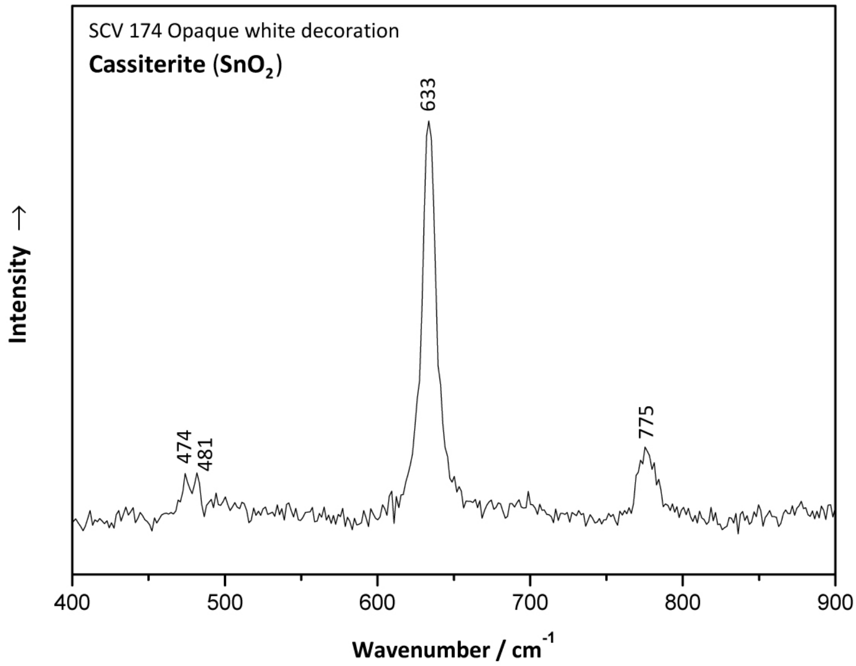

Figure 3.1: Raman spectrum of cassiterite (SnO_2), identified in the crystalline phase of the opaque white glass present in the decoration of fragment SCV 174.

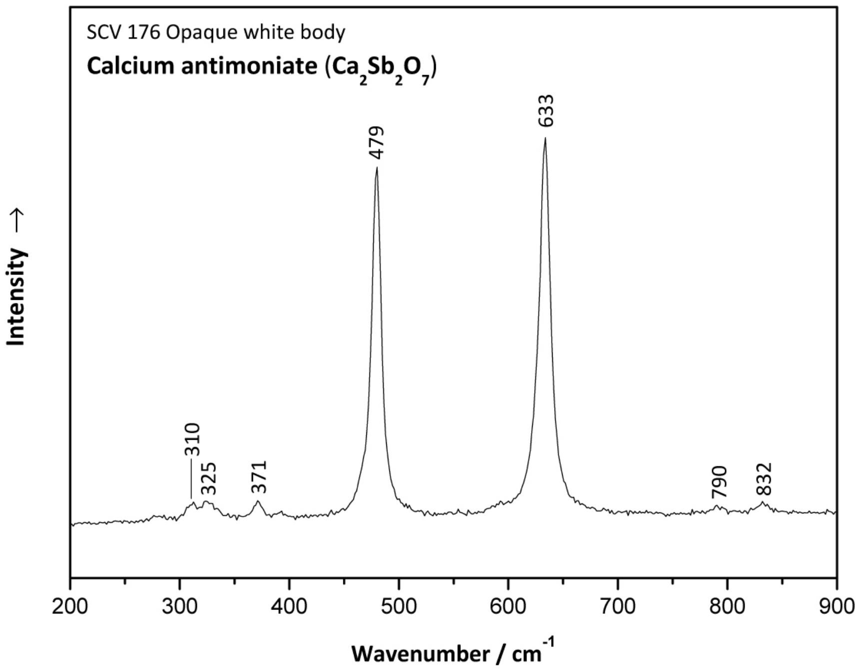

Figure 3.2: Raman spectrum of calcium antimonate, in its $Ca_2Sb_2O_7$ form, identified in the crystalline phase of the opaque white glass of body of fragment SCV 176.

The Raman signature of cassiterite are the bands at 633 - 775 cm^{-1}, and frequently an additional less intense band is observed at ca. 474 cm^{-1}. These frequencies are almost identical to the signature

Raman bands of $Ca_2Sb_2O_7$, at ca. 480 and 633 cm^{-1}, although it is still possible to distinguish the spectra of both through the intensities ratios of the bands and also by the additional bands of $Ca_2Sb_2O_7$ (at ca. 318, 367, 781 and 820 cm^{-1}). [23-25]

In the production of opaque white glass, or *lattimo*, the term used in the Venetian documents and in glass recipes from the beginning of the 15th century onwards, the opacifier was prepared by calcining metallic lead and tin and separating the white calx (mixture of lead and tin oxides) formed on the surface. This calx was added to the batch: the lead oxide dissolved in the melt and crystals of tin oxide (cassiterite) precipitated within the glass matrix. [11] Variable amounts of lead (8.06-29.2 wt%) were found in the *Millefiori* tin opacified white glasses indicating that this procedure was used in these glasses. The ratio PbO/SnO_2 varies from 1/1 to 10/1, which indicates that no specific recipe was adopted in all the fragments.

Calcium antimonate has already been identified in white opaque glasses from Ancient Egypt, Roman Age, Renaissance and Modern times. [11][23-25] It was the preferred opacifier of Roman glassmakers but for some unclear reason its use declined in Late Antiquity and early Middle Ages when it was replaced by other opacifiers, including tin oxide. Antimony as an opacifier was reintroduced in Venice during the 16th century. [11] Calcium antimonate may crystallize in two forms: $CaSb_2O_6$ or $Ca_2Sb_2O_7$, being the latter the one found in a few 16th-18th century Venetian glass vessels analyzed by Raman microscopy. [23] According to recipes reported in the *Darduin* treatise, written in Venice in the first half of 17th century, the antimony opacifier was prepared by heating soda ash (some of it purified), quartz pebbles, minium (lead oxide, Pb_3O_4) and antimony at relatively low temperatures and for approximately eight hours. As a result of the reaction between calcium oxide (contained in the plant ash) and antimony, crystals of calcium antimonate were formed. This frit was then added to the base glass to produce the antimony opacified white glass. [11]

Opaque red glass

According to analytical studies on ancient and historical opaque red glasses, red colouration can be produced by nanocrystals of metallic copper dispersed in the glass matrix as well as by dendritic crystals of cuprous oxide. Batch composition and melting conditions are the key parameters controlling the state of oxidation of copper. Elements as iron, lead, antimony and tin have been suggested to act as reducing agents. [25-28] The eleven opaque red glasses analyzed in this study contain CuO from 0.36 - 1.25 wt% and Fe_2O_3 from 1.68 - 6.10 wt%. The mean concentration of CuO is 0.91 wt% and of Fe_2O_3 is 3.89 wt%. In general way, the amounts of CuO and Fe_2O_3 found in our glasses are in agreement with those reported in literature for some 16th-17th century opaque red glasses. [11][27]

Small amounts of antimony, lead and tin were also found, suggesting that small quantities of tin-lead calx and antimony were deliberated added to the base glasses, as recommended by some historical recipes to aid in the formation of the red colour. Nevertheless, identical quantities of these elements are also present in other transparent colours, as for instance in the blue and green glasses of fragments SCV 171 and V 74, which suggests the use of cullet glass. Comparison of compositions among the analyzed red glasses showed that the red glasses of fragments SCV 171, V 67 and V 74 are comparable and in fragment SCV 174 it was used the same red glass in the body and decoration, as well as in fragment SCV 175. The red glass of fragment SCV 176 contains an extraordinarily high amount of manganese (1.49 wt%). The average content of this oxide in the other red glasses is 0.52 wt%. Manganese is usually added to the melt to neutralize the colouring effect of iron, which is irrelevant in red glasses, however in this case it may have been added to change the red hue colour. [27] In a study of a Venetian polychrome goblet dating from the 16th century, Verità has also noted an anomalous content of manganese in the red glass applied in the decoration suggesting that this oxide contributed to the a slight violet hue of the red glass. [11]

Concerning the identification of the exact colouring agent – Cu^0 or Cu^{1+} (Cu_2O) –, it was not possible to reach any conclusion using the available analytical techniques. Crystallites of cuprite (0.5-1μm) were recently identified in Roman opaque red glasses by Raman microscopy. [24-25] In this work, Raman microscopy did not identify this crystallite, which could be due to the poor scattering behaviour of cuprite or the red colour being given by nanocrystals of metallic copper, and therefore not rendering a first order Raman spectrum.

Aventurine

The term aventurine refers to a glass with a sparkling gold aspect, invented by the Muranese glassmakers in the first half of the 17th century, according to Venetian documents. However aventurine glass is already present in a Venetian goblet dating from the second half of the 16th century. [11] The characteristic golden sparkling effect results from the formation of small crystals of metallic copper during the very slow cooling of a melt in a well controlled reducing atmosphere. According to Weyl [29], the difference between opaque red and aventurine glasses lies on the size of the crystals of metallic copper: a few nm in opaque red glasses and up to 1 mm in aventurine.

In the analyzed *Millefiori* fragments, aventurine is present in the decoration of fragments SCV 173 and 176. The results show that copper, iron, antimony, lead and tin were added to the base glass, similarly to what has been already observed in the red opaque glasses. However, the copper content is higher in the aventurine glass (1.82 and 2.00 wt%) than in the red glasses. Iron plays again the role of a reducing agent (3.17 and 4.54 wt%) and contrarily to what has been suggested for most of the red opaque glasses, it seems that in both aventurine glasses a small amount of lead-tin calx was also added with this same purpose. Regarding antimony oxide, it is present in such small amounts and in similar quantities as in the transparent blue glasses that it was most likely introduced with cullet glass.

Turquoise blue

Bluish green transparent glass is present in the body of fragment SCV 171 and in the applied sections of canes of fragment V 108. The colour is produced by copper ions in its divalent state, Cu^{2+}, and is obtained by melting the glass in oxidizing conditions. [29-30] The presence of divalent copper was confirmed in fragment SCV 171 by its characteristic broad band with a maximum wavelength between 780 and 810 nm in the UV-Vis absorption spectrum (**Figure 3.3**). Quite unusual is the content of copper oxide in fragment V 108 (4.03 wt%), about four times more than the amount detected on fragment SCV 171 (1.09 wt%). The explanation can be related with the thickness of the glass: if the glass is to be used in a very thin layer, a high quantity of colourant is required otherwise the glass will seem colourless when applied. When the end use is the body of an object, less colourant is needed because the thickness is higher. Small amounts of lead and tin are also present in both glasses, almost certainly due to the recycling of a certain amount of cullet glass.

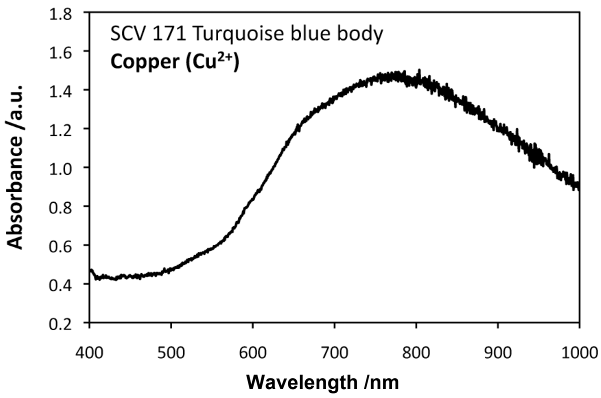

Figure 3.3: UV-Vis absorption spectrum of the turquoise blue glass of fragment SCV 171.

Blue

The blue colour is given by the cobalt ion Co^{2+} in a tetrahedral environment. Cobalt oxide is present in the composition of four of the seven blue glasses analyzed. It is interesting to note that it was detected in decoration glasses in concentrations of 0.11, 0.43, 0.65 and 0.75 wt%. Contents higher than 0.10 wt% rarely appear in blown blue glass [11] but, as stated earlier, a high content of colourant is required when the coloured glass is applied in a thin layer.

In the bodies of fragments V 68 and V 108 the ion Co^{2+} was identified by means of UV-Vis absorption spectroscopy (**Figure 3.4**) through its characteristic triple band at 540, 590 and 640 nm. [30] In the glasses where cobalt is present, arsenic, iron and nickel were also detected in small amounts (the presence of zinc, sought in the analysis, was not detected). These elements coexist with cobalt in the mineral added for colouring the blue glass. According to comparative studies performed by Gratuze [31-32], the association of Co, Fe, Ni and As indicates that the mineral used in these glasses was probably from the mines of Schneeberg, in Erzgebirge, Germany.

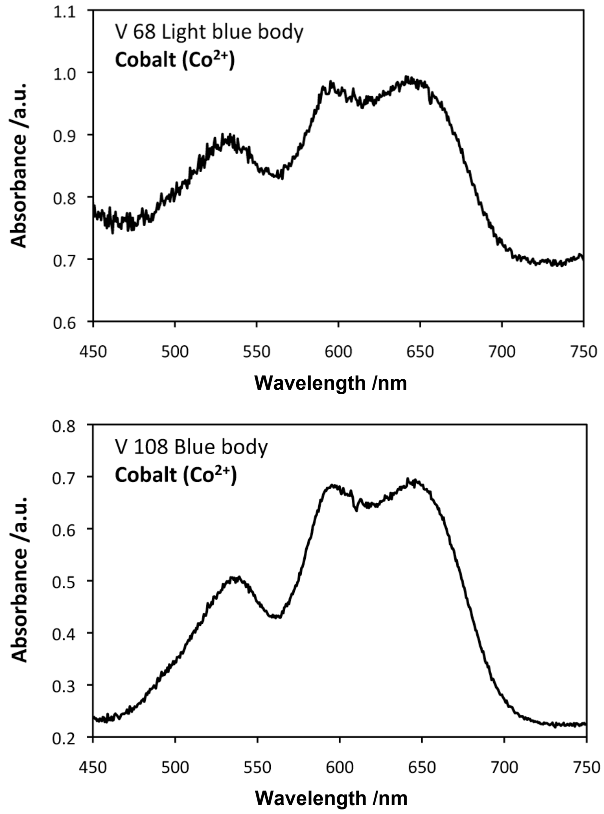

Figure 3.4: UV-Vis absorption spectra of the blue glasses of fragments V 68 and V 108.

Yellow and Green

The green to yellow hues observed in the bodies of fragments V 66, V 67 and V 74 may be called "natural colours", as colouration is produced by iron involuntary introduced in the glass through impurities present in the raw materials, instead of being deliberately added. The content of iron in these glasses ranges from 0.94 - 2.15 wt% and the manganese concentration from 0.33 - 1.39 wt%, which indicates that the final colour was the result of a partial decolouration. In a silicate glass, the ferric ion, Fe^{3+}, and the ferrous ion, Fe^{2+}, produce yellow and light blue colours, respectively. The green colour is obtained when both Fe^{2+} and Fe^{3+} ions are present in the glass. The ion Fe^{3+} was identified in the body of fragment V 66 through its characteristic bands at 380, 420 and 440 nm (**Figure 3.5**). [30]

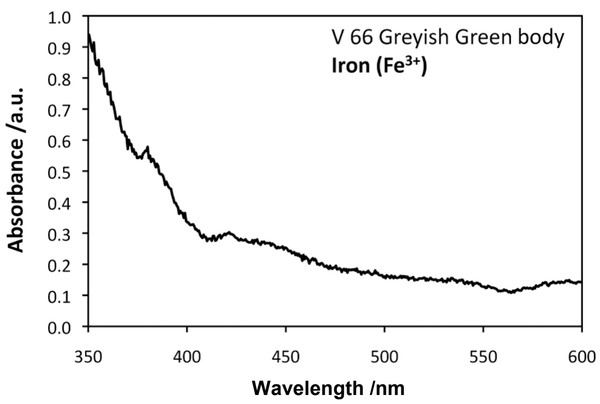

Figure 3.5: UV-Vis absorption spectrum of the greyish green glass of fragment V 66.

Manganese

According to the resulting compositions manganese oxide is present in all of the analyzed glasses, in concentrations from 0.10 - 1.49 wt%. As referred above, this oxide was added either as decolourant, to neutralize the colour given by iron, or with the purpose of altering the hue of the red colour, as in the case of the opaque red glass.

3.2 Compositions and raw materials

All of the base glasses are of soda-lime-silica type, containing Na_2O from 13.5 - 19.4 wt% and CaO from 3.11 - 11.4 wt%. The use of coastal plant ash is suggested by the relatively high content of MgO (3.31 ± 0.93 wt%), K_2O (3.46 ± 1.32 wt%) and P_2O_5 (0.36 ± 0.13 wt%), as well as by the presence of chlorine.

The blue glasses present in the decoration of fragments SCV 173 and SCV 176 can be classified as *cristallo* glass due to their low concentration of CaO, MgO and P_2O_5 (**Figure 3.6**) and high content of SiO_2 (**Figure 3.7**). These concentrations reveal that a purified ash and a source of silica of high purity were used. It should be noted the quite unusual MgO content of fragment V67 body (6.67 wt%), which was excluded from the plot showed in Figure 3.6.

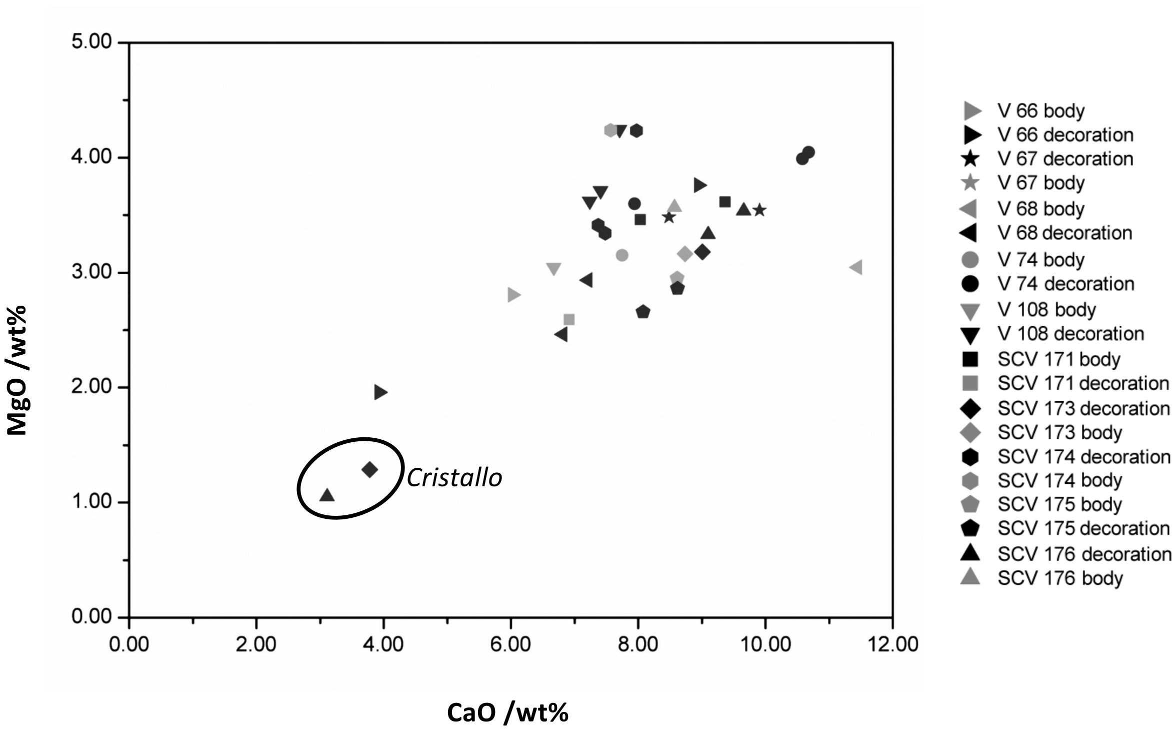

Figure 3.6: Concentration of CaO *vs.* MgO in the base glasses (wt%).

The plot alumina *vs.* silica (**Figure 3.7**) shows that four different sources of silica were used in the manufacture of the analyzed glasses, which allowed their classification in the following compositional groups: low alumina (< 2 wt%), low alumina – *cristallo* (< 2 wt% and SiO_2 > 70 wt%) medium alumina (2 - 3 wt%), high alumina (3 - 6 wt%) and very high alumina (> 6 wt%).

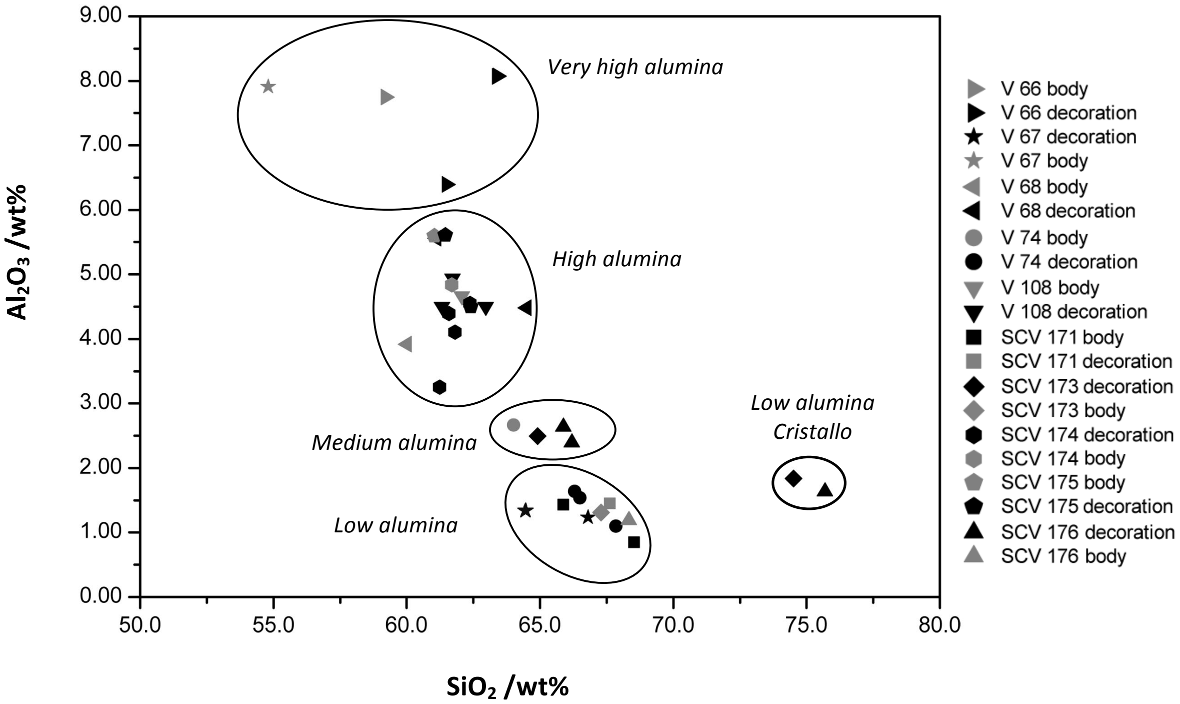

Figure 3.7: Concentration of SiO_2 *vs.* Al_2O_3 in the base glasses (wt%).

In **Table 3.3** are identified the samples assigned to each group.

Table 3.3: Glasses assigned to each compositional group, distributed by their alumina and silica content, in weight percent of oxides.

Concentration (wt%)	Classification of composition	Fragment and/or glass
$Al_2O_3 < 2$	Low alumina	SCV 171, SCV 173 Opaque bluish white, SCV 176 Opaque white, V 67 decoration, V 74 decoration
$Al_2O_3 < 2$ ($SiO_2 > 70$)	Low alumina - *cristallo*	SCV 173 Blue and SCV 176 Blue
$2 < Al_2O_3 < 3$	Medium alumina	SCV 173 Aventurine and SCV 176 Opaque red and aventurine, V 74 body
$3 < Al_2O_3 < 6$	High alumina	SCV 174, SCV 175, V 68 and V 108
$Al_2O_3 > 6$	Very high alumina	V 66 and V 67 body

The plot alumina vs. potassium oxide (**Figure 3.8**) suggests that there is a linear relation between these two oxides, excluding fragments V 67 body and V 66. The potassium related to aluminium comes from feldspathic minerals in the sand; a certain amount of sodium, calcium and magnesium also come from these feldspars, but a much larger amount of these elements comes from the soda plant ash. The amount of potassium not related to aluminium (the trend line intersection with the Y axis) is approximately 1.5 wt% of potassium oxide. This amount of potassium introduced in the glass through the soda plant ash is probably underestimated.

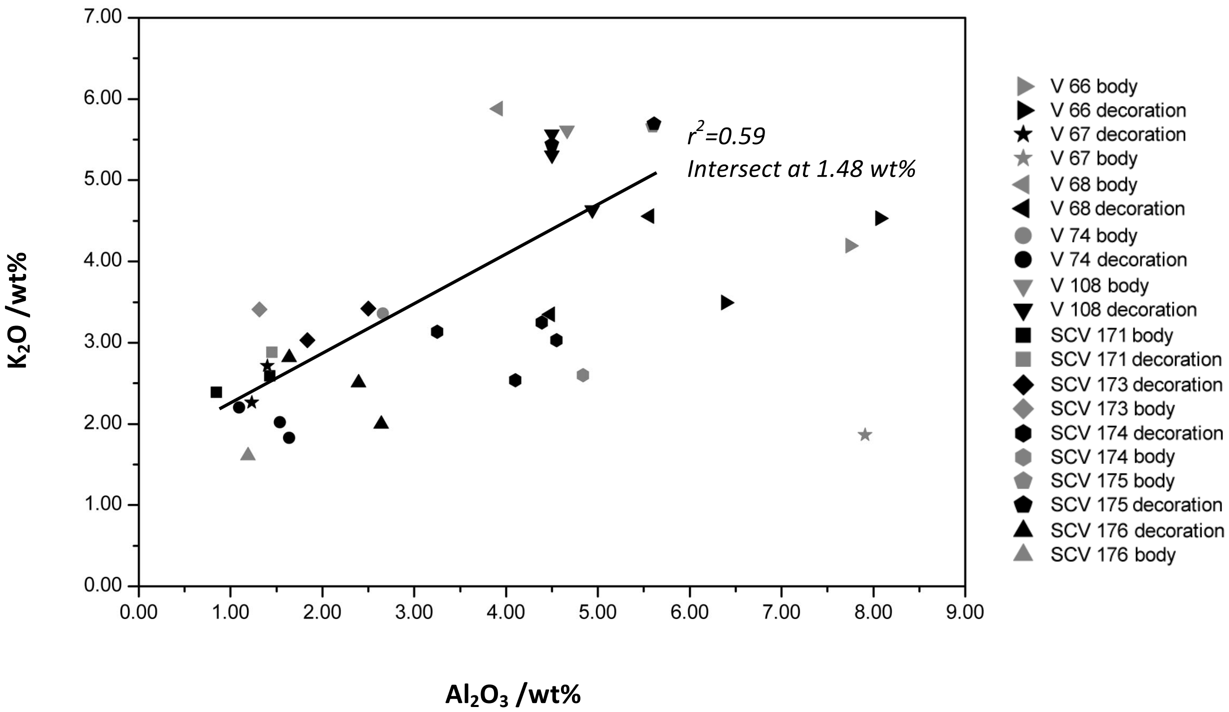

Figure 3.8: Concentration of Al_2O_3 *vs*. K_2O in the base glasses (wt%).

3.3 Comparison with Venetian and *façon-de-Venise* compositions

In the following paragraph the possible provenance of each group of glasses will be discussed.

As previously mentioned, in section 1.4, the content of alumina in Venetian and *façon-de-Venise* glasses is always below 2 wt%, except for the "Tuscany Barilla" and "Tuscany Levantine" groups. The red and aventurine glasses may show a slight higher content of this oxide because as iron had to be added to the batch the use of a less pure source of silica was irrelevant. Thus, according to the amounts of alumina and potassium oxide, the glasses included in the low alumina group may be genuine Venetian or Spanish II production. However, fragments SCV 173 and SCV 176 can be considered Venetian production, as they are identical in style and also in composition to a Venetian goblet recently studied by Verità. [11]

The medium alumina group comprises the red and aventurine glasses of fragments SCV 173 and 176, already assigned to Venetian production, and the V 74 body. The latter features a composition not comparable to the studied *façon-de-Venise* glasses because the amount of alumina is above 2 wt% and the amount of potassium oxide is below 4 wt%.

The fragments included in the high alumina group – SCV 174, SCV 175, V 68 and V 108 – and very high alumina group – V 66 and V 67 body - show a much higher amount of alumina when compared to that found in the Venetian and *façon-de-Venise* glasses. They were made using less pure silica sources. The concentration of alumina of fragments SCV 174, SCV 175, V 68 and V 108, as well as the concentration of the other elements, is comparable to the Tuscany production. However, to confirm this hypothesis the analysis of trace elements would be essential. It is important to refer that in spite of a difference of one century this provenance cannot be excluded. The fragments V 67 and V 74 are probably the most interesting samples as the glasses from body and decoration feature very different compositions. As referred above, the composition of the decoration glasses is comparable to Venetian and Spanish II productions but the glass of the bodies shows high amounts of alumina, suggesting that these objects were decorated using glass produced in a different place.

4. Conclusions

Chemical analysis, by X-ray electron probe micro-analysis, allowed the characterization of both body and decoration of ten 17th century *Millefiori* glass fragments. Some relevant conclusions can be drawn from the obtained compositions. All glasses are of soda-lime-silica type. The use of coastal plant ash is suggested by the relatively high content of MgO, K_2O and P_2O_5, as well as by the presence of chlorine. Raman microscopy and UV-VIS absorption spectroscopy were also used as complementary techniques in the study of opacifiers and colourants, which allowed the identification of tin oxide (SnO_2, cassiterite) or calcium antimonate ($Ca_2Sb_2O_7$) in the opaque white glasses, and of the colourants cobalt in the blue glasses, copper in the turquoise, iron in the yellow and greenish glasses and iron and copper in the opaque red and aventurine glasses.

Based on the concentrations of alumina and silica it were identified four different sources of silica, which allowed the classification of the glasses in five compositional groups: low alumina (< 2 wt%), low alumina – *cristallo* (< 2 wt% and SiO_2 > 70 wt%) medium alumina (2 - 3 wt%), high alumina (3 - 6 wt%) and very high alumina (> 6 wt%). Comparison with genuine Venetian and *façon-de-Venise* compositions showed that fragments SCV 173 and SCV 176 are genuine Venetian production, fragment SCV 171 is comparable to Venetian production or Spanish glass (type II) [18], fragments SCV 174, SCV 175, V 68 and V 108, all the glasses of the "high alumina group", are only comparable to Tuscany production. The composition of fragment V 66, included in the "very high alumina group" is not comparable with any composition of the glasses with known provenance and the alumina content suggests the use of very impure sand, rich in feldspathic minerals. Fragments V74 and V 67 show a particular characteristic: body and decoration have different origins. The body of fragment V 67 may have been produced in the same place as fragment V 66 but the composition of the glasses used in the decoration indicates that the rods may have been produced in Venice or Spain (type II). Body of fragment V 74 shows a composition not comparable to that of the others fragments of unknown provenance, already referred. The glass from decoration may also have been produced in Venice or Spain (type II).

As a final conclusion, excluding the two fragments attributed to Venetian production (SCV 173 and SCV 176) and the fragment SCV 171 which composition is comparable to Venetian production or Spanish glass (type II), the provenance of the remaining *façon-de-Venise Millefiori* glasses from the Monastery of Sta. Clara-a-Velha, can be attributed to three unknown distinct places.

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