Received: 13 January 2022 | Revised: 16 June 2022 | Accepted: 22 July 2022

DOI: 10.1111/ijag.16605

INTERNATIONAL JOURNAL OF Applied Glass SCIENCE

RESEARCH ARTICLE

Red glass in Kunckel's *Ars Vitraria Experimentalis*: The importance of *temperature*

Márcia Vilarigues[1,2] | **Andreia Ruivo**[1,2] | **Thijs Hagendijk**[3] | **Mario Bandiera**[1,2] | **Mathilda Coutinho**[4] | **Luis C. Alves**[5] | **Sven Dupré**[3]

[1]Department of Conservation and Restoration, NOVA School of Science and Technology, Caparica, Portugal

[2]R&D Unit VICARTE – Vidro e Cerâmica para as Artes, NOVA School of Science and Technology, Caparica, Portugal

[3]Utrecht University, Utrecht, The Netherlands

[4]Laboratório HERCULES – CityUMacau Chair in Sustainable Heritage – IFAA, Évora, Portugal

[5]C2TN, IST/CTN, Universidade de Lisboa, Sacavém, Portugal

Correspondence

M. Vilarigues and A. Ruivo, Department of Conservation and Restoration, NOVA School of Science and Technology, Caparica, Portugal.
Email: mgv@fct.unl.pt and a.ruivo@fct.unl.pt

Funding information

European Research Council, Grant/Award Number: 648718; Portuguese Foundation for Science and Technology, Grant/Award Numbers: UID/EAT/00729/2019, UIDP/00729/2020, UIDB/00729/2020, UIDB/04349/2020, UIDB/04449/2020, PD/BD/136673/2018, CEECIND/00349/2017, 2020.00252. CEECIND

Abstract

The role of the melting conditions and furnaces used to the obtained final colors has always been a question raised when investigating formulations and recipes of historical glasses. The focus of the present work is the reproduction of three recipes of red enamel glass of the manuscript by Neri, *L'arte vetraria* (1612) following the translation and comments by Kunckel's in *Ars Vitraria Experimentalis* (1679). The reproductions include the production of each individual compound of the selected recipes following instructions, and the final glass production in electric and wood-fire furnaces to assess the effect of different melting conditions. A multianalytical approach was used to fully characterize the produced samples allowing the study of the enamel chemical composition, color, crystals formations, and thermal properties. The results indicate that no significant color differences may be attributed to the melting conditions. However, it revealed that the samples produced in the electric furnace at 1200°C present a high crystallinity degree and the formation of white crystals at room temperature in a short period of time. The formation of crystals on glass is critical, and historically, to avoid it, these recipes must have been made at temperatures between 1050 and 1100°C.

KEYWORDS

furnaces, historical recipes, Kunckel, reconstructions, red enamels

1 | INTRODUCTION

During the last decade, several publications on the study of historical written treatises and recipe books on the production of glass objects and glass-based paints were published. Although some of the works focus mainly on translations and interpretations of the texts (e.g., Ref. [1–3]), others developed experiments on the reproduction of recipes and relating reconstructions with the chemical composition of historical objects and glass-based paints (e.g., Ref. [4–6]).

These historic glass recipe books often include a step-by-step structure, providing information on glassmaking

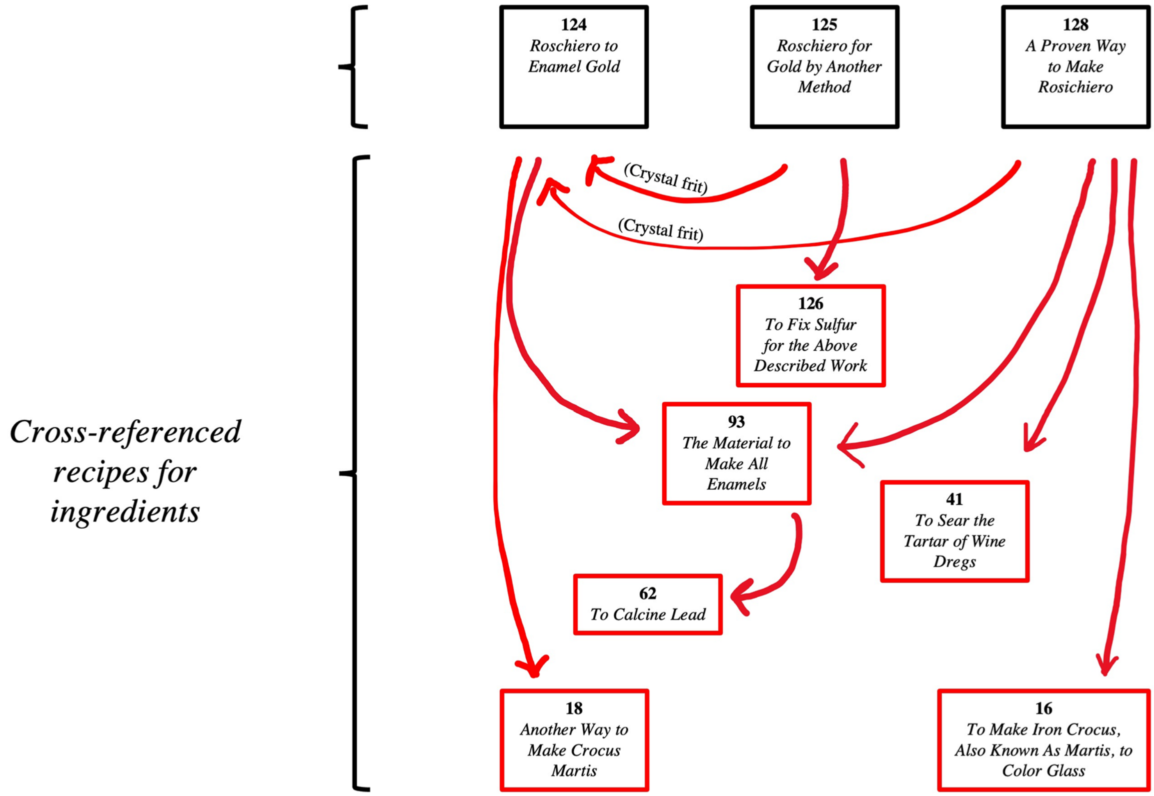

FIGURE 1 Overview of the three *rosichiero* recipes (Chapters 124, 125, and 128) published by Neri and later translated by Kunckel. The red arrows indicate references to other recipes containing instructions for preparing specific ingredients. *Source*: Based on Ref. [8]

processes and on the materials and equipment used, including tools for glass shaping, mold production, and furnaces. Furthermore, along with new recipes, glass recipe books are often critical translations and may contain commentaries, annotations, and additional recipes from previous treatises.[3] Thus, these documents offer a precious source of information on the evolution of chemical and material sciences and their relationship to glassmaking. This is the case with Kunckel's *Ars Vitraria Experimentalis* (1679), which includes a transcription of the manuscript by Neri, *L'arte vetraria* (1612), with Kunckel adding a second part to the text based on his own experiments with glass production.

In Hagendijk et al.,[7] the process of the deconstruction and reconstruction of four recipes for *rosichiero* glass (a transparent red glass) is discussed. The procedure started with the recipes' historical texts transformed into step-by-step protocols for chemical synthesis and production of each compound and final glasses, following Knuckles' instructions and comments (Figure 1).

In this paper, the production of Kunckel's translation[9] of three recipes originally written by Neri for red glass used as enamels (*rosichiero*) is analyzed, focusing on the production conditions, particularly the melting atmosphere and temperature of different furnaces. The recipes under study are (i) recipe 124 (*Eine Rofen-farbichte Smalte oder Schmeltzglaß zu machen/von den JtaliåRofichiero genandt/mit welchen das Gold bemahlet wird*), (ii) recipe 125 (*Eine andere Rofen farbichte Smalte oder Schmeltzglas zum Gold*), and (iii) recipe 128 (*Eine bewåhrte Manier/das Rofen-farbichte Smalte o-der Schmaltz-Glas zu machen*). A fourth recipe for red glass production can also be found, 127 (*Ein Blut-Rothes Glas/welches an statt der Rofen-farbichten Smalte dienen kan*); however, it diverges significantly from the other recipes—it uses a different glass base, and it lacks the addition of *crocus martis*, an artificially produced iron oxide.[8]

The chemical characterization of the individual compounds as well as of the final enamels are presented and discussed, with particular attention to the differences observed in the enamels production using different melting conditions.

1.1 | Raw materials and process of *rosichiero* glass recipes at *Ars Vitraria*

The *rosichiero* glass is a translucent red glass mainly used as an enamel by goldsmiths in the middle ages and the Renaissance.[10] Its color results from the presence of submicrometric particles of metallic copper or cuprite (Cu^0 or Cu_2O) in the glass matrix. Given the poor solubility of metallic copper in glass, it is necessary to introduce copper in the form of oxide and then create the required reducing conditions inside the melt by using an adequate furnace with a reducing atmosphere or by adding to the glass elements capable of reducing copper to its elementary state.[11,12]

The process starts by preparing a first base enamel glass, composed of a crystal frit and “a calx of lead and tin,” to which the other components are added. The different ingredients in the preparation of *rosichiero* glass described in the recipes that Kunckel translated from Neri into German are the following[7,8]:

(i) In all recipes, a colorless glass called “crystal frit” is prepared. This glass will be the matrix for the final enamel composition. The production of the crystal frit is provided in Chapter 124 and it is made from “white and finely powdered Tarso” (quartz), which is calcined in a furnace with the “salt from the Levantine powder” (ashes from salsola from the Levantine[3]).

(ii) The second step is the addition of the “calx of lead and tin.” The author refers to another chapter (recipe 93) (*Die Materia/aus welcher alle Schmeltzgläßer oder Smalten bereitet warden*) to explain how this ingredient should be prepared. As described in the recipe, pieces of lead and tin in a ratio of 30/33 are calcined together until a yellow substance is formed. Chapter 125 adds another source of lead-oxides in the form of minimum. The combination of the ingredients (i) and (ii) originates the base enamel glass.

(iii) The third ingredient mentioned in the recipes is “cream-of-tartar” (*Weinstein*), which is either calcined first (recipes 124 and 128) or used raw (recipe 125).

(iv) The fourth ingredient that needs to be added is calcined copper (*Hammerschlag*, CuO). In Chapters 24, 25, and 28, the instructions to produce copper oxide from metallic copper are described.

(v) The recipes for *rosichiero* glass prescribe the addition of iron oxide (Fe_2O_3). Some of the iron oxides described by Kunckel were sourced minerals, such as hematite. For the other iron-oxides (which appear in the recipes as *crocus martis*) Kunckel provides recipes starting from steel or iron. Two of the recipes (124 and 128) introduce this compound in the form of *crocus martis*.[8] The *rosichiero* recipe 125 prescribes the use of bloodstone or natural hematite. Kunckel indicates two sources of iron to produce *crocus martis*: the flakes produced from the beating of incandescent iron beaten on the anvil and unprocessed or calcined steel. These products are mixtures of metallic iron and different iron oxides. Most recipes suggest correcting the final color with small additions of iron compounds.[7,8]

The final factor for the success of the production of the *rosichiero* glass is the melting conditions. This topic is here explored by asking about the role of different furnaces and furnace conditions on the final chemical, optical, and thermal properties. The study of the melting conditions on the final red color has been the focus of several studies.[13–15] However, a comparative study among furnaces with different atmospheric conditions is still lacking. In this study, a comparison among different melting conditions is made by using *rosichiero* glass following recipes found in *Ars Vitraria*, as a case study.

2 | MATERIALS AND METHODS

For this study, three recipes were selected to be reconstructed. To limit the variables to be compared, it was chosen only the recipes with identical base glass composition, raw materials and with the same colorant, copper.

The selected recipes were reproduced based on Kunckels and Neri’s instructions and set of comments. The samples were melted both in an electric furnace (EF) and a wood furnace (WF), enabling one to compare the results obtained in the different melting atmospheres. Both raw materials and final glass were chemical and morphologically characterized by a multianalytical approach. The color, composition, and crystallography of the final product of all produced glasses were fully characterized through reflectance spectroscopy, optical microscopy, particle-induced X-ray emission (PIXE) spectrometry, and X-ray diffraction (XRD). The thermal properties of glass obtained were characterized by differential scanning calorimetry (DSC), allowing the study of the glass transition temperature and crystals formation of the produced glasses.

2.1 | Recipes reproduction

The production of the *rosichiero* described in the historical recipes is divided into the production of selected base enamel-glass; production of metal oxides from metal scraps (or use of earth pigments); mixture and melting of all components in a step-by-step process. In Table 1 are presented the different elements used to produce the *rosichiero* enamels.

To produce the base enamel-glass, we started with the crystal frit: 10 lb of “white and finely powdered Tarso” (pebbles from the Tarso river of almost pure quartz[16]),

TABLE 1 Different elements used to produce rosichiero enamels, correspondent obtained product, and recipe number (cf. Section 1)

Crystal frit	Colorless glass	124
Calx of lead and tin	Metallic lead and tin after calcination	93
Base enamel glass	Combination of the crystal frit + calx of lead and tin	124
Cream of tartar	Potassium bitartrate	

melted with 10 lb of "salt from the Levantine powder" (ashes from salsola from the Levantine[3]). The crystal frit composition was obtained from recipe 124,[9] which includes a detailed description of the frit recipe to be used. Following the literature[17] on the chemical compositions of plant ashes used in the production of glass, in particular the composition of *Salsola vermiculata* from Aleppo, the crystal glass was produced with the following mixture to obtain at the end of the melting process 100 g of crystal frit: 45.1-g SiO_2, 63-g Na_2CO_3, 5-g K_2CO_3, 17.6-g $CaCO_3$, 9.3-g $MgCO_3$. The mixture was melted at 1200°C (heating rate 5.5°C/min) for 4 h in commercial alumina crucibles. The melt was dropped into cold water to obtain a glass frit and dried before use. The calx of lead and tin is the other component required to obtain the base enamel glass. This was produced by calcining 1:1.1 (wt%) metallic lead and tin in a ceramic crucible in an EF at 650°C for 12 h, mixing periodically. The result was a dark to light yellow powder. The base enamel-glass used in *rosichiero* recipes is obtained by melting the mixture of these two elements.

Calcined cream of tartar was produced at 600°C, in a ceramic crucible, for 20 min. For most of the colors of enamels presented in *Ars Vitraria*, this compound is part of the base glass recipe; however, in the *rosichiero* recipes 125 and 128, it is added afterward (Table 1).

Calcined copper and iron were obtained by burning low-carbon steel and standard commercial copper plates. The metals were cut into small pieces, separately placed in crucibles, and taken to several heating cycles (until 850°C) in a furnace to promote the oxidation of the metal. Both were individually ground into a fine powder before being mixed with the melt.

In the present work, four *crocus martis* recipes were used: Iron filings calcined in the presence of sulfur (Chapter 16), or treated with vinegar (17), *aqua fortis* (18), or *aqua regia* (19). A detailed reproduction of *crocus martis* recipes is described elsewhere,[7,8] as well as a comparison of the possible influence of each preparation method of the *crocus martis* on the final color of the produced glass. The first glass was made with the *crocus martis* originally prescribed by the recipe (prepared with sulfur). In the other three samples, the originally prescribed variety of *crocus martis* was substituted for different varieties (prepared with vinegar, *aqua fortis*, and *aqua regia*). The other ingredients were kept the same, and all samples were collectively melted in the same electric and wood-fired furnace.

Recipe 125 includes the addition of fixed sulfur, the production of which is described in recipe 126 ("how one should fix the sulfur for aforementioned use"). An amount of 1.6 g of sulfur was heated at 210°C with 50 ml of olive oil for 1 h, after which 100 ml of vinegar was added. When the sulfur settled on the bottom of the recipient, the liquid was removed. Kunckel, in his commentary, argues that the "fixed sulfur does not serve any purpose here. It can easily be left out as well as being added."[8] To validate Kunckel's comment, recipe 125 was produced with and without sulfur. In Table 2 it can be found the various components used to make the different recipes.

The original Recipe 124 resulted in an opaque, almost black glass. To compare the red shade of the glass, a version with a lower amount of the calx of lead tin and cream of tartar mixture was produced (124*).

The *rosichiero* glass was produced in a bottom-up EF and melted at 1200°C (heating rate 5.5°C/min) following the step-by-step order described in the recipes (Table 2). The crystal frit was put in an alumina crucible and melted for 1 h. Afterward, the different ingredients were added with 1-h intervals between each addition and mixed by stirring.

The same procedure was followed in the WF in Oficinas do Convento, Montemor-o-Novo, but in this case, the furnace temperature was fixed around 1050–1100°C. As described previously,[7,8] this WF is designed vertically and is used to fire ceramics. It has two holes near the ground, in which fire is made. The two fire holes are on opposite sides and end up in the main chamber on top that contains the crucibles. The oven is built as such to create a downdraft. The heat and flames are reflected by the ceiling, go down again, touch the crucibles, and leave the chamber through the chimney opening at the bottom in the back. Thus, the Montemor-o-Novo furnace resembles the experimental furnace that Kunckel described in his book that he used for glass tests (Figure 2).

Kunckel describes a specific and versatile furnace used for his glass tests and experiments "with various useful things."[8] Its performance is more than satisfying, according to Kunckel: "Once it is truly hot," he explains, "it could melt everything that is meltable." It is also fuel-efficient "once it is hot, it consumes not too much wood." On top of that, the furnace contains a fire channel by which its residual heat can be used to feed a smaller furnace for various smaller operations, such as calcined or "digest" (dissolve) substances. Kunckel explains that his furnace can conduct "twenty tests on a small scale" [*ins kleine*]. The glass tests produced in this furnace were made in small crucibles. Evidence of Kunckel tests was found in

TABLE 2 Composition (normalized to 100 g) of the produced glasses according to Kunckel's recipes

	Recipe number											
	124			**124***			**125**			**128**		
	quantity (g)	**obs**	**order**	**quantity (g)**	**obs**	**order**	**quantity (g)**	**obs**	**order**	**quantity (g)**	**obs**	**order**
Crystal frit	59.2		1	80		1	94.7		1	90.9		1
Calx of lead and tin	19.2		2	8		2	.7		2	3.0		2
Cream of tartar	19.2	Calcined	2	8	Calcined	2	.7		4	3.6	Calcined	5
Calcined/burnt copper	2		3	2.7		3	.7		4	.9		3
Iron oxide	.4	*Crocus martis* prepared with *aqua fortis*	4	.5	*Crocus martis* prepared with *aqua fortis*	4	.2	Burned iron w/fixed sulfur	5	.9	*Crocus martis*	4
Other								Minium	3	.6	Soot	4

FIGURE 2 Sketch of Kunckel's compendious furnace that contains several small crucibles used for testing (F). Especially noteworthy is the fire channel (K) that could be used to hook up another and smaller furnace.[9] *Source*: Photo © Thijs Hagendijk

archeological excavations of the remains of his glass laboratory on the Pfaueninsel carried out in the 1970s. Many small crucibles were discovered containing glass of various colors, ranging from green to red–brown, including shards of what appears to be gold ruby glass, Kunckel's most famous production.[18,19] Moreover, the size of the excavated crucibles (~6.5-cm high and 3.5-cm diameter) matches the size of the alumina crucibles used in this work (6.5-cm high and 4.7-cm diameter). The excavations thus not only show that downscaling was a typical historical operation but also give an impression of the general size of Kunckel's tests.

2.2 | Analytical methods

All produced samples were fully characterized through Reflectance spectroscopy, Optical Microscopy, PIXE spectrometry, XRD, and DSC, allowing the study of the color, composition, crystals formation, and glass transition temperature of the produced glasses.

TABLE 3 Corning C standard glass compositions in wt%

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	Fe_2O_3	CoO	NiO	CuO	ZnO	SrO	SnO_2	BaO	PbO
CMoG C reference[a]	1.07	2.76	.87	36.2	.14	–	2.84	5.07	.79	.34	.18	–	1.13	.052	.29	.19	11.4	36.7
CMoG C analyzed	1.17	2..34	.72	34.24	.19	.35	2.55	4.47	.91	.32	.18	.005	1.14	.03	.17	.54	10.64	39.93

[a]Brill RH. Chemical analyses of early glasses. vol. 2. New York: The Corning Museem of Glass; 1999. 544p.

2.2.1 | μ-PIXE

For the μ-PIXE analysis, the ion beam analytical facilities at the Instituto Superior Técnico, Polo de Loures, were used. They comprise a 2.5-MV Van de Graaff accelerator and an OM150 Oxford Microbeams scanning nuclear microprobe. Elemental distribution maps were obtained with the microprobe beam scanning system, and specific regions of interest were selected for quantitative analysis. Operation and basic data manipulation were achieved using OMDAQ software; quantitative analysis was done with the GUPIX program. Each sample was analyzed in three different areas, and the results in oxides weight percentage form were normalized to 100 wt%. To validate the obtained concentration results, the Corning C standard reference glass was also analyzed (Table 3).

2.2.2 | X-ray diffraction

XRD was applied to identify crystallographic phases. It was performed on a benchtop X-ray diffractometer Rigaku model MiniFlex II, using a monochromatic X-ray source (Cu K_α line) operated at 30 kV of acceleration voltage and 15-mA current. The spectra were acquired at 2°/min. The identification was made by comparison with the RRUFF database and EVA software database.

2.2.3 | Colorimetry and reflectance spectroscopy

The color of the samples was measured numerically using the colorimetric coordinates, CIELab coordinates (L^*, a^*, b^*) and optical reflectance spectroscopy were performed (FORS). MAYA 200 PRO from an Ocean Optics spectrophotometer with a single-beam dispersive optical fiber was used together with a 2048 CCD Si detector, and the light source was an HL-200-HP 20W halogen with a single optical path between 360 and 2500 nm. The spectra were taken on the glass surface, in reflectance (R) mode, with a 45° configuration (illumination angle/acquisition) and ca. 2-mm diameter of the analyzed area. The calibration was made using a Spectralon surface as a reference, and the spectra were obtained in the range between 380 and 1050 nm, with an integration time of 8 ms. The color coordinates were obtained considering the illuminant D65 as the source and with an angle of observation of 10°.

2.2.4 | Optical microscopy

The morphology of the samples was observed by transmitted light optical microscopy under plane and cross-polarized light. The microscope was an Axioplan 2ie Zeiss, equipped with halogen light HAL100 and a digital camera (Nikon DMX1200F).

2.2.5 | Differential scanning calorimetry

The produced glass thermal behavior was analyzed using a differential scanning calorimeter, Pegasus DSC 404 F. Measurements were conducted under nitrogen gas N5.0 (99.999% p.a.) in a furnace that reaches temperatures of up to 1550°C. The samples were placed in a platinum crucible (ca. 50 mg), and the reference crucible was filled with alumina using the same quantity. A heating rate of 10°C/min was applied.

3 | RESULTS AND DISCUSSION

This study focuses on reconstructing red enamel glasses, reproducing all the steps described in historical recipes, focusing on Kunckel's instructions.

3.1 | Chemical composition and crystalline phases of the individual recipe elements

To obtain the final enamel, all individual recipe elements were prepared and analyzed: (i) "crystal frit"; (ii) "calx of lead and tin"; (iii) cream of tartar; (iv) calcined red copper, and (v) iron oxide (Fe_2O_3).

3.1.1 | Crystal frit

The crystal frit described in the recipes has in their composition almost pure quartz and ashes of salsola (see Section 2.1) which translates to a nominal composition of 45.26% SiO_2, 36.98% Na_2O, 3.42% K_2O, 9.89% CaO, 4.45% MgO (wt%).

TABLE 4 Nominal crystal frit composition and chemical composition (wt%) of the crystal frit obtained by μ-PIXE (particle induced X-ray emission)

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	NiO	ZnO	ZrO_2	BaO
Nominal crystal frit	36.98	4.45	–	45.26	3.42	9.89	–	–	–	–	–	–
Analyzed crystal frit	33.74	3.55	3.20	46.42	3.45	9.08	.08	.14	.005	.011	.113	.20

TABLE 5 Chemical composition (wt%) of Pb–Sn calx, crystalline phase of the individual recipe elements obtained by μ-PIXE (particle induced X-ray emission) and X-ray diffraction and the correspondent powder diffraction file (PDF)

Recipe element			Crystalline phase	PDF file
Pb–Sn calx	Composition (wt%)		SnO_2 PbO $PbSnO_4$ $Pb_2Sn_2O_6$	77-0447 77-1971 24-0689 72-0002
	SnO_2	PbO		
	50.9	49.1		
Calcined cream of tartar			$K_2CO_3{\cdot}1.5H_2O$	11-0655
Calcined copper			CuO	72-0629
Calcined iron			Fe_2O_3	33-0664
Hematite			Fe_2O_3	33-0664
Crocus martis prepared with sulfur (16)			Fe_2O_3 FeS	33-0664 22-1120
Crocus martis prepared with vinegar (17)			Fe_2O_3	33-0664
Crocus martis prepared with *aqua fortis* (18)			$Fe_4NO_3(OH)_{11}{\cdot}2H_2O$	44-0519
Crocus martis prepared with *aqua regia* (19)			Fe_2O_3	33-0664
Fixed sulfur			Sulfur	78-1889

The glass frit produced was analyzed by μ-PIXE, and the compositions were determined (Table 4). Few differences can be observed compared with the nominal composition and are most likely due to contaminations from the crucibles into the melt.

The obtained composition differs from that prescribed by other authors. For example, considering other Venetian glassmaking treatises, in particular those by Darduin (1644), Brunoro (1645), the Montpellier manuscript (1536), and The Anonimo recipe book written by an unknown Venetian glassmaker around 1560, they prescribe the use of potash, mixed alkali glass but mainly of common or *vitrum blanchum* glass.[6] Kunckel remarks on the poor quality of crystal frit in Chapter 124. He says that with this frit "everything will look unpleasant and spotty and nothing will be right and no beauty will come from it."[8]

3.1.2 | Individual elements of the recipes to be added to the glass frit

As mentioned in Section 2.1, all the compounds were prepared following the written recipes. The different crystalline phases of the prepared compounds are presented in Table 5.

The final products were those expected. The powder obtained from the calcination of the lead–tin has a ratio of ca. 1/1 lead–tin and is a mixture of different crystalline phases of lead–tin oxides. The calcined tartar resulted in hydrated potassium carbonate. The analysis confirms that the product resulting from the fixed sulfur recipe is sulfur.

The metal copper calcination gives rise to CuO. The CuO is fundamental to increasing the color homogeneity, as mentioned before, it spreads more easily than the metallic copper in the glass matrix due to a higher solubility. Concerning the iron source, all the prepared *crocus martis* gave rise to Fe_2O_3, except in the case of *aqua fortis* (18), Table 4, which originated $Fe_4NO_3(OH)_{11}{\cdot}2H_2O$. The iron in Fe_2O_3 in the oxidation state 3+ will not be able to reduce the CuO to Cu^0, which is mandatory to obtain the red glasses.[20,21] This indicates that other compounds such as sulfur and/or cream of tartar are needed to reduce Fe^{3+} to Fe^{2+} or Fe^0. This can justify that only in the *rosichiero* recipe 128, the cream of tartar is added after the iron, probably to reduce it, as it is the only recipe where the iron is added as Fe_2O_3 and without any sulfur. In all the other Kunckel's recipes,

TABLE 6 Recipes nominal composition in wt%

Oxides	Recipes 124	125	128
SiO_2	37.50	42.98	42.09
Na_2O	30.64	35.11	34.39
K_2O	7.56	3.65	5.28
CaO	8.19	9.39	9.20
MgO	3.69	4.23	4.14
SnO_2	4.22	.36	1.56
PbO	4.07	3.28	1.51
CuO	2.80	.70	.92
Fe_2O_3	1.35	.20	.92
S	–	*.1*	–

the cream of tartar is added to the base glass (124) or before the iron addition (125).

Different mixtures resulted from the distinctive preparation methods of the *crocus martis*, with the results of the reproduction presented in Refs. [7, 8] clearly showing the impact of the production method on the color and crystallographic properties of the obtained iron oxide.

3.2 | Chemical composition and crystalline phases of the final *rosichiero* glass

In Table 6 is presented the glass nominal composition of all the produced glasses. The overall base compositions are similar except for the elements used to reduce the copper, like potassium, which is also added in the tartar, lead and tin, lead–tin calx, and iron oxides. A substantial difference is also observed in the higher copper content of recipe 124. The glass samples produced were analyzed by μ-PIXE, and the compositions were determined (Suplementary material, Table S1).

The crystalline phases of the produced red glasses were determined by XRD analysis (Table 7). All diffractograms showed the presence of a characteristic broad hump due to the scattering peaks of the vitreous material. The pattern of metallic copper was detected in all produced glass samples (ICDD card 01-085-1326), except for samples 125 WF, 128 (17) 1100°C—EF, and 128 (19)—WF. The submicrometric particles of metallic copper are responsible for the glass' red color, which corroborates the results obtained by reflectance spectroscopy in Section 3.3. They were formed through the reduction of copper oxide during firing. Moreover, related to the reductive condition in which the glasses were produced, metallic lead (128 (18)—EF, 128 (19)—EF), and FeO (wustite) (125 EF) were also identified. Other crystallized products, such as sodium calcium and sodium aluminum silicates, were also detected in some glass samples. Crystals rich in Ca–Si or Na–Ca–Si are common devitrification products that have been reported in Roman copper-based red opaque glass.[22] Some of these polyphase minerals could be identified due to the presence of multiple phases. Few of these silicates are probably transitional phases formed during the firing and cooling of glass.

Additionally, several glass samples presented a pattern that could be assigned to hydrated sodium carbonate (thermonatrite). This compound is probably a corrosion product due to the low stability of the glass composition with a low content of SiO_2 and high content of Na_2O and may be formed during the quenching of the glass using water.

3.3 | *Rosichiero* glass optical properties

All the produced *rosichiero* glass resulted in opaque deep red samples with heterogeneous colors (Figure 4). In recipe 125, according to Neri's, "fixed sulfur" should be added to the glass in addition to the other ingredients. However, Kunckel argues that the "fixed sulfur does not serve any purpose here. It can as easily be left out as well as being added." This reproduction, with and without the addition of fixed sulfur, demonstrated that, in recipe 125, this ingredient is essential for the final red color of the glass. Without the sulfur, the enamel presents a pale turquoise green (associated with Cu^{2+}), whereas with the sulfur, and contrary to Kunckel's claim, the glass turned red (Figure 3). The iron introduced in the experiment without the fixed sulfur (.2-wt% nominal), which will act as a reducing agent, is not enough to reduce Cu^{2+} to Cu^0. This can be related to the fact the introduced iron needs to be reduced to allow the copper reduction. Furthermore, another experiment was performed using sulfur without adding iron. Similarly, no red color was obtained.

The obtained red color referring to the recipe 128, Kunckel states "one should not think/that he will obtain right transparent red glass from it/nay/that is not concerned here/yet it is transparent insofar/when one takes a small piece/and/that/beaten from each other/being hold against the Light of the Sun on the Nail [*auff den Nagel*]/then it looks beautiful red. However, if one uses it for Blowing Glass/it will become Tile-Colored [*Ziegel-Farb*] on the Instrument or on the Pipe." So, although *rosichiero* should refer to a light transparent enamel,[10] Kunckel already identified the opaque nature of the final product obtained with these recipes. The production of recipe 128 with the different *crocus martis*, both in electric and WFs, resulted in various shades of red in the glass (Table 8, Figure 4), but it is not clear how these

TABLE 7 Crystalline phase of the produced red glasses obtained by X-ray diffraction

Recipe reference	*Crocus martis*	Crystalline phase
124*	18	Glass + metallic Cu (PDF 01-1241) + devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448)
125—WF	Burnet iron w/fixed sulfur	Glass
125—EF	Burnet iron w/fixed sulfur	Glass + metallic Cu (PDF 01-1241) + FeO (wustite, PDF 46-1312) + devitrification products ($Na_4Ca_{2.8} \cdot (Si_6O_{18})$, combeite, PDF 78-1649)
128—EF	16	Glass + metallic Cu (PDF 01-1241) + devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448)
128—EF	17	Glass + metallic Cu (PDF 01-1241) + devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448; $Na_4CaSi_3O_9$, sodium calcium silicate, PDF 12-0670)
128—EF	17–1100°C	Glass+ devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448; $Na_4CaSi_3O_9$, sodium calcium silicate, PDF 12-0670)
128—EF	18	Glass + metallic Cu (PDF 01-1241) + metallic Pb (PDF 01-0995) + devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448)
128—EF	19	Glass + metallic Cu (PDF 01-1241) + metallic Pb (PDF 01-0995) + $Na_2CO_3 \cdot H_2O$ (thermonatrite, PDF 08-0448)
128—WF	16	Glass + metallic Cu (PDF 01-1241) + devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448; Ca_2SiO_4, PDF 06-0476)
128—WF	17	Glass + metallic Cu (PDF 01-1241) + metallic Pb (PDF 01-0995) + devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448; Ca_2SiO_4, PDF 06-0476)
128—WF	18	Glass + metallic Cu (PDF 01-1241) + devitrification products ($Na_2CO_3 \cdot H_2O$, thermonatrite, PDF 08-0448; Ca_2SiO_4, PDF 06-0476)
128—WF	19	Glass + FeO (wustite, PDF 46-1312) + devitrification products ($Na_2CO3 \cdot H_2O$, thermonatrite, PDF 08-0448; Ca_2SiO_4, PDF 06-0476)

Abbreviations: EF, electric furnace; WF, wood furnace.

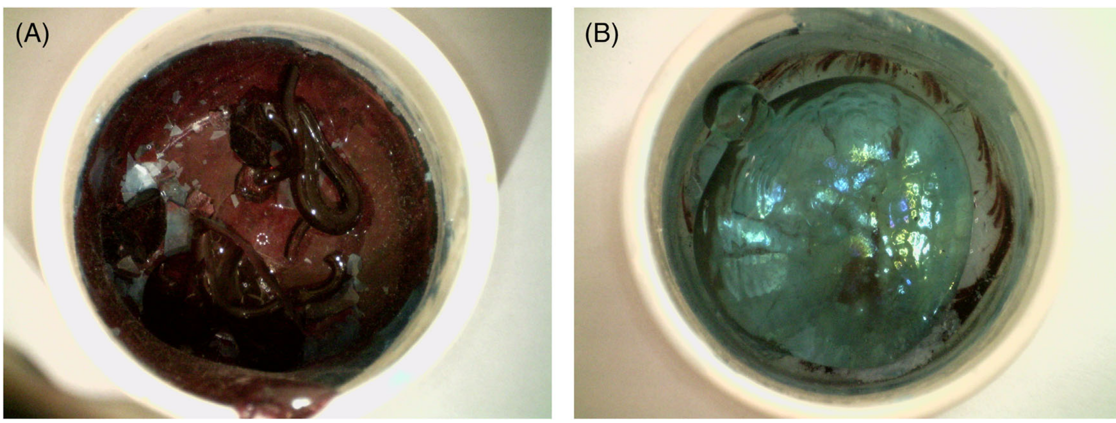

FIGURE 3 Recipe 125 prepared (A) with fixed sulfur and (B) without fixed sulfur

color differences arise as a result of different preparation methods of the *crocus martis*. The color obtained in the various glasses presents a high degree of heterogeneity, especially in recipe 124, where the cream of tartar was added at the end of the glass production.

Copper red glasses are prepared by introducing copper compounds on a base glass, followed by the ion copper reduction to metal atoms and further nucleation to form nanoparticles, or by their reduction to cuprite and crystals formation.[11] The reduction and nucleation can be obtained through different reducing agents such as tin or antimony.[11,22] Several reducing agents, in various concentrations, were applied in the studied recipes, such as tin, sulfur, tartar, and iron. The lower content of copper and reducing agents, like tin and iron, commonly give rise to a red hue that changes to a brown color as the concentration

TABLE 8 CIELab coordinates of the obtained glasses by using different recipes, including recipe 128 produced with the different *crocus martis*

Recipe reference	*Crocus martis*	*L**	*a**	*b**
124*	18	2.8 ± 8.1	13.7 ± 7.5	4.6 ± 6.6
125	Burnet iron w/sulfur	8.4 ± 1.7	8.5 ± 2.9	.02 ± 2.0
128—EF	16	34.0 ± 1.7	16.6 ± 2.1	5.2 ± .4
128—EF	17	33.1 ± 1.1	25.0 ± 1.0	10.6 ± 3.7
128—EF	18	33.0 ± .5	4.9 ± .9	−1.6 ± .5
128—EF	19	35.5 ± 4.2	17.3 ± 3.3	8.3 ± 1.1
128—WF	16	29.9 ± 1.5	6.3 ± 1.5	.6 ± 1.5
128—WF	17	34.1 ± 1.1	30.9 ± 1.0	17.0 ± 1.6
128—WF	18	25.8 ± 3.2	22.5 ± 4.2	11.5 ± 1.9
128—WF	19	16.5 ± 1.7	9.6 ± 2.3	3.8 ± 1.1

Abbreviations: EF, electric furnace; WF, wood furnace.

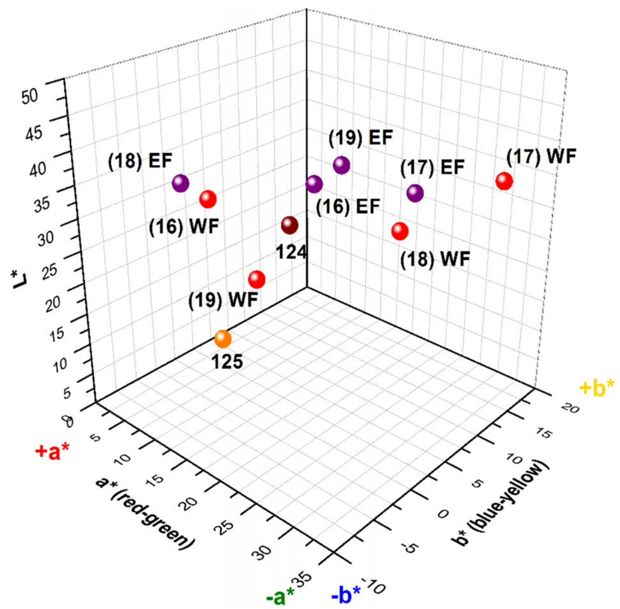

FIGURE 4 *L*a*b** color coordinates of the various red glasses obtained using recipes 124, 125, and 128. Red dots correspond to the glasses obtained in the wood furnace (WF) and purple dots in the electric furnace (EF) for recipe 128.

of these elements increases, as previously described.[6,21] However, the obtained glasses are very heterogeneous. The measured color coordinates vary from red–purple to orange–red and brown, being difficult to correlate the color with the copper and reducing agents concentration.

The opacity of the samples could result from the intentional use of lead–tin calx. Lead–tin calx is an intermediate product prepared to produce white opaque glass or to be used as an opacifier of transparent colored glass. It is the main white opacifier prescribed not only by Neri and Kunckel but also in the Renaissance Venetian recipes. Generally, these recipes recommend preparing a calx with a Pb/Sn ratio of 1. This ratio can be observed for recipes 124 and 128 (Table 5); however, recipe 125 presents a higher lead content, being the recipe that shows more significant differences when compared to the other samples, mainly in the *L* value (Figure 4). Despite the assumption that lead–tin calx is a commonly used opacifier, it was impossible to identify SnO_2 in any red glasses XRD patterns. Consequently, the obtained opacity can be attributed to copper, cuprite nanoparticles, or other precipitates as hematite, which can also scatter light.

3.4 | Electric furnace versus wood furnace

A detailed study of recipe 128 red glass production using an EF and a WF was performed to understand how different furnaces, or oxidation atmospheres, could influence the red color formation.

The glasses produced in the EF (1200°C), except the one made at 1100°C, presented a higher crystallization when compared with the samples produced in the wooden furnace (1050–1100°C), see Figure 5. With time, these glasses made in the EF also show a much higher degree of corrosion, observed by the formation of a white corrosion layer.

The samples produced in the different furnaces were characterized by a noticeable heterogeneity, with several layers of light to dark red hues formed (Figure 6). The heterogeneous, red-banded samples present large dark zones and opaque red layers. Two of the glasses produced in the WF, WF 18 and WF 19, besides the red color, also present in some regions a transparent blue color (Figure 6B), probably due to Cu^{2+}.[11] In several samples, numerous glittering round crystals are clearly visible by optical microscopy (Figure 6C).

The red color of all the synthesized 128 glasses was characterized by colorimetry and reflectance spectroscopy. The different red colors were differentiated through the reflectance percentage and the first derivate transformations from the reflectance spectra, which allow the calculation of the inflexion points.[23,24] The reflectance value will be indicated as *R* (%) (Figure 7A) and the first derivative value as derivative (Figure 7B).

The samples present an inflexion point between 575 and 598 nm (Figure 7B). Color in copper glasses is commonly caused by the interaction of electromagnetic radiation with metallic colloidal particles, giving rise to an absorption band, generally with a maximum around 560 nm,[25] which corresponds to the observed inflexion points in the reflectance spectra. The unique optical properties of the metal nanoparticles, with origin on the surface plasmon resonance, result from the absorption and scattering of

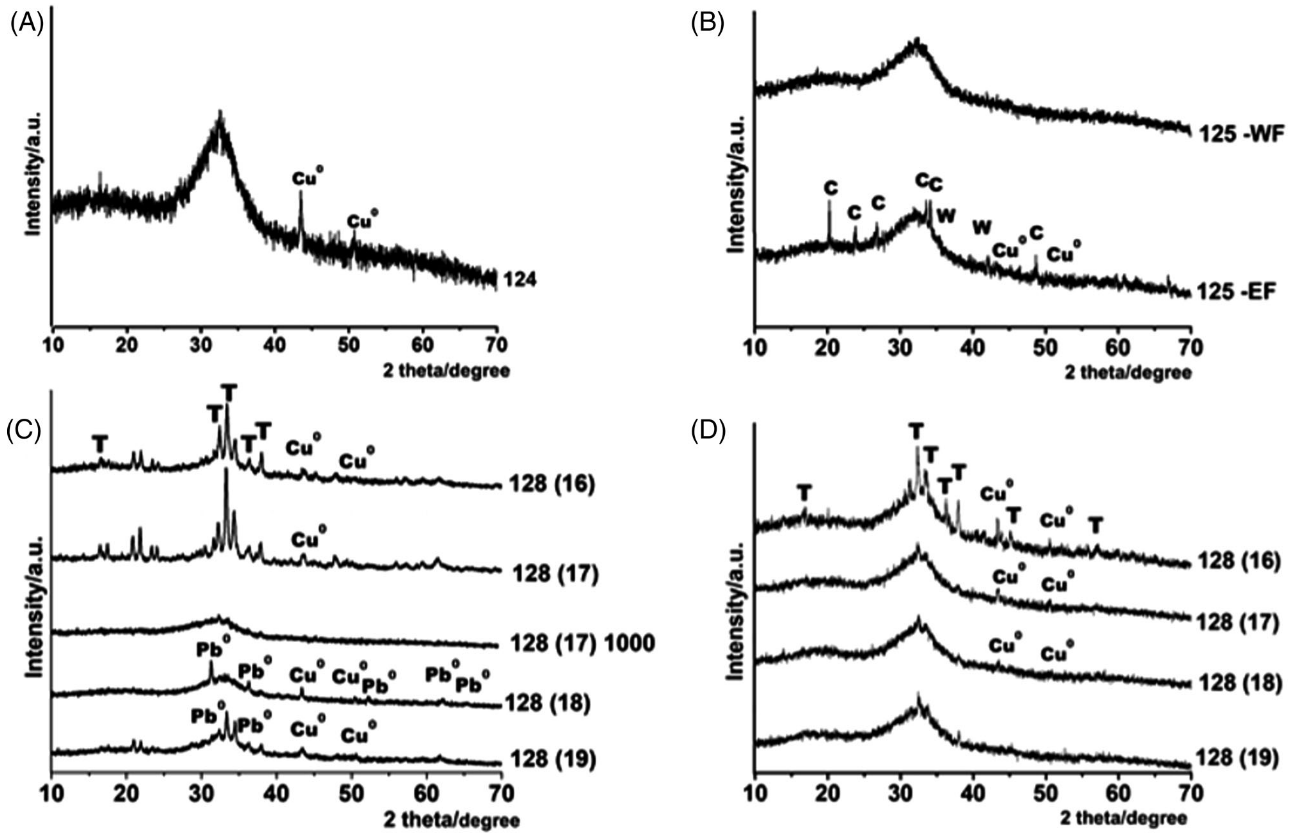

FIGURE 5 X-ray diffraction diagrams of the final glasses: (A) recipe 124*; (B) recipe 125 and (C) recipe 128 produced in an electric furnace; and (D) recipe 128 produced wood furnace. C, combeite; Cu^0, metallic Cu; N, sodium aluminum silicate; Pb^0, metallic lead; T, thermonatrite

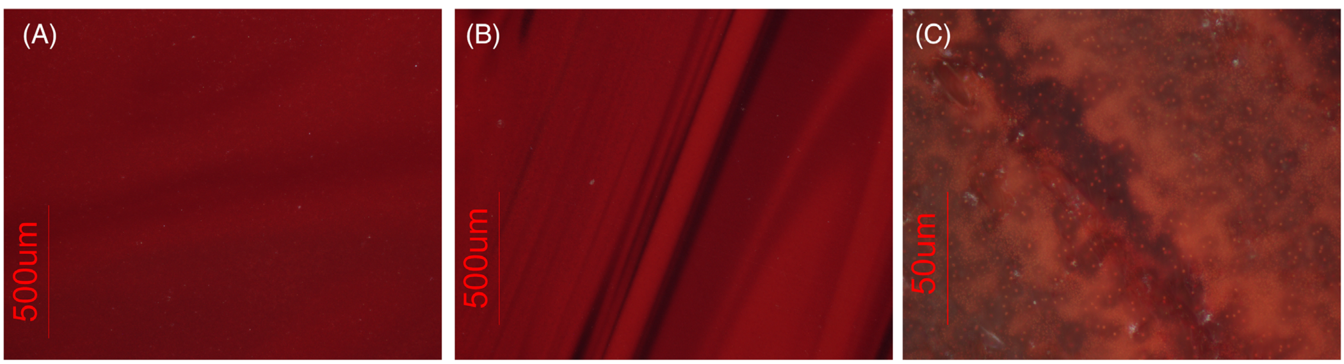

FIGURE 6 Representative microscope images of the final glass produced in an electric furnace or wood furnace. (A) Homogeneous region, (B) region of transparent dark cords, (C) particles of metalic copper

light due to the match between the incident light frequency and the intrinsic electron oscillation frequency.[26] This absorption band's wavelength and shape depend mainly on the metal nanoparticles' size, shape, dielectric properties, and the surrounding matrix.[27] The shift of the inflection point to a longer wavelength could be due to the increase of the number and sizes of the Cu^0 particles, making the glass opaque and not transparent.[25] One of the causes of these results could be the too strong reducing conditions provided by several potential reducing agents (iron, presence of stannous oxide, sulfur). Still, no systematic differences in using different furnaces can be indicated. However, more tests and analyses are needed to reach further conclusions.

The reflectance percentage demonstrates that samples WF 16 and EF 18 present a darker color in the range between 700 and 900 nm. In addition, samples 128—WF (18) and 128—WF (19) present an absorption band in the

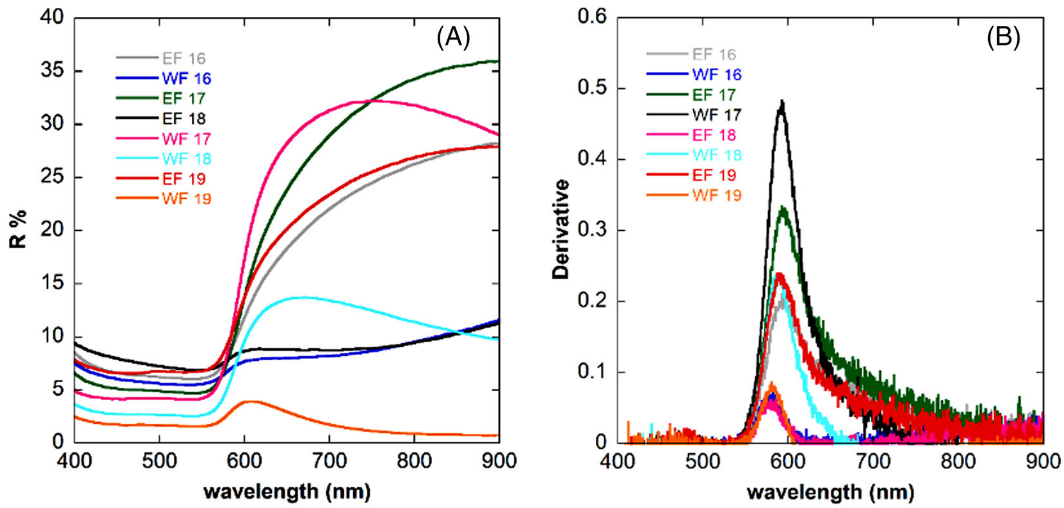

FIGURE 7 (A) Reflectance spectra of the different red glasses produced through recipe 128, using different *crocus martis*, both in an electric furnace and in a wood furnace and (B) the correspondent calculated first derivative

TABLE 9 T_g, T_c, and T_S values for each glass produced from recipe 128, obtained by differential scanning calorimetry (DSC), determined at the midpoint and peak, respectively

	Glass recipes								
	128 (16)		128 (17)		128 (18)		128 (19)		128 (17)—1100°C
	EF	WF	EF	WF	EF	WF	EF	WF	EF
T_g	420	410	424	420	429	430	419	434	449
T_c (°C)	577	582	559	595	570	609	572	633	628
T_S (°C)	157	172	135	175	141	179	153	199	179

Abbreviations: EF, electric furnace; WF, wood furnace.

near-infrared region, with a maximum at around 800 nm, which corresponds to the electronic transition $^2E \rightarrow {}^2T_2$ of Cu^{2+}, showing the heterogeneity and mixture of different copper oxidation states in the various samples.

The presence of Cu^{2+} underlines that the redox states were not homogeneously distributed in the melt during both melting temperatures and cooling phases, or probably the ideal reducing conditions were not achieved.

As the thermal properties significantly influence the nanoparticles crystallization, DSC analyses were performed. The different samples' thermal behavior, obtained by DSC, are similar, presenting an endothermic effect around 420°C, corresponding to the various glass transition temperatures (T_g) (Figure 8 and Table 9).

The T_g is a crucial parameter for glass materials and can define the temperature where the glass network gains more freedom[28] and copper nanoparticles can be formed. The T_g value obtained for the crystal frit is similar to those obtained for the different samples, indicating that adding the colorants on the base glass does not promote significant differences in this value.

The second peak in the DSC plot refers to an exothermic crystallization process (T_c). This peak can be attributed to copper as the observed peak is around the same temperature as the one observed for the copper nanoparticles crystallization, which can be found at 563°C.[29] The crystal frit and the base glass, see the Supporting Information section, do not present the crystallization peak at ca. 550°C, opposite to the final red glasses, which have the copper nanoparticles formation. The difference between T_c and T_g can be used to define the glass thermal stability (T_S), representing the kinetic resistance to crystallization. Higher T_S values correspond to a higher delay in the nucleation process and, therefore, greater resistance. In the developed recipes, it can be observed that the samples produced in a WF present higher T_S, which correlates with the fact that these glasses have a vitreous appearance and not a crystalline aspect as the ones made at the EF. The DSC of the sample heated at 1100°C in the EF was performed, and the obtained T_c and T_S results were similar to the WF glasses. These results confirm the hypothesis previously suggested that the glass differences result from the furnace's temperatures and not different oxidizing atmospheres.

Beyond the need to add a specific compound to the batch or the molten glass to form Cu^0, the redox atmosphere is

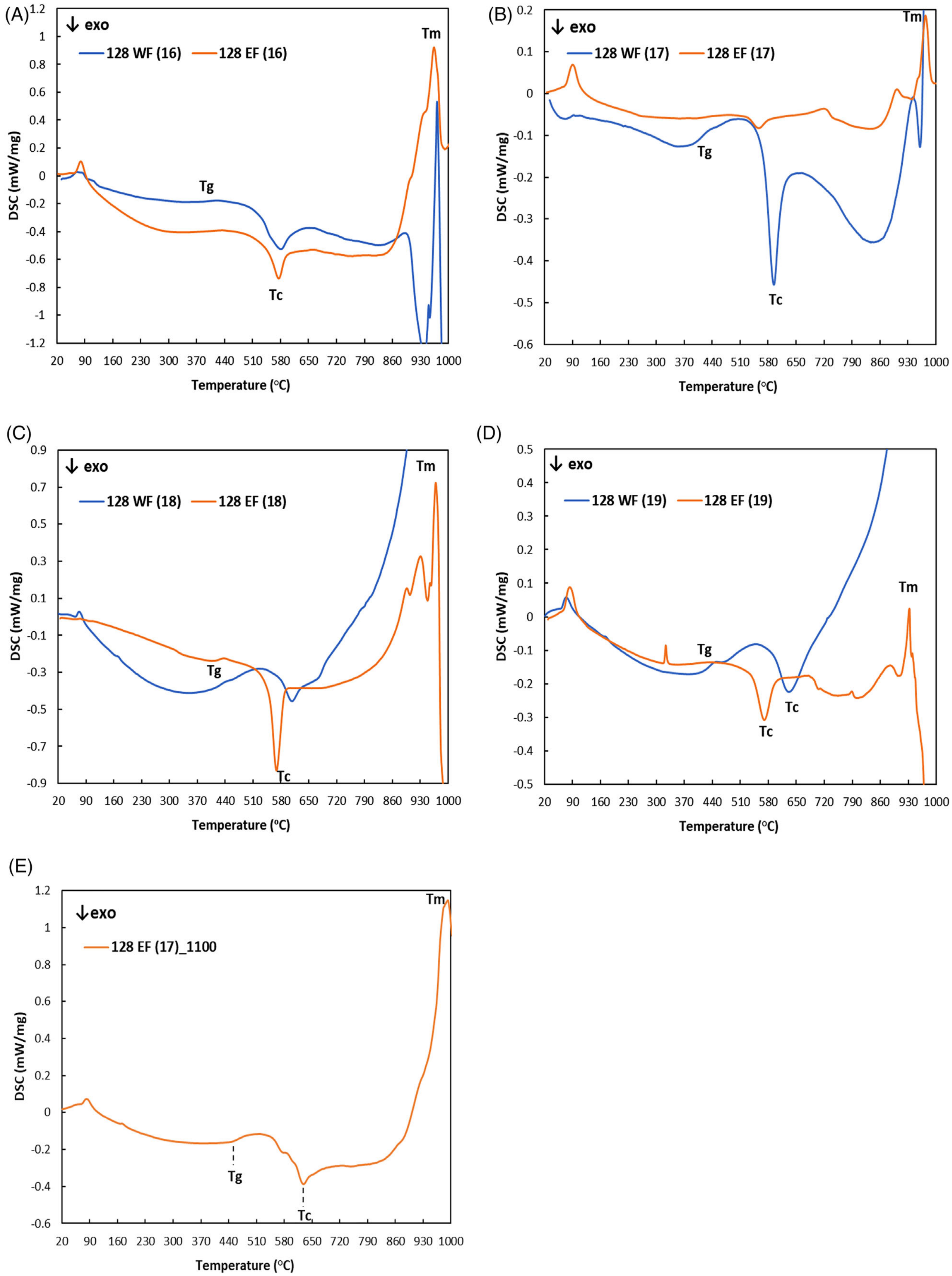

FIGURE 8 Differential scanning calorimetry (DSC) curves of the final glass produced from recipe 128 by using different *crocus martis*, in an electric furnace (EF) or wood furnace (WF): (A) 128 (16)—EF and WF; (B) 128 (17)—EF and WF; (C) 128 (18)—EF and WF; (D) 128 (19)—EF and WF; (E) 128 (17)—EF 1100°C

another important factor in producing red glaze and red glass.[11] However, it is not mentioned in the recipes studied in this work. Moreover, the red glass formed in these experiments underlines that other factors could cause the chromatic differences between the several tests. One of these factors could be the temperature which affects the oxidation state of the melt. Indeed, the oxidation state of the multivalent elements present in the melt, which should react to promote the formation of Cu^0, is affected by the melting temperature; the higher the temperature, the lower the oxidation state.[30–33] However, the results obtained have shown that while the heat source in the furnace (electric or wood) does not result in different glass properties (including the final color), the temperature plays a key role, not in color, but in the glass crystallization, being fundamental for the quality of the final product. The different temperatures reached in the furnaces promoted different nucleation rates and growths of not only Cu^0 but other crystallization particles. However, more studies are needed to define the role of the furnace oxidation state and the different temperatures in synthesized copper red glass production.

4 | CONCLUSIONS

This paper describes the results of the reconstruction of three recipes from *Ars Vitraria Experimentalis*, aiming to obtain *rosichiero* glass (a red translucent glass used as enamel) in different furnace conditions. All the recipes' reconstructions gave rise to red copper glasses. Furthermore, Kunckel provided extensive commentaries on them. These commentaries present practical issues and improvements identified by Kunckel, thus providing additional information on Neri's original recipes.

Although Kunckel refers that recipe 128 will not result in a translucence glass, no remarks are made for recipe 124 or 125. Associated with this lack of information and the fact that the use of fixed sulfur, discarded by Kunckel, is fundamental to obtaining the red color on recipe 125, we propose that not all recipes were tested by the author as already suggested in Refs. [7, 8].

Kunckel argues that the color of glass is sensitive to the way ingredients are sourced and processed and emphasizes the importance of furnace management in optimizing the color of glass. Kunckel does in fact provide advice on fire management and adequate timing in glassmaking: "when the Fire is much too Strong, the Color that one obtains will perish and another will appear that one does not desire nor wants to have."[8] In this study, all the produced glasses presented the characteristic amorphous properties of vitreous materials and the diffraction patterns of metallic copper. The significant difference observed in the produced glasses was obtained when different melting temperatures were used. The results at 1200°C exhibit a higher crystallization/devitrification when compared with the samples produced at 1100°C, both in the electric and the wooden furnace. Using this glass composition, it can be concluded that temperature control is more important than having control of the furnace atmosphere. There are no critical differences in the obtained color as no correlation was observed between the colors obtained on the EF and WF. Still, significant differences in the glasses' amorphous degree are observed. The temperature plays a key role, whereas their melting at the right temperature is fundamental for the quality of the final product.

Even though controlled experiments are of utmost importance in answering scientific questions, controlled experiments often significantly deviate from historical circumstances. Understanding historical glassmaking practices requires that we enlarge our understanding of historical technologies as well. In the present work, this allowed us to study and map factors that are usually omitted from controlled experiments but that do explain the background of historical recipes, including the motivation for specific instructions and ingredients.

ACKNOWLEDGMENTS

The authors wish to acknowledge the European Research Council (Grant agreement ID: 648718) and the Portuguese Foundation for Science and Technology for funding through UID/EAT/00729/2019, UIDP/00729/2020, UIDB/00729/2020, UIDB/04349/2020, UIDB/04449/2020, PD/BD/136673/2018, CEECIND/00349/2017, 2020.0025-2.CEECIND.

ORCID

Márcia Vilarigues https://orcid.org/0000-0003-4134-2819

Mario Bandiera https://orcid.org/0000-0002-4144-2767

REFERENCES

1. Lautier C, Sandron D. Antoine de Pise : l'art du vitrail vers 1400. Paris: CTHS, Comité des travaux historiques et scientifiques; 2008. ISBN: 978-2735506590
2. Moretti C, Toninato T. Glass recipes of the Renaissance: transcription of an anonymous Venetian manuscript. Watts Pub; 2011. ISBN: 0956211615, 9780956211613.
3. Moretti C, Hreglich S. Raw materials, recipes and procedures used for glass making. In: Modern methods for analysing archaeological and historical glass. Oxford, UK: John Wiley & Sons Ltd; 2013. p. 23–47. ISBN: 978-0-470-51614-0.
4. Palomar T, Díaz Hidalgo RJ, Vilarigues M. Pigments, vinegar, and blood: interpretation and reproduction of glassy materials from the medieval manuscript H-490. Int J Appl Glass Sci. 2018;9(4):555–65. https://doi.org/10.1111/ijag.12354
5. Vilarigues M, Machado C, Machado A, Costa M, Alves LC, Cardoso IP, et al. Grisailles: reconstruction and characterization

of historical recipes. Int J Appl Glass Sci. 2020;11(4):756–73. https://doi.org/10.1111/ijag.15793
6. Bandiera M, Verità M, Zecchin S, Vilarigues M. Some secrets of Renaissance Venetian opaque red glass revealed by analyses and glassmaking treatises. Glass Technol: Eur J Glass Sci Technol A. 2021;62(1):24–33.
7. Hagendijk T, Vilarigues M, Dupré S. Materials, furnaces, and texts: how to write about making glass colours in the seventeenth century. Ambix. 2020;67(4):323–45. https://doi.org/10.1080/00026980.2020.1826823
8. Hagendijk T. Reworking recipes: reading and writing practical texts in the early modern arts. PhD dissertation. Utrecht University; 2020.
9. Kunckel J. Ars Vitraria Experimentalis, Oder Vollkommene Glasmacher-Kunst (Franckfurt und Leipzig, 1679). All translations are ours unless otherwise indicated. All transcriptions of Kunckel's Ars Vitraria were obtained from the Deutches Textarchiv: http://www.deutschestextarchiv.de/kunckel_glasmacher_1679
10. Kerssenbrock-Krosigk D, Brain C. Glass of the alchemists: lead crystal-gold ruby, 1650–1750. Corning, NY: Corning Museum of Glass; 2008. ISBN: 0872901696
11. Weyl WA. Coloured glasses. Sheffield, England: Society of Glass Technology; 1951; ISBN 9780900682063.
12. Doremus R, Kao SC, Garcia R. Optical absorption of small copper particles and the optical properties of copper. Appl Opt. 1992;31(27):5773–8. http://doi.org/10.1364/AO.31.005773
13. Wakamatsu M, Takeuchi N, Ishida S. Effect of heating and cooling atmospheres on colors of glazes and glass containing copper. J Non-Cryst Solids. 1986;80:412–21. https://doi.org/10.1016/0022-3093(86)90425-4
14. Wakamatsu M, Takeuchi N, Nagai H, Ishida S. Chemical states of copper and tin in copper glazes fired under various atmospheres. J Am Ceram Soc. 1989;72:16–9. https://doi.org/10.1111/j.1151-2916.1989.tb05946.x
15. Padovani S, Sada C, Mazzoldi P, Brunetti B, Borgia I, Sgamellotti A, et al. Copper in glazes of Renaissance luster pottery: nanoparticles, ions, and local environment. J Appl Phys. 2003;93(12):10058–63. http://doi.org/10.1063/1.1571965
16. Machado A. Historical stained glass painting techniques technology and preservation. PhD dissertation. FCT NOVA; 2018. http://hdl.handle.net/10362/56803
17. Barkoudah Y, Henderson J. Plant ashes from Syria and the manufacture of ancient glass: ethnographic and scientific aspects. J Glass Stud. 2006;48:297–321. http://www.jstor.org/stable/24191157
18. Rau Günter, Rau M. Das Glaslaboratorium des Johann Kunckel auf der Pfaueninsel in Berlin. Berlin: Staatliche Museen zu Berlin, Preußischer Kulturbesitz; 2009.
19. Schulze G. Kunckels Glaslaboratorium auf der Pfaueninsel – Bericht über chemische Untersuchungen an einigen Fundobjekten. Medizinhist J. 1976;11(1/2):149–56. http://www.jstor.org/stable/25803482
20. Freestone IC. Composition and microstructure of opaque red glass. In: Bimson M, Freestone IC, editors. Early vitreous materials; British Museum Occasional Paper No.56. London, UK: British Museum; 1987. p. 173–91. ISBN 978-0861590568.
21. Bandiera M, Verità M, Zecchin S, Vilarigues M. Riproduzioni in laboratorio del vetro rosso bruno opaco. In Atti delle XX Giornate di Studio del Vetro. Comitato Italiano AIHV; 2019, (in press, May 2022).
22. Bring T, Jonson B, Kloo LA, Rosdahl J. Colour development in copper ruby alkali silicate glasses: Part 2. The effect of tin (II) oxide and antimony (III) oxide. Glass Technol –A. 2007;48:142–48.
23. Bandiera M, Verità M, Lehuédé P, Vilarigues M. The technology of copper-based red glass sectilia from the 2nd century AD Lucius verus villa in Rome. Minerals. 2020;10(10):875. http://doi.org/10.3390/min10100875
24. Aceto M, Agostino A, Fenoglio G, Idone A, Gulmini M, Picollo M, et al. Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry. Anal Methods. 2014;6(5):1488. http://doi.org/10.1039/c3ay41904e
25. Nagao H, Misonou M, Kawahara H. Mechanism of coloration in copper-stained float glass. J Non-Cryst Solids. 1990;120(1–3):199–206. http://doi.org/10.1016/0022-3093(90)90204-y
26. Schwartzberg AM, Zhang JZ. Novel optical properties and emerging applications of metal nanostructures. J Phys Chem C. 2008;112(28):10323–37. http://doi.org/10.1021/jp801770w
27. Liz-Marzán LM. Tailoring surface plasmons through the morphology and assembly of metal nanoparticles. Langmuir. 2006;22(1):32–41. http://doi.org/10.1021/la0513353
28. Shelby JE. Introduction to glass science and technology. Cambridge, England: Royal Society of Chemistry; 2007. ISBN 0854045333
29. Somlyai-Sipos L, Janovszky D, Sycheva A, Baumli P. Investigation of the melting point depression of copper nanoparticles. IOP Conf Ser Mater Sci Eng. 2020;903(1):012002. https://doi.org/10.1088/1757-899x/903/1/012002
30. Banerjee S, Paul A. Thermodynamics of the system Cu-O and Ruby formation in borate glass. J Am Ceram Soc 1973;57(7):287–90. https://doi.org/10.1111/j.1151-2916.1974.tb10902.x
31. Paul A. Effect of thermal stabilisation on redox equilibria and colour of glass. J Non-Cryst Solids. 1985;71:269–78. https://doi.org/10.1016/0022-3093(85)90296-0
32. Schreiber HD. Redox processes in glass-forming melts. J Non-Cryst Solids. 1986;84:129–41. https://doi.org/10.1016/0022-3093(86)90770-2
33. Chopinet M-H, Lizarazu D, Rocanière C. L'importance des phénomènes d'oxydo-réduction dans le verre, Academie des Sciences. C R Chim. 2002;5(12):939–49.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Vilarigues M, Ruivo A, Hagendijk T, Bandiera M, Coutinho M, Alves LC, et al. Red glass in Kunckel's *Ars Vitraria Experimentalis*: The importance of *temperature*. Int J Appl Glass Sci. 2023;14:201–215. https://doi.org/10.1111/ijag.16605