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# Against the Dying of the Light: Enamel Analysis and the Conservation Problems of Art Nouveau Windows

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***Contre la mort de la lumière. Analyse de l'émail et problèmes de conservation des fenêtres Art nouveau – Résumé***

*L'utilisation de l'émail est l'une des caractéristiques typiques du vitrail catalan Art nouveau. En comprendre les causes de dégradation permet d'adopter des stratégies de conservation plus précises. L'article donne un aperçu historique de l'utilisation des émaux, ainsi que les résultats d'analyse chimique des échantillons et des matières premières originales utilisés par l'atelier Rigalt i Granell (Barcelone, 1861-1914). Les échantillons historiques issus des vitraux catalans ont été réalisés par les ateliers les plus renommés de l'époque. Le verre et l'émail ont été étudiés par calorimétrie à balayage différentiel DSC, par microscopie électronique à balayage (MEB), par diffractométrie de rayons X (DRX) et par LA-ICP-MS. La stabilité de l'émail dépend de sa composition chimique ainsi que de plusieurs autres paramètres tels que le verre de base utilisé, la température du four, de son mélange à d'autres émaux, des conditions atmosphériques externes, etc.*

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***Against the Dying of the Light: Enamel Analysis and the Conservation Problems of Art Nouveau Windows – Abstract***

*The use of enamel is one of the typical features of Catalan Art Nouveau stained glass. Understanding the reasons for enamel deterioration of that period may help in devising more precise conservation strategies. The current article gives some historical background of the use of enamels and the results of the chemical analysis of the samples and original raw materials from the Rigalt i Granell studio. The historical samples from Catalan stained-glass windows analysed here were made by the most renowned studios of that time. The glass and enamel were investigated by DSC, SEM imaging, X-ray diffraction, and LA-ICP-MS. Enamel stability depends on its chemical composition, as well as on several other parameters such as the substrate glass used, the temperature of the kiln, whether it is mixed with other enamels or, external atmospheric conditions, etc.*

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## Introduction

Enamels were applied to most of the stained glass made in Barcelona at the end of the 19th and beginning of the 20th century, one of the most relevant periods in quantity and quality. Since fired enamel is basically a finely ground coloured glass fused to the surface of a supporting glass, the mechanisms associated with glass corrosion also occur in the enamel. Most of the enamels show some decay, but the blue and green appear particularly affected.[1]

The present document summarizes the results of long-term research on Art Nouveau enamels used in Catalan stained-glass windows. *J.M. Bonet vitralls S.L*. provided the original raw materials from *Rigalt & Granell* studio and also from historical windows covering the most renowned studios of the period: *Rigalt, Bordalba*, *Amigó*, *Maumejean and Buxeres i Codorniu.*

The first part of this research work, on the chemical and thermal properties of the *Rigalt & Granell* studio enamels, was published at the Corpus Vitrearum forum in Cambridge in 2017.[2] A low softening temperature lead-rich borosilicate glass (with zinc in some cases) was determined. Despite boron being mentioned in historical documentation as a source of instability,[3] analyses proved that if the composition of the enamel is correctly chosen, this is not necessarily true. To obtain a well adhered

[1] Olivier Shalm, Veerle Van der Linden, P. Frederickx, S. Luyten, Geert Van der Snick, Jost Caen, and others, "Enamels in Stained-glass windows: Preparation, Chemical Composition, Microstructure and Causes of Deterioration", *Spectrochimica Acta - Part B Atomic Spectroscopy*, 64.8, 2009, 812–20.

[2] Martí Beltran, Jordi Bonet, Trinitat Pradell, "Properties of Modernist Enamels and Stained Glass from the City of Barcelona", in Sarah Brown, Claudine Loisel, Aletta Rambaut, Ivo Rauch, Sebastian Strobl, Sophie Wolf (publ.), *Stained Glass: Art at the Surface* (Cambridge, 3-5 Sept. 2017) The international scientific committee for the conservation of stained glass, York, 2017, p. 102–12.

[3] Christopher Whall, *Stained Glass work*, D. Appleton, New York, 1905, p. 112, p. 370; William Mackail, *The life of William Morris*, Haskell House Publishers, 1920, first published 1899, p. 59; Lewis F. Day, *Windows. A book about stained glass*, B.T. Batsford, London, 1897, p. 85

layer required a good praxis, compatible compositions between enamel and substrate glass and adequate firing temperature (~580ºC).[4]

## Old Materials and Methods: Current Problems

Enamel is a crucial part in the conservation of the windows of this period, however the reasons for each alteration are not yet clear. This paint plays a relevant role in the aesthetics of the windows, but it is also a characteristic feature of the Catalan windows of the period especially because 17th- and 18th-century enamelled stained-glass windows are so rare in the country. There is a great need to get a better understanding of the nature of enamel decay, leading to more accurate conservation plans that could preserve its otherwise vanishing identity.

*Fig. 1. Typical white aspect of enamel on a face painted by Amigó Studio, 1903. Sant Jaume of Calaf Church.*

Enamel deterioration appears in different phenomenon ranging from pitting to full vanishing.[5] In order to build better strategies, it must be understood why well mixed, applied and fired enamel is decaying (fig. 1). Some altered enamel fades away due to what might be considered wrong practices of the painter: the use of poorly cleaned substrate glass, accidental–insufficient heat in the kiln, a random mixture of enamel or the use of too thick paint layers.

In Catalonia most craftsmen did not write about their own experience, so most of the old painting techniques are only known from the oral record. The exception is the few articles by Antoni Rigalt Blanc (1861-1914),[6] probably the best Catalan artist working on stained glass at the end of the 19th century. Despite the high quality of his articles, no manual such as those by Whall,[7] Jaenicke,[8] Oidtmann,[9] was ever written by any of the Catalan professionals.

The best and only description about how paint was applied by a Catalan studio is written by him:[10] "When it comes to making three or four [paint] layers, we begin by applying the first one dissolved in

[4] BELTRAN, BONET, PRADELL, 2017, p. 112.

[5] Alison GILCHRIST, "Severe Paint Loss from Stained-Glass Windows: Causes and Conservation Challenges" in Sarah BROWN, Claudine LOISEL, Aletta RAMBAUT, Ivo RAUCH, Sebastian STROBL, Sophie WOLF (publ.), *Stained Glass: Art at the Surface*, The international scientific committee for the conservation of stained glass, York, 2017, p. 7–25; Stefan TRÜMPLER, "Les vitraux néo-gothiques de l'église Sainte-Élisabeth à Bâle. Analyse et conservation des peintures" in Jacques BARTLET (publ.), *Grisaille, jaune d'argent, sanguine, émail et peinture à froid* (in Sites et fouilles de la région wallone Commission royale des monuments, Liège 19-22 juin) Liège, 1996, p. 21–27; Alison GILCHRIST, "The tears wept by our Windows", *Vidimus*, 64, December 2012, https://www.vidimus.org/issues/issue-64/news/ [accessed December 2019].

[6] Núria GIL FARRÉ, "*El taller de vitralls modernista Rigalt, Granell & Cia. (1890-1931)*" Barcelona: Universitat de Barcelona. Departament d'Història de l'Art, 2013 [accessed 2 December 2019].

[7] WHALL, 1905.

[8] Frederick JAENNICKE, *Handbuch der Glasmalerei* (P. Reff, ed.), Stuttgart. 1890.

[9] Heinrich OIDTMANN, *Die Glasmalerei*, J.P. Bachem, Köln,1893.

water with a small part of potash silicate, the second one with gum and water, the third one with turpentine spirit and the fourth one with water. […] It can also be made all with water, but it is a few of them who do that since the minor error leads to the total loss of the work."

Before the work is finished, the back of the pieces is painted with *despulit,* also named *couberte*[11] in other publications, to soften the penetration of bright light. In the same text, Rigalt mentions that the enamel must be utilized only if its use is impossible to avoid and recommends its use on the external side.

This glazier generation defended the use of mosaic stained glass and blamed the use of enamel, or painted windows for the past degeneration of the craft. Nonetheless, Rigalt studio could not skip its use and some windows are fully painted.

Rigalt i Granell studio purchased many of the Adolphe Lacroix enamels. The French maker offered since 1858[12] a ready to use enamel, which was already thinly ground and had the right amount of flux. Some of the texts by the Catalan artist are influenced by the publications written by Lacroix, the formulation and recommendations for firing are similar. Lacroix describes that his product is finely ground and offers an economic advantage and saves time to the makers since they did not have to grind the colours themselves.

One of the peculiarities of Catalan stained glass, is that most of the raw materials used by the studios were imported from France, England, United States or Germany and, consequently, the possibility to combine glasses and enamels that were not chemically compatible was high.

## Analytical Methods

The composition of the powders and replica enamels prepared from the *Rigalt, Granell & cia* workshop and historical enamels were analysed by LA-ICP-MS. Polished sections were observed both in reflected light with an optical microscope (OM), and back-scattered electron images (BSE) were also recorded in a scanning electron microscope (SEM). Microanalysis was obtained by an EDS attached to the SEM. Synchrotron X-ray microdiffraction ($\mu$-XRD) were obtained from cross sections of the enamels at the ALBA Synchrotron Light (Cerdanyola, Spain). UV-Vis-NIR Transmittance and Diffuse Reflectance measurements were obtained using a double beam UV-Vis spectrophotometer.

## Sampling and Results from Replica Enamels

Raw enamels were purchased by Xavier Bonet from *Granell & Cia* company in the late 1980's when the studio ceased working on stained glass. Green, blue, purple, red and yellow samples of the prepared enamel powder were taken as well as a sample of a *flux* used in the workshop.

Composition of original enamels shows that the enamel glassy phase is a high lead (zinc) borosilicate (60-70%PbO, 5-20%$B_2O_3$, 10-25%$SiO_2$, 0-5%ZnO) to which colourants and/or pigment particles were added. The composition, the colourants and the pigment particles determined are shown in Table 1**.** It is a dense transparent glass with a low softening temperature and a thermal expansion coefficient matching that of the substrate glass, while retaining a good resistance to water corrosion.

A borosilicate glass consists of a three-dimensional network built of silica ($SiO_2$) tetrahedral and metaborate ($BO_3$) trigonal units. The addition of network-modifiers like lead or zinc oxide to the borosilicate glass instead of depolymerizing the silica network gives rise to the formation of tetrahedral ($BO_4$) units responsible for the increase in the chemical resistance, decrease of the thermal expansion and enlargement of the softening temperature range. Depending on the type/amount of network-modifier, a maximum of ($BO_4$) units is reached and equilibrium is established between trigonal and tetrahedral borate units, lower or higher PbO (ZnO) content results in a degradation of the properties of

[10] Antoni Rigalt, "Presentación de algunas muestras de vidrieras de color, y explicación de los procedimientos seguidos para pintar y construir las mismas, desde la aparición de este arte, hasta nuestros días". *Memorias de La Real Academia de Ciencias y Artes de Barcelona*, 2 (3a època), 1900, p. 291–297.

[11] Barbara Trinchereau, Claudine Loisel, "The nineteenth-century restoration process of Louis Germain Vincent-Larcher at the Cathedral of Troyes", in Sarah Brown, Claudine Loisel, Aletta Rambaut, Ivo Rauch, Sebastian Strobl, Sophie Wolf (publ.) *Stained Glass: Art at the Surface*, The International Scientific Committee for the Conservation of Stained Glass, York, 2017, p. 60–75.

[12] Adolphe Lacroix, *Des couleurs vitrifiables et de leur employ pour la peinture sur porcelain, faience, vitraux*, Chez A. Lacroix, Paris, 1872.

the enamel. The enamels used in the workshop, in particular those from Lacroix, have the right compositions for a soldering glass with softening temperature ~ 580ºC.

*Table 1. Chemical composition (typical error 5%) of the replica enamels produced from the raw materials found in the Rigalt i Granell workshop determined by LA-ICP-MS. Sulphur was not measured. Crystalline pigment particles identified by XRD.*

| Color | | Company | wt% | | | | | | | | | | | | | | | | | | ppm | | | Colourants | Pigment Particles |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **$B_2O_3$** | **$SiO_2$** | **ZnO** | **PbO** | $Na_2O$ | MgO | $Al_2O_3$ | $K_2O$ | CaO | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CoO | CuO | $SnO_2$ | $Sb_2O_5$ | Se | Cd | Ni | Ag | Au | | |
| Purple | E14 | Lacroix | 21.1 | 8.6 | 11.2 | 53.2 | 2.1 | 0.1 | 0.3 | 0.2 | 0.9 | | | 0.1 | | | 1.8 | | | | | 1112 | 2117 | | Ag-Au, $SnO_2$ |
| | E107 | | 19.8 | 8.9 | 13.8 | 52.6 | 0.9 | | 0.2 | 0.3 | 0.6 | | | 0.1 | | | 2.6 | | | | | 19 | 82 | | Ag-Au, $SnO_2$ |
| xRed | E23 | Lacroix | 16.6 | 9.3 | 14.0 | 40.8 | 0.8 | | 0.3 | 0.1 | 0.6 | | | 0.0 | | | 7.6 | | 2.0 | 8.0 | 19 | | | | CdS,$CdS_xSe_{1-x}$, CdSe, $SnO_2$ |
| | E25 | | 12.1 | 7.9 | 9.9 | 62.7 | 0.4 | | 0.4 | 0.2 | 0.4 | 3.5 | | 0.1 | | | 2.3 | | | | | | | | PbO·Pb($CrO_4$), $SnO_2$ |
| | E124 | | 17.8 | 7.5 | 13.7 | 56.7 | 1.4 | 0.2 | 0.5 | 0.1 | 0.7 | | 1.2 | 0.1 | | | | | | | 10 | | | $Mn^{3+}$ | |
| Yellow | E3 | Lacroix | 7.0 | 30.4 | 0.0 | 53.0 | 5.1 | 0.1 | 0.3 | 0.1 | 2.6 | 1.3 | | 0.1 | | | | | | | | | | $Cr^{6+}$ | |
| | E4 | | 16.2 | 7.2 | 13.8 | 59.4 | 1.0 | | 0.5 | 0.2 | 0.4 | 0.5 | 0.6 | 0.1 | | | | | | | | | | $Cr^{6+}$ | |
| | E106 | | 7.9 | 22.4 | 4.1 | 54.6 | 2.1 | | 4.8 | 0.4 | 0.5 | | | 0.2 | | | 0.5 | 2.4 | | | 10 | | | | $SiO_2$, $Pb_2(Sn,Sb)_2O_7$ |
| | E119 | | 20.4 | 8.2 | 13.9 | 53.4 | 1.1 | | 0.2 | 0.3 | 0.5 | 0.5 | | 0.1 | | | 1.4 | 0.0 | | | | | | $Cr^{6+}$ | |
| Green | E34 | Lacroix | 8.1 | 10.7 | 1.9 | 49.8 | 2.0 | 0.4 | 5.9 | 0.5 | 0.3 | 10.8 | | 0.2 | 6.5 | 0.3 | 0.9 | 1.2 | | | 1269 | | | | $Co(Al,Cr)_2O_4$, $Pb_2(Sn,Sb)_2O_7$ |
| | E89 | | 16.4 | 8.5 | 12.4 | 53.9 | 1.7 | | 0.5 | 0.2 | 0.7 | 0.2 | | 0.2 | 0.0 | 5.3 | 0.1 | | | | 18 | | | $Cu^+$-$Cu^{2+}$ $Cr^{3+}$ | |
| | E121 | | 15.2 | 6.9 | 13.9 | 59.2 | 0.9 | | 0.5 | 0.2 | 0.5 | 0.4 | | 0.1 | 2.0 | | 0.0 | 0.1 | | | 290 | | | $[Co^{2+}]_4$,$Cr^{3+}$ | |
| Blue | E33 | Wengers | 11.1 | 11.4 | 9.2 | 41.9 | 2.8 | 0.5 | 13.9 | 0.1 | 0.7 | | | 0.4 | 7.7 | | 0.2 | 0.1 | | | 732 | | | | $CoAl_2O_4$ |
| | E122 | L'Hospied | 3.8 | 23.2 | 0.2 | 71.2 | 0.2 | | 0.8 | 0.0 | 0.2 | | | 0.1 | 0.1 | | 0.0 | | | | 48 | | | $[Co^{2+}]_4$ | |
| | E114 | Lacroix | 15.4 | 8.7 | 15.1 | 57.3 | 0.6 | | 1.4 | 0.3 | 0.4 | | | 0.0 | 0.3 | | 0.5 | | | | 28 | | | | $SnO_2$, $CoAl_2O_4$ |
| | E115 | | 18.3 | 7.7 | 14.6 | 56.5 | 0.7 | | 0.5 | 0.3 | 0.4 | | | 0.1 | 0.8 | | 0.2 | | | | 79 | | | $[Co^{2+}]_4$ | $SnO_2$ |
| *Grisaille* | G1 | Granell | 0.0 | 20.0 | 0.0 | 50.4 | 0.2 | | 0.5 | 0.1 | 0.1 | | 6.5 | 21.9 | | | | | | | 97 | | | | $Fe_2O_3$, $Pb_2(Fe,Mn)_2Si_2O_9$ $(Fe,Mn)_2O_3$,$FeMn_2O_4$ |
| Flux | F1 | Lacroix | 9.2 | 9.2 | 0.1 | 80.1 | 0.1 | | 0.9 | 0.0 | 0.2 | | | 0.1 | | | | 0.1 | | | 2 | | | | |

To ensure a good adherence the enamel has to be fired above the glass transition temperature but below the deformation temperature of the substrate glass. Considering that blown substrate glasses were of the soda-lime type (~15%$Na_2O$, 15%CaO and 70%$SiO_2$) with a glass transition temperature of 575°C and deformation temperature of 615°C, the glaziers had a relatively narrow firing temperature range.

The *flux* found in the workshop is a high lead borosilicate glass (85%PbO, 9% $B_2O_3$, 8% $SiO_2$) characterised by a very low softening temperature of 477°C. However, the composition is outside the balanced range and it is less stable and more susceptible to water corrosion. Although this *flux* was probably added to the enamels by the glaziers to increase their adherence, it made them less stable and more prone to deterioration.

Finally, the *grisaille*, is made of a high lead glass (70%PbO, 30% $SiO_2$) mixed with iron oxide and manganese oxide particles. After firing, both iron and manganese oxides react with the glass producing iron-manganese lead silicate and oxide particles.

The enamels show a large variety of pigment particles and colourants:

Purple is based on the ancient recipe of Cassius and is a co-precipitate of gold nanoparticles and tin. The enamels contain silver-gold alloy nanoparticles. This formula is mentioned by Lacroix,[13] Encyclopaedia Roret[14] and Rigalt.[15]

Three different types of red enamels are found: (E23) contains cadmium sulphide selenide particles together with cassiterite; another (E25) contains particles of lead oxy-chromate, together with cassiterite; and (E124) associated with Mn III dissolved in the glass. The first selenium reds follow Franz Welz glass patents,[16] manganese and chrome are mentioned at the Roret encyclopaedia (1913 edition)

[13] LACROIX 1872, p. 5.
[14] M.-E.-F. REBOULLEAU, M. Désiré MAGNIER et Adolphe ROMAIN *Peinture sur verre sur porcelaine et sur email*, L. Mulo, Paris, 1913 p. 81.
[15] RIGALT 1900, p.291–297.
[16] Franz WELZ, *Patent No. 417.676*, Unites States, 1892.

as *ferrate de chrome*[17] and iron oxide particles. Selenium does not appear in these manuals, as it probably was a new recipe; nevertheless, it can be found in some 1919 publications stating its use.[18]

Three of the yellow enamels (E3, E4 and E119) contain hexavalent chromium, Cr VI, dissolved in the glass and E119 contains also cassiterite particles. E106 contains particles of lead-tin antimonate or Naples yellow.

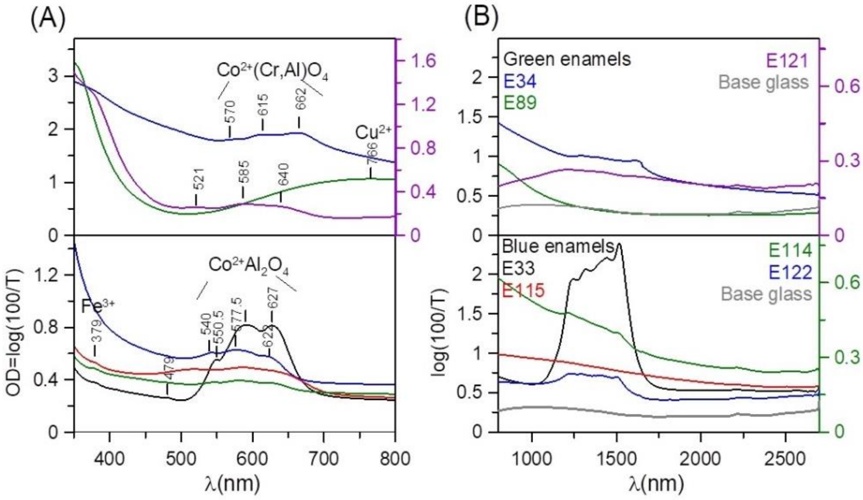


*Fig. 2. (A) UV-Vis and (B) NIR absorption spectra corresponding to the green and blue enamels from the Rigalt i Granell workshop.*

Green enamel E34 contains cobalt-chromium aluminate together with some Naples yellow particles, while E121 contains Co II and Cr III ions dissolved in the glass (fig. 2A). E89 contains mainly Cu II dissolved in the glass.

All the blue enamels contain cobalt, Co II, either as particles of a cobalt aluminate (E33 and a few in E115) or dissolved in the glass (E122 and E114). E114 and E115 contain also cassiterite particles to increase the opacity. The UV-Vis-NIR spectrum of blue and green enamels show the three characteristic absorption peaks in the 500-650 nm range of Co II in tetrahedral coordination ($CoO_4$) responsible for the blue-green colour (fig. 2A), and also of an enhanced absorbance in the NIR range between 1250 and 1750 nm, especially high for those containing cobalt aluminate particles (an increase of 30 % for E33) and between 600 nm to 1000 nm by Cu II (fig. 2B).

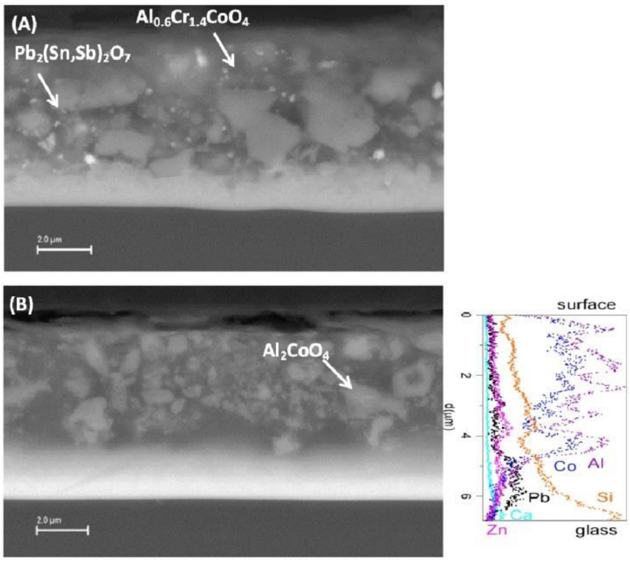


*Fig. 3. SEM-BSE images of the cross sections of the (A) green (E34) and (B) blue (E33) enamels showing the presence of the particles cobalt-chromium aluminate and cobalt aluminate particles respectively. The accumulation of the particles near the surface of the enamel and the resulting chemical inhomogeneous layered microstructure are clearly seen.*

It is also important to observe that the low density of the cobalt aluminate particles and, to a lesser extent the cobalt chromium aluminate particles, compared to that of the enamel glassy phase is a very relevant feature as the particles tend to float and accumulate on the surface (fig. 3), resulting in a layered structure, with a lead rich layer at the enamel-glass interface (~54 % PbO and negligible amounts of boron, fig. 3). SEM-BSE images of the cross sections of the (A) green (E34) and (B) blue (E33) enamels showing the presence of the particles cobalt-chromium aluminate and cobalt

[17] M.-E.-F. Reboulleau, M. Désiré Magnier et Adolphe Romain *Manuel Roret, Verrier. Glaces et cristaux*, L. Mulo, Paris, 1913, p. 65.

[18] F. A. Kirkpatrick et George G. Roberts, "Production of Selenium Red Glass", *Journal of the American Ceramic Society*, volume 2, issue 11, November 1919, p. 895-904.

aluminate particles respectively. The accu-mulation of the particles near the surface of the enamel and the resulting chemical inhomogeneous layered microstructure are clearly seen.

## Sampling and Results of Historical Enamelled Stained Glass

***Table 2***. *Chemical composition (typical error 5%) of the historical enamels determined by LA-ICP-MS. Sulphur was not measured*

| Location | Workshop | color | wt% | | | | | | | | | | | | | | | | | | ppm | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **$B_2O_3$** | **$SiO_2$** | **ZnO** | **PbO** | $Na_2O$ | MgO | $Al_2O_3$ | $K_2O$ | CaO | $Cr_2O_3$ | MnO | $Fe_2O_3$ | CoO | CuO | $SnO_2$ | Ag | Au | Cl | P | Ti | Ni | As | Sr | Zr | Sb | Ba |
| Private house (Badalona) c.1900 | Buxeres i Codorniu | yellow stain | | 70.1 | | | 18.2 | 0.1 | 0.6 | 0.4 | 8.3 | | | | | | | 1.3 | | 0.7 | 12 | 154 | 1 | 1083 | 40 | 19 | 20 | 42 |
| | | blue | 5.2 | 28.3 | 8.1 | 42.2 | 4.9 | 0.1 | 3.6 | 0.1 | 1.2 | 1.8 | 0.4 | 1.9 | 1.6 | | | | | 0.2 | 192 | 139 | 467 | 179 | 132 | 10 | 77 | 2065 |
| | | brown | 0.2 | 53.2 | 0.0 | 18.9 | 12.5 | 0.1 | 1.3 | 0.3 | 6.1 | | 1.4 | 5.2 | | | | | | 0.5 | 256 | 284 | 21 | 980 | 85 | 18 | 149 | 270 |
| | | purple | 1.2 | 52.1 | 1.2 | 17.6 | 12.9 | 0.1 | 0.7 | 0.4 | 5.8 | | 0.3 | 1.5 | | | 4.2 | 0.2 | 0.5 | 1.2 | 122 | 179 | 18 | 625 | 49 | 15 | 77 | 214 |
| | | green | 7.5 | 26.5 | 2.2 | 40.5 | 6.3 | 0.1 | 1.9 | 0.2 | 7.1 | 2.9 | 0.1 | 0.4 | 1.6 | 1.6 | | | | 0.5 | 157 | 112 | 339 | 226 | 4823 | 10 | 126 | 741 |
| Casa Burés (Barcelona) 1900-1905 | | purple | 0.1 | 62.7 | 0.1 | 4.5 | 8.1 | 0.2 | 1.2 | 0.8 | 9.8 | | 1.2 | 0.9 | | 0.1 | 9.0 | 0.0 | 0.9 | 0.1 | 105 | 306 | 42 | 384 | 67 | 39 | 302 | 506 |
| Església de Sant Jaume (Calaf) 1903 | Amigó | red | 0.4 | 63.9 | 0.5 | 6.9 | 11.4 | 3.4 | 1.1 | 0.5 | 7.4 | | 0.6 | 3.4 | 0.1 | | | | | 0.1 | 176 | 513 | 359 | 436 | 39 | 53 | 52 | 184 |
| | | green | 0.6 | 50.4 | 0.2 | 27.1 | 4.4 | 1.8 | 2.3 | 0.4 | 4.0 | 1.4 | 0.7 | 4.4 | 1.2 | | | | | 0.1 | 2366 | 473 | 246 | 509 | 277 | 41 | 71 | 215 |
| | | purple | 0.5 | 64.9 | 0.1 | 8.9 | 9.9 | 3.3 | 1.5 | 0.6 | 6.8 | 0.5 | | 0.5 | 0.5 | | 1.1 | | 0.1 | 0.3 | 1473 | 505 | 97 | 507 | 34 | 54 | 173 | 74 |
| Estació Nord (Barcelona) 1910-1912 | Maumejean | green | 15.7 | 15.8 | 1.9 | 61.3 | 1.4 | 0.0 | 0.8 | 0.1 | 0.8 | 0.2 | | 0.1 | | 1.6 | | | | 0.1 | 212 | 128 | 2 | 88 | 15 | 11 | 328 | 115 |
| | | yellow | 14.5 | 15.0 | 7.5 | 58.4 | 1.5 | 0.0 | 0.5 | 0.1 | 1.0 | 1.3 | | 0.1 | | | | | | | 165 | 97 | 1 | 79 | 11 | 8 | 433 | 74 |
| Palau Justicia (Barcelona) 1911-1914 | Rigalt i Granell | purple | 0.1 | 65.8 | 0.1 | 5.4 | 11.0 | 0.2 | 0.5 | 0.3 | 12.8 | | 0.2 | 0.3 | | | 1.8 | 0.1 | 0.2 | 0.5 | 149 | 147 | 17 | 79 | 122 | 28 | 49 | 4529 |
| | | Yellow stain | | 68.1 | | | 11.8 | 0.1 | 0.4 | 0.2 | 14.5 | | 0.2 | 0.2 | | | | 3.5 | | 0.3 | 27 | 142 | 2 | 7 | 119 | 28 | 1 | 4946 |
| Seu Districte Sants Montjuic (Barcelona) 1915 | Rigalt i Granell | blue | 0.2 | 60.2 | 0.1 | 5.3 | 10.5 | 0.1 | 3.1 | 0.1 | 12.3 | 3.8 | 0.2 | 0.2 | 2.9 | | 0.1 | | | 0.6 | 38 | 175 | 3 | 5 | 55 | 29 | 1 | 111 |

The enamels have been exposed to environmental conditions and they all appear corroded, with little exception. The samples cover all relevant makers and the most common colours. In many cases, the enamel layer is extremely thin (below 10 µm) with the consequent analytical difficulties. The chemical analyses are shown in Table 2 and the colourants, pigment particles and alteration compounds in Table 3.

***Table 3***. *Colourants, pigment particles and alteration compounds identified in the historical enamels, determined by UV-Vis-NIR and µ-XRD*

| Location | Workshop | color | colourants | Pigment particles | Alteration compounds |
|---|---|---|---|---|---|
| Private house (Badalona) c.1900 | Buxeres i Codorniu | Yellow stain | | Ag° | |
| | | blue | | $(Cr,Co,Zn)Al_2O_3$ | $PbSO_4$, $Pb(OH)Cl$ |
| | | brown | | $Fe_2O_3$, $MnO_2$, $SiO_2$, $Pb_2(Fe,Mn)_2Si_2O_9$ | |
| | | purple | | Ag-Au° | |
| | | green | $Cu^+$-$Cu^{2+}$ | $(Cr,Co,Zn)Al_2O_4$, $FeSiO_4$ | |
| | | grisalle | | $Fe_2O_3$, $MnO_2$, $Pb_2(Fe,Mn)_2Si_2O_9$, $SiO_2$ | |
| Casa Burés (Barcelona) 1900-1905 | | purple | | Au-Ag° | $SnO_2$ |
| Església de Sant Jaume (Calaf) 1903 | Amigó | flesh | | $Fe_2O_3$, $(Mn,Fe)_3O_4$ Spinel | $PbSO_4$, $CaSO_4\cdot(H_2O)_2$, $Pb(OH)Cl$ |
| | | red | | $Fe_2O_3$ | |
| | | green | $Cu^+$-$Cu^{2+}$ | $(Cr,Co,Zn)Al_2O_4$ | |
| | | purple | | Ag-Au°, Sn, $(Cr,Co,Zn)Al_2O_4$ | |
| | | grisalle | | $Fe_2O_3$, $Pb_2(Fe,Mn)_2Si_2O_9$ | |
| Estació Nord (Barcelona) 1910-1912 | Maumejean | green | $Cu^+$-$Cu^{2+}$, $Cr^{3+}$ | - | - |
| | | yellow | $Cr^{6+}$ | - | - |
| | | grisalle | | $(Fe,Cu,Mn)_3O_4$ Spinel | - |
| Palau Justícia (Barcelona) 1911-1914 | Rigalt i Granell | purple | | Ag-Au° | $PbSO_4$, $CaSO_4\cdot(H_2O)_2$ |
| | | grisalle | | $(Fe,Cu,Mn)_3O_4$ Spinel, $Pb_2(Fe,Mn)_2Si_2O_9$ | |
| | | Yellow stain | | Ag° | |
| Seu Districte Sants Montjuic (Barcelona) 1915 | Rigalt i Granell | blue | | $(Cr,Co)Al_2O_4$ | |
| | | grisalle | | CuO, $(Fe,Cu,Mn)_3O_4$ Spinel, $Pb_2(Fe,Mn)_2Si_2O_9$ | $Pb_3(CO_3)_2(OH)_2$, $CaCO_3$ |
| | | Matt grisaille | | CuO, $(Fe,Cu,Mn)_3O_4$ Spinel, $Pb_2(Fe,Mn)_2Si_2O_9$, $SnO_2$ | |

## 1. Private house (Badalona)

This private house, located in Badalona, a coastal city close to Barcelona, hosts a collection of stained glass signed by *Buxeres i Codorniu*. The sample is part of an ornamental decoration with blue, brown, purple and green enamels, yellow silver stain and *grisaille*. The blue, green and purple paint contain cobalt and cobalt-chromium aluminate particles and silver-gold nanoparticles. The brown enamel contains the same particles as the *grisaille* but is richer in iron oxide particles and more vitrified. The alteration compounds determined are lead sulphate and hydroxyl-chloride.

## 2. Casa Burés (Barcelona)

The private residence of the family of Francesc Burés i Borràs was built in 1900 by the architect Francesc Berenguer i Mestres. The skylight is remarkable for its size, beauty and design. It was built by *Antoni Bordalba*, a stained glass maker who worked in a few important commissions, such as the windows of Cercle del Liceu private club, and who has been studied lately by art historians.[19] It has little enamelled glass, mainly a few minor details painted with a thin layer of purple of Caussius enamel worked with a badger brush, the enamel shows pin holes all over the surface.

## 3. Sant Jaume Church of Calaf

This late 16th-century church has a set of windows made in 1903 by the *Amigó*'s workshop, a studio run by Eudald Ramon Nonat Amigó i Dou (1818-85) and considered the technical innovator of stained glass in the mid-19th century.[20] The enamels from this studio are often referred to as weak and unstable.[21] The windows are very characteristic of the religious work of this studio; a central figure of a saint standing under canopies and surrounded by complex geometric patterns. Some were severely damaged by hail storms and many fragments fell fourteen meters to the nave ground floor. The church was also partly burned during the Spanish civil war.

The fragment of stained glass analysed belongs to a complex painted design of a face, painted with carnation and red enamels for the skin and lips, green and purple draperies and tracing and modelling grisailles. Carnation, like the grisaille, contains iron and manganese oxide particles, while the red lips contain only iron oxide particles. The green and purple enamels contain copper II and cobalt-chromium or zinc aluminate particles and silver-gold alloy nanoparticles respectively. The alteration compounds determined are lead and calcium sulphates and lead hydroxyl-chlorides (fig. 4). The pieces appear very fragmentary, on one side only grisaille was painted and on the other tracing grisaille, modelling grisaille, and enamel are mixed.

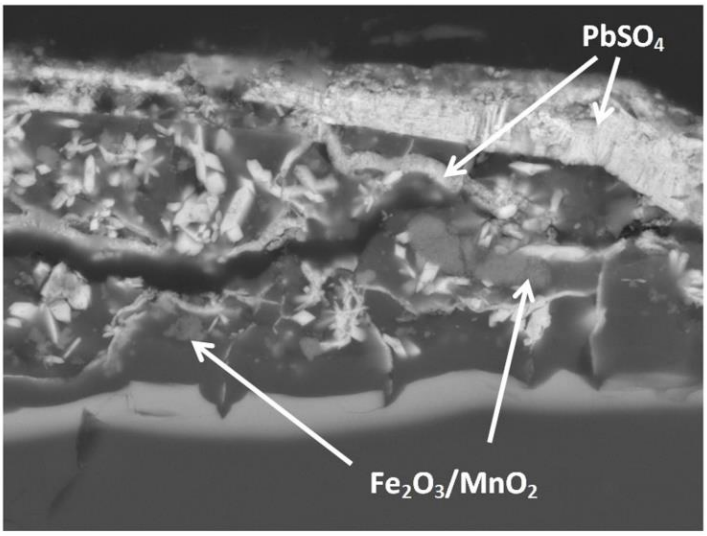


*Fig. 4. SEM-BSE images of the contour grisaille in a sample of enamelled glass from the Sant Jaume Church of Calaf (C13) showing the presence of large cracks filled with lead sulphate (anglesite, $PbSO_4$). Analysis shows the presence of kentrolite/melanotekite and different particles as iron and manganese oxides and also lead manganese silicate. Some alterations in the surface with lead sulphates particles can be observed.*

[19] Núria Gil, "La decoración con vidriera artística en el mueble domestico modernista catalán", *Virtuosisme Modernista. Tècniques del moble*, Associació per a l'Estudi del Moble i Museu del Disseny de Barcelona, Barcelona, 2019, p. 131-147.

[20] Sílvia Cañellas & Núria Gil, "La Fábrica de Vidrieras de los Amigó", *Cuadernos del Vidrio*, núm. 3, Real Fábrica de Cristales de la Granja. Fundación Centro Nacional del Vidrio, Diciembre 2014, p. 42-59.

[21] Sílvia Cañellas & Núria Gil, "El taller Amigó de la tradició al progrés. El camí cap al vitrall modernista", Lluís Bosch, Mireia Freixa, *CDf International Congress*, Barcelona, 2017.

### 4. Estació del Nord (Barcelona)

The train station made in 1861 was reformed by the architect Demetri Ribes i Marco,[22] between 1910 and 1915, incorporating in the waiting rooms a set of windows with a floral *coupe de fouet* style pattern made by *Maumejean*'[23] workshop. The windows have always been interior and not affected by atmospheric corrosion. The maker, *Maumejean* a large French stained glass studio; originally located in the city of Pau, which also opened offices in Paris, Madrid, San Sebastian, and Barcelona. In Catalonia the studio was located in Rambla Catalunya 120 for only two years.

The sample is an acid etched copper red flashed glass with yellow and green enamel and black tracing *grisaille*. The green and yellow enamels are fully amorphous and the colourants are Cu II and Cr VI. The piece was badly broken with large losses and during a conservation campaign in 1991 a new copy was made starting from the original pieces. The enamel is simply applied with a brush and not thinned with a badger brush; it looks mildly cloudy but does not show any other sign of decay.

### 5. Palau de Justícia (Barcelona)

The large skylight was made in 1908 by the *Rigalt i Granell* workshop.

The full building is a design by the architects Domenech Estapà and Enric Sagnier. The sample was obtained during the full restoration of the stained glass carried out in 2009. The skylight was covered by a glass roof, as usual. Since it was quite difficult to reach for maintenance, dust and dirt deposited and accumulated for decades.

The sample is part of the silver stained pattern that has a light purple background which in some parts appears to be vanishing. The *grisaille* and paint are applied to the internal side of the panels while yellow silver stain is applied at the exterior side. The purplish enamel is very thin, containing silver-gold nanoparticles applied diluted and worked with a badger brush. The *grisaille* contains iron copper manganese oxide particles. The alteration compounds found are lead and calcium sulphates.

### 6. Seu del Districte de Sants Montjuic (Barcelona)

Large set of windows drawn by the artist Francesc Labarta (1883-1963) and built also by the studio of *Rigalt i Granell* in 1914. The windows installed in the main facade of a very busy street with dense traffic were vandalized during a riot in May 2014. The external side of the enamels shows a whitish appearance. The glass sample consists of a mixture of blue and green enamel applied over a yellow cathedral glass. The blue and green enamel has cobalt chromium and zinc aluminate particles and dissolved copper II; it appears mixed with some *grisaille* painted motives, with iron manganese copper oxide and copper oxide particles. On the other side, a matt *grisaille* containing also tin oxide particles to reduce the light entering the building is present (fig. 5). The alteration compounds found are lead and calcium carbonates.

## Mechanisms of Alteration

The historical enamels appear to be depleted in lead, boron and zinc, enriched in silicon, calcium and sodium; lead and calcium sulphate, lead hydroxil-chloride or lead and calcium carbonates precipitated within the cracks and bubbles. Lead sulphate is found in the Palau de Justicia and in the church of San Jaume de Calaf and in the private house in Badalona; lead sulphate is a typical alteration compound in an atmosphere rich in sulphur dioxide. Chlorine which in some cases result also in the formation of lead hydroxyl-chloride precipitates is related either to the proximity to the seashore (Badalona and Barcelona) but also perhaps to the effect of the smoke from candles. Phosphorous is also found in most of the enamels and is related to the presence of bird droppings. Basic lead carbonate and calcium carbonate are found in the stained glasses from Seu del Districte de Sants Montjuic, which although nowadays is integrated to Barcelona, for a long time it was in a suburb area. The enamels from Estació del Nord, being placed inside buildings appear mainly unaltered.

[22] http://invarquit.cultura.gencat.cat/Cerca/Fitxa?index=0&consulta=&codi=40487 Inventory of Catalan arquitectural Heritage. (Last visited 25/11/2019).

[23] Benoît Manauté, *Flambe ! Illumine ! Embrase ! La place de la manufacture de vitrail et mosaïque d'art Mauméjean dans le renouveau des arts industriels franco-espagnols (1862,1957)*, UPPA, 2012, p. 58-60.

This alteration is in good agreement with atmospheric corrosion of a lead glass involving an interdiffusion controlled lead leaching and silica dissolution and reprecipitation. Atmospheric sulphur, carbon and nitrogen dioxide gases are dissolved in water incorporated to the enamel and metal sulphates and carbonates precipitate. Boron and nitrates are highly soluble while on the contrary, calcium and lead carbonates or sulphates are highly insoluble.

After only 162 hours of exposure to moisture, typical leached thicknesses of 1-2 µm[24] are found for historical glasses in laboratory corroding conditions. Considering the thickness of our enamels (10-50 µm) the corrosion layer might build up in a relatively short period (months to few years) after continuous exposure.

The historical enamels show less saturation of colour than the replicated ones due to the presence of lead and calcium sulphate or carbonate precipitates which are white. This is the very common white appearance of enamel, especially noticeable on the external side with reflected light.

Temperature variations will also promote the formation of cracks and favour the solubility/recrystallization cycle of the alteration compounds (of particular importance for calcium sulphate) precipitated in cracks.

Besides corrosion, some painting practices, like mixing *grisaille* and enamel, which has been found in the Amigó and Buxeras i Codorniu stained glass, or adding more *flux* to a ready-to-paint enamel, are bad practices. The consequent modification of the enamel chemistry may result in a material of reduced stability.

The enamels containing pigment particles with a lower density (blue and green cobalt and chromium aluminate pigment particles) than the glassy matrix give rise to a layered structure (fig. 5B) with the particles floating in a lead poorer glass over a lead richer enamel-substrate glass reaction layer. The leakage of lead will affect the stability of these enamels more drastically advancing the surface flaking.

Another source of instability is the greater absorption in the near infrared region of the blue cobalt centres ($CoO_4$) or by Cu II; an effect which is more dramatic when the enamel contains cobalt aluminate particles (fig. 2). This enhanced absorbance will produce an increase in the overall temperature of the enamel and also a thermal mismatch between particles, enamel glass and substrate glass.

## Conclusions

The enamels are made of a lead-zinc borosilicate glass (60-70%PbO, 5-20%$B_2O_3$, 10-25%$SiO_2$, 0-5%ZnO) characterised by a low sintering temperature and softening point, while keeping a reasonable stability against water corrosion, mixed with a wide variety of colourants and pigment particles.

The analysis of the historical enamels shows that the whole thickness of the enamels independently of the colour is affected by atmospheric corrosion. Boron, lead and zinc are depleted from glass shortly after its exposure to the atmosphere, while the enamels appear to be silicon, sodium and calcium enriched. Lead leaching from the enamel in the presence of humidity and of atmospheric gases/pollutants results in the subsequent precipitation of lead and calcium sulphates and carbonates. The difference between the corrosion precipitates is related to the atmosphere of the environment. The resulting products are mainly leached to the surface where they are dissolved and rinsed by rainwater and therefore do not generate a crust or corrosion layer, but some precipitate inside cracks and bubbles as lead and calcium sulphates, carbonates hydroxyl-chlorides and also phosphates, which are white yellowish reducing the colour saturation of the enamels.

The chemical composition of the blue and green enamels is the same. Nevertheless, the blue and green enamels containing cobalt and cobalt chromium aluminate particles show a layered microstructure, with a lead depleted layer with pigment particles floating near the surface and a lead enriched interface at the substrate glass. This heterogeneity is expected to be in part responsible for the enhanced flaking of the enamels exposed to weathering. The enhanced absorbance in the Near Infrared of enamel containing ($CoO_4$) or Cu II causes an increase in the temperature of these enamels which may be responsible for the formation of cracks and tension between the glass and the enamel.

[24] Susan Wood and J.R. Blachere, "Corrosion of lead glasses in acid media: I, leaching kinetics", *J. Am. Ceram. Soc.* 61, 7–8, 1978, p. 287–292.

Some paint practices, such as the addition of *flux* to the enamel or the mixture of enamel and *grisaille* give rise to a more unstable composition which might be the reason for the low stability of the paints in some of the studios of the period.

The conservation of the enamelled stained glass will require better protection from humidity and atmospheric gasses and the use of a filter of infrared light, especially important in Mediterranean climates.

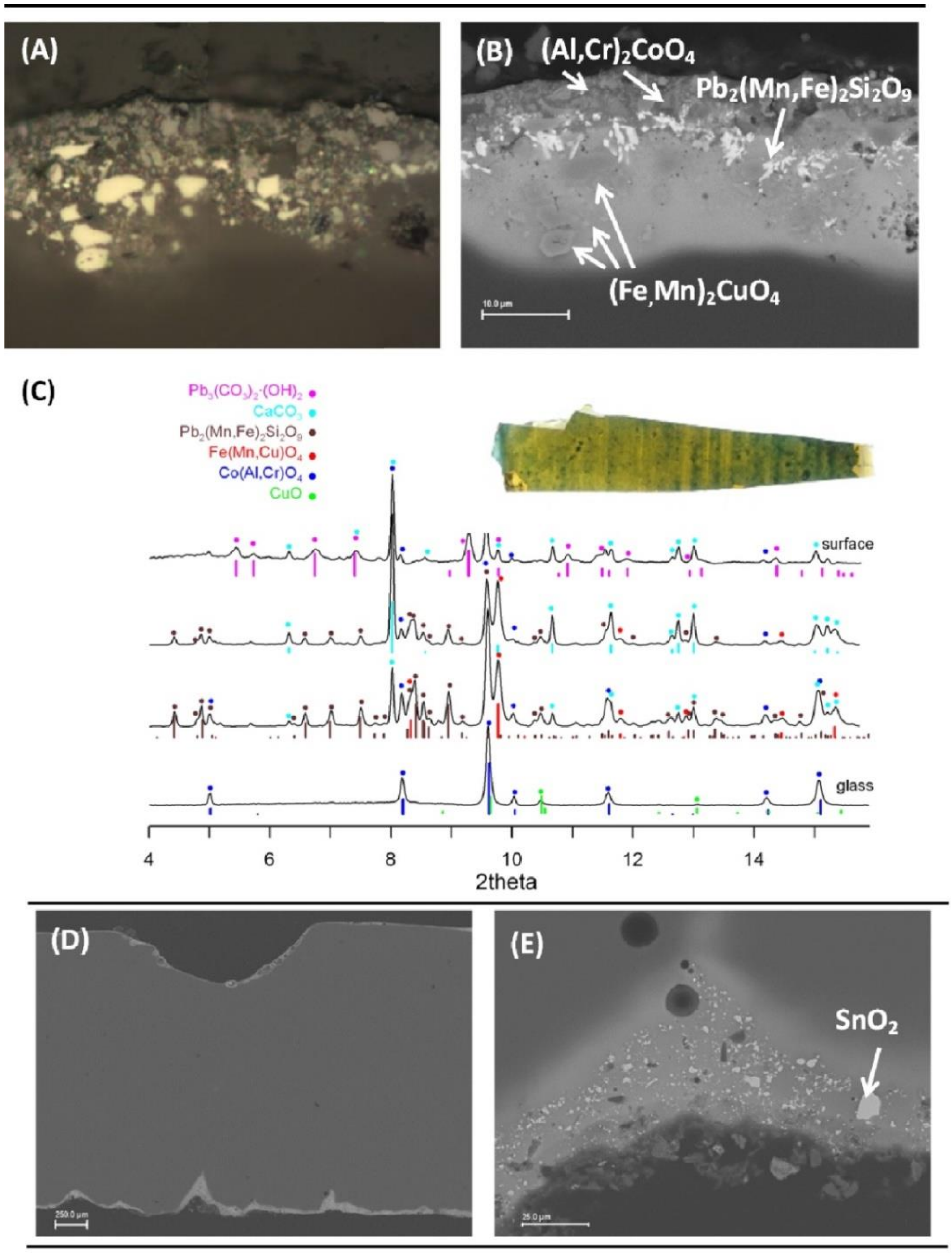


*Fig. 5. (A) Blue enamel mixed with grisaille over a yellow glass fragment from the Seu del Districte Sants-Montjuic by Rigalt & Granell; (B) SEM-BSE image showing the presence of particles of $(Al,Cr)_2CoO_4$ from the blue enamel and of $Pb_2(Mn,Fe)_2Si_2O_9$ from the grisaille (C) µ-XRD patterns obtained across the enamel layer showing the enamel and grisaille particles, $(Al,Cr)_2CoO_4$, $(Fe,Mn)_2CuO_4$, CuO and $Pb_2(Fe,Mn)_2Si_2O_9$, and also the presence of $CaCO_3$ and $Pb_2(CO_3)_2(OH)_2$ compounds on the surface. (D) and (E) SEM-BSE images showing the grisaille and blue enamel on the internal side and grisaille with $SnO_2$ particles outside a cathedral glass.*