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**INVESTIGATION OF THE
LOSS OF COLOUR IN
SMALT ON DEGRADATION
IN PAINTINGS USING
MULTIPLE SPECTROSCOPIC
ANALYTICAL TECHNIQUES**

Keywords: smalt, alteration, painting, SEM-EDX, micro X-ray absorption spectroscopy, Raman micro-spectroscopy, infrared micro-spectroscopy, synchrotron

ABSTRACT

Smalt is a potash glass with a blue colour given by cobalt, common as an artists' pigment between the 16th and 18th centuries. It often deteriorates, losing its colour and causing dramatic changes in the appearance of paintings. The changes in structure and elemental composition accompanying the loss of colour in the glass were examined in samples from paintings in the National Gallery, London and the Louvre using synchrotron micro X-ray absorption spectroscopy, synchrotron reflectance FTIR microspectroscopy, Raman microspectroscopy and SEM-EDX. The leaching of potassium was found to be responsible for concurrent structural modifications in the glass: increase in polymerisation of the silicate network and change in cobalt coordination from tetrahedral towards octahedral, leading to colour change in the pigment. These results also form valuable reference data for examinations with lab-based techniques to distinguish between smalt that is degraded or a pale grey variety deliberately chosen by the artist.

RÉSUMÉ

Le smalt est un verre potassique dont la couleur bleue est due au cobalt, communément employé comme pigment par les artistes du XVI^e siècle au XVIII^e siècle. Il se détériore souvent, en se décolorant et en entraînant des modifications radicales dans l'apparence des tableaux. Les changements de structure et de composition élémentaire qui accompagnent la décoloration du verre ont été examinés sur des échantillons provenant de tableaux du Louvre et de la National Gallery, à Londres, par microspectroscopie d'absorption X par

INTRODUCTION

The blue pigment smalt was commonly used by artists between the 16th and 18th centuries. It is a potassium silicate glass coloured by cobalt ions. The smalt found in paintings of this period also contains other elements, such as arsenic, iron, nickel and bismuth associated with the cobalt ore. Historic documentary sources show that several grades were sold that varied in colour intensity as a consequence of differences in both particle size and cobalt content (Mühlethaler 1993).

Smalt often deteriorates, losing its colour and causing dramatic changes in the appearance of paintings.

On degradation, potassium is leached from the glass (Boon 2001, Spring 2005), and in oil paintings it can react with fatty acids in the oil to form soaps. These can migrate to the paint surface where they react further with sulphates, carbonates and other environmental pollutants to create a crust of complex potassium salts (Spring 2005, van Loon 2008). The change in appearance of smalt-containing paint is therefore a complex combination of many processes and not simply due to loss of colour in the smalt but also to changes in the binding medium and paint structure.

The focus of this paper is specifically the structural changes within the smalt glass associated with the loss of colour. It is now well established that it is associated with loss of potassium, but the exact physico-chemical origin of the colour change has not been fully explored. Leaching of the cobalt colouring ion has been sometimes cited as a cause (Hornblower 1962, Altavilla 2004), but although this has been shown to have occurred in some severely degraded cases (Spring 2005) many examples exist where smalt has lost its colour without significant loss of cobalt and this is not therefore the primary mechanism. It has also been suggested that a change in the cobalt oxidation state is involved (Giovanoli 1970) but the most feasible proposed mechanism is change in speciation or environment around the cobalt ion, from tetrahedral coordination, known to be responsible for the blue colour, to octahedral coordination (Boon 2001, Spring 2005).

Like any silicate glass, smalt consists of a disordered silicate network partially depolymerised by the alkali and other cations present in the glass. The elemental composition influences the chemical structure and the properties

rayonnement synchrotron, microspectroscopie de réflectance infrarouge à transformée de Fourier par rayonnement synchrotron, microspectroscopie Raman et microscopie électronique à balayage couplée à la spectrométrie de rayons X à dispersion d'énergie. Le lessivage du potassium a été jugé responsable des modifications structurelles concomitantes dans le verre : augmentation de la polymérisation du réseau de silicate et modification de la coordination du cobalt, qui de tétraédrique devient octaédrique, ce qui entraîne un changement de couleur du pigment. Ces résultats sont également des données de référence utiles pour les examens basés sur des techniques de laboratoire, puisqu'ils permettent de faire la distinction entre du smalt dégradé ou une variété de gris pâle délibérément choisie par l'artiste.

RESUMEN

El esmalte es un vidrio potásico con un color azul dado por el cobalto, un pigmento artístico común entre los siglos XVI y XVIII. Se deteriora a menudo y pierde su color causando graves cambios en la apariencia de las pinturas. Se examinaron los cambios en la estructura y la composición elemental que acompañan a la pérdida de color en el vidrio en muestras de pinturas de la Galería Nacional de Londres y del Louvre, utilizando microespectrometría de absorción de rayos X sincrotrónicos, microespectrometría de reflectancia IRTF sincrotrónica, microespectroscopía Raman y MEB-EDX. Se descubrió que la lixiviación del potasio era responsable de las modificaciones estructurales simultáneas en el vidrio: un aumento de la polimerización de la red de silicato y cambios en la coordinación de cobalto, de tetraédrico a octaédrico, lo que provoca el cambio de color en el pigmento. A partir de estos resultados también se consiguen valiosos datos de referencia para los exámenes con técnicas de laboratorio, que permiten distinguir entre un esmalte degradado y una variedad de gris pálido elegida deliberadamente por el artista.

of a glass, such as viscosity, colour and melting temperature. Complete understanding of discoloration of smalt can only therefore be reached by examining concurrently the elemental composition and structural chemistry of the glass. The range of analytical techniques available to achieve this is limited by the non-crystalline nature of the pigment. In addition, the smalt particles in the paint layers are 10-50 μm in size, necessitating the use of micro-beam techniques with a high spatial resolution so that individual particles that have degraded to varying degrees can be analysed separately and directly on cross-sections. For this reason the following techniques were selected:

- Raman and synchrotron Fourier transform infrared (FTIR) microspectroscopy, probing the chemical structure of the silicate network
- synchrotron micro X-ray absorption spectroscopy (XAS) examining the local environment and structure around the cobalt ion
- scanning electron microscopy with energy dispersive X-ray microanalysis (SEM-EDX) providing quantitative elemental composition of the glass.

A description of the details of instrumental and experimental conditions and the complex data analysis involved for the above techniques, is beyond the scope of this short paper; this will be published elsewhere in separate articles on the XAS results and the vibrational spectroscopy (Robinet 2011). The purpose of this contribution is instead to bring together the information obtained on smalt degradation from all these techniques, to present an overview of what has been learned about changes in structure and composition and to place it in a context relevant to conservation and art historical issues such as the interpretation of the original appearance of paint affected by this type of deterioration.

SAMPLES AND EXPERIMENTAL METHODS

The smalt-containing samples in this study were taken from paintings from different periods and geographical origin belonging to the National Gallery, London and the Centre de Recherche et de Restauration des Musées de France (C2RMF) (Table 1). They were prepared as cross-sections mounted in polyester resin and were selected because they contain smalt particles showing different degrees of degradation (some blue well-preserved, others partially or completely altered) that were sufficiently large to be analysed by the various micro-beam techniques. Silica gel (dry and hydrated), and cobalt-containing glass, including modern smalt, were used as references for XAS.

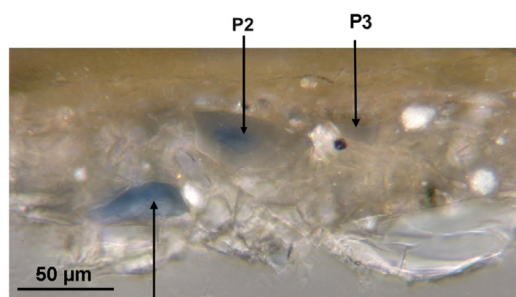
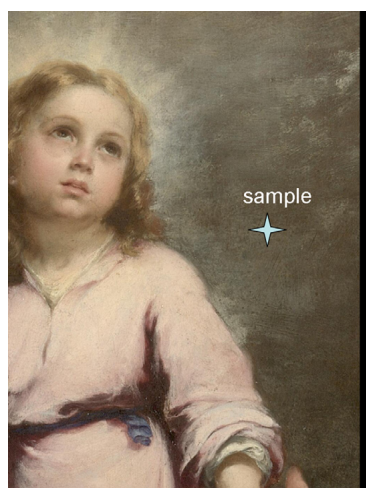
Optical microscopy was carried out with a Leica DM4000M microscope under visible light and ultraviolet light (filter block A: excitation filter BP: 340–380 nm, emission filter LP: 430 nm).

Quantitative SEM-EDX analysis was conducted in a Zeiss Evo®MA10 SEM with an Oxford Instruments 80mm² X-max EDX detector under variable pressure conditions (30 Pa, water vapour, 20 kV, 200 pA beam current), to avoid carbon coating and allow further analysis by other techniques.

Table 1

Details of the paintings examined in this study

Artist, painting title, date and location	Description of the area sampled
Paolo Veronese, <i>The Consecration of Saint Nicholas</i> (NG 26), 1562, oil on canvas, National Gallery, London	Brown discoloured shadow of the bishop's blue drapery (ref. NG2656)
Paolo Veronese, <i>Les Dieux de l'Olympe</i> , 1557, detached wall painting replaced on a canvas, Louvre Museum	pale grey-blue paint, probably from the sky (ref. L2925)
Paolo Fiammingo, <i>Landscape with the Expulsion of the Harpies</i> (NG5467), around 1590, oil on canvas, National Gallery, London	Light blue area of the sky (ref. NG546751)
Bartolomé Esteban Murillo, <i>The Heavenly and Earthly Trinities</i> (NG 13), 1675–1682, oil on canvas, National Gallery, London	Brownish grey sky (ref. NG1358)
François Lemoine, <i>Hercule tuant Cacus, Morceau de réception à l'Académie</i> , 1718, oil on canvas, Louvre Museum	Greyish drapery of Cacus (ref. L4346)



P1

Figure 1

Bartolomé Esteban Murillo's *The Heavenly and Earthly Trinities*. © National Gallery, London (NG13). Detail of the degraded smalt-containing sky

Figure 2

Cross-section of sky paint from *The Heavenly and Earthly Trinities* showing unaltered (P1), partially altered (P2) and severely altered (P3) smalt particles

Raman spectra were collected on a Thermo Scientific DXR Raman microscope over the spectral range 200–1600 cm^{-1} (532 nm laser, 2 μm beam size, 25 μm confocal hole, power at the sample 1–5 mW).

Micro-FTIR spectroscopy was undertaken on the SMIS beamline at SOLEIL synchrotron on a Continuum XL microscope with a Nicolet 5700 spectrometer (Thermo Scientific). A beam size of 11 \times 11 μm was used. The spectra were collected in reflection mode, spectral range 4000–700 cm^{-1} and spectral resolution of 8 cm^{-1} , averaging 512 scans.

Micro-X-ray absorption spectra were collected at the cobalt K-edge up to 8 keV on the LUCIA beamline at SOLEIL synchrotron with a beam size of 2 \times 4 μm . The beamline configuration and measurement conditions are detailed elsewhere (Robinet 2011).

RESULTS AND DISCUSSION

The results from each technique were very consistent. Between five and ten particles were analysed in each sample from each painting and this relatively large body of data demonstrated that the trends seen held true across all the degraded smalt examined. A single example that was typical will be used here to illustrate the observations. This was taken from the greyish-blue sky of Murillo's *The Heavenly and Earthly Trinities* (1675–1682, oil on canvas, National Gallery, London) (Figure 1).

In the cross-section (Figure 2) there are a few smalt particles which are still blue, including one with a blue core and colourless degraded rim, amongst smaller particles that are colourless or very pale. The quantitative SEM-EDX analyses demonstrate a clear relationship between the colour and the potassium content (Table 2). In the most intense blue particle (P1) almost 13 weight percent (wt%) potassium oxide is present, while in the small very degraded particle (P3) potassium has been leached and was measured at only around 2 wt%. There is around 9 wt% potassium in the blue area of the partially degraded particle (P2) suggesting it is partially leached even in the core, dropping to 3.5 wt% in the degraded rim. The quantitative results for these three particles are included so that the degree of leaching of potassium can be correlated with the features in the XAS,

FTIR and Raman spectra, as they are from the same areas. The other cations, including cobalt, are retained in the structure and although small variations in their concentration can be seen in Table 2, these are due to inherent difficulties with EDX analysis, such as the greater contribution to the spectra of small particles from elements outside the smalt such as lead from lead white pigment, due to scattering under variable pressure conditions in the SEM. There are also inconvenient overlaps in the peaks of the elements such as Pb/As, Pb/Bi and As/Mg which affect the EDX results. Nevertheless, the cobalt content in the Murillo sample can be established at around 3 wt% (the apparently greater amount in degraded particles is due to normalisation) and there is a considerable amount of arsenic associated with it (around 4 wt%). The well-preserved smalt in the group of paintings studied had potassium contents of 12–16 wt % and cobalt contents of 2–7 wt %, the Murillo being at the lower end of this range.

Table 2

Quantitative SEM-EDX analyses of well-preserved and degraded smalt in the cross-section from the painting by Murillo

Wt % normalised	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO	CoO	NiO	As ₂ O ₃	PbO	Bi ₂ O ₃
P1: blue particle, bottom left	0.7	0.3	1.1	69.9	12.7	1.8	3.4	2.9	0.6	4.1	1.4	1.3
P2: blue core of particle in the centre	0.1	-	0.8	77.4	8.8	0.4	3.1	3.7	0.8	3.4	1.1	0.4
P2: degraded rim of particle in the centre	-	0.1	0.9	81.6	3.5	0.4	3.1	3.8	0.9	3.5	1.5	0.8
P3: small degraded particle, top right	-	-	1.1	80.8	1.9	0.6	3.2	3.8	0.5	3.8	3.6	0.7

The X-ray absorption near edge spectroscopy (XANES) region of the XAS spectrum (7670–7755 eV, Figure 3) gives information on the oxidation state and coordination environment around the cobalt ion, while the distance and number of nearest neighbours can be calculated from the extended X-ray absorption fine structure (here only partial EXAFS, 7756–8000 eV). All the spectra showed a pre-edge peak centred at 7711 eV (inset, Figure 3) and a single white line centred at 7727 eV. This indicates that the oxidation degree is not modified with the alteration.

The well-preserved particle P1 and the very degraded particle P3 do, however, show some clear differences in the profile of both regions of the spectra. The similarity of the XAS spectra profile of the well-preserved particles in the paintings with the blue reference samples measured (including blue silica gel, Figure 4), as well as the Co–O distances and the coordination number calculated from the EXAFS region, indicate the presence of Co²⁺ mostly in tetrahedral coordination (Robinet 2011).

A blue colour in cobalt-containing compounds is associated with tetrahedral coordination of the cation, while a pinkish colour is expected in octahedral coordination. Glasses follow a similar trend, and although they can exhibit a range of coordination geometries, including some not encountered in crystalline silicates, studies have shown that tetrahedral structure is more

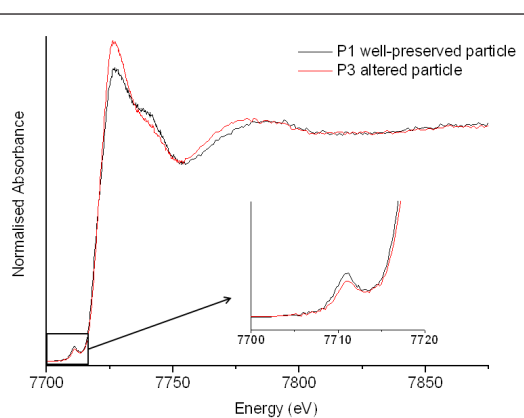


Figure 3

Comparison of the X-ray absorption spectra of well-preserved and altered smalt in the cross-section in Figure 2

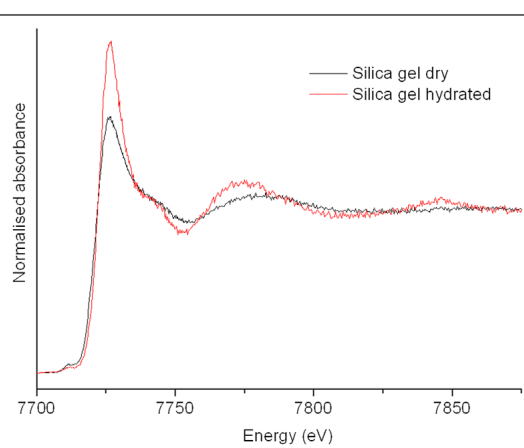


Figure 4

Comparison of the X-ray absorption spectra of pink hydrated and blue dry silica gels

stable than octahedral for cobalt in alkali silicate glass (Llusar 2001). There is a direct link between the environment around the cobalt ion and the alkali ions that can be understood by looking at their role in the glass structure. Potassium ions are present as modifiers as well as charge-compensating cations. Co^{2+} can only adopt tetrahedral coordination, and therefore give a blue colour, if alkali is present to compensate its charge. Terczynska-Madej (2010) has demonstrated that potassium is able to stabilise tetrahedral coordination more effectively than sodium in alkali silicate glasses, leading to a blue colour of higher intensity. This explains why potassium in combination with cobalt in glass gives a purer blue colour (Weyl 1951) and why smalt is almost always a potash glass, reflected in some of the historical recipes where the potassium-rich tartar is mentioned as an ingredient (Stege 2004).

The spectrum of the altered smalt in the painting by Murillo displays a decrease in the intensity of the pre-edge peak and an increase in intensity of the white line in the XANES region, as well as a shift of the first oscillation towards lower energy in the EXAFS region (Figure 3). These same spectral modifications can be seen in Figure 4 resulting from the change in coordination of cobalt from tetrahedral in blue dry silica gel to octahedral in pink hydrated silica gel. In addition the Co–O distances and coordination number calculated from the EXAFS region are increased relative to those in the well-preserved particle indicating that, on alteration, Co^{2+} coordination increases towards an octahedral state. Consideration of the elemental composition and the cobalt environment in combination revealed that the cobalt coordination is dependent on the alkali:cobalt ratio in the glass. Leaching of the potassium ions has a direct impact as it decreases the number of charge-compensating ions available in the structure, which can create a charge deficiency around the cobalt. As a result, cobalt cations cannot retain their tetrahedral coordination and it increases towards octahedral coordination leading to the colour change.

Vibrational spectroscopy probes the silicate network, the vibrations of which are sensitive to its degree of polymerisation and the chemistry and concentration of the surrounding cations. As FTIR and Raman rely on different selection rules, they give complementary information on modifications in the medium range order in the glass on degradation. Synchrotron FTIR in reflectance mode made it possible to obtain good spectra from individual particles within the paint layer so that differences between degraded and well-preserved particles could be investigated without interference from the binding medium and made a good comparison with the extensive reflectance FTIR studies on the corrosion of glass (MacDonald 2000). Because the infrared silicate vibrations occur between 900 and 1200 cm^{-1} , the minimum possible beam size without diffraction effect in the spectra was $11\text{ }\mu\text{m}$, which was sufficient to examine individual particles but led to averaging where the degree of degradation differed within a particle. Raman microscopy was able to examine a much smaller volume ($2\text{ }\mu\text{m}$ beam size), allowing

structural differences within single smalt particles to be followed from the well-preserved blue core to the degraded rim.

The Raman spectrum of the well-preserved particle in the Murillo sample is characteristic of an alkali silicate glass, having an intense peak centred at 1091 cm^{-1} , associated with the vibration of silicate species coordinated to alkali ions (Figure 5) (Robinet 2008). Similarly, in the FTIR spectrum of the same particle the peak at around 995 cm^{-1} can be assigned to the stretching of Si-O^- coordinated to potassium (Figure 6), although it is less well defined than in the Raman spectrum.

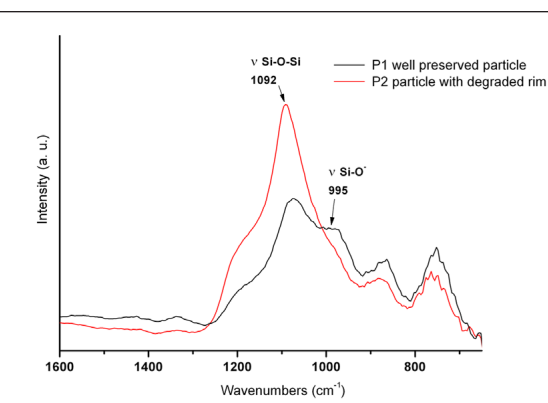
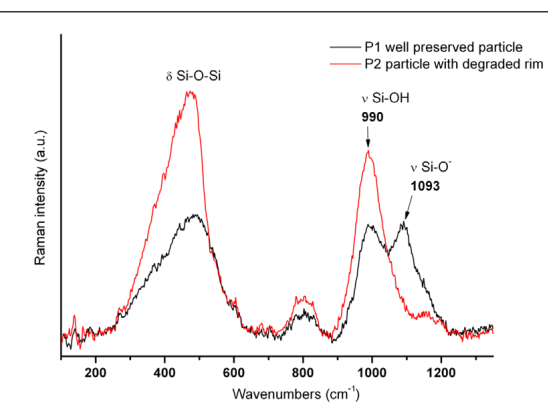
The leaching of potassium is the result of an ion-exchange reaction with protonated species (H_3O^+ , H^+ or H_2O). In vibrational spectra, as potassium is leached from the smalt, the contribution to the spectrum from the non-bridging bond Si-O^- coordinated to alkali decreases. The differences in the vibrational spectra between the well-preserved particle and the degraded rim of the partially preserved particle illustrate this modification very clearly (Figures 5 and 6) and it is more evident in the Raman spectra than in the FTIR spectra. The silanols ($\equiv\text{Si-OH}$) formed through the ion exchange are observed in the Raman spectrum with an intense band around 990 cm^{-1} . These species partly undergo condensation reactions creating more bridging Si-O-Si . As a result, in the FTIR spectra the Si-O-Si stretching appears to become more intense and to shift to higher wavenumber (Figure 6) whilst an intensity increase in the Si-O-Si bending vibration is observed in the Raman spectra (Figure 5). In both cases, the spectra of degraded particles more closely resemble those of vitreous silica and the silicate network becomes more highly polymerised. The extent of these changes correlates to the potassium concentration measured by SEM-EDX in individual particles and, taking the results from all the samples as a whole, the position of the most intense peak in the silicate region of the FTIR spectra relates closely with the degree of degradation.

Figure 5

Raman spectra of the well-preserved and altered smalt in the cross-section in Figure 2

Figure 6

Reflectance FTIR spectra of the well-preserved and altered smalt in the cross-section in Figure 2



CONCLUSION

This investigation of smalt degradation has provided fundamental information on the structural changes occurring in the glass itself, with accompanying loss of colour. The SEM-EDX analysis confirms that potassium is leached on degradation, as found in earlier studies. Relatively few results of quantitative elemental composition of smalt have been published but it proved valuable for establishing the degree of leaching in the individual particles. The depletion of potassium ions creates a deficiency in charge-compensating ions around cobalt. As a result, the colouring cation, present in the glass as Co^{2+} , changes from mostly tetrahedral towards octahedral coordination, as shown by μXAS on separate particles exhibiting varying degrees of degradation, only possible at the synchrotron. This structural change around cobalt is directly responsible for the discoloration observed in the pigment. The hypotheses regarding leaching of cobalt or change in oxidation state of cobalt were discarded. The ion exchange not only causes

loss of potassium and changes in the structure around the cobalt ion, but induces a structural rearrangement of the silicate network, with condensation of part of the silanols leading to the formation of a more polymerised structure as revealed by vibrational spectroscopy techniques.

Historical documentary sources show that smalt was available in different grades, varying in shade from strong blue to pale grey. An added benefit of this study is that it illustrates that a combination of quantitative SEM-EDX, FTIR and Raman spectroscopy can be reliably used to determine whether the smalt has degraded or whether the artist deliberately chose a weakly coloured variety, which would display the analytical features of an unaltered smalt. The differences in elemental composition determined by SEM-EDX, and in both the Raman and FTIR spectra of well-preserved and degraded smalt particles are very evident, making them valuable reference data for examinations with lab-based techniques for this purpose. This is a commonly recurring question from conservators and curators, which in the past has been difficult to address effectively, and is fundamental in our interpretation of the original appearance of paintings in which smalt has been used as a pigment.

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