

Della Robbia blue glaze: micro-Raman temperature study and X-ray fluorescence spectroscopy characterization

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Micro-Raman temperature study and X-ray fluorescence (XRF) spectroscopy were used for characterization of the blue glaze on *Saint John the Baptist* – majolica terracotta relief attributed to Andrea Della Robbia and *Saint John the Baptist with Cross* – majolica terracotta statue attributed to Giovanni Della Robbia. Both objects are on permanent exhibition in the John and Mable Ringling Museum of Art in Sarasota, FL. This study proves that the detection of the 548 cm⁻¹ Raman band alone cannot serve as evidence for presence of lazurite crystallites in the pigment in the glaze. It was established that the famous Della Robbia blue is due to the combined effect of Co–Ni–Cu–Zn atoms and S₃⁻ ions embedded in a lead silicate matrix. It is proposed that the Della Robbia family used Co-containing sulfide ores as a source for manufacturing their blue pigments. Copyright © 2009 John Wiley & Sons, Ltd.

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Introduction

Luca Della Robbia is credited for his invention of '*Terracotta invetriata*', glazed terracotta. His specific glazing technique imitates carved marble, and Giorgio Vasari characterizes it as 'a new, useful, and beautiful art' of the Renaissance era, 1450–1600.^[1] Leon Battista Alberti recognized the artist of the Florentine Renaissance and wrote: 'arte e scienza non udite e mai vedute'; 'arts and science not heard and never seen.'

Luca's glazed terracotta artworks are throughout Florence at the Duomo, Orsanmichele, Museo Bardini, Santa Trinita, Santa Maria del Fiore, the Convent of San Marco, San Jacopo at San Miniato, the Pazzi Chapel in Santa Croce, National Museum of the Bargello and Serristori Palace. A family workshop for glazed terracotta artworks was established in 1446 by brothers Luca and Marco Della Robbia. Marco's son Andrea (1435–1525) and grandson Giovanni (1469–1529) kept the family workshop alive for more than a century. All art objects were created for humid and cold mountainous environments, 'where no painting could be preserved for even a few years,' according to Vasari.^[2] As works of religious art, their intent was practicality and durability, positioned in sites of architectural and historic significance possibly preferred over more fragile thus vulnerable paintings or carved wood sculptures.

Within the John and Mable Ringling Museum of Art collections, there are various works of art acquired by John Ringling from the Emile Gavet collection when sold from the Gothic Room at the Marble House Mansion, Newport, Rhode Island. His acquisitions, assisted by Lord John Duveen at the auction, include majolica terracotta relief from the workshop of Andrea della Robbia: *Saint John the Baptist*, a tondo (29") and colored tin enamel glazed terracotta statue (36" × 14.5" × 8") attributed to Giovanni della Robbia: *Saint John the Baptist with Cross*, Fig. 1.

Few autographed works and elusive documentation regarding commissions and provenance create the need for a variety of research investigations into the materials and techniques used by

the Della Robbia family. Elemental analysis of Della Robbia blue and white glazed terracotta have been performed by other authors using various techniques – particle-induced X-ray emission (PIXE) analysis,^[3,4] X-ray fluorescence (XRF) spectroscopy,^[3] scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS),^[4] inductively coupled plasma combined with mass spectroscopy (ICP/MS)^[4] and inductively coupled plasma combined with atomic emission spectroscopy (ICP/AES).^[4] Molecular characterization utilizing micro-Raman spectroscopy was reported previously for the yellow glaze of the Della Robbia majolica altar conserved at St. Mary of the Angels in Assisi (Perugia, Italy) dated 1490 by Sakellariou *et al.*,^[5] and our group reported a study carried out on the *Saint John the Baptist* terracotta relief at the John and Mable Ringling Museum of Art.^[6]

The aim of the present study is to apply micro-Raman temperature study and complement it with XRF spectroscopy to characterize the composition of the blue glaze applied on two art objects attributed to Della Robbia family workshop in order to identify the source of the blue pigments.

Experimental

Raman spectra were obtained using a Leica DMLP microscope (100× objective) coupled to a Raman system manufactured by

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Figure 1. On-site handheld EDXRF data collection *Saint John the Baptist* (tondo) (a) and *Saint John the Baptist with Cross* statue (b).

Kaiser Optical Systems, Inc. The RamanRxn1 analyzer incorporates a thermoelectrically cooled CCD detector for maximum sensitivity, an Invictus NIR semiconductor laser (785 nm) and a holographic grating to provide fast and simultaneous full spectral collection of Raman data. The laser spot diameter on the sample was around $8\ \mu\text{m}$, and the total laser power incident on the specimen was kept below 0.7 mW ($1.4\ \text{kW cm}^{-2}$). Microscopic samples of the glaze were studied under optical microscope and significant statistics were collected at various locations. Raman spectra were collected at room temperature and at $500\ ^\circ\text{C}$ utilizing a Linkam THMS 600 heating stage in static air.

On-site, nondestructive XRF characterization was implemented by using a TRACeR III-V handheld analyzer manufactured by Bruker AXS, Fig. 1. TRACeR III-V is an energy dispersive X-ray fluorescence (EDXRF) spectrometer with a high-resolution Si PIN diode detector (170 eV resolution) which allows quick and easy analysis of elements as low as magnesium. The PXRF software program provides qualitative and quantitative analysis, in addition to the voltage and current control of the X-ray tube, which makes possible a widest range of elemental analysis, combined with the ability to select the optimum filter/secondary target. In this study, X-ray emission up to 40 keV from a Rh target is used as the X-ray excitation source.

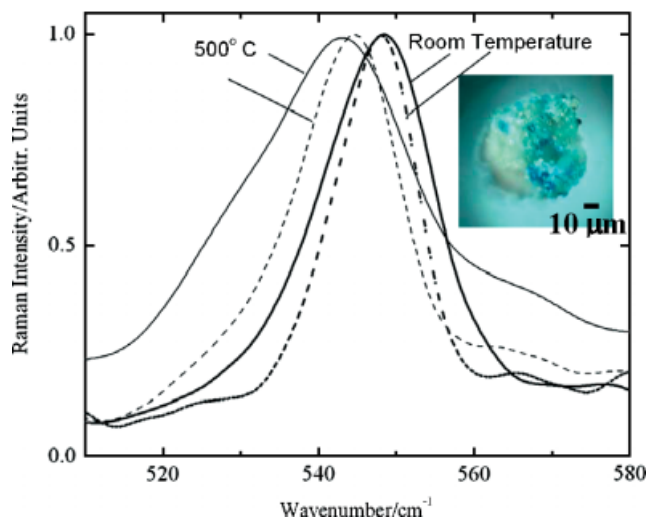


Figure 2. The $548\ \text{cm}^{-1}$ Raman band of the pigment in the blue glaze (solid lines) and the same band in lazurite reference sample (dashed lines) at room temperature and at $500\ ^\circ\text{C}$. The image of the actual blue inclusion in the glaze from which the spectrum is taken (inset).

Results and Discussion

Micro-Raman spectroscopy

The most prominent Raman band appearing in our spectra collected from the blue microcrystals in the blue glaze of the two Della Robbia art objects is at $548\ \text{cm}^{-1}$, Fig. 2. This band usually is attributed to S_3^- ion stretching vibration in lazurite,^[7–11] which constitutes an aluminosilicate matrix. In our previous work on the *Saint John the Baptist* majolica glazed tondo,^[6] we observed the characteristic band of the sulfur chromophore at $548\ \text{cm}^{-1}$. In order to get some insight into the elemental composition of the matrix in which the sulfur chromophore is embedded, we conducted laser-induced surface modification experiments. The Raman spectra of amorphous phases are sometimes difficult to interpret because of the low content of spectral features. However, laser-induced modification can be used in order to transform materials into phases that exhibit Raman spectral features. After the laser-induced micro-recrystallization was carried out, characteristic Raman bands assigned to lead sulfate and lead oxide appeared at the same spot where the $548\ \text{cm}^{-1}$ was prominent initially. Based on this finding, we suggested that the sulfur chromophore is embedded in some type of lead-rich matrix, rather than aluminum-rich matrix, such as the matrix of the lazurite. Moreover, it appears that the interatomic forces between each matrix and the chromophore are such that the stretching vibration of the sulfur chromophore at $548\ \text{cm}^{-1}$ remains unchanged by the matrix.

In order to isolate the effect of the matrix on the $548\ \text{cm}^{-1}$ band of the S_3^- chromophore, Raman spectra of the Della Robbia blue glaze and the naturally occurring lazurite sample at two different temperatures were collected, and the temperature shift and the broadening of the band were compared. The spectra from the lazurite mineral served as a reference. It is well known that the temperature band-shift and broadening are sensitive to the interatomic force constants modification, thereby altering the phonon decay mechanisms.^[12,13] Spectra were collected at room temperature and at $500\ ^\circ\text{C}$ from the blue glaze and from the lazurite mineral. In Fig. 2 we compare the temperature shift of the band in the glaze (solid lines) to the temperature shift of the

same band detected in naturally occurring lazurite (dashed lines). The temperature shift is -3 cm^{-1} for the lazurite and -5 cm^{-1} for the Della Robbia glaze compared to the position of the band at room temperature. The full width at half-maximum (FWHM) of the band is 13 cm^{-1} for the lazurite and 17 cm^{-1} for the glaze. The relative broadening of the bands at the elevated temperature is 23% (lazurite) and 35% (glaze). Although, the Raman band position of the stretching mode at room temperature is the same in both materials, its temperature behavior is different. Such difference in the temperature shift and band broadening is attributed to the fact that the chromophore is embedded in different matrices: aluminosilicate (lazurite) and lead silicate (Della Robbia glaze).

XRF spectroscopy

In this study, the findings from the micro-Raman characterization are complemented and broadened by the XRF analysis of the same glazes. The XRF spectra collected at 15 kV, 11 μA from the tondo (trace I in Fig. 3(a)) and from the statue (trace II in Fig. 3(a)) are compared with the spectra obtained from lazurite mineral (trace III in Fig. 3(a)), which we use as a reference. As can be seen, both glazes have high lead content, confirming the results obtained from the micro-Raman characterization. Representative XRF spectra collected at 40 kV and 1.1 μA , are shown in Fig. 3(b). To optimize for particular elemental groups, we filtered the emitted X-rays from the Rh target, thereby impacting the sample just above the absorption edges of the element(s) of interest. The depth of the analyzed sample is also very much a function of both the X-rays energy used to probe the material and the element that is being excited. In acquiring the 40-kV spectra, Fig. 3(b), we used the following filters: 304.8 μm Al, 25.4 μm Ti and 25.4 μm Cu. These settings allow all the X-rays above 14 keV to reach the sample, thereby efficiently exciting high Z elements ($Z > 50$). After analyzing spectra collected at various experimental conditions, we concluded that the main components of the two art objects are Si, Pb, Sn, Ca and Fe, which categorize the glaze as a tin-opacified lead glaze. Elements such as Co, Ni, Cu and Zn are identified as characteristic of the blue pigment in the glaze, and their presence and proportion depend on different types of ores employed in the manufacturing process of blue pigments.^[14] Cobalt occurs in copper- and nickel-containing minerals or in combination with sulfur and arsenic in the sulfidic cobaltite (CoAsS), safflorite (CoAs_2) and skutterudite (CoAs_3) minerals.^[15] The tondo glaze pigment has Ni and Cu, and the statue pigment has Cu and Zn in addition to the Co. The fact that no As was detected in either of the blue glazes and the identification of sulfur chromophores by Raman spectroscopy lead to the suggestion that Della Robbia used sulfide ores such as sphalerites $[(\text{Zn},\text{Fe})\text{S}]$ and pyrites (FeS_2), containing small amounts of Cu, Co and Ni as a source for the blue pigment.

Previously, the elemental composition of Della Robbia blue glaze on 12 sculptures on exhibit at Museo Nazionale del Bargello in Florence was studied by Pappalardo *et al.*^[3] with PIXE-alpha system and XRF spectroscopy. They reported average oxide concentrations that are in a good agreement with our findings: SiO_2 – 34%, PbO – 31%, CaO – 11%, K_2O – 3.5% (not detected in one of the samples), Al_2O_3 – 3% (not detected in two of the samples), iron oxides – 1.1% and CoO – 0.8%; NiO was reported for one of the samples. Moreover, our elemental analysis is in agreement with that of other European ceramics with blue decoration prior to 16th century.^[14]

Al $K\alpha$ (1.49 keV) and Si $K\alpha$ (1.74 keV) XRF lines of the reference lazurite sample and the blue pigment area of the Della Robbia

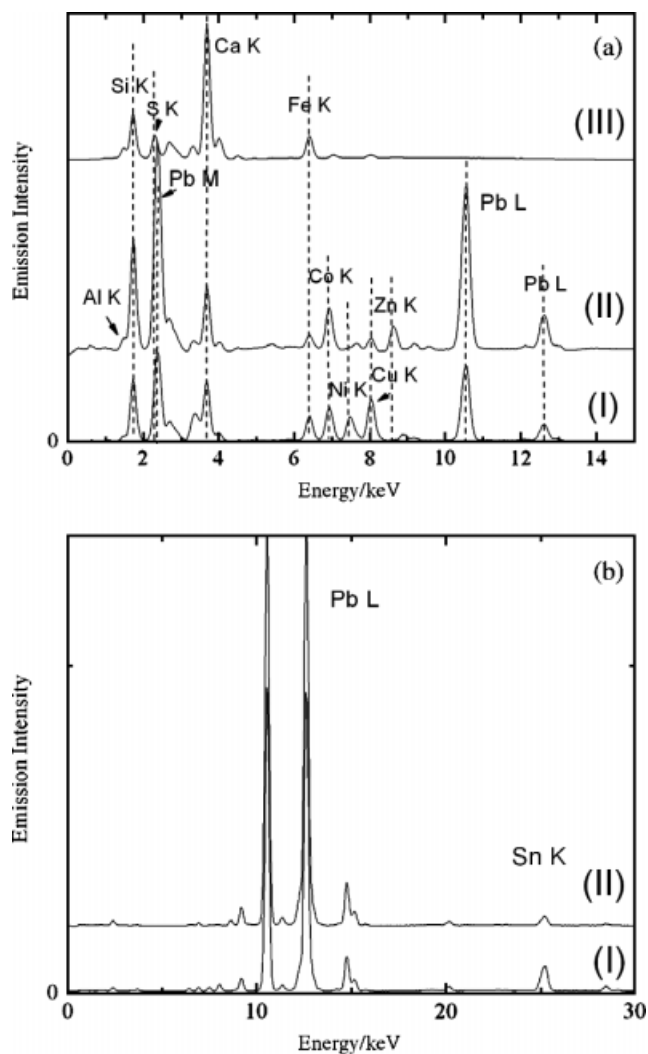


Figure 3. EDXRF spectra of the blue glaze of the tondo (trace I), the statue (trace II) and the reference lazurite (trace III) 15 kV (a); EDXRF spectra of the blue glaze of the tondo (trace I), the statue (trace II) 40 kV (b).

glaze are compared in Fig. 4. The two spectral lines are fitted with Gaussian functions, and the ratio of their integral intensities ($\text{Si } K\alpha/\text{Al } K\alpha$) is compared in both samples. It is well known that the observed photon rate from the analyte element in the specimen is a function of many factors. Most notably, it depends on the weight fraction of that element.^[16] Using the Si $K\alpha$ line as an internal reference, the relative amount of Al in each sample was estimated. For the Della Robbia blue glaze, the Si/Al ratio is evaluated to be 14.2, as compared to the same ratio evaluated from the spectrum of the reference lazurite sample, 4.8. Following the same considerations and fitting procedures, we calculated the integral intensity ratio of Si $K\alpha$ and Ca $K\alpha$ lines. For the Della Robbia blue glaze, the Si/Ca ratio is estimated to be 0.8 as compared to the same ratio of the reference lazurite sample, 0.5. The estimates for the relative proportions of the components in the blue glaze (Si, Al, Ca) indicate different proportions from those found in the naturally occurring lazurite sample. Therefore, elemental analysis strongly supports the proposed suggestion from our previous Raman study involving micro-recrystallization^[6] and the current temperature study of the 548 cm^{-1} band, that the matrix in which the blue pigments are embedded in the Della Robbia glazes

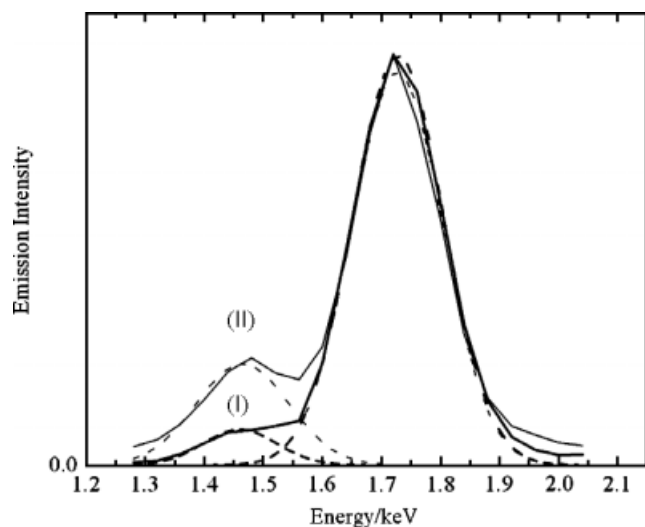


Figure 4. Al $K\alpha$ and Si $K\alpha$ lines for the blue glaze of the tondo (trace I) and the reference lazurite (trace II).

does not resemble the aluminosilicate matrix composition of the lazurite.

Since the Pb M lines overlap with the S K lines in the XRF spectra, a relative rough estimate of the amount of sulfur in the presence of large amounts of lead can be done by calculating the ratios of the integral photon rate for the Pb M (at 2.39 keV) and Pb L (at 10.55 keV) lines, Fig. 3(b). The result obtained from the Della Robbia blue glaze was compared with the same ratios calculated from the spectra of stoichiometric PbO_2 and $PbSO_4$ samples. All spectra were collected under the same conditions: 15 kV, 20 μ A, in vacuum, Ti filter, and accumulation time of 60 s. The Pb M/Pb L integral intensity ratio for the oxide is 0.12, for the sulfate it is slightly larger 0.15, and for the Della Robbia blue it turned out to be larger than 0.12, suggesting the presence of S in the Della Robbia blue pigment. Moreover, the presence of sulfur was unambiguously confirmed by the micro-Raman spectroscopy analysis with the assignment of the 548 cm^{-1} band to S_3^- chromophore.

Conclusions

Detection of the 548 cm^{-1} Raman band alone does not justify the presence of lazurite crystallites in the pigment of a glaze.

The 548 cm^{-1} Raman band is indicative of the presence of the S_3^- chromophore, but not of the composition of the matrix in which it is embedded. Based on the micro-Raman temperature study and XRF analysis, we can conclude that the famous Della Robbia blue is due to the combined effect of Co–Ni–Cu–Zn atoms and S_3^- ions embedded in a lead silicate matrix. In addition, the analysis suggests that the Della Robbia family workshop used Co-containing sulfide ores, such as pyrites and sphalerites, as the source for their blue pigment.

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