

Article

Material and Technical Study of Symeon Savvidis' *Ring Around the Rosie* (ca. 1908) Using VNIR Hyperspectral Imaging with Mobile Raman and h-EDXRF

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Abstract

This study presents the first technical examination of *Ring Around the Rosie* (ca. 1908), an easel painting by the Greek artist Symeon Savvidis (1859–1927). Despite Savvidis' significance within Greek modernism, little is known about his materials and working practices from a scientific perspective. To address this gap, the painting was analysed using VNIR hyperspectral imaging (HSI), portable Raman spectroscopy, and handheld energy dispersive X ray fluorescence (h-EDXRF). The integration of imaging, molecular, and elemental data enabled the identification of several pigment classes, including cobalt blue, ultramarine, lead chromates, ochres, lead white, and a tentative Cu-As green pigment, while also providing information on their spatial distribution across the surface. HSI classification and the examination of a representative NIR image revealed relationships among the coloured passages and suggested the widespread use of a cobalt-containing background paint. The results further indicate that several compositional elements may have been applied directly over previously, although the absence of stratigraphic information prevents definitive conclusions regarding paint layering and mixtures. Overall, the study demonstrates the value of combining HSI, Raman spectroscopy, and h-EDXRF for the non-invasive investigation of artists' materials and highlights the contribution of technical studies to a broader understanding of Savvidis' artistic practice and modern Greek painting traditions.

Keywords: hyperspectral imaging; technical art history; non-invasive analysis; Symeon Savvidis; Munich school

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1. Introduction

From the mid-19th century to the 1930s, a conspicuous number of Greek artists moved to Germany to attend the Academy of Fine Arts in Munich [1–4]. This trend marked the emergence of an artistic movement of academic realism, commonly referred to in Greek scholarship as the *Munich School*.

The Munich School has been extensively studied in art-historical scholarship, initially with emphasis on its formal academic characteristics [4–6] and subsequently in relation to its role in the emergence of modern artistic tendencies [7]. Its thematic and ideological dimensions have been explored through analyses of Orientalism, genre painting, and the construction of Greek national identity [6,8–11], as well as later socially oriented artistic practices [12]. Additionally, the Munich School has been reframed as part of a broader transnational network of artists, institutions, and exchanges [1–4,9,13], highlighting the complexity of the cultural environment in which these artists developed their practices.

Greek artists trained within the Munich School were not isolated from broader European developments but actively engaged with other artistic currents, particularly those emerging in France [14–16]. This is evident, for instance, in the Impressionist tendencies observed in painters such as Thalia Flora-Karavia (1871–1960) [8], as well as in the Symbolist influences identified in the work of Frixos Aristeus (1878–1951) [17].

Despite this well-established art-historical framework, limited attention has been devoted to the material and technical aspects of these artists' practices. To date, only few studies have addressed this issue, including a preliminary technical investigation of a painting by Thalia Flora-Karavia [18] and a broader analytical study of selected works from the National Gallery of Greece [19]. Consequently, the material choices and working processes associated with both the academic phase and the later artistic development of these painters remain poorly understood.

Among these artists, Symeon Savvidis (Savvides, 1859–1927) represents a significant case. Trained at the Munich Academy, he spent most of his professional life in Germany, remaining there for approximately 45 years, while travelling periodically to Anatolia and eventually retiring to Athens in 1925 [20,21]. His work is often associated with Orientalist themes, particularly depictions of Ottoman life [21], while also reflecting a gradual engagement with broader European artistic developments. Karras [9] has suggested the influence of French Realism and Impressionism in his work, alongside a marked interest in colour theory and chromatic relationships [9,21].

The case study chosen for detailed investigation is a painting created during a transitional phase in Savvidis' career, when his academic training in Munich began to give way to a more open and modern pictorial approach informed by broader European developments. This position makes the painting particularly suitable for investigating the materials and techniques employed during a crucial period in the artist's career [20,21]. Although the work is preserved in a major public collection, it has received little individual scholarly attention and has not been examined from a technical art-historical or scientific perspective.

To address these questions, a multi-analytical approach was employed, combining molecular (portable Raman spectroscopy, p-Raman) and elemental (handheld X-ray fluorescence, h-EDXRF) point analyses with a chemical imaging technique (VNIR hyperspectral imaging, HSI). This fully non-invasive, in situ methodology enables the investigation of both surface and subsurface materials while preserving the integrity of the artwork.

Hyperspectral imaging (HSI) has increasingly been applied in the study of easel paintings [22,23], where it enables the non-invasive mapping of pigments and mixtures across the pictorial surface. Previous research has demonstrated its usefulness not only for pigment identification [24,25] but also for the visualisation of underdrawings [26] and

the investigation of painting stratigraphy, particularly when combined with complementary techniques such as Raman spectroscopy and X-ray-based methods [25].

VNIR HSI was used in conjunction with Raman and h-EDXRF data to enhance the characterisation of pigments and mixtures across the pictorial surface. In addition, a classification method commonly applied in the analysis of paintings, spectral angle mapping (SAM) [24–26], was implemented to examine the spatial distribution of identified materials. Beyond material identification, the study also seeks to investigate aspects of the artistic process underlying the creation of the work, thereby contributing to a broader understanding of the painter's technique and informing future research directions.

Given the absence of sampling and cross-sectional examination, this work is intended as an exploratory investigation of Savvidis' materials and technique. The analytical methods employed provide complementary molecular, elemental, and imaging information, but they differ in penetration depth and analytical sensitivity. Therefore, questions concerning pigment mixtures, superimposed paint layers, binder composition, and preparatory materials cannot always be resolved unambiguously. The results should therefore be interpreted as a framework for future technical studies rather than as definitive evidence of the painting's material structure.

2. Materials and Methods

2.1. Materials

The artwork selected for this investigation is *Ring Around the Rosie* (Inv. no. P.2071, Figure 1), an oil painting on wood measuring 180 × 240 mm (H × W) and dated to approximately 1908. This painting is currently preserved in the permanent collection of the National Gallery–Alexandros Soutsos Museum, Athens. It was executed during Savvidis' so-called '*German period*', at a stage when the artist was consolidating his artistic personality following international exposure. The work was therefore selected to investigate both the materials employed and aspects of the artist's working process during a transitional phase of his career.



Figure 1. *Ring around the Rosie*, inv. no. P.2071, National Gallery–Alexandros Soutsos Museum, Athens; (a) original image; (b) spots of analysis of all analytical techniques (supervised HSI endmembers extraction, Raman, h-EDXRF). The labels' colours refer to the colour of the areas that were examined.

Selected areas were analysed using portable Raman spectroscopy (p-Raman) and handheld X-ray fluorescence (h-EDXRF), and corresponding hyperspectral endmembers were extracted from the VNIR-HSI image at the same locations to enable direct comparison between molecular, elemental, and chemical imaging data.

Analysis points were selected according to three complementary criteria: (i) representativeness of the main chromatic components of the palette (blue, green, yellow, brown, pink, red, and white paints), (ii) the inclusion of structurally and functionally dis-

tinct pictorial elements, specifically background areas, clothing, hair decoration, and flesh tones, and (iii) minimisation of fluorescence interference in the Raman spectra in order to ensure sufficient spectral quality for reliable pigment identification. A detailed description of the selection criteria for the spots is provided in Table 1.

Table 1. Summary of the results for all techniques (HSI, h-EDXRF, and Raman). The major elements of h-EDXRF are marked in **bold** text, while the minor elements are in *italics*. The tentative interpretations are indicated with a question mark.

Paint	Pictorial Feature	Proposed Identification	h-EDXRF Results	Vis-NIR Results			Raman Results		
				Band (nm)	Assignment	Reference	Band (cm ⁻¹)	Assignment	Reference
Blue 1	Dress (head ribbon)	Ultramarine blue	10 kV: Fe, Cr, Ba, Co, Ca, S * 40 kV: Pb, Zn, Cu, As	600(ab)	Ultramarine blue	[27]	548	$\nu_1(\text{S}^{3-})$, ultramarine	[28,29]
Blue 2	Dress (dress band)	Cobalt blue; lead white	10 kV: Co, Cr, Ca, Fe 40 kV: Pb, Cu, As, Co, Hg, Cr, Fe	420(ab), 480(ab), 546(ab), 583(ab), 631(ab), 645(ab)	Cobalt blue	[30–33]	-	-	-
Green 1	Background	Cobalt blue; lead chromate?	10 kV: Cr, Co, Ca, Fe, Mn 40 kV: Pb, As, Cu, Sr, Co, Fe, S, Cr	546(ab), 583(ab), 631(ab)	Cobalt blue	[30–32]	-	-	-
Green 2	Clothing (dress)	Cobalt blue; lead white?	10 kV: Co, Cr, Ca, Fe 40 kV: Pb, Cu, As, S, Co	420(ab), 480(ab), 546(ab), 583(ab), 631(ab), 645(ab)	Cobalt blue	[30–32]	-	-	-
Green 3	Background (feature)	Cu-green?; cobalt blue	10 kV: Cr, Ca, Co, Fe, Cd 40 kV: Pb, As, Cu, S	520(R _{max}), 631(ab), 645(ab)	chrome yellow, cobalt blue	[30–32,34,35]	-	-	-
Yellow 1	Clothing (dress)	Lead chromate (yellow); yellow earths; cobalt blue	10 kV: Cr, Fe, Ca 40 kV: Pb, As, Cu	455(ab), 498(ab), 519(λ_m), 542(ab), 577(ab), 628(ab), 643(ab), 880(ab)	yellow earths, chrome yellow, cobalt blue	[34–37]	838, 376, 359	$\nu_1(\text{CrO}_4^{2-})$, $\nu_2(\text{CrO}_4^{2-})$, $\nu_3(\text{CrO}_4^{2-})$, chrome yellow/orange	[38,39]
Yellow 2	Background (feature)	Lead chromate (yellow); yellow earths; cobalt blue (underlying?)	10 kV: Co, Cr, Ca 40 kV: Pb, As, Cu	431(ab), 495(ab), 519(λ_m), 643(ab), 880(ab)	yellow earths, chrome yellow	[34–37]	-	-	-
Brown 1	Flesh tones	Red earths	-	490(ab), 577(ab),	red earths	[36]	-	-	-

				660(λ_m), 880(ab)					
Brown 2	Flesh tones	Red earths; α -HgS / red lead?	-	583(λ_m), 634(ab)	red lead? / α -HgS?, red earths	[37,40]	-	-	-
Pink	Background (feature)	Ochres; α -HgS	10 kV: Fe, Ca, Cr, Ba, Co, S 40 kV: Pb, Zn, Hg, As, Sr	-	-	-	341, 283, 252	v(α -Hg-S)	[40]
Red	Clothing (head rib- bon)	α -HgS	-	589(λ_m)	α -HgS?	[40]	-	-	-
White	Clothing (dress)	Lead white; Ba-, Zn- based ma- terial	10 kV: Ba, Fe, Ca, Co 40 kV: Pb, Zn, Cu	-	-	-	1048	lead white	[41]

Legend: λ_m inflection point; *ab*: absorption band; R_{max} : reflectance maximum; * the element is tentatively assigned owing to the overlap between the Pb-L and S-K lines, as the presence of sulfur cannot be unequivocally excluded.

Although a larger number of Raman measurements was collected, only spectra containing interpretable analytical information are presented and discussed in this work

2.2. Methods

2.2.1. HSI

VNIR hyperspectral imaging (HSI) was employed to investigate the electronic transitions of materials in the painting. Data were collected using a Specim IQ push-broom camera (Spectral Imaging Ltd., Oulu, Finland) operating in the 400–1000 nm spectral range with an average spectral resolution of 7 nm.

Radiometric calibration was performed using a white reference panel (Specim Ltd.) positioned within the acquisition area. Separate measurements of the reference panel and the painting were recorded under identical illumination conditions. White calibration and background correction were carried out using the instrument software to obtain apparent reflectance data.

Data were collected without spectral binning (204 channels per pixel), with a spatial resolution of approximately 0.6 mm/pixel and an integration time of approximately 80 ms. Illumination was provided by two continuous-wavelength halogen lamps (50 W, quartz-bulb lamps, colour temperature of 3200 K) positioned at a distance of approximately 1.5 m from the painting. To minimise detector saturation caused by the high gloss of the paint surface, relatively low illumination levels were employed. The lighting geometry (approximately 40° relative to the object surface) was adjusted to optimise diffuse illumination and reduce specular reflections. The light sources were projected directly onto the object and onto a scattering surface (white) only in those cases when the radiation was not sufficiently spread. A fluxmeter was used to monitor irradiance prior to each acquisition to ensure consistent and controlled illumination conditions.

HSI data processing, including endmember extraction, hypercube classification, and extraction of HSI slices, was carried out using the ENVI 5.3® software (L3Harris Geospatial, Broomfield, CO, USA). Endmembers were extracted from 3 × 3 pixel regions of inter-

est. Spectral data processing and graphic representation of reflectance spectra were carried out using OriginPro 8.5 (OriginLab Corporation, Northampton, MA, USA).

The spatial distribution of materials was evaluated using the Spectral Angle Mapper (SAM) algorithm, a supervised classification method based on n-dimensional spectral angle comparison [42]. An initial classification threshold of 0.100 rad was adopted following ENVI recommendations and subsequently optimised for each endmember. Higher tolerance angles were required for selected blue and green classes, whereas lower thresholds were used for yellow, brown, and red classes to minimise both over-classification and under-classification. In particular, the green 1 endmember proved highly sensitive to threshold variation, with small increases in the SAM angle resulting in extensive misclassification of spectrally similar regions. This behaviour was taken into account during the interpretation of the classification results.

To investigate subsurface features, a near-infrared representation was generated using a single spectral band located near the long-wavelength limit of the detector sensitivity. This band was selected to maximise penetration depth while maintaining an acceptable signal-to-noise ratio.

2.2.2. h-EDXRF

Handheld energy-dispersive X-ray fluorescence (h-EDXRF) data were collected to study the elemental composition for the painting materials. H-EDXRF spectra were collected with a handheld Innov-X Delta Premium commercial analyser (Olympus Corporation, Waltham, MA, USA) coupled with a polychromatic Rh X-ray tube and a Large-Area Si-CCD detector (145 eV at Mn K α). The h-EDXRF data were collected at two analytical conditions: one was used for the analysis of high-Z elements (from Al onwards); another for the detection of the low-Z elements. The analytical conditions for I) were as follows: 40 kV voltage, 38.7 μ A current, 300 s integration time, and with an aluminium filter placed before the sensor to reduce the signal from the low-Z elements (including the Rh excitation lines) and enhance the signal from the higher Z-elements. The analytical conditions of II) were as follows: 10 keV voltage, 50.8 μ A current, 300 s integration time, no filter. The measurements were performed using a collimated beam of approximately 3 $\times$ 3 mm². Spectra were processed and qualitatively interpreted using PyMCA 5.3.1 [43].

2.2.3. p-Raman

Mobile Raman data was collected to obtain compositional details of the pigments used in the painted mixtures of case study no. 1. P-Raman spectra were collected with a mobile i-Raman® Plus 785S analyser by B&W Tek/Metrohm LTD (Herisau, Switzerland). The spectrometer is a commercial device equipped with a fibre-optics sampling unit, a 785 nm excitation source, and a high-quantum-efficiency charge-coupled device (CCD) array detector with thermo-electrical (TE) cooling for data collection and operated with a tethered laptop. The system registered data in the spectral range 65–3350 cm^{−1} at a spectral resolution better than 4.5 cm^{−1} (912 nm). Number of accumulations and laser density at the spot were adjusted manually by observing the optimal signal-to-noise ratio and at the shortest measuring time to avoid any damage to the painting (ablation, photo-quenching, and crystalline rearrangements). The software BWSpec® 4.15 was used for data collection, while the Thermo Grams/AI 8.0 ® suite by Thermo Fisher Scientific was adopted for data exploration and interpretation. Wavelength calibration was performed daily with the following products used for wavelength calibration: sulfur, epsilon-caprolactone (Acros Organics, Geel, Belgium), cyclohexane (VWR International, part of Avantor, Leuven, Belgium), polystyrene pellets (Sigma-Aldrich, St. Louis, MO, USA) and acetonitrile (Panreac Química S.A., Barcelona, Spain)/ toluene (UCB Chemicals, Brussels, Belgium) (mixed in

50/50 volume%) [44]. The spectra shown in the paper were neither smoothed nor background-subtracted.

All spectra were plotted with OriginPro 8.5, and the spots of analysis for all techniques are given in Figure 1 (right).

3. Results and Discussion

3.1. Material Characterisation

The technical examination of *Ring Around the Rosie* (inv. no. P.2071) aimed to identify (i) the materials used by Symeon Savvidis and (ii) aspects of his working process during a transitional phase of his career. Because the painting was produced at a time when the artist was experimenting with iconographic themes, colour theory, and diverse artistic influences, the study sought to clarify the technical characteristics of this period. Material characterisation was carried out using a VNIR HSI camera to obtain information on the electronic transitions of the pigments, a portable Raman spectrometer to collect vibrational spectroscopic data, and a h-EDXRF analyser to determine elemental composition. The reconstruction of Savvidis' artistic process relied primarily on HSI classification maps and the VNIR slice. The results of the material characterisation are summarised in Table 1.

Two pigments were identified in the blue paints (blue 1 and blue 2, Figure 2, Table 1). The HSI endmember of blue 1 describes a single, large band of absorption $Ab_{S_{max}}$ centred at ca. 600 nm and falling in the 580–620 nm range (Figure 2b) that closely resembles the spectral response of blue ultramarine. A pigment sourced either naturally or synthetically, the composition, physical and optical properties of ultramarine pigments stem mainly from minerals from the sodalite family, primarily lazurite ($Na_7Al_6Si_6O_{24}S_3$). Lazurite is an aluminosilicate whose colour arises from electronic exchanges (ETs) between several chromophores trapped within, specifically polysulfide radical ions and some sulphates [27,28]. The most widely accepted opinion is that trisulfide radical ions are the principal chromophores responsible for its hue [27,29]: as a matter of fact, $Ab_{S_{max}}$ of blue 1 falls in the expected range for unpaired S_3^- ET (580–620 nm) [28]. The hypothesis of the presence of ultramarine could only be supported with the Raman data (Figure 2d) since the h-EDXRF data did not detect any fingerprinting fluorescence line (Figure 2c). The Raman spectra show only a single band of the $\nu_1 S_3^-$ mode at 548 cm^{-1} [28,29].

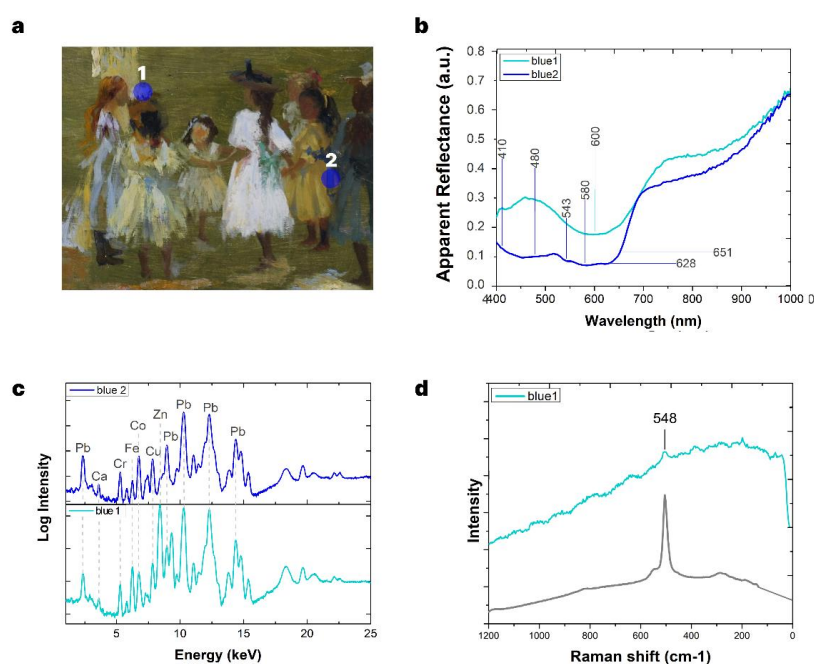


Figure 2. Representative spectra of the blue paints: (a) position of the spots; (b) UV-Vis-NIR spectra (HSI endmembers); (c) h-EDXRF spectra; (d) Raman spectrum. The grey spectrum in (d) shows a sample spectrum of ultramarine blue.

Blue 2 shows two series of consecutive absorption bands, one at 410 and 480 nm (series 1) and the other at 513, 546, 631, and 645 nm (series 2, Figure 2c). The position of the bands of series 2 is compatible with degenerate ligand-to-metal charge transfers (LMCT) of the d-d orbitals in Co^{2+} in tetrahedral coordination (T_d) [37], thus being evidence of the presence of a Co-based pigment. A strong fluorescence background dominated the Raman spectra of these spots, preventing the acquisition of useful analytical information. By contrast, the h-EDXRF data supported this interpretation through the intense fluorescence lines of Co detected in this spot (Figure 2d). Historically, common Co-based pigments for this period are Thénard blue (also called cobalt blue, CoAl_2O_4) and cerulean blue (Co_2SnO_4) [30–32]. Research by Angelin et al. [31] reports these bands, showing that their position falls within the range expected for CoAl_2O_4 ; moreover, the h-EDXRF data do not show the presence of the Sn lines.

The same bands as blue 2 were similarly observed in two endmembers for the green mixtures (green 1 and green 2, Figure 3a, Table 1).

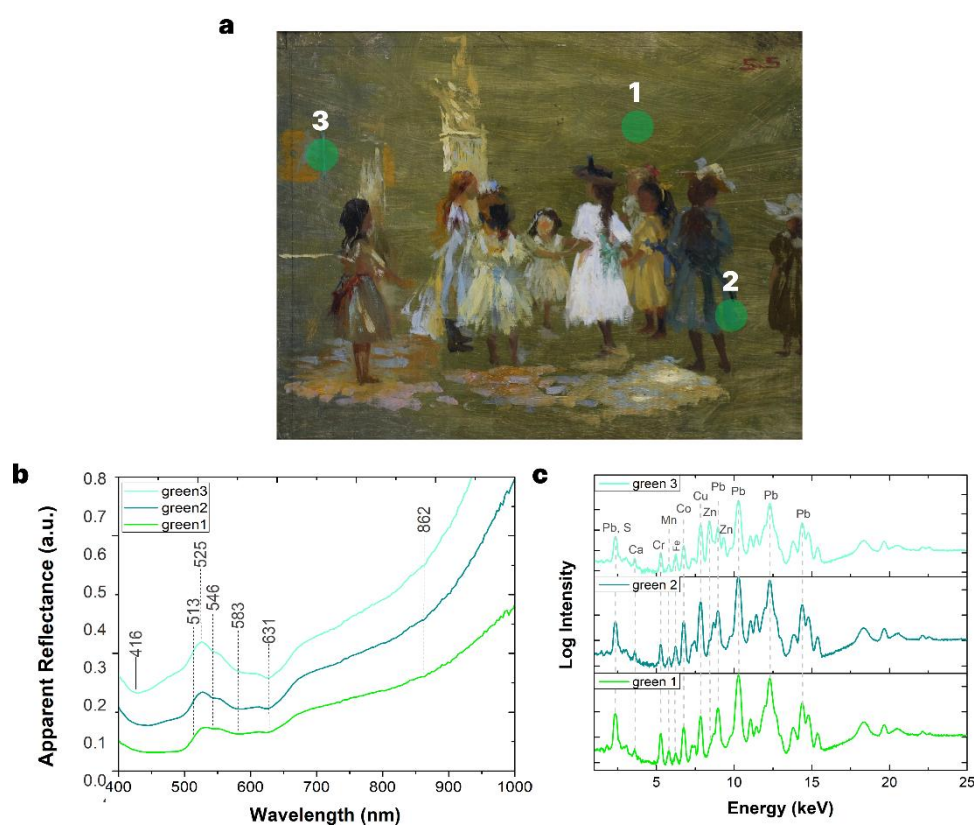


Figure 3. Representative spectra of the green paints: (a) position of the spots; (b) UV-Vis-NIR spectra (HSI endmembers); (c) h-EDXRF spectra.

Additionally, green 1 shows an inflection point λ_m at 519 nm (Figure 3b), a feature compatible with yellow and orange yellow of chrome ($\text{PbCr}_{1-x}\text{S}_x\text{O}_4$, with $0 \leq x \leq 0.8$). In VNIR spectra, this pigment is identified through a Direct Electronic Recombination (DER) band, whose position ranges from 532 nm ($\text{PbCr}_{0.2}\text{S}_{0.5}\text{O}_4$) to 559 nm (PbCrO_4) according to [34], while [35] report its position approximately at 500 nm for the bright yellow quality ($\text{Pb}(\text{Cr,S})\text{O}_4$) and at 520 nm for the dark yellow pigment (PbCrO_4) [38]. The position of λ_m for green 1 is consistent with the values reported by [35] for chrome yellow varieties and,

when considered together with the intense S fluorescence line observed in this spot, may indicate the presence of a sulphur-rich lead chromate pigment (Figure 3c). Green 2 shows the same feature along with the bands, characteristic of cobalt blue, yet the region in the 450–500 nm range shows a different spectral behaviour. The elemental profiles of both spots show intense fluorescence lines for S, Co, Pb, and Cr, especially in the green 1 spot. Raman spectra, however, are dominated by fluorescence in all green spots, preventing confirmation of this interpretation. Therefore, the assignment of a lead chromate in the green paints should be regarded as tentative.

In green 2, minor Cu and As were also detected (Table 1). The third endmember (green 3) shows stronger Cu and As signals, and its VNIR spectrum differs significantly, displaying a main reflectance band $R_{\max}$ centred at 520 nm and strong absorption in the region until 800 nm. These features are compatible with a copper arsenite [38], although these data are not sufficient to determine the specific pigment type, which may correspond to either emerald green or Scheele's green [45]. While the available data do not allow for a definitive identification, they support a tentative assignment at the pigment class level, whereas complementary techniques (e.g., Raman spectroscopy) could not provide usable analytical information.

Similar characteristics to those observed in green 1 were identified in the yellow areas (yellow 1 and yellow 2, Figure 4b), although with stronger Pb and Cr signals in the h-EDXRF spectra (Figure 4c). Their Raman spectra exhibit three bands emerging from a strong fluorescence background at 838, 376, and 359 cm^{-1} (Figure 4c). Previous studies have assigned these bands to the $\nu_1(\text{CrO}_4^{2-})$, $\nu_2(\text{CrO}_4^{2-})$, and $\nu_4(\text{CrO}_4^{2-})$ modes respectively, which are characteristic of lead chromate pigments $[\text{PbCr}_{1-x}\text{S}_x\text{O}_4]$ [39,45,46].

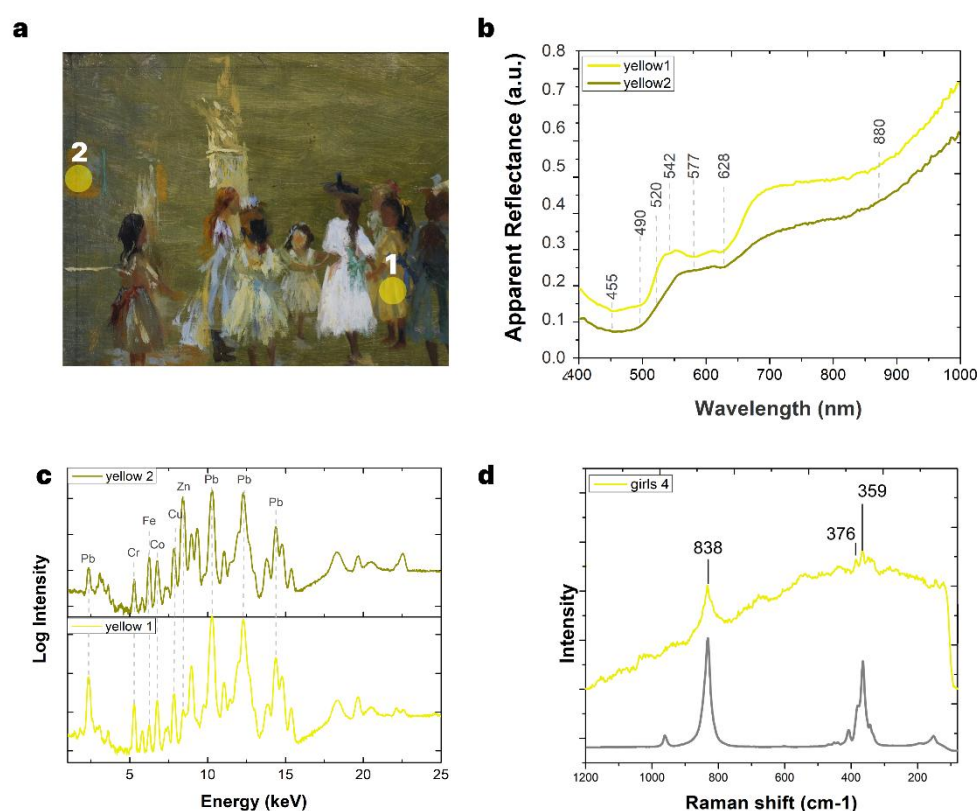


Figure 4. Representative spectra of the yellow paints: (a) position of the spots; (b) UV-Vis-NIR spectra (HSI endmembers); (c) h-EDXRF spectra; (d) Raman spectrum. The grey spectrum in (d) shows a sample spectrum of chrome yellow.

The inflection point λ_m of both yellow VNIR reflectance spectra occurs at 520 nm, consistent with the data by [35] for a dark yellow lead chromate. This feature is slightly more well-defined in yellow 1. Together, the Raman, h-EDXRF and VNIR HSI data are compatible with a dark yellow lead chromate; however, the compositional variability of lead chromates and the macroscopic nature of the analytical techniques employed limit the degree of confidence with which a specific lead chromate variety can be assigned. Consequently, the pigment identification is intentionally restricted to the level of chrome yellow, while the precise composition and sulphate content remain tentative and require verification using higher-resolution analytical approaches.

The brown and red mixtures were represented by brown 1, brown 2, and red 1 (Figure 5, Table 1). All VNIR spectra (Figure 5b) exhibit two shoulders at 490 and 570 nm and broad absorption bands at 654 and 874 nm. These features are consistent with crystal field transitions (CFT) of ochres, particularly those containing hematite (Table 1) [36,37]. However, the λ_m of the region 560–590 nm falls slightly outside the range reported for both red and orange ochres (orange ochres, 565–580 nm; red ochres, 575–580 nm [37]). H-EDXRF data were not available for the brown spot, but the spectra from the red spots showed intense fluorescence lines for Fe and Hg. The Raman spectra showed a prominent band at 252 cm^{-1} . The same band was also seen in the Raman spectra of red 1 along with two more at 341 and 283 cm^{-1} ; collectively, these bands are characteristic markers of mercury sulphide (α -HgS) [40]. In VNIR RS spectra, this pigment should exhibit a marked inflection point at ca. 600 nm; however, the red endmember however shows it at 590. This value lies midway between those of α -HgS and red lead (Pb_3O_4 , 580 nm [40]), thus complicating straightforward interpretation based solely on HSI data.

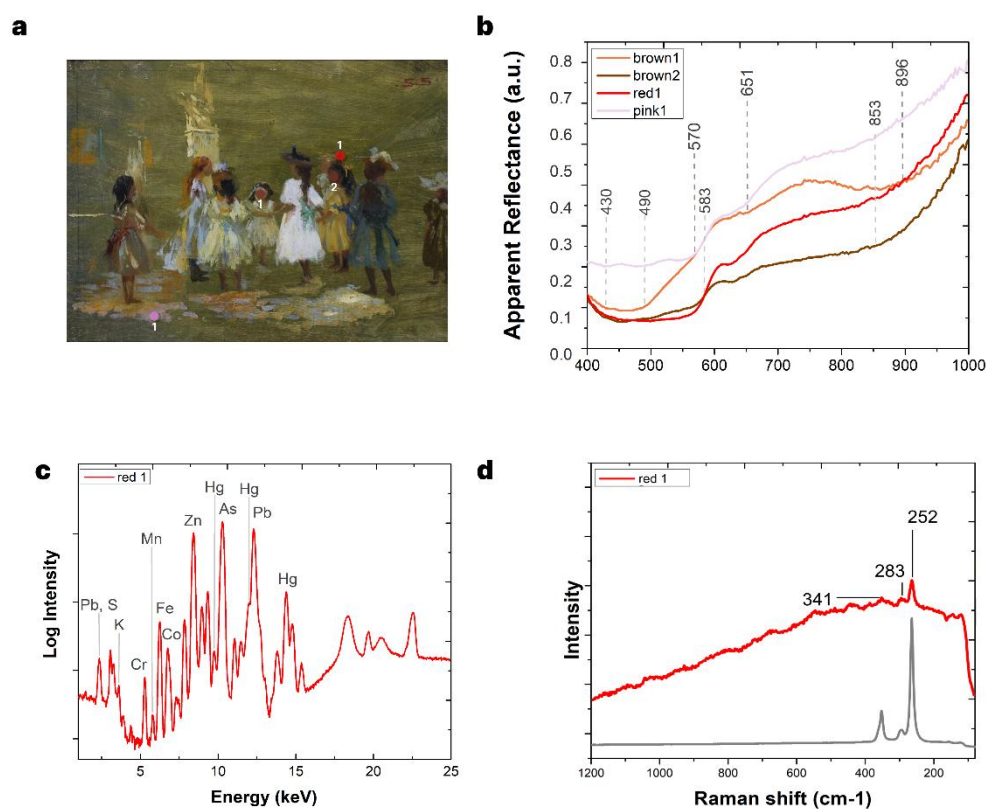


Figure 5. Representative spectra of the brown, red, and pink paints: (a) position of the spots; (b) UV-Vis-NIR spectra (HSI endmembers); (c) h-EDXRF spectrum (pink paint); (d) Raman spectrum (pink paint). The grey spectrum in (d) shows a sample spectrum of α -HgS.

The white pigment could be characterised with the sole Raman and h-EDXRF data: lead white along with other materials (Table 1, [41]). Regarding these, the h-EDXRF data show the presence of intense Ba and Zn contemporaneously. Unfortunately, the Raman data could not support a clearer identification, so it could not be established whether this response arose from a zinc white (ZnO), baryte (BaSO₄), or a mixed Ba-Zn material like lithopone (BaSO₄ ZnS). Additionally, several spots also showed the contemporaneous presence of Ba and Zn intense fluorescence lines.

3.2. Analysis of the Artistic Technique

Information about the paint application and an exploratory analysis of sub-surface features was attained with SAM classification of the HSI data and extraction of single-spectral channel slices, shown in grayscale. When superimposed, the distribution maps of the endmembers (Figure 6) offered a picture of their use across the painting, showing above all that green 1, tentatively assigned to a mixture of cobalt blue and a lead chromate, appears to be the most extensively distributed material and is observed throughout much of the background. The occurrence of spectral features attributable to Co²⁺ transitions supports this interpretation, being also observed in the yellow endmembers, particularly in yellow 1. However, in the absence of microsamples and stratigraphic information, this interpretation remains tentative, and it cannot be determined whether these materials occur as physical mixtures, superimposed paint layers, or contributions from underlying strata.

Unlike green 1, the other two green classes show a more limited distribution. The green 2 class includes areas corresponding to the lighter tones of dress worn by the second girl from the right, whereas green 3 class is observed both in a background feature and a ribbon fastened at a waist of one of the girls.

Less straightforward is the interpretation of the distribution of the yellow mixtures. Areas classified as the light-yellow paints (yellow 1 class) appear to be associated with multiple pictorial elements, including highlights of a girl's dress, a background feature at the feet of the girls, and a clock positioned behind the group. The yellow 2 class comprises areas corresponding with shadows and mid-tones of yellow-coloured elements, such as dresses, the clock in the rear, the yellow decorative pattern at the girls' feet, while occurring independently only in two features in the left side of the painting. However, the areas interpreted as shadows and highlights of yellow-coloured elements are simultaneously classified as both yellow 1 and yellow 2 (Figure 6b,c), complicating a straightforward interpretation. Furthermore, the yellow dresses of the girls classified as yellow 1, together with portions of the clock appear brighter in a NIR slice (982 nm, Figure 6d) and are therefore more reflective in the near-infrared than the surrounding areas. The brushstrokes around the clock also exhibit a different orientation from those observed in the background, which appears to be painted predominantly using horizontal strokes, whereas the clock was rendered with more vertically oriented brushwork. Although NIR imaging alone cannot unequivocally distinguish between superimposed layers and pigment mixtures, the combined differences in reflectance and brushwork may suggest the superimposition of paints. One interpretation is that the yellow paint was applied directly on top of the green background, rather than being fully integrated within a single mixed layer. However, further confirmation would require stratigraphic analysis.

Blue paints appear to be used more selectively, being employed primarily in the lower portion of the dress of the girl at the centre-left and in several ribbons worn around the girls' waist. Similarly, red paints were used both for the ribbons and for highlights in the flesh tones of some arms and legs. Notably, Simeon Savvidis' signature at the topmost corner appears to have been executed with a material classified as red 1.

Some areas of the painting could not be reliably classified. These include the dresses of three girls and a large area in the lower-right corner of the composition. For the white dresses, Raman and h-EDXRF analyses supported the presence of lead white together with an unidentified Ba- and Zn-bearing material. However, no representative white endmember was extracted from the HSI data and, consequently, no SAM classification could be performed for a white paint class. Furthermore, a substantial area in the lower-right quadrant of the painting was not assigned to any of the defined SAM classes. This observation may indicate the presence of additional materials not represented by the selected endmembers or alternatively reflect differences in paint stratigraphy. However, in the absence of complementary analytical evidence, this interpretation remains tentative and requires further investigation.

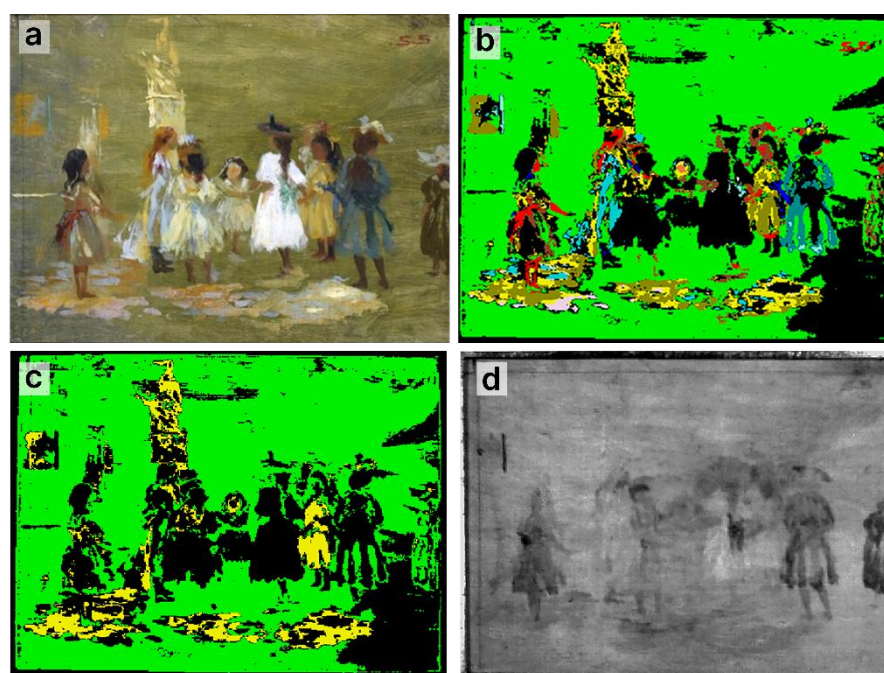


Figure 6. HSI classification of P.2071, (a) Vis representation; (b) SAM distribution map of the endmembers. Parameters for the classification (SAM tolerance angles): ● blue 1 (0.120 rad); ● blue 2 (0.150 rad); ● green 1 (0.095 rad); ● green 2 (0.100 rad); ● green 3 (0.110 rad); ● brown 1 (0.070 rad); ● brown 2 (0.085 rad); ● pink 1 (0.070 rad); ● red 1 (0.085 rad); ● yellow 1 (0.075 rad); ● yellow 2 (0.065 rad); (c) distribution maps of sole green 1 and yellow 1; (d) single slice (982 nm). The SAM classification is dependent on the selected endmembers and the user-defined tolerance values; the applied tolerance values are reported to facilitate interpretation of the distribution maps.

The NIR slice of the painting was also examined to investigate the possible presence of a preparatory drawing. Inspection of the image revealed that several features of the Vis image become less apparent or disappear in the NIR region, including the pendulum clock on the background, the yellow flowers on the meadow, and portions of the girls' faces. By contrast, the exposed flesh tones of the girls appear relatively IR-absorbing, as does the green detail located on the left side of the composition. These observations can be interpreted considering the spectral behaviour of the identified pigments. Chrome yellow becomes increasingly transparent in this region, whereas the iron-rich pigment identified in the brown areas and the areas with the tentative Cu-As green remain comparatively absorbing [47,48]. Consequently, the yellow paint appears sufficiently transparent, or sufficiently diluted, to allow underlying pictorial features to become visible in the NIR image. In particular, the upper paint layer is not fully opaque, allowing the texture and directional flow of the underlying paint application to be observed.

Despite these optical effects, neither a preparatory drawing nor sketch could be identified using the present imaging technique and data-processing workflow. The only previously concealed features observed were two intersecting lines along the upper and left margins of the painting. Their function and relationship to the execution of the composition remain uncertain. Additional investigation using imaging or chemical-imaging techniques operating in a broader spectral range, particularly in the SWIR region, may provide further information on possible underdrawings and subsurface features and help clarify these observations.

The palette identified in *Ring Around the Rosie* is broadly consistent with the materials available to artists working in Europe during the late 19th and early 20th centuries. Some of the identified materials are traditional pigments, like lead white, α -HgS, the tentative minium, ultramarine, and earths. Other pigments are synthetic pigments introduced between the late 18th century and the 20th century: cobalt blue, lead chromates, Cu-As green and the tentative Ba-Zn white pigment.

Cobalt blue was first produced in the 18th century and became commercially available after Thénard developed a more efficient manufacturing method in 1803 [49,50]. Reported in relation to numerous 19th c. painters, it was highly valued for its brilliance and ability to quickly promote polymerisation of oil media, despite its high cost [49–53]. Cobalt blue was widely used across European artistic production. In Germany, it has been reported in paintings by Caspar David Friedrich (1774–1840) [54]. In France, it has been identified in the palettes of Impressionist painters represented in the National Gallery, including those by Monet (1840–1926) [49,52,55–58], Manet (1832–1883) [49,52,59–61], Renoir (1841–1919) [49,52,62], Sisley (1839–1899) [49,52], Van Gogh (1853–1890) [39,63,64] and Seurat (1859–1891) [65]. Outside the Impressionist context, cobalt blue is also documented in Portuguese art-technical sources [66] and has been consistently identified in the palette of artists like Henrique Pousão (1859–1884) [53] and António Carneiro (1872–1930), particularly in works dated after the 1920s [67]. Additionally, Rousaki et al. [19] reported its presence in other paintings by Savvidis (*Boats in the waters of Bosphorus* and *Portrait of the painter Georgios Roilos*), *Furniture maker* (ca. 1850) by the Greek painter Francesco Pige (1822–1862) and *Fishing Captain* (1850–1853) by Andreas Kriezis (1813–1878), further supporting its widespread use in Greek painting of the period.

Lead chromates similarly found extensive use in 19th and 20th-century artistic productions, following their introduction in the late 18th century [35]. These pigments have been reported in the palettes of the artists mentioned above [49–67], often in association with cobalt blue. Callen notes that Impressionist painters frequently produced green hues through combinations of blue and yellow pigments and that this practice is documented in historical sources [52]. Analytical studies based on micro-invasive approaches have also reported their co-occurrence [56,62,67]. However, chromium-based pigments are more commonly reported in association with viridian ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), likely to modulate chromatic properties and enhance colour brilliance [52,58,668]. Similar associations have been observed in artists linked to the Munich School [19]. In these cases, however, the data are primarily derived from non-invasive analyses, limiting the possibility of assessing pigment interactions at the stratigraphic level. Therefore, although the co-presence of cobalt- and chromium-based pigments is both historically and technically plausible, the existence of a deliberate Co–Cr mixture cannot be demonstrated based on the present data, and further interpretation of their technical function remains speculative.

The tentative identification of an arsenical copper green pigment would also be consistent with contemporary artistic practice. Green pigments based on copper arsenites and copper acetoarsenites, including Scheele's green and emerald green, were widely marketed and used throughout the 19th century and remained available during the early decades of the 20th century. Their occurrence has been documented in technical studies of

European paintings of late 19th-century and early 20th-century painters [68], supporting the historical plausibility of their use in *Ring Around the Rosie*.

Further considerations concern the white pigments, Hg-based reds, and ultramarine. Raman spectroscopy supported the presence of lead white, a pigment that remained widely used throughout the nineteenth and early twentieth centuries despite the growing awareness of its toxicity. During this period, lead white continued to serve multiple functions, including ground preparation, paint modification, and the rendering of highlights and light tones. At the same time, h-EDXRF analysis revealed the presence of Zn. While this element may be associated with zinc white (ZnO), one of the principal alternatives to lead white introduced during the nineteenth century, other Zn-bearing materials were also commercially available at the time. These include lithopone ($\text{BaSO}_4\text{-ZnS}$), introduced in the 1870s as an economical and comparatively non-toxic white pigment, as well as zinc chromate pigments and other Zn-containing paint components.

Because no Zn-bearing compound was identified by Raman spectroscopy, the source of Zn cannot be determined unambiguously. Consequently, it is not possible to establish whether the detected Zn derives from a white pigment, such as zinc white or lithopone, from a chromate-based yellow pigment, or from another paint constituent. This limitation further highlights the constraints of the present non-invasive analytical approach and the need for complementary stratigraphic and molecular investigations. Similarly, both Hg-based reds and ultramarine were commercially available in both natural and synthetic forms during the period in which *Ring Around the Rosie* was executed. However, the analytical data obtained in this study do not allow discrimination between natural and synthetic sources.

Overall, the materials identified in *Ring Around the Rosie* are largely consistent with pigments and painting materials commonly employed in European artistic production during the late 19th and early 20th centuries, including works by artists associated with the Munich School. The identified pigments indicate reliance on a restricted range of widely available commercial colours. The analytical approach adopted in this study provided information on the distribution of materials at the painting surface, allowing the visualisation of colour relationships and patterns of paint distribution, but offering only limited insight into paint stratigraphy and layer build-up.

Taken together, these observations suggest that the technical complexity of the painting derives less from an extensive range of materials than from the spatial organisation and superimposition of a limited number of pigments.

The spatial distribution of the identified materials suggests that several coloured passages may have been applied directly over the background paint layer. However, in the absence of evidence for a preparatory drawing or sketch, this interpretation remains tentative. Further studies involving other paintings by Savvidis would be valuable to determine whether this apparent working method represents a recurring feature of the artist's practice or is specific to *Ring Around the Rosie*.

4. Final Considerations on the Analytical Approach

The combined use of HSI, Raman spectroscopy, and h-EDXRF enabled a non-invasive investigation of the material composition and surface distribution of paint materials in *Ring Around the Rosie*. The complementarity of the three techniques proved particularly valuable: Raman spectroscopy provided molecular information for selected pigments, h-EDXRF supplied elemental data over a larger sampling volume, and HSI allowed the visualisation of spectrally distinct materials across the painting surface. Together, these methods supported the identification and mapping of several pigment classes and provided preliminary insights into the artist's working process.

At the same time, the study highlights several limitations inherent to the chosen analytical workflow. Most notably, the characterisation of binding media was not possible. This limitation arises from both instrumental and compositional factors. The spectral range covered by the HSI system is primarily sensitive to electronic transitions associated with pigments and offers only limited sensitivity to organic functional groups. Similarly, most Raman spectra were dominated by an intense fluorescence background, preventing the reliable identification of organic materials. Consequently, the interpretations presented in this work are largely restricted to pigment characterisation and cannot address potential relationships between pigments, binders, and painting technique.

The different information depths of the analytical methods further complicate data interpretation. h-EDXRF can probe a substantial volume of material and may detect signals originating from several superimposed paint layers as well as underlying preparatory or ground layers. In contrast, HSI and portable Raman spectroscopy predominantly provide information from near-surface regions of the paint stratigraphy. Furthermore, the Raman instrument employed in this study was not equipped with confocal optics and sampled a relatively large area, potentially integrating information from multiple paint layers within the analysed region. As a result, the datasets are not strictly comparable in terms of analytical depth and may reflect different portions of the painting structure.

These constraints are particularly relevant for the interpretation of the pigment composition. Although several materials could be identified with confidence, certain questions remain unresolved. Iron was detected by h-EDXRF in many blue and green areas but could not be associated with a specific pigment phase, since it may derive from earth pigments, impurities, or underlying paint layers. Likewise, the distribution of chromium suggests the possible presence of lead chromates beyond the yellow paint passages, yet the available data do not allow their precise spatial or stratigraphic assignment. Similar uncertainties affect the interpretation of the Zn- and Ba-bearing materials, which may correspond to zinc white, lithopone, baryte, mixtures thereof, or Zn-containing yellow pigments. Without stratigraphic information, it is not possible to determine whether these materials served as white pigments, extenders, paint modifiers, or constituents of coloured paint mixtures.

Additional questions concern the provenance and formulation of several pigments. The analytical data do not allow discrimination between natural and synthetic forms of ultramarine, vermilion/cinnabar (α -HgS), or the tentative red lead. Similarly, although the presence of a Cu-As green pigment appears likely, it was not possible to distinguish between different arsenical copper green formulations. The source of the Cd detected in the green 2 area likewise remains unexplained. Resolving these questions could contribute to a more detailed understanding of pigment circulation, commercial paint manufacture, and artistic material choices in early twentieth-century Greece.

From a technical-artistic perspective, the principal limitation concerns the absence of direct stratigraphic information. While the spatial distribution of pigments suggests possible relationships between paint layers and supports tentative interpretations of the painting sequence, the data do not permit unambiguous distinction between pigment mixtures, superimposed paint layers, and contributions from underlying strata. Similarly, the NIR images did not reveal a preparatory drawing; however, the absence of detectable features cannot be interpreted as proof that no preparatory drawing exists. The accessible spectral range may simply be insufficient to reveal buried carbon-based or weakly contrasting preparatory materials.

Future investigations could address these limitations through the integration of complementary imaging and analytical methods. Hyperspectral imaging extended into the SWIR region could provide additional information on both organic materials and concealed compositional features. Likewise, MA-XRF or μ -XRF scanning would enable the

spatial mapping of elemental distributions and help clarify questions concerning pigment associations and stratigraphy. Raman mapping or scanning systems equipped with microscopic fibre-optic probes and confocal capabilities could further improve pigment discrimination and spatial resolution. The application of exploratory multivariate approaches, including PCA, k-means clustering, and multimodal data fusion, may also reveal compositional relationships that remain inaccessible through visual inspection alone.

Although such methodologies would greatly enhance the level of interpretation, their implementation must also be considered considering practical constraints. High-resolution scanning approaches often require long acquisition times and controlled analytical conditions that may not be compatible with the display environment of publicly accessible museum collections. Nevertheless, the present study demonstrates that the integration of portable and non-invasive techniques can provide a meaningful characterization of artists' materials while simultaneously identifying the key knowledge gaps that should guide future investigations of Savvidis' work and broader modern Greek painting traditions.

5. Conclusions

This study explored the potential of integrating VNIR-HSI hyperspectral imaging, portable Raman spectroscopy, and h-EDXRF for an explorative, non-invasive investigation of the early 20th century painting *Ring Around the Rosie* by Symeon Savvidis. The complementary use of these techniques enabled the identification of several pigment classes and the visualization of their spatial distribution across the painting surface, while highlighting the benefits and limitations of each method when applied to complex painted stratigraphies.

The results support the presence of a palette comprising both traditional and modern materials, including lead white, ultramarine, vermillion, earth pigments, cobalt blue, lead chromates, and a tentative Cu-As green pigment. Comparison with published technical studies indicates that these materials are largely consistent with those employed by European artists of the late nineteenth and early twentieth centuries, including painters associated with the Munich School and contemporary Greek artistic production.

The application of spectral classification methods to the HSI dataset provided insights into the distribution of paint materials and suggested relationships among coloured passages and the underlying background. However, the absence of stratigraphic information prevents unambiguous distinction between pigment mixtures, superimposed paint layers, and contributions from underlying strata. Likewise, no preparatory drawing could be detected using the analytical workflow employed, although its existence cannot be excluded.

Overall, the study showcases the value of combining VNIR HSI, Raman spectroscopy, and h-EDXRF for explorative, non-invasive investigations of easel paintings using a work by a Greek modernist painter as a case study. The study also highlights the analytical value of integrating imaging and point-analysis approaches. At the same time, the results demonstrate that the selected analytical methodologies are insufficient to address questions relating to paint stratigraphy, binder composition, and artistic working methods. Future comparative studies involving additional works by Savvidis, together with the application of extended-range spectral imaging and elemental mapping techniques, may contribute to a broader understanding of the artist's material practices and their relationship to early twentieth-century European painting traditions.

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Abbreviations

The following abbreviations are used in this manuscript:

λ_m	Inflection point
Ab	Absorption band
DER	Direct Electronic Recombination
EPT	Electronic Pair Transition
ET	Electronic transition
R_{max}	Reflectance maximum
Gth	Goethite
HC	Hypercube
h-EDXRF	Handheld energy-dispersive X-ray fluorescence spectroscopy
Hem	Hematite
HSI	Hyperspectral imaging
O_h	Octahedric coordination symmetry
SAM	Spectral angle mapper
T_d	Tetrahedral coordination symmetry

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