Eur. Phys. J. Plus (2025) 140:187
https://doi.org/10.1140/epjp/s13360-025-06104-7

THE EUROPEAN PHYSICAL JOURNAL PLUS

Regular Article

Unravelling the mysteries of the fifteenth century 'Saint Vincent Panels' by combined in situ and micro-Raman spectroscopy

Eva Vermeersch[1,a], **Anastasia Rousaki**[1], **Sylvia Lycke**[1,2], **Sara Valadas**[3,4], **Virgínia Glória Nascimento**[4,5,6,7], **Rita Oliveira**[3,6,7], **José Mendes**[6], **Susana Campos**[6], **Joaquim Caetano**[6,7], **António Candeias**[3,4,5], **Peter Vandenabeele**[1,2]

[1] Raman Spectroscopy Research Group, Department of Chemistry, Ghent University, Ghent, Belgium
[2] Research Group Archaeometry and Natural Sciences, Department of Archaeology, Ghent University, Ghent, Belgium
[3] HERCULES Laboratory, Laboratório In2PAST (Associate Laboratory for Research and Innovation in Heritage, Arts, Sustainability and Territory, Institute for Advanced Studies and Research), University of Évora, Évora, Portugal
[4] City University of Macau Chair in Sustainable Heritage, University of Évora, Évora, Portugal
[5] Centro de Investigação E de Estudos Em Belas-Artes (CIEBA), Faculdade de Belas-Artes, Universidade de Lisboa, Lisbon, Portugal
[6] The Project of Study, Conservation and Restoration of St. Vincent Panels, Museu Nacional de Arte Antiga, Lisbon, Portugal
[7] Museus E Monumentos de Portugal EP, Museu Nacional de Arte Antiga, Lisbon, Portugal

Received: 15 November 2024 / Accepted: 8 February 2025

Abstract 'The Saint Vincent panels' are produced by the painter Nuno Gonçalves, and it is a fifteenth century polyptych consisting of six panels. The uniqueness of the work, together with the documentation scarcity about Nuno Gonçalves, highlights the importance of the research of characterizing the colour palette. Raman spectroscopy, both in situ and laboratory instrumentation, was used for this. The mobile Raman spectroscopy campaign is part of the multidisciplinary research project 'Study, Conservation and Restoration of Saint Vincent Panels'. A mobile EZRaman-I dual Raman analyser (785 and 532 nm) was used during the opening hours of the museum to investigate the panels and their pigments. The polyptych was heavily varnished and as such, the 785 nm laser was preferred for the characterization. It proved to be efficient in characterizing most of the pigments: vermilion, lead tin yellow type I, lazurite, carbon black, gypsum, lead white and calcite were identified. Intervention areas were characterized by the presence of titanium dioxide. Only for a few colours (blue, pink/purple and green), identification with the 785 nm laser was ambiguous and additional characterization with the 532 nm laser was hampered by the strong fluorescing varnish. As a result, micro-samples of these regions were collected for further analysis with benchtop micro-Raman instrumentation. Next to the confirmation of the in situ results, azurite and copper resinate were identified. As such, the combination of both approaches was successful in unravelling the colour palette of the Saint Vincent panels.

1 Introduction

The Saint Vincent Panels (Fig. 1) are the most significant work of Portuguese painting from the fifteenth century, and the six panels feature 58 figures surrounding a double representation of a holy deacon.

This set, attributed to Nuno Gonçalves, is characterized by the fidelity in the representation of reality and the monumental scale used in the representation of the figures. It can be framed in the movement of transformation of representation that took place during the fifteenth century in the main European artistic scene.

Unfortunately, documentation about the life of Nuno Gonçalves is rather scarce. The Saint Vincent panels are the only paintings that can officially be ascribed to Nuno Gonçalves. Originally, the panels were painted for an altarpiece that existed in the main chapel of the cathedral in Lisbon, as reported by Francisco de Holanda in 1548. Regarding the history of the altarpiece, it is known that in 1460, the archbishop of Lisbon ordered alms to be collected throughout the diocese to pay for a new altarpiece and that the works were still taking place in 1469. Throughout the sixteenth and seventeenth centuries, there are several references to the altarpiece, which was dismantled and replaced by a new stone altar in 1690. In the eighteenth century (before the 1755 earthquake), the paintings were moved to Quinta dos Patriarcas in Marvila, Lisbon. In 1895, the six paintings were found in the rooms of the Paço de São Vicente de Fora in Lisbon [1], arising the interest of the Royal Academy of Fine Arts and some specialized foreign press. The Burlington Magazine published its photographic reproduction in July 1909, before the panels' restoration [1]. After the

[a] e-mail: raman@ugent.be (corresponding author)

Published online: 03 March 2025

Fig. 1 Saint Vincent Panels. Nuno Gonçalves, c. 1470

restoration by Luciano Freire, the polyptych was musealized, remaining until today as part of the permanent exhibition of the Museu Nacional de Arte Antiga (MNAA).

In 2020 the project of study, conservation and restoration started with the aim to identify and characterize the paint set materials and techniques, bringing to light new information about Nuno Gonçalves, his workshop methods and creative processes. In addition, identifying subsequent interventions, and this with a focus on the restorations that were carried out throughout the twentieth century, first by Luciano Freire (1909) and later by Fernando Mardel (1955).

This ongoing project can be seen by the visitors of Museu Nacional de Arte Antiga, and it applies a multidisciplinary approach that uses imaging techniques, in situ (micro-) analysis and laboratory techniques, to provide scientific support during the conservation and restoration intervention. Considering the scarce documentary records and the small set of remaining paintings from this period and painter, this research is a unique opportunity to increase the knowledge, and to better understand the profound artistic changes that took place in Portugal during the fifteenth and sixteenth century.

The approach of the study ranges from elemental (macro-XRF, SEM–EDS, LC–MS) to molecular techniques (Raman spectroscopy, micro-FTIR), each having its own complimentary advantages. Raman spectroscopy has grown as a quite important technique in conservation studies and cultural heritage research [2]. More particular, the advantage of performing in situ measurements on a whole range of cultural artefacts, such as wall paintings [3, 4], manuscripts [5], mosaics [6], jewellery [7]. This non-invasive approach is especially interesting when analysing paintings of high cultural importance such as the Saint Vincent panels. Hence, a mobile measurement campaign was set up to analyse the colour palette of the Saint Vincent panels. Unfortunately, a mobile set-up also has its limitations and shortcomings: larger spot size, lower spectral resolution, smaller spectral range, wavenumber instability, sensitivity of the detector [2, 8]. This can ensure that identification might be troubled, and that mobile instrumentation will not succeed in characterization. In addition, Raman spectroscopy is based on scattering of visible light, as such any interference of visible light is to be avoided and measurements are often performed in a dark environment [2, 9]. However, when working in a museum that is open to the public, the darkening of the environment is not readily possible during the opening hours. It is thus clear that working with mobile equipment can be complicated and taking samples cannot be completely ruled out if a complete characterization of the colour palette is wanted.

In this work, the identification of the colour palette of the Saint Vincent panels with Raman spectroscopy is discussed. The results include the measurements of the mobile Raman spectroscopy campaign, which was undertaken in the national museum of Ancient Art in Lisbon, Portugal. As well as the identification performed with benchtop micro-Raman spectroscopy of samples taken from regions of the paintings where mobile instrumentation was insufficient in the characterization of the components.

2 Experimental

2.1 The painting

The polyptych of Saint Vincent was executed around 1470, and it consists of six oil paintings on oak support [10–12]. They depict from left to right (Fig. 1): The Panel of the Friars, The Fishermen, The Prince, The Archbishop, The Knights and lastly the panel of The Relic. The sizes of the panels are circa 204 cm in lengths and the widths of the outer four panels are ± 64 cm, while the two central panels (Prince and Archbishop) measure 128 cm wide.

Fig. 2 Pictures taken during the in situ measurement campaign in MNAA

2.2 In situ analysis

All in situ measurements were performed with a portable fibre-optics EZRaman-I Dual Raman analyser (TSI Inc. Irvine, USA). This dual spectrometer has a diode laser (785 nm), and a frequency doubled Nd:YAG laser (532 nm) with a spectral range of 126–2205 cm^{-1} and 108–3122 cm^{-1}, respectively. A spectral resolution of *ca*. 7 cm^{-1} is obtained for both wavelengths. Detection of the Raman scattering is achieved by a thermo-electrically cooled (-50 °C) charge-coupled device (CCD). The power of the system can be chosen by the user itself using adjustable power controls of which the maximum laser power is 300 mW and 50 mW, for, respectively, the 785 nm and 532 nm laser.

The measurements were performed with the standard lens (STD), having 7 mm of working distance, yielding a spot size of ca. 120 μm [13]. The 3 m fibre-optic cable was mounted on an articulating arm which can be moved in XYZ direction, this in order to precisely focus on the desired spot. Most of the spectra were recorded with the 785 nm laser, and the power was kept sufficiently low in order not to hamper or damage the paint layer of the panels. The power was set at circa 45% and this resulted in 33, 1 mW (measured with a power meter); the power of the laser is thus not linear with the control input. Typically, the measurements have short acquisition times ranging from 3 to 30 s with a maximum of 10 accumulations. A wavelength calibration was performed each day to correct for wavelength instability. The following products were used for this purpose: sulphur, epsilon-caprolactone (Acros Organics), cyclohexane (Kaiser), polystyrene pellets (Aldrich) and acetonitrile (Panreac)/toluene (UCB) (mixed in 50/50 volume%) [14].

The Saint Vincent Panels are showcased in a room behind a glass wall, ensuring that the visitors of the museum get a glance at the restoration and conservation process. However, as a consequence, this room cannot be darkened, and the mobile Raman measurements are exposed to ambient light. This has to be avoided, and typically black cloths are used during in situ measurements [3, 7, 16, 17]. In this measurement campaign, black cloths were also to be used. However, due to the sizes of the panels (± 2 m in height), it was impossible to cover the entire panel. Therefore, a small frame that created a shadow over the painting was proposed to block out the ambient light (Fig. 2b, c). This set-up was rather time-consuming and limited the overall practicality and flexibility of the Raman measurements. As time was limited for the in situ measurements, the influence of the ambient light on the Raman spectra was evaluated. This involved taking measurements from the different areas (darkened vs. exposed to ambient light), the obtained spectra were then compared, and no significant interference of the ambient light was observed. The remaining panels (excluding the panel of the Fisherman) were therefore measured without darkening interventions. Furthermore, a dark and environment spectra were taken on a daily basis to correct for interferences. The first for the internal set-up of the spectrometer, while the latter is for spectral subtracting in case of artefacts due to the ambient light.

To acquire spectra of the desired spots, the articulating arm was used [18–21]. However, due to the limits of the arm in height and the orientation of the panel, in some cases the laser probe combined with a cap was used directly on the artwork [13]. This cap ensures the optimal working distance and a dark environment for collecting the signal. A protective foam layer was also added at the front end of the cap.

The measurements were typically performed with the 785 nm laser as excitation source, as it is better in suppressing the fluorescence background [9] giving that the panels were heavily varnished. On some measuring spots, the varnish was partially removed, but still interference was noted. In specific regions (e.g. green or blue coloured areas), the 532 nm laser was tested as it typically gives better results for the identification of these colours [22], but the thick varnish had a too strong influence on the spectra.

2.3 Laboratory analysis

Samples were taken of specific regions in panels of which in situ Raman analysis provided no characterizable spectra. This was done in non-varnished parts by either scraping some of the paint layer onto a glass plate or using a cotton swab (Q-tip) [15, 23], as when rubbing the dry cotton swab over the painting miniscule pigment fragments are transferred. An overview of the sampling method and their positions on the painting can be found in Figure S1 and Table S1.

Analysis of the samples was performed by using a benchtop micro-Raman confocal Bruker Senterra R200-L spectrometer. It is equipped for two excitation wavelengths, a 785 nm diode laser and a 532 nm Nd:YAG frequency doubled laser. A thermo-electrically cooled (− 65 °C) CCD is used as detector. The system is coupled to an Olympus microscope, equipped with a turret containing the following objectives 5x, 20x, 50x and 100x, with, respectively, numerical apertures (NA): 0.1; 0.4; 0.75; 0.9. Spot sizes were visually estimated to be 50 μm, 10 μm, 4 μm and 2 μm, respectively. The power of the lasers is controlled with neutral density fillers ranging from 1%, 10%, 25%, 50% and 100% transmittance. The maximum nominal laser power, for, respectively, the 785 nm and 532 nm laser, is 100 mW and 20 mW. A spectral resolution of 3–5 cm^{-1} can be achieved. The system is controlled by OPUS software (Bruker).

Given the small size of the sample particles, measurements were acquired using the 50x objective. The lowest power (1%) was chosen, as damaging the sample was to be avoided. This resulted in a laser power of 0.73 mW and 0.12 mW at the sample surface (measured with a power meter), for, respectively, the 785 nm and 532 nm laser. In order to account for organic materials (e.g. pigments, varnish, binder), the spectral range covered two regions (80–2627 cm^{-1} (785 nm) and 50–2735 cm^{-1} (532 nm)). As a consequence, the measuring time was doubled. Almost all spectra were recorded with the 785 nm laser, except for some measurements on blue grains, which were suspected to be lazurite ($Na_7Ca(Al_6Si_6O_{24})(SO_4)(S_3)\cdot H_2O$). A 532 nm laser was used in these cases to (possibly) induce resonance enhancement.

Typically, an integration time ranging from 30 to 90 s was chosen, while the accumulations varied from 30 to 60.

All post-processing of the spectra (in situ and laboratory) was done by using Thermo Grams/AI 9.3 suite software (Thermo Fischer Scientific).

3 Results and discussion

Raman spectroscopy was applied to investigate the artistic palette of the Saint Vincent panels painted by Nuno Gonçalves. It is the first time that Raman spectroscopy was used to identify the pigments of this masterpiece. Giving the documentation scarcity of the painter and his works, this study is important in unravelling new information and gaining more knowledge. This involved a mobile measurement campaign undertaken during the museum's opening hours, as well as laboratory analysis of samples taken of colours/regions in which mobile Raman measurements failed to produce characterizable spectra.

In the following paragraphs, the pigment identification will be discussed, first the in situ analysis, followed by the laboratory analysis of the samples taken during the measurement campaign.

3.1 In situ analysis

The mobile Raman spectroscopy analysis identified the following components of the artist´s palette: azurite ($Cu_2(CO_3)2Cu(OH)_2$), lazurite ($Na_7Ca(Al_6Si_6O_{24})(SO_4)(S_3)\cdot H_2O$), lead tin yellow type I (Pb_2SnO_4), vermilion (α-HgS), carbon black, calcium sulphate ($CaSO_4$ x H_2O), titanium dioxide (TiO_2), lead white ($2PbCO_3Pb(OH)_2$) and calcite ($CaCO_3$). In Table 1, a summary of the pigments identified in each panel is given. The presence of titanium dioxide in two panels is linked to areas of intervention, from a later period (twentieth century).

In Fig. 3, some spectra obtained from the Panel of the Prince are shown, together with the measuring spots. In all spectra, a higher background is observed and most of the spectra are characterized by rather weak bands. This can be attributed to many factors: the bigger spot size of the mobile instrumentation, compared to benchtop instrumentation, and thus a bigger influence of the matrix on the spectra; influence of the binder and varnish; focussing optics; shorter measuring times (typically 10 s × 6 accumulations, longest measuring time was 30 s × 10 accumulations). In addition, it must be noted that most of the pigments identified (Table 1) are rather good Raman scatterers, such as vermilion. It is easily characterized by its most prominent band at 252 cm^{-1} (Fig. 3b) [24, 25]. Even through a thick varnish layer the Raman bands of vermilion were visible. For certain areas, the mobile instrumentation was inconclusive. Of the pink and purple regions, no easily characterizable spectra were obtained. From previously taken and embedded samples (cross sections), it could be microscopically observed that these colours were obtained by a mixture of red and blue pigments [12]. Hence, when measuring any of these colours with Raman spectroscopy at least two materials should be identified. Mobile Raman spectroscopy was able to detect lazurite ($Na_7Ca(Al_6Si_6O_{24})(SO_4)(S_3)\cdot H_2O$) as one of the blue pigments by its main band centred around 545 cm^{-1} [26, 27]. A very intense band (more intense than the lazurite band at 545 cm^{-1}) could be observed in these spectra at circa 1310 cm^{-1} (Fig. 3a). A band in this region has often been linked to a natural (*lapis lazuli)* origin of the pigment, as it is said to be fluorescence bands caused by the mineral impurities (e.g. diopside ($CaMg(Si_2O_6)$), sodalite ($Na_4(Si_3Al_3)O_{12}Cl$), pyrite (FeS_2)) [26–28]. However, as mentioned before, based on cross sections it was evident that a mixture of red and blue was at the origin

Table 1 An overview of the identified pigments during the in situ measurement campaign obtained with portable Raman spectroscopy

Panel	Azurite [24, 39, 40]	Lazurite [26, 27]	Lead tin yellow type I [22, 24]	Vermilion [24, 25]	Carbon Black [46]	Calcium Sulphate [47]	Titanium Dioxide [43, 44]	Lead White [22, 24]	Calcite [22, 48]
Panel of the Fisher-men	X?	X?		x	X			X	x
Panel of the Prince	X?	x	x	x	X	x	x	x	
Panel of the Friars	X?				X	x		x	x
Panel of the Knights	X?	X?	x	x				x	
Panel of the Relic	X?	X?		x	X		x	x	
Panel of the Arch-bishop	X?	X?	x	x		x		x	

? refers to an non-conclusive characterization

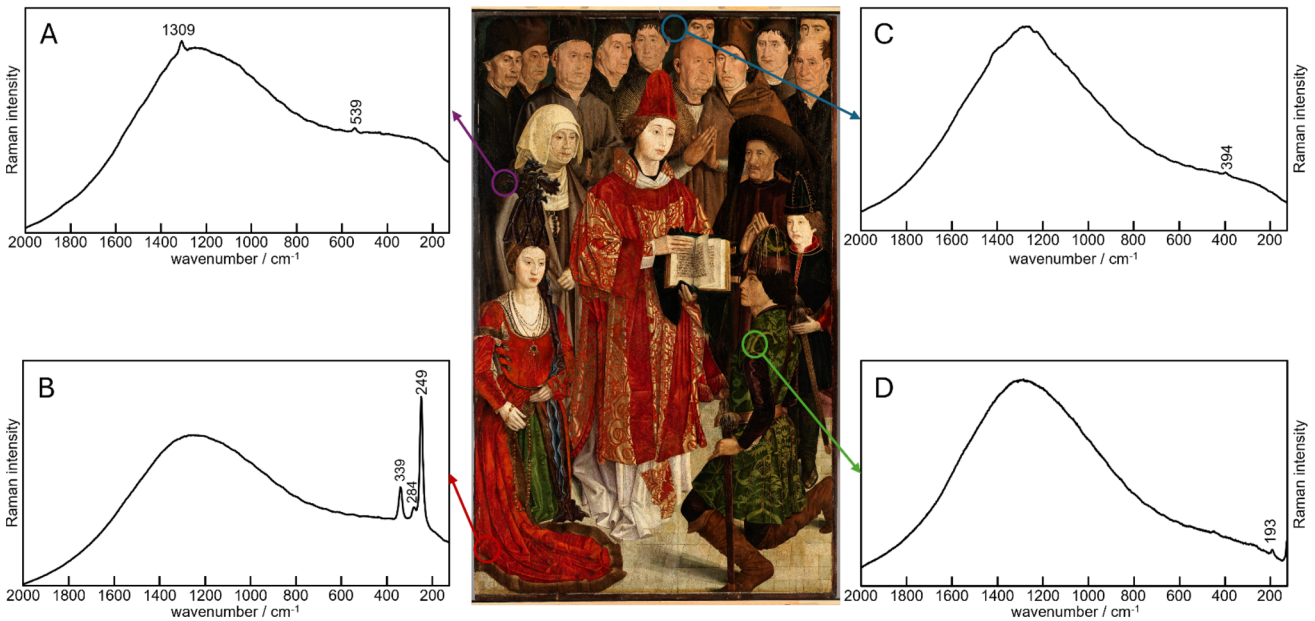

Fig. 3 Spectra obtained during the in situ campaign with the mobile equipment (laser wavelength 785 nm) of the following colours and their identification: Purple—lazurite (A), Red–Vermilion (B), Turquoise–Azurite? (C), Green–Lead Tin Yellow Type I (D). Experimental conditions: 785 nm, 33.1 mW (50%), 10 s × 6 acc (A), 3 s × 10 acc (B), 30 s × 10 acc (C), 30 s × 5 acc (D)

of the purple/pink colours. The lack of red lead (Pb_3O_4) or vermilion (α-HgS) identification by Raman spectroscopy in this region suggested an organic origin (e.g. a carmine or madder lake) for the red colourant. Moreover, it is well-known that Nuno Gonçalves used dyes [12]. These organic components typically tend to have stretching and bending vibrations in this region (800–1800 cm^{-1}) [29–31]. Unfortunately, they are rather weak Raman scatterers [22] and often surface-enhanced Raman spectroscopy (SERS) is used for their identification [32–35]. As such, samples from these colours were taken for further analysis in the laboratory using micro-Raman spectroscopy. SERS was no option for these samples giving the limited quantity and the extensive sample preparation required for it.

In addition, some samples were taken in green coloured regions as these also proved to be difficult to characterize using the mobile set-up. Cross sections from these colours (taken in 2012) showed that the green colour was not produced by mixing blue and yellow pigments [12], but that a green pigment was used. XRF (EDXRF and MA-XRF) measurements showed that Cu was present in these coloured layers and as such, the green pigment was copper-based. Green pigments such as malachite ($CuCO_3 \cdot Cu(OH)_2$), acatamites ($CuCl_x$), copper resinates, verdigris ($Cu_x(CH_3COO)_y(OH)_z \cdot n\ H_2O$) are not easily identified with Raman spectroscopy using the 785 nm laser [22, 36, 37], and the fluorescing varnish layer hampers the use of the 532 nm laser. In situ measurements of

dark green coloured regions did not yield characterizable spectra. However, when lighter green coloured regions were measured, the Raman spectrum (Fig. 3d) showed the bands of lead tin yellow type I (Pb_2SnO_4) [22, 24]. The most intense band of LTYI (ca. 129 cm^{-1}) falls right at the edge of the spectral range of the mobile instrumentation; however, this band can be noticed at the end of the spectral range of the spectrum (Figure S2). This yellow pigment was probably used to brighten the green hue.

The dark turquoise colour in the background is believed to be painted using azurite ($Cu_2(CO_3)_2 \cdot Cu(OH)_2$). This pigment is also not easily characterized with a 785 nm laser [22], especially when working with mobile instrumentation. Raman measurements of this background colour often resulted in no clearly identifiable spectra with a high fluorescence background. In some spectra (Fig. 3c), a very minor band could be seen at circa 394 cm^{-1}. This band might originate from the Cu–O bending vibration in an azurite molecule [38]. An even weaker band around 1094 cm^{-1} can be observed in some spectra, but it is barely above signal-to-noise ratio. An unambiguous assignment cannot be made based on (a single) weak Raman band(s). Therefore, samples were taken from the background for further analysis in the laboratory with a micro-Raman system.

Other painted zones were easily measured, and identification was rather straightforward. The skin colour, for example, was obtained by a mixture of vermilion and lead white ($2PbCO_3 \cdot Pb(OH)_2$), of which the latter was characterized by its Raman band at 1050 cm^{-1} [22, 24].

Overall, it can be concluded that mobile Raman spectroscopy was successful in obtaining an overview of the colour palette of the paintings. Some paint layers could not be identified, but for most of the regions the in situ measurements were successful in characterizing the pigments. As such, it was possible to rather rapidly obtain a first impression of the artistic colour palette.

3.2 Laboratory analysis

As mobile instrumentation could not provide a complete overview of all the pigments used, micro-Raman measurements were performed on a limited number of samples (Supplementary Fig. 1).

In Table 2, an overview is presented of the samples analysed with micro-Raman spectroscopy together with their identification. The pigments that were identified during the in situ measurements could be confirmed with micro-Raman spectroscopy, and only in a limited number of cases, where in situ measurements did not yield satisfying results, the micro-Raman measurements were necessary to identify the pigments.

For instance, micro-Raman spectroscopy proved to be successful in acquiring spectra of azurite (Fig. 4), where the intense Raman band at 400 cm^{-1} (Cu–O stretching vibration), the C = O symmetric stretching vibration at 1095 cm^{-1} and the other Cu–O vibrations [38–40] can easily be identified. From this, it is obvious that micro-Raman spectroscopy is more suited to identify this pigment than the mobile instrumentation that was used. As with mobile instrumentation, only a very weak and broad band at circa 394 cm^{-1} could be observed in some spectra.

Another challenge during the in situ campaign was the characterization of the material responsible for the red hue in the purple and pink layers. As mentioned, previous microscopic analysis showed a combination of red and blue material. However, in the laboratory, when focussing on the sample with the microscope, the blue particles were dispersed in a more or less uniform red material which had variations in intensity. As such, measurements were performed on all the different colour hues present. Unfortunately, characterization of the red component could not be achieved, based on the acquired spectra. However, lazurite was identified by its Raman band at 545 cm^{-1} [27, 28]. In agreement with the mobile measurements, an additional band at 1310 cm^{-1} was apparent. Micro-Raman spectroscopy did not provide any new information, and the characterization of this band is still ambiguous. It might originate from the mineral impurities of the ultramarine pigment [27, 28], that in that case would be present in every grain that was measured. However, the band could also suggest a red colourant [31, 41]. It is known that Nuno Gonçalves used red dyes such as madder and carmine as was revealed by HPLC in 2017 [12]. They appear in overlapping layers, and in certain cases, they are used in mixture with pigments to create various colours such as greys, browns and flesh tones. Madder is extracted from the roots of *Rubia Tinctorum L.* herb and has its main Raman band at circa 1480 cm^{-1} [41]. Whereas carminic acid ($C_{22}H_{20}O_{13}$), the main colouring component of cochineal, has its most prominent Raman band at ca. 1303 cm^{-1} [29, 30]. This could hint that the unidentified band in the acquired spectra might be of this colourant; however, a conclusive characterization cannot be obtained based only on this Raman band.

Another colour where the mobile equipment proved to be insufficient was the green zones. Laboratory analysis equally turned out to be quite troublesome. Many different experimental conditions were tested, including long and shorter measuring times, combined with stepwise increasing the laser power, yet still controlling that the samples were not damaged or burned. Both lasers, the 532 nm and the 785 nm, were tested, to avoid absorption of the laser light. Spectra were obtained with weak bands at 1438 and 729 cm^{-1}, and a medium band at 200 cm^{-1} (Fig. 5).

It should, however, be noted that these spectra still display a lot of noise and that the weak bands are barely above the signal-to-noise ratio. This band pattern suggests a copper resinate origin for the green colour [36, 42]. A slight shift in band positions can be observed, but this can be linked to the ageing of the paint [42] as well as the fact that copper resinates are not a single, well-defined pigment. It is a generic term for a green glaze, consisting of a solution of a green-copper salt in a resin or oily medium [36]. A spectrum of a copper resinate (Kremer 12200) was acquired with the benchtop instrument under the same experimental conditions (Supplementary Fig. 3), and it is observed that the Raman bands are similar. This seems to support the idea that the green pigment is a copper resinate. However, previous analysis with μ-FTIR of the green pigments showed various spectral contributions associated with the presence of verdigris, particularly in the Fishermen, Prince and Relic Panels [12]. Verdigris can be characterized by Raman

Table 2 An overview of the identified pigments with micro-Raman spectroscopy

Panel	Sample name	Description	Azurite [24, 39, 40]	Lazurite [26, 27]	Lead tin yellow type I [22, 24]	Vermilion [24, 25]	Carmine [22, 29, 30]	Cu-resinate [36, 42]	Carbon black [46]	Calcium sulphate [47]	Titanium dioxide [43, 44]	Lead white [22, 24]	Calcite [22, 48]	Quartz [49, 50]
Archbishop	A1	Background Blue/green	X									X	x	X
	A2	Green shadow			X			X?	X	X	x	x		
	A3	Black vermilion?	X		X	X			X		X			
	A4	Brown rope			X	X			X	X		X		
Prince	I1	Violet	X	x	X	X	X?					X		
	I2	Red				X			X		X			
	I3	Pink	X	X	X	X	X?		X	X	X	X	X	
	I4	Purple		X			X?		X					
	I5	Green			X			X?	X	X			X	
	I6	Background	X			x			X		X	X	X	
	I7	Background original?	X									X	X	
Fishermen	P1	Background	X		X				X				X	
	P2	Blue	x		X				x				X	
	P3	Green			X			X?				x		

? refers to an non-conclusive characterization

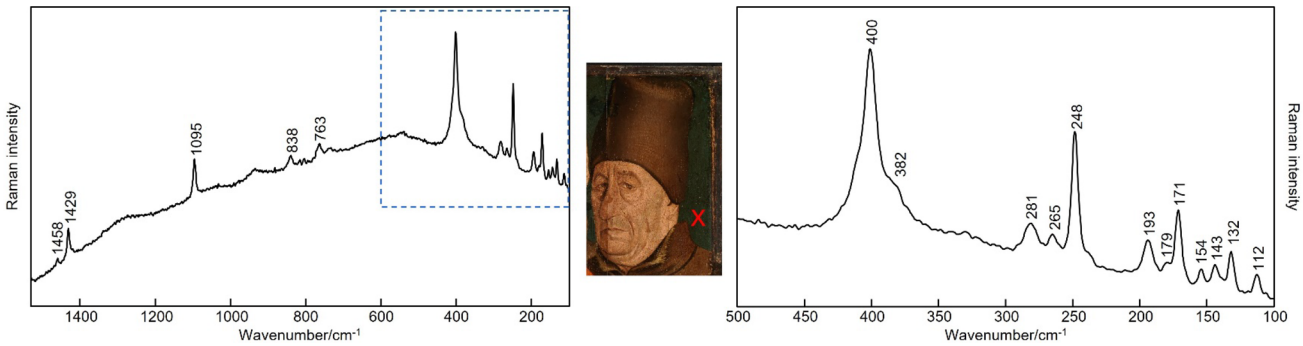

Fig. 4 Raman spectra of identified azurite of the panel of the Archbishop. Full spectral range spectrum (Left), the sampling spot (Middle) and the lower spectral range spectrum (Right). Experimental conditions: 50 × objective, 785 nm, 0.73 mW (1%), 60 s × 60 acc

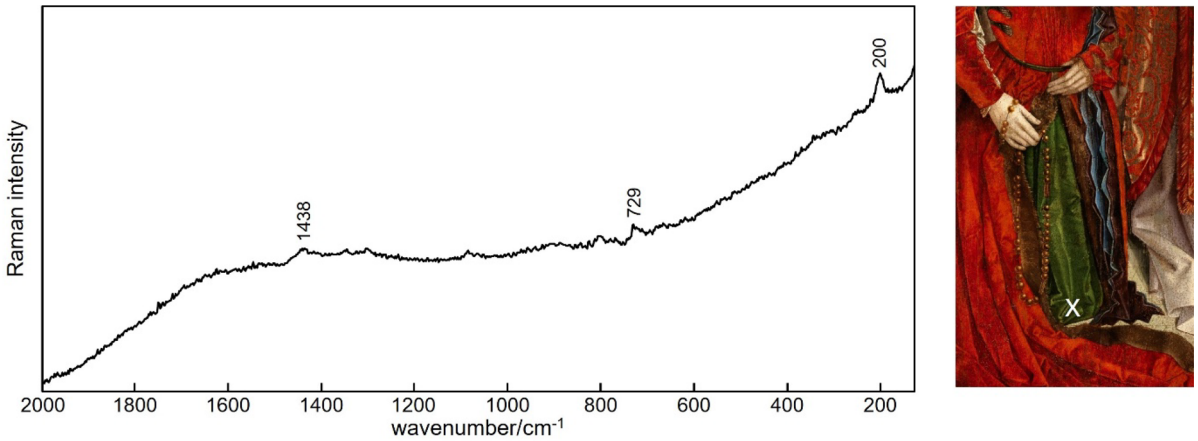

Fig. 5 Raman spectrum of a green particle taken from the green paint layer of the panel of the Prince. The sample spot is given on the right. Experimental conditions: 50 × objective, 785 nm, 0.73 mW (1%), 60 s × 60 acc

spectroscopy with the 785 nm laser by its bands at 948 (m), 320 (m), 180 (vs.) cm^{-1} [37]. This is in disagreement with the Raman results obtained from the samples; however, Nuno Gonçalves could have used a mixture of both components for obtaining his green colours. Lead tin yellow type I was also identified in some spectra. Interestingly, the main Raman band at 197 cm^{-1} of LTY I is slightly broader in these spectra than in the ones obtained of other paint colours. The most prominent band of Cu-resinate is at 200 cm^{-1}, so it is possible that these bands overlap and that the resulting band has some contributions of both pigments.

Titanium dioxide was also found in some spectra of the samples by a weak band around 140 cm^{-1} [43, 44]; however, their presence is most likely linked to mineral impurities rather than an intervention nature. Many of the pigments the artist Nuno Gonçalves used can have a mineral origin, and traces of other minerals, such as titanium dioxide, can then be present in the pigment [45].

Micro-Raman spectroscopy was, as such, able to help with further identifying the pigments used by the painter Nuno Gonçalves for his polyptych 'Saint Vincent Panels'.

4 Conclusion

The Saint Vincent panels are the only paintings that are certainly attributed to Nuno Gonçalves and were as such used to gain knowledge regarding the painter and his works. For this, Raman spectroscopy was used to help identify the artists' colour palette. A mobile measurement campaign was performed to analyse the polyptych during the opening hours of the museum. This set-up had some implications regarding the focus and the dark environment required for Raman spectroscopy. The paintings were also heavily varnished, which complicated the measurements and the choice of laser (785 vs. 532 nm laser). The mobile Raman instrumentation was able to identify most of the pigments used in the different coloured paint layers, even through the thick varnish layers when using the 785 nm laser. The following pigments were characterized: lazurite, lead tin yellow type I, vermilion, carbon black, calcium sulphate, calcite and lead white. In intervention regions, the mobile instrumentation was able to detect titanium dioxide. Unfortunately, in situ Raman spectroscopy had difficulties identifying some colouring components in specific regions (e.g. turquoise background, any green or pink, purple area). As such, samples were taken of these colours to further investigate with laboratory micro-Raman instrumentation. The micro-Raman system was able to further identify some pigments responsible for the blue and

green colours: azurite and copper resinates. Identification of the pink and purple colours, which are a combination of blue and red components, is however still ambiguous. The red component could not be characterized, but vermilion or red lead as colourant is excluded, hinting to a red lake as colourant. The combined approach of in situ and laboratory Raman spectroscopy has thus given a more concise overview of the colour palette that the painter Nuno Gonçalves used for his works.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1140/epjp/s13360-025-06104-7.

Acknowledgements This study was part of the research for 'The Project of Study, Conservation and Restoration of Saint Vincent Panels', sponsored by Millennium BCP Foundation. The authors would like to thank the people of the National Museum of Ancient Art for their hospitality and help with any problems. Sylvia Lycke would like to thank the faculty of sciences of Ghent University for the FCWO grant for participating in the in situ campaign. Anastasia Rousaki greatly acknowledges the Ghent University-Special Research Fund (UGent-BOF) for her postdoctoral fellowship.

Author contributions Conceptualization was performed by Anastasia Rousaki, Peter Vandenabeele and Eva Vermeersch; methodology, formal analysis, writing—original draft preparation and visualization were done by Eva Vermeersch; investigation was performed by Sylvia Lycke, Anastasia Rousaki and Eva Vermeersch; writing—review and editing was performed by Susana Campos, António Candeias, Sylvia Lycke, Virgínia Glória Nascimento, Rita Oliveira, Anastasia Rousaki, Sara Valadas, Peter Vandenabeele and Eva Vermeersch; funding acquisition was performed by Joaquim Caeteno, António Candeias and Sylvia Lycke; resources were provided by Joaquim Caeteno, António Candeias and Peter Vandenabeele; supervision was performed by António Candeias and Peter Vandenabeele.

Funding This research was partially funded by FCWO of the faculty of sciences of Ghent University and is part of the research project 'Study, Conservation and Restoration of the Saint Vincent Panels' which is sponsored by the Millennium BCP Foundation.

Data availability The data that support the findings of this study, which are not included in the manuscript, are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

References

1. A. M. Gonçalves, Restauro dos Painéis de São Vicente de Fóra (1960)
2. A. Rousaki, P. Vandenabeele, J. Raman Spectrosc. (2021). https://doi.org/10.1002/jrs.6166
3. G. Barone, D. Bersani, A. Coccato, D. Lauwers, P. Mazzoleni, S. Raneri, P. Vandenabeele, D. Manzini, G. Agostino, N.F. Neri, Appl. Phys. A (2016). https://doi.org/10.1007/s00339-016-0370-7
4. A. Rousaki, E. Vargas, C. Vázquez, V. Aldazábal, C. Bellelli, M.C. Calatayud, A. Hajduk, O. Palacios, L. Moens, P. Vandenabeele, TrAC Trends Anal. Chem. **105**, 338–351 (2018). https://doi.org/10.1016/j.trac.2018.05.011
5. D. Lauwers, V. Cattersel, L. Vandamme, A. Van Eester, K. De Langhe, L. Moens, P. Vandenabeele, J. Raman Spectrosc. (2014). https://doi.org/10.1002/jrs.4500
6. A. Rousaki, M. Costa, D. Saelens, S. Lycke, A. Sánchez, J. Tuñón, B. Ceprián, P. Amate, M. Montejo, J. Mirão, P. Vandenabeele, J. Raman Spectrosc. **51**(9), 1913–1923 (2020). https://doi.org/10.1002/jrs.5624
7. G. Barone, D. Bersani, J. Jehlička, P.P. Lottici, P. Mazzoleni, S. Raneri, P. Vandenabeele, C. Di Giacomo, G. Larinà, J. Raman Spectrosc. (2015). https://doi.org/10.1002/jrs.4649989
8. E. Vermeersch, F. Kosek, J. De Grave, J. Jehlička, A. Rousaki, J. Raman Spectrosc. (2024). https://doi.org/10.1002/jrs.6646
9. P. Vandenabeele, *Practical Raman Spectroscopy*, 1st edn. (Wiley, Chichester, 2013), pp.1–39
10. A. J. Cruz (1994). Do certo ao incerto: o estudo laboratorial e os materiais do políptico de S. Vicente. In Nuno Gonçalves. Novos Documentos. Estudo da pintura portuguesa do séc. XV. Instituto Português de Museus – Reproscan.
11. P. Klein, L. Esteves. "Dendrochronological analyses in Portuguese panel paintings." La peinture et le laboratoire: procédés, méthodologie et applications. 2001.
12. J. Mendes (2012) A obra de Nuno Gonçalves: estudo técnico. PhD theses on easel painting conservation. Universidade Católica Portuguesa, Porto. http://hdl.handle.net/10400.14/13434
13. D. Lauwers, A.G. Hutado, V. Tanevska, D. Bersani, P. Vandenabeele, Spectrochim. Acta A (2014). https://doi.org/10.1016/j.saa.2013.08.088
14. D. Hutsebaut, P. Vandenabeele, L. Moens, Analyst (2005). https://doi.org/10.1039/B503624K
15. A. Burnstock, K.J. van der Berg, J. House, in: *Art Matters, Netherlands Technical Studies in Art* (Waanders, Zwolle, 2005), Vol. 3, p. 47
16. K. Osterrothová, L. Minaříková, A. Culka, J. Kuntoš, J. Jehlička, J. Raman Spectrosc. (2014). https://doi.org/10.1002/jrs.4541
17. J. Jehlička, A. Culka, D. Bersani, P. Vandenabeele, J. Raman Spectrosc. (2017). https://doi.org/10.1002/jrs.52141289
18. P. Vandenabeele, T.L. Weis, E.R. Grant, L.J. Moens, Anal. Bioanal. Chem. (2004). https://doi.org/10.1007/s00216-004-2551-z
19. A. Deneckere, F.P. Hocquet, A. Born, P. Klein, S. Rakkaa, S. Lycke, K. De Langhe, M. Martens, D. Strivay, P. Vandenabeele, L. Moens, J. Raman Spectrosc. (2010). https://doi.org/10.1002/jrs.2679
20. L. Van de Voorde, M. Vandevijvere, B. Vekemans, J. Van Pevenage, J. Caen, P. Vandenabeele, P. Van Espen, L. Vincze, Spectroschim Acta B (2014). https://doi.org/10.1016/j.sab.2014.10.007
21. A. Rousaki, P. Pincé, S. Lycke, A. Harth, M. Martens, L. Moens, P. Monsieur, P. Vandenabeele, EPJ+ (2019). https://doi.org/10.1140/epjp/i2019-12754-3
22. M.C. Caggiani, A. Cosentino, A. Mangone, Microchem. J. (2016). https://doi.org/10.1016/j.microc.2016.06.020
23. R. Klockenkamper, A. Von Bohlen, L. Moens, W. Devos, Spectrochim. Acta (1993). https://doi.org/10.1016/0584-8547(93)80029-T
24. R. Sefcu, S. Chlumska, A. Hostasova, Herit Sci (2015). https://doi.org/10.1186/s40494-015-0045-2

25. D. Chiriu, M. Pala, F.A. Pisu, G. Cappellini, P.C. Ricci, C.M. Carbonaro, Dyes Pigments **184**, 108866 (2021). https://doi.org/10.1016/j.dyepig.2020.108866
26. A. Paz, D.-V. Ana, J.T.L. De la María, R.-D. Ramón, M.J. Ayora-Cañada, Appl. Phys. A (2016). https://doi.org/10.1007/s00339-016-0537-2
27. M. Gonzalez-Cabrera, P. Arjonilla, A. Doninguez-Vidal, M.J. Ayora-Canada, Dyes Pigm. (2020). https://doi.org/10.1016/j.dyepig.2020.108349
28. C.M. Schmidt, M.S. Walton, K. Trentelman, Anal. Chem. (2009). https://doi.org/10.1021/ac901436g
29. E. Svobodova, Z. Bosakova, M. Ohlidalova, M. Novotna, I. Nemec. Vibr. Spectrosc. (2012). https://doi.org/10.1016/j.vibspec.2012.09.003
30. M.S. Kozachuk, M.O. Aviles, R.R. Martin, B. Potts, T. Sham, F. Lagugne-Labarthet, Appl. Spectrosc. (2018). https://doi.org/10.1177/0003702818773760
31. S. Bottura-Scardina, P. Vandenabeele, C. Miguel, A. Candeias, J. Raman Spectrosc. (2023). https://doi.org/10.1002/jrs.6501
32. A.V. Whitney, R.P. Van Duyne, F. Casadio, J. Raman Spectrosc. (2006). https://doi.org/10.1002/jrs.1576
33. E. Van Elslande, S. Lecomte, A. Le Ho, J. Raman Spectrosc. **39**(8), 1001–1006 (2008). https://doi.org/10.1002/jrs.1994
34. A. Idone, M. Aceto, E. Diana, L. Applonia, M. Gulmini, J. Raman Spectrosc. (2014). https://doi.org/10.1002/jrs.4491
35. F. Pozzi, K.J. Berg, I. Fiedler, F. Casadio, J. Raman Spectrosc. (2014). https://doi.org/10.1002/jrs.4483
36. C. Conti, J. Striova, I. Aliatis, E. Possenti, G. Massonet, C. Muehlethaler, T. Poli, M. Positano J Raman Spectro (2014). https://doi.org/10.1002/jrs.4455
37. A. Coccato, D. Bersani, A. Coudray, J. Sanyova, L. Moens, P. Vandenabeele, J. Raman Spectrosc. (2016). https://doi.org/10.1002/jrs.4956
38. R.L. Frost, W.N. Martens, L. Rintoul, E. Mahmutagic, J.T. Kloprogge, J. Raman Spectrosc. (2002). https://doi.org/10.1002/jrs.848
39. G. Marucci, A. Beeby, A.W. Parker, C.E. Nicholson, Anal. Methods (2018). https://doi.org/10.1039/C8AY00016F
40. S.E. Jorge-Villar, H.G.M. Edwards, J. Raman Spectrosc. (2021). https://doi.org/10.1002/jrs.6118
41. F. Pozzi, J.R. Lombardi, M. Leona, Heritage Science (2013). https://doi.org/10.1186/2050-7445-1-23
42. C. Paz, L.-R. Rodriguez-Simon, E. Manzano J Cult Heri (2023). https://doi.org/10.1016/j.culher.2022.12.004
43. U. Balachandran, N. G. Eror, J. Solid State Chem. Gfs (1982) *42*(3), 227-241.
44. H.G.M. Edwards, N.F. Nik, P.S. Hassan Middleton, Ana Bioanal Chem **384**(6), 1356–1365 (2006). https://doi.org/10.1007/s00216-005-0284-2
45. M. Aru, L. Burgio, M.S. Rumsey, J. Raman Spectrosc. (2014). https://doi.org/10.1002/jrs.4469
46. A. Coccato, J. Jehlička, L. Moens, P. Vandenabeele, J. Raman Spectrosc. (2015). https://doi.org/10.1002/jrs.4715
47. N. Prieto-Taboada, O. Gómez-Laserna, I. Martínez-Arkarazo, M.A. Olazabal, J.M. Madariaga, Anal. Chem. (2014). https://doi.org/10.1021/ac501932f
48. W.J.B. Dufresne, C.J. Rufledt, C.P. Marshall, J. Raman Spectrosc. (2018). https://doi.org/10.1002/jrs.5481
49. M.L. Frezzotti, F. Tecce, A. Casagli, J. Geochem. Explor. (2012). https://doi.org/10.1016/j.gexplo.2011.09.009
50. X. Zhong, A. Loges, V. Roddatis, T. John, Contr. Mineral. Petrol. (2021). https://doi.org/10.1007/s00410-021-01845-x