Comparison of Different *Non-invasive* μ -Raman Set-ups for Studying Pigments in Art Works

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ABSTRACT

Micro-Raman spectroscopy is widely used for the identification of pigments on art works. Due to the priceless value of artistic objects, non-invasive measurements are strongly preferred over sampling strategies. However, the non-invasive spectra response is often lower if compared to measurements carried out on a sample. In this study, spectral intensity of measurements performed with various non-invasive Raman set-ups was compared with spectral intensity from a traditional micro-Raman set-up. The comparison was done on pure pigments reference swatches first, to test the methodology. Then a painting was investigated, as case study on a real artefact, directly on its surface and on taken samples under the microscope. For the non-invasive measurements, four horizontal beam set-ups and an external measuring head connected to the spectrometer by fibre optics were used. Two lasers were used: 785 and 532 nm. The results were determined as counts (Raman signal intensity) per second of measurement and per Watt of laser intensity (Cnts/Ws). A method to compare performances among the different experimental conditions is proposed in this work. The horizontal beam configurations showed spectral responses in signal intensity very similar to those of the traditional microscope but the ones from the fibre optics were only at about 10% of that of the microscope. These results show the potential of horizontal set-ups for the analyses of artworks, as their performance is equivalent to the traditional microscope configuration. However, the more challenging positioning for the horizontal beam set-ups can hamper the acquisition of a good spectrum, since either the Raman spectrometer or the artwork has to be moved with μ m scale precision to position the laser spot on the area of interest. This often requires improvements especially regarding the mechanical stability of the analytical set-up as well as the artwork.

Keywords: Raman Spectroscopy, Pigments, Non-Invasive, *in situ* Analyses, Signal Intensity

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1. Introduction

Raman-spectroscopy is one of the most imported methods for the identification of pigments in paintings (Clark, 2002; Smith & Clark, 2004; Vandenabeele et al., 2007) or other works of art (Deneckere, Schudel, Van Bos, Wouters, & Bergmans, 2010). Indeed, pigments are high Raman active compounds that makes micro-Raman spectroscopy an ideal tool to identify them, both inorganic and organic ones, on ancient as well as on contemporary objects. The analysis of pigments is used to study art works for questions of technical art history or forensic sciences.

No matter the reason of the study of an artwork, a non-sampling approach and, if possible, *in situ* measurements are strongly preferred over sampling the artwork. The second important advantage of completely non-invasive measurements is that all accessible areas of the painting can be analysed, whereas samples can only be collected from limited, and thus less representative areas (Deneckere et al., 2010; Vandenabeele et al., 2005, 2007).

Depending on the analytical circumstances, the most suitable working set-up needs to be chosen: the traditional

Raman microscope, the horizontal beam with extension tubes of different length or the measuring head with fibre optic. If the object is small enough, e.g. watercolours or miniature paintings (Röhrs & Stehr, 2014), non-invasive measurements can be carried out directly under the microscope with its traditional set-up. In this configuration, the object can also be easily moved (x-, y- and z-wise) with a motorized microscope stage and the focusing is fast and straight forward.

However, if the objects dimensions do not allow such a measurement, the object needs to be placed in front of the instrument. Typically, the non-invasive set-up of a laboratory instrument directs the laser beam onto the sample either by deflecting the laser by a mirror or by guiding it via fibre optics. Using the deflecting mirror, an extension tube of adapted length which holds the objective is required to focus the laser on the surface of the object. If an object cannot be placed in front of to the instrument, e.g. a mural painting, a measuring head, which is connected to the spectrometer via fibre optics can be used alternatively. This fibre can guide the light of the laser though a several meters long cable to the measuring head, where the focusing optics are installed. In this case, the measuring head must be positioned precisely to focus on the chosen spot.

Many publications compare between bench and portable Raman spectrometers, but the performances of non-invasive set-ups of a laboratory instrument were seldom discussed in publications. Portable instruments often show some disadvantages such as: 1) they provide a narrow spectral window (Bersani et al., 2006. Perez-Alonzo et al., 2004, Reiche et al., 2004), sometimes with a cut-off filter at 200 cm⁻¹; 2) often there are fewer lasers available (Aceto et al., 2012; Bersani et al., 2006), frequently only one, or 3) they provide lower laser power (Aceto et al., 2012; Boschetti, Corradi, & Baraldi, 2008; Trentelman & Turner, 2009). When comparing the Raman response, portable set-ups also show in general a lower signal to noise ratio (Ziemann, 2006).

Nevertheless, the aim of this study is to obtain a better understanding of the loss of signal by using our non-invasive micro-Raman laboratory device in comparison to the traditional microscope set-up. This will help us to choose the most appropriate spectrometer configuration for a given analytical problem. For the performance tests, measurements were carried out on pure pigment reference samples and, as a case study, non-invasively on a painting and on samples from the same painting.

2. Material and Methods

2.1. Pure pigments (reference samples)

The reference samples consisted of pellets of pure pigments: cinnabar, red ochre, ultramarine blue, yellow chrome and copper phthalocyanine blue. The choice of the pigments relied on their homogeneity and presence in the case study painting.

Pure pigments were prepared as pellets. The small size of the pellets (13 mm diameter) made the spectra acquisition straightforward. The samples were mounted on a sample holder, to easily move from one pellet to the next.

Six pigments were initially chosen to estimate the spectroscopic performance of the different set-ups: ultramarine blue (Na₈₋₁₀Al₆Si₆O₂₄S₂₋₄), chrome yellow (PbCrO₄), cinnabar (HgS) and minium (Pb₃O₄) from Kremer Pigments, anatase (TiO₂) from Hombitan and phthalocyanine blue (C₃₂H₁₆CuN₈ – PB15:1 - copper phthalocyanine) from BASF (Heliogen Blau L 6930).

These were prepared as pellets using a pellet-making die. Since a pellet of pure pigment would be too brittle, the pellet has a second layer of cellulose and Plexigum in extremely low concentration is used as pigment binder. No trace of cellulose or Plexigum was seen in the Raman spectra. For each pigment's preparation the following method was followed:

1. 100 mg of cellulose (Somar Mix) were weighted on the pellet making die and pressed for ca. 20 s with 3 t.
2. 50 mg of pure pigment were well mixed in an agate mortar with 150 µL of a 2 % (w/w) solution of Plexigum (Polymer in powder form based on iso-butyl methacrylate), let to dry and mixed again.
3. This mixture was added to the pellet-making die (on top of the cellulose layer) and pressed at 8 t for ca. 20s.

Homogeneity of the pure pigment's references was tested by Environmental scanning electron microscopy (ESEM) with an energy-dispersive X-ray analyser (EDX).

2.2. Case study painting

The case study concerns a falsified painting. The painting "Cubist still life" (1913) had been wrongly believed to be by Fernand Léger (1881-1955) and is painted with oil on canvas (H 55.4 cm x B 38.0 cm). Samples of the painting had already available in the *Rathgen Research Laboratory* from analysis carried out in the past.

The presence of synthetic pigments evidenced in samples from the painting allowed excluding the year 1913 as the proposed production date. Fig 1 shows the painting with sampling positions from the previous measurement campaign and the area analysed by non-invasive analyses (this study).

Fig 1. *Cubistic still life*, oil on canvas, formerly attributed to Fernand Léger, (55.4 cm x 38.0 cm). P no.: sampled spots; M no.: non-invasively measured spots.

3. Experimental

3.1. Environmental scanning electron microscopy (ESEM) with an energy-dispersive X-ray analyser (EDX)

A Quanta 200 environmental scanning electron microscope from Fei equipped with an energy-dispersive X-ray analyser (Flash X 4010 Bruker) was used to map element distributions. Measurements were carried out in an atmosphere of 0.75 torr of water vapour to prevent electrical charging of the sample surface.

To test the homogeneity of the pellets of pure pigments, the distribution of the main elements was measured by an EDX chemical mapping of the ROI (Region of Interest) of characteristic x-ray lines.

3.2. Raman spectroscopy

A Horiba XploRa Micro-Raman system, equipped with a 532 nm and a 785 nm laser, was used. The maximum power of each source is 25 mW and 90 mW respectively. The excitation wavelength influences, for example, the spectral response of a certain pigment and fluorescence interference, hence, different lasers were used to increase the signal-to-noise ratio. The laser power is controlled using different filters. The reference samples were

measured with filters with transmissions of 1 % or 10 % and the painting with 1 %, 10 % and 25 %. The spectral resolution is managed through different gratings. The grating used was 1200 lines/mm. The spatial resolution is ca. 2 μ m in the plane of the sample surface.

A 50x objective with long focal length was used (Olympus LMPlanFLN50x/0.50, ∞ /0/FN 26.5). For the fibre optics set-up, a 20x objective (Olympus MPlanFNL 20x/0.45, ∞ /0/FN 26.5) was used with the microscope to focus laser into the glass fibre and the 50x with the video-head.

Time of acquisition varied between 0.1 and 20 s and cycles (accumulations) between 1 and 20. Wavelength scale calibration was carried out using a Si standard (520.5 cm^{-1}). Data acquisition and spectra elaboration was performed with NGSLabSpec software. "SuperHead" fibre probes from Horiba for both lasers were also used. With these set-ups, the laser visible light is connected via optic fibre to the remote optical head and a second fibre connects the head to the spectrometer. All measurements were performed in darkness.

To obtain the pigments intensity of the Raman signal the baseline was subtracted from each spectrum and the amplitude of the strongest band in counts was compared. The results were determined as counts (Raman signal intensity) per second of measurement and per Watt of laser intensity (Cnts/Ws). Parameters, such as intensity, objective, grating, time of acquisition and accumulations were kept constant whenever possible. Several sets of measurements were made for the reference samples. Each of them consisted in: 1) measuring the standard crystalline silicon sample to verify the intensity of its characteristic Si-O stretching band at ca. 520 cm^{-1} ; 2) measuring all the samples with all the set-ups available and 3) measure again the silicon standard to ascertain that the intensities of the lasers did not change during the session. Only sets of measurements (three in total) without significant change in the intensity of the silicon band (< 5%) were considered. All the values presented here are an average of the three measurements.

The traditional microscope setup (configuration 1 in Fig 2), was compared with setups for analyses directly on the object (configurations 2a-d in Fig 2), where the laser path is deviated by 90° (using a so-called macro accessory which contains a 45° sloped mirror) and with the fibre optics setup, which allows the examination of an object few metres away from the Raman instrument (configuration 3 in Fig 2).

Table 1 summarises the characteristics of the setups that are schematised in Fig 2

Table 1: Summary of the different set-ups

Setup	Set-up characteristics			Suitable for:
1	traditional microscope configuration			collected samples or small, flat and thin objects
2 a-d	90° deviated laser path by a 45° sloped mirror	a	macro accessory	flat surfaces of small objects
		b	macro accessory + self-made extension tube	flat surfaces
		c	macro accessory + commercial extension tube	any desired surface spot, as long as it is possible to focus the laser on it
		d	commercial stable extension tube	
3	fibre optics'			

As evidenced in Fig 2, due to the microscope design, configuration 2a does not allow the measurements of spots more than ca. 15 cm away from the border of the painting, because of the design of the Horiba system. Only for small paintings (ca. 30 cm) without frame, it is possible to reach all positions. Extension tubes allow the analyses of broader and bulkier objects.

Therefore, an extension tube of 3 cm, placed between the 45° mirror piece and the objective, was self-made (configuration 2b in Fig 2). With this extra accessory, it is possible to analyse canvas (or any other flat object) of any size. There are two types of extension tubes (ca. 20 cm) commercially available. These were also tested and are represented in Fig 2. A simple tube, that can be screwed to the macro accessory (Fig 2c) and an extension, which includes the 45° inclination mirror and is attached directly to the microscope (Fig 2d). The later solution seems to be mechanically more stable as it is fixed in the mounting for the revolving nosepiece.

For the fibre optics' configuration set-up, as seen in Fig 2 configuration 3. This configuration is the most versatile as it allows the analyses of objects with almost any shape.

The painting was analysed only with the 785 nm laser since the Raman spectra acquired from the collected samples in the preceding analysis were acquired only with this laser and comparisons are only made using the same laser. Additionally, not all sampling spots (P) were accessible with all set-ups (e.g. configurations 2a and 2b in Fig 2).

Further restrictions have been implied by the absence of the 785 nm measuring head and the simple commercial extension tube (configuration 2c in Fig 2) due to organisations issues for the measurements of the reference sample.

Samples from the “Cubist still life” were collected and analysed with the experimental configuration 1. The sampling spots are marked as “P” in Fig 1. Subsequently, the painting was analysed with the non-invasive set-ups,

as seen in Fig 3 using the 785 nm laser, since the 532 nm laser caused too high fluorescence signals. The analysed spots are marked ‘M’ in Fig 1. With configuration 2a) it was not possible to reach all spots in the painting as the painting was larger than 30 cm.

Fig 2. Schematic views of configuration 1: traditional microscope setup with the 50x objective; 2: with the a) macro accessory (45° mirror) and b) the short extension tube; c) the simpler commercial tube and d) the more stable one and 3: measuring head connected via fibre optics.

3.3. Raman setup performance evaluation procedure

It has been proposed to use the limit of detection (LOD) as a parameter to compare two different experimental approaches (Vandenabeele, 2013; Vandenabeele & Moens, 2012). In the following, a procedure to calculate the LOD is proposed with the intention to obtain a value to compare experimental set-ups. The authors are aware of the fact that the calculated values may not represent the realistic detection limit given in concentration.

Generally, the smallest signal that can be identified with certainty as a peak in a spectrum should be three times larger than the fluctuation of the total background (shot noise) at the peak position. In counting statistics, i.e. spectra, the fluctuations of the background are equal to the square root of the background. The spectral background is generated by the total shot noise, which contains contributions of scattered light and background fluorescence radiation from the matrix in the analytical volume and noise from various sources. The background subtraction (eq.2) was used to determine the intensity of the background, I_B , by the difference of the intensity of the peak before the background subtraction, I_p , and the intensity of the Raman signal, I_R , after the background subtraction.

$$I_p = I_B + I_R \quad (\text{eq. 1})$$

$$I_B = I_p - I_R \quad (\text{eq. 2})$$

The minimum intensity of a detectable peak sitting on a background of I_B is therefore given as

$$LOD_I = 3\sqrt{I_B} \quad (\text{eq. 3})$$

The LOD_C in concentration is calculated by equation 4, where b denotes the response of the spectrometer on a specific peak of a compound in Cnts/wt%. In quantitative analytical this value is obtained from the calibration curve where b is the slope of the curve.

$$LOD_C = \frac{3\sqrt{I_B}}{b} \quad (\text{eq. 4})$$

As an estimation of b the I_R values of the measurements of the pure pigments was used assuming a straight calibration curve from the concentration at zero to the measured value for a concentration of 100 % of the pigment. The b value for the pure pigment can be calculated as given in the following equation, with x indexing the instrumental set up used:

$$b_{pure}^x = \frac{I_R^x}{100 \text{ wt}\%} \quad (\text{eq. 5})$$

For the measured spectra of anatase the values for LOD_I , LOD_C and b_{pure}^x are given in Table 2. The given values were derived from spectra where the measurement time and accumulations were not always kept constant. The parameters times and accumulations have been adapted for each set up in order to obtain the best possible spectra from the analysed volume, in the way as an operator would work analytical measurements on an art work.

The limit of detection (LOD) was calculated for anatase assuming I_p is the signal (counts) of the strongest peak (143 cm^{-1}) before baseline subtraction and I_R after

subtraction. With values I_B and b the LOD was calculated according to the following equation.

$$LOD_C = \frac{3\sqrt{I_B}}{b_{pure}} \quad (\text{eq. 6})$$

The LOD_C values can be used for a direct comparison of the set-ups whether the LOD_I values give an indication of the peak high necessary for a detectable signal. It is important to be aware of this difference as a configuration with a poor sensibility (as configuration 3 in our study) can have a low LOD_I but a high LOD_C . To avoid misunderstandings we like to emphasize that we do not believe that the LOD_C values are obtained in a way, which would allow using them as a reliable value for the actual limit of detection but are for reference only. The LOD_C values are not believed to give a realistic limit of detection of a setup but are used as index to compare the performance of the set-ups.

4. . Results and Discussion

Measuring reference pure pigments prepared as homogeneous and flat pellets does not represent a real case study but allowed in a simple way to characterize the sensitivity of *in-situ* set-ups, which was the aim of this study.

4.1. Results on reference samples by Environmental scanning electron microscopy (ESEM) with an energy-dispersive X-ray analyser (EDX)

Before the Raman measurements, the pellets of anatase, chrome yellow, cinnabar, minium, phthalocyanine blue and ultramarine were analysed with the ESEM-EDX to ascertain that their composition was homogeneous and not contaminated.

As it can be seen from the ESEM chemical maps in, elements in the ultramarine pellet are heterogeneously distributed. For example, Ca-rich grains (probably calcite) of ca. $10 \mu\text{m}$ diameter are present. These are larger than the Raman spot size (about $2 \mu\text{m}$) and their heterogeneous distribution could lead to very different bands or bands' intensities in the Raman spectra depending on the actual spot analysed. Therefore, this sample was discarded.

4.2. Raman spectroscopy results of reference samples

The spectra obtained for phthalocyanine are shown as example in Fig 4 (Bell, Clark, & Gibbs, 1997; Bouchard & Smith, 2003; Burgio & Clark, 2001; Scherrer, Zumbühl, Delavy, Fritsch, & Kuehnen, 2009).

Fig 3. Device including 45° inclined mirror and tube and fibre optic configuration

Table 2. ESEM chemical mapping of the six pure pigments pellets. The shown chemical elements are indicated in the respective colour for each map.

Fig 4. Uncorrected Raman spectra of Phthalocyanine with setups 1, 2a, 2b, 2d, 3

In the following graphics (Fig 5 and Fig 6), the intensities of each set-up and for each pigment are compared to those obtained with the setup 1 (traditional microscope, configuration 1 in Fig 2) normalized to 1.

The performance index for anatase on a pure pigment was calculated as a LODC, calculated as described in the equations (eq.1-6). The results are summarised in detection of a set-up but are used as index to compare the performance of the set-ups. For a more realistic estimation, other experiments are needed and a more precise determination of b is needed in table 3 and are based on the average of three measurements. The LODC values are not believed to give a realistic limit of the values for the LODC of the configurations 1 and 2 values are lower than for configuration 3. These values confirm the trend of the performance observed during the experiments with various set-ups

Fig 5. Intensities (average of 3) normalised to the performance of configuration 1 measured with each set-up with the 532 nm Laser.

Fig 6. Intensities normalised to the performance of configuration 1 from each set-up with the 785 nm Laser.

Table 3. LOD_I, LOD_C and b for pure pigment calculated for anatase measured with lasers 532 nm and 785 nm (all measurements given for 10% transmission filter)

Set-up	Laser 532 nm			Laser 785 nm		
	LOD _I (Cnts/s)	LOD _C (wt%)	b _{pure anatase} (Cnts/s.wt%)	LOD _I (Cnts/s)	LOD _C (wt%)	b _{pure anatase} (Cnts/s.wt%)
1	274*	0.1*	2690*	69	0.4	165
2a	304	0.1	3113	67	0.4	171
2b	301	0.1	2928	70	0.4	159
2c	Setup not available for these measurements					
2d	295	0.1	2488	70	0.5	142
3	22	8.0	3	Setup not available for these measurements		

* 1 % filter was used; intensity values were multiplied by ten

Fig 7. Uncorrected Raman spectra of sample P9 (setup 1) and spot M20 (setups 2b, 2c, 3)

Fig 8. Intensity normalized to performance of configuration 1 from each setup

4.3. Case study

The pigments identified were: anatase, lazurite/ultramarine, mangan violet, cinnabar, minium, baryte, chrome yellow and Cu phthalocyanine blue. Example spectra of anatase obtained with different setups are seen in Fig 7.

The intensities from the most intense pigment lines obtained from the ‘Cubist still life’ are shown in the following (Fig 8). The values show much more variations than those for the reference samples. Intensities from some for non-invasive configurations are even higher than those obtained with the traditional microscope set-up on a collected sample.

As for the pure pigment the LOD for anatase was calculated and is shown in table 4. A value for the configurations 2c and 3 are not available as the corresponding *b* values were not available. The LOD_C values for configurations 1, 2a, 2b and 2d were all slightly higher than compared to the results on the pure anatase. With values from 0.3 wt% to 0.8 wt% the LOD_C value indicate still a better performance than the external measuring head on the pure pigment with 8 wt%.

Table 4. LOD_I taken from the background of the measurements of the case study, LOD_C and *b* for pure pigment calculated for anatase measured with the laser 785 nm

Set-up	Laser 785 nm		
	LOD _I (Cnts/s)	LOD _C (wt%)	<i>b</i> pure anatase (Cnts/s.wt%)
1)	47	0.3	165
2a)	91	0.5	171
2b)	72	0.4	159
2c)	no <i>b</i> available for this setup		
2d)	117	0.8	142
3)	no <i>b</i> available for this setup		

4.4. Comparison of the set-ups

The use of the procedure established in this article to calculate the LOD_C value for the comparison of the performance of an experimental set-up gives us the possibility to benchmark the various experimental configurations with regard to the obtained signal and background intensities.

All instrumental configurations allowed identifying the pigments anatase, chrome yellow, minium, cinnabar and copper-phthalocyanine blue in the samples. Depending on the set-up, variations were found in the intensity of the signals of the pigments. The horizontal beam configurations (2a, 2b and 2d) on the reference samples showed spectral responses of 0.8 to 1.2 of the intensities measured with the microscope (configuration 1). The intensities from the fibre optics (configuration 3) dropped to 0.1. The intensities from the horizontal beam set-ups were comparable to the microscope whether the use of fibre optics introduced a significant loss of signal.

This drop of intensity leads also to a less favourable LOD_C value for the configuration 3. All configurations without external measuring head gave a LOD_C value of about 0.1 wt% in contrast to the value of 8 wt% for the configuration 3. These results show the potential of horizontal beam set-ups for the analyses of artworks as their performance is equivalent to the traditional microscope configuration. On the painting, the non-invasive response from the horizontal beam set-ups (2a-d) shows much larger fluctuations in intensity with respect to the microscope configurations: from 0.15 to 1.85. Compared to the reference samples, the paint layer of the painting is much more heterogeneous as it is composed of pigment mixed with filler and binding media at μ m scale. This induces a momentum of random to the composition of the analysed volume, influencing the intensity regardless of the set-up used. Again, the intensities of the fibre optic set-up dropped to ca. 0.1. This suggests that the choice of the measurement spot on the painting is more important than the choice between the different set-ups of configuration 1 and 2. However, comparing configurations 1 and 2, difficulties in positioning the horizontal beam set-up can hamper the acquisition of a good spectrum. Either the Raman spectrometer or the artwork has to be moved in a μ m scale to position the laser spot to the area of interest. This requires often improvements of the experiment, especially regarding the mechanical stability of the analytical set-up as well as the artwork and its support or the use of a precision motor driven stage to move the art work.

5. Conclusions

In this work, different non-invasive micro-Raman set-ups were compared to the traditional microscope set-up with respect to their spectral response efficiency. For the non-invasive measurements, four horizontal beam set-ups and an external measuring head connected to the spectrometer by fibre optics were used. Using limit of detection values as index, their performances were compared. Reference pigment samples and a painting were studied.

The horizontal beam configurations showed spectral responses in signal intensity very similar to those of the traditional microscope. These results show the potential of horizontal set-ups for the analyses of artworks, as their performance is equivalent to the traditional microscope configuration. Neither the laser's path deviation nor the extension tubes (self-made or commercial) affected significantly the spectral response.

All measurements performed with the fibre optics' set-up originated a significant lower spectral response (lower signal intensity in the range of 10% compared to the other configurations). These are the finds of our equipment and may not be generalized to all fibre based configurations. .

The mode of operation for measurements on the painting was quite different from the measurement on paint samples. Working with the traditional set-up allows a much better choice of the measurement spot. It is possible to avoid binding media, dirt and other extraneous materials or layers and to focus on a spot, which contains a high proportion of pigment. In contrast, non-invasive measurements with the horizontal set-ups and the fibre optics measurement head are bound to access the painting via its surface with all its dirt and varnish layers. Therefore, it was more difficult to focus on a pigment grain.

The movement of the object relative to the focal spot of the Raman spectrometer requires a precision in positioning in the range of several micrometres, which is difficult to obtain without the help of a precision motor-driven xyz-stage. An additional challenge working with a canvas painting is to keep the object steady, especially the canvas in the central area of the painting can vibrate, during the measurements, which is very difficult to prevent under the necessary precautions to prevent mechanical damage to the painting.

Despite the challenge of positioning set-up in front of the object, any of the horizontal beam set-ups are proficient options for a non-invasive measurement. An inherent advantage of the non-invasive approach is the possibility to probe much more spots on the objects as in would be possible with a sampling. Therefore, the

horizontal beam set-up allows to obtain a much more complete understanding of the pigments palette used without the risk that samples do not represent the full pigments palette and at the same time using a very effective configuration of the Raman spectrometer with high spectral response.

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7. Conflict of Interest

Authors declared no conflict of interest.

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