

# Pigment and Binder Concentrations in Modern Paint Samples Determined by IR and Raman Spectroscopy

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**Abstract:** Knowledge of the techniques employed by artists, such as the composition of the paints, colour palette, and painting style, is of crucial importance not only to attribute works of art to the workshop or artist but also to develop strategies and measures for the conservation and restoration of the art. While much research has been devoted to investigating the composition of an artist's materials from a qualitative point of view, little effort has been made in terms of quantitative analyses. This study aims to quantify the relative concentrations of binders (acrylic and alkyd) and inorganic pigments in different paint samples by IR and Raman spectroscopies. To perform this quantitative evaluation, reference samples of known concentrations were prepared to obtain calibration plots. In a further step, the quantification method was verified by additional test samples and commercially available paint tubes. The results obtained confirm that the quantitative method developed for IR and Raman spectroscopy is able to efficiently determine different pigment and binder concentrations of paint samples with high accuracy.

In the last few decades, the field of heritage science of contemporary art has become very important at the international level due to the importance of preserving modern cultural heritage with suitable science-based treatments.<sup>[1]</sup> With the development of synthetic organic chemistry at the beginning of the 20th century, many different kinds of organic materials have been used for the creation of artistic objects; among the most employed in the field of art are alkyd and acrylic polymers that are largely used as binders. Alkyd binders are oil-modified polyester resins made up of a poly-

hydric alcohol (or polyol) and a polybasic carboxylic acid.<sup>[2]</sup> The majority of alkyd paints uses glycerol or pentaerythritol as a polyol and phthalic anhydride as the polybasic acid. The addition of oil and free fatty acids allows a flexible polymer suitable for a paint film to be obtained.<sup>[3]</sup> Due to their low costs and fast drying times combined with good optical properties, these polymers have become the modern substitutes of traditional drying oils.<sup>[4]</sup> However, the most common and versatile synthetic polymers are the acrylates. Acrylic copolymers, usually composed of methyl methacrylate (MMA) and either ethyl acrylate (EA) or *n*-butyl acrylate (nBA), are often used as painting binding media.<sup>[2]</sup> Their stability, excellent optical and mechanical properties, and rapid drying have made them the most used synthetic polymeric binders in the field of art materials.<sup>[4]</sup>

The synthetic inorganic pigments chosen in this study, namely, artificial ultramarine blue, hydrated chromium oxide green, and cadmium sulphide, represent 80 % of the inorganic pigments presently used in the world.<sup>[5]</sup> Compared to dyes of organic origin, they are made of grains of insoluble materials in a dispersing phase, forming a suspension of different consistency.<sup>[6]</sup> The three pigments selected possess high chemical and physical stability, making them the most suitable pigments for quantitative analysis.<sup>[7]</sup>

The qualitative identification of binders and pigments in paints by non-invasive analytical techniques is currently highly elaborated.<sup>[8,9]</sup> Methods such as IR and Raman spectroscopies, as well as X-ray fluorescence, which does not require sample removal from the art object and allows investigations in situ, are the methods of choice for qualitative analyses of pigments and binders.<sup>[8–10]</sup> Concerning the quantification of paint mixture components and their ratios by non-invasive techniques, relatively little research has been done.<sup>[11,12]</sup>

The aim of this study was to explore the potential of ATR (attenuated total reflectance)-FTIR and Raman spectroscopies to quantify the relative concentrations of pigments and binders in paint samples. Samples of known pigment and binder concentrations were prepared and analysed by ATR-FTIR and Raman spectroscopies in order to find a fitting quantification method. In a further stage, characteristic spectral features that may act as signatures for the composition of pigment and binder had to be defined. To create calibration curves, the integration method to obtain the spectral band areas ascribed to different pigments and binders had to be evaluated. As a proof of concept, the quantification method was tested by additionally prepared samples and a commercially available paint tube, where we could show

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that the proposed method can be used to quantify the composition of two-component paint mixtures.

To obtain detailed information about the pigments and binders under consideration, their chemical identification is necessary. This evaluation is not only important for qualitative analysis but also fundamental for developing a fitting quantitative method. In the first step, the pure pigments (PG18, PB29, and PY37) and binders (alkyd and acrylic) were analysed by ATR-FTIR and Raman spectroscopies (see the Experimental Section, Table S1 and Figures S1–S4 in the Supporting Information), and the chemical species identified (Table 1, Table 2, Table 3, Table 4).

During the qualitative analysis, differences between ATR-FTIR and Raman spectroscopy measurements are observed, depending on the type of pigment and binder. In the ATR-FTIR results, the two binders considered in this study are distinguished by the presence of the phthalic component in the alkyd binder (1254–1069–747–709  $\text{cm}^{-1}$ ). With Raman spectroscopy, this distinction is more detailed, as the different polarizabilities of the two binders' molecules lead to a more specific characterization of the functional groups, which are

**Table 1:** ATR-FTIR band assignment of pigments.<sup>[3, 8, 10, 13, 14]</sup>

Pigments	Wavenumber [ $\text{cm}^{-1}$ ]	Assignment
PY37	< 600	below detector cut-off
PB29	981	Si–O vibrations
PG18	3077	O–H vibrations
	547–483	Cr–O vibrations

**Table 2:** Raman shift assignment of pigments.<sup>[15–17]</sup>

Pigments	Wavenumber [ $\text{cm}^{-1}$ ]	Assignment
PY37	290	optical longitudinal mode
	595	2° optical longitudinal mode
PB29	255	lazurite $\delta$ ( $S_3^-$ )
	547	lazurite $\nu$ ( $S_3^-$ )
	1097	lazurite $\nu$ ( $S_3^-$ )
PG18	488	hydrated oxide
	578	hydrated oxide
	271	hydrated oxide

**Table 3:** ATR-FTIR band assignment of binding media.<sup>[3, 18–21]</sup>

Acrylic Plextol D498 wavenumber [ $\text{cm}^{-1}$ ]	Alkyd Medium 4 wavenumber [ $\text{cm}^{-1}$ ]	Absorption band assignment
2955–2874	2925–2854	C–H stretching (sym-asym)
1726	1720	C=O stretching
	(oil and phthalate)	
1450	C–H bending	C–H bending
1237–1144	1250	C–O–C stretching (asym)
	(phthalate)	
	1170	C–O stretching
	(oil)	
	1114	C–O–C stretching (sym)
	(phthalate)	
	1069	C=C unsaturated in-plane deformation
	(phthalate)	
	747–709	aromatic out-of-plane bending
	(phthalate)	

**Table 4:** Raman shift assignment of binding media.<sup>[20, 22]</sup>

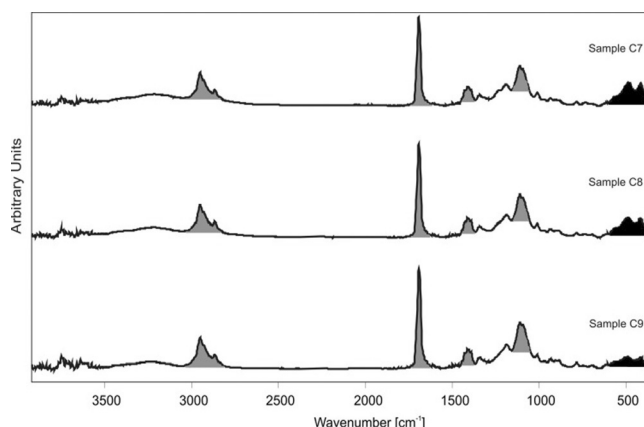
Acrylic Plextol D498 wavenumber [ $\text{cm}^{-1}$ ]	Alkyd Medium 4 wavenumber [ $\text{cm}^{-1}$ ]	Band assignment
594	–	C=O bending
–	651	C=O wag
808–839	–	C–H rock
–	873	C–O–C stretching, symm. (aliph. ether)
–	1003–1042	ring breathing (o-phthalate)
–	1166	C–O stretching (alcohol)
1299	1299	C–H twist/rock
1449	1442	C–H bending
–	1601	C=C stretching (aromatic)
1726	1725	C=O stretching
–	2854	C–H stretching (–CH <sub>2</sub> – symm.)
2876	–	C–H stretching (–CH <sub>3</sub> )
2933	2900	C–H stretching (–CH <sub>2</sub> – asymm.)
–	3070	C–H stretching (aromatic)

less visible in the ATR-FTIR analysis. Regarding the pigments, in the case of ATR-FTIR, artificial ultramarine blue is only identified by the vibration of the Si–O bond (981  $\text{cm}^{-1}$ ), while with Raman, it is possible to identify more vibrational modes of the molecule (255–547–1097  $\text{cm}^{-1}$ ). Using this technique, it is also possible to distinguish artificial ultramarine blue from the natural one.<sup>[15]</sup> In the case of hydrated chromium oxide green, the identification is more simple by ATR-FTIR spectroscopy, which characterizes both the hydrated part of the molecule (3077  $\text{cm}^{-1}$ ) and the vibration of the oxide bond (547–483  $\text{cm}^{-1}$ ). With Raman, however, this attribution is not yet completely clear and generally, the two resulting bands are attributed to the hydrated oxide part.<sup>[16]</sup> Finally, the cadmium sulfide yellow pigment can only be identified by Raman spectroscopy, as this pigment has no absorption bands in the mid-IR region.<sup>[23]</sup>

After qualitative characterization of the materials used for the test samples by ATR-FTIR and Raman spectroscopies, a quantitative analysis method was established. This requires a detailed study of the spectral features that may act as signatures of composition (pigment and binder concentrations). For this reason, samples with different pigment/binder ratios were prepared (Tables 9 and 10) and subsequently analysed by ATR-FTIR and Raman spectroscopy. The method proposed for a precise and accurate determination of the relative concentration of binders and pigments is common for both techniques and is based on the best possible calibration curves obtained by the homemade reference samples of known pigment and binder concentration. For this, it is assumed that the area of each spectral band is directly proportional to the concentration of the chemical group associated with it<sup>[24]</sup> and hence their relationship is represented by a straight line with the equation  $y = mx$ . Straight line calibrations can be obtained by linear regression of the experimental points representing the ATR-FTIR or Raman spectral band area versus the relative concentration of the corresponding pigment or binder present in a mixture of

reference samples. It has to be taken into account that the value of the area of any spectral band depends on the choice of the baseline used for the integration. Usually, the baseline for integration is calculated automatically by the specific software of the IR and Raman spectroscopy instruments applied. It is defined on the basis of standard values of the range of the absorption bands in the mid-IR or Raman shifts characteristic of the vibrational mode of the chemical group responsible for the band. To better estimate the quality of the automated baseline integration from the software, it was compared to manually choosing the baseline integration, which is discussed later.

Figure 1 depicts the manually chosen integration range for the ATR-FTIR spectral bands of the test samples (C7–C9, Table 9), containing different ratios of acrylic binder (Plextol D498) and hydrated chromium oxide green (PG18) as



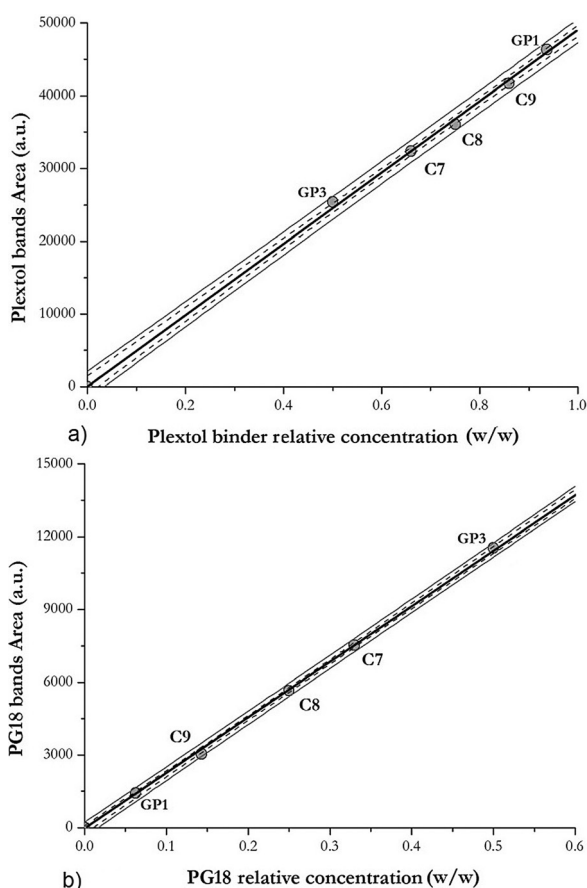
**Figure 1.** Calculated band areas of ATR-FTIR spectra of the reference samples with a pigment/binder ratio of 1:2 (C7), 1:3 (C8), and 1:6 (C9): the grey areas represent bands of acrylic binder (Plextol D498), and the black ones represent the bands of hydrated chromium oxide green pigment (PG18).

a pigment. The grey areas represent the bands for the main functional groups of the acrylic binder, and the green ones represent the bands of the hydrated chromium oxide green pigment. It is clearly visible that with an increasing amount of binder in the mixture ( $C7 < C8 < C9$ ), the absorption band areas of the pigment decrease. The same integration procedure was also performed with the obtained Raman spectra (Figure S5). All of the different pigment and binder mixtures summarized in Table 9 were determined and evaluated automatically by software, and the integration of the spectral bands was manually optimized. The values of these calculated spectral band areas are the basis for the calibration curves. To obtain accurate and precise data for calibration, we propose that the criterion of choice of the integration range of the spectra (either software automated or manually) is one, which allows a maximum value of the correlation coefficient  $R^2$  (acceptability range between 0.95 and 1.00) of the linear regression with zero intercept. This is in agreement with the expected proportionality between band area and concentration of the related chemical species. This entails the narrowest confidence and prediction band.

The calibration lines were developed for six different pigment and binder combinations, and for each one, five different P/BM ratios were considered. Table 5 shows the composition of the sample mixtures used for the calibration linear equation and the related  $R^2$  values for the automated software baseline integration and the optimized ones (Table 5, values A and B, respectively). The comparison of

**Table 5:** Comparison of the correlation coefficients  $R^2$  of the linear calibration obtained by integration of the spectral bands based on the wavenumber ranges determined by the software (A) and on those optimized by the above-described procedure (B).

Ratio (Table 9)	Components Binder/Pigment	Method	$R^2$ coefficient values		B range [ $\text{cm}^{-1}$ ]
			A	B	
C1 C2 C3	acrylic binder	ATR-FTIR	0.97358	0.99958	2980–2711
BP1 BP3		Raman	–	–	–
		ATR-FTIR	0.97567	0.99956	1024–875
	artificial ultramarine blue	Raman	0.95069	0.99972	357–514
BA2 BA3 NC4 NC5 NC6		ATR-FTIR	0.96595	0.99977	2898–2667
	artificial ultramarine blue	Raman	–	–	–
		ATR-FTIR	0.97178	0.99976	1024–875
		Raman	0.94581	0.99962	357–514
C7 C8 C9 GP1 GP3	acrylic binder  chromium oxide green	ATR-FTIR	0.95975	0.9998	2980–2711
		Raman	0.97079	0.99946	2846–3099
		ATR-FTIR	0.98011	0.99981	669–499
		Raman	0.97496	0.99983	339–463
GA1 GA3 NC10 NC11 NC12	alkyd binder  chromium oxide green	ATR-FTIR	0.96645	0.99982	2898–2667
		Raman	0.95852	0.99968	2853–3056
		ATR-FTIR	0.97099	0.99954	669–499
		Raman	0.93107	0.99966	339–463
YP1 YP3 C13 C14 C15	acrylic binder  cadmium yellow	ATR-FTIR	0.96444	0.99967	2980–2711
		Raman	0.98181	0.99933	2846–3099
		ATR-FTIR	–	–	–
		Raman	0.96122	0.99961	82–273
YA2 YA3 NC16 NC17 NC18	alkyd binder  cadmium yellow	ATR-FTIR	0.94867	0.99961	2898–2667
		Raman	–	–	–
		ATR-FTIR	–	–	–
		Raman	0.95849	0.99965	82–273

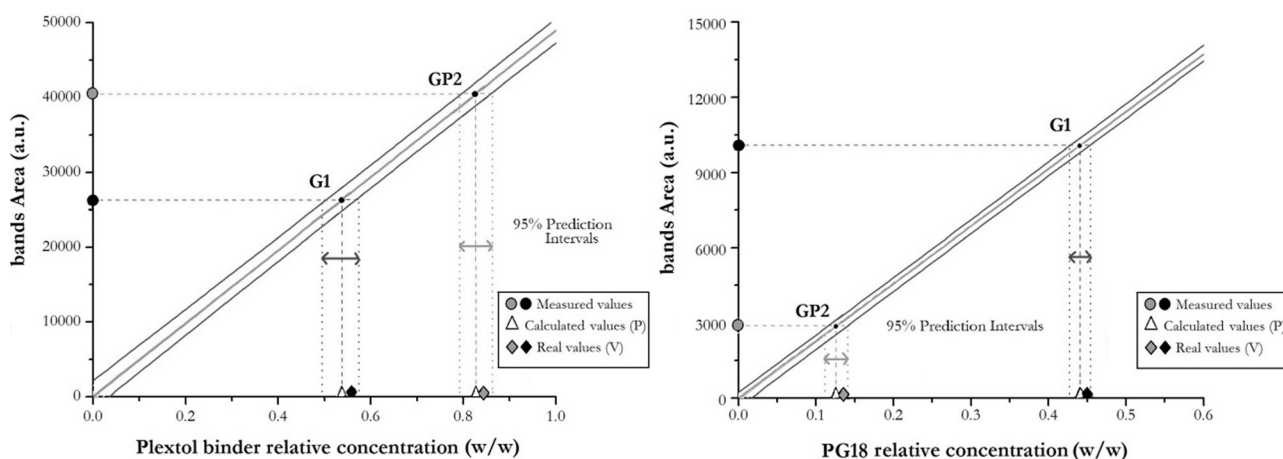


**Figure 2.** Linear calibration ( $y = mx$ ) of the Plextol acrylic binder (a) and PG18 (hydrated chromium oxide green) pigment (b) obtained by ATR-FTIR results of the reference samples (C7–C9, GP1, GP3, see Table 9): a) Plextol band areas of the main functional groups of acrylic binder versus relative concentration of binder of the reference samples. b) PG18 band areas of the main functional groups of hydrated chromium oxide green versus relative concentration of PG18 of the reference samples. Grey and black dotted lines represent the prediction and confidence bands, respectively.

$R^2$  values A and B clearly shows higher  $R^2$  values for the optimized ones, for all mixtures. An example of the obtained calibration curves is presented in Figure 2. It shows the linear trend for the binder (a) and pigment (b) calculated from the ATR-FTIR spectra which were obtained from 5 different test sample mixtures of PG18 and Plextol D498 (Table 9: C7–C9, GP1, GP3). The straight line equation represents the best linear fitting of the points with zero-crossing of the intercept. The calibration curves for the other pigments obtained by ATR-FTIR and Raman spectroscopic measurements are shown in Figures S6–S9.

Once the precision of the calibration model with the test samples was verified, it was possible to validate the proposed quantification method by calculating the different relative binder and pigment concentrations of 12 samples prepared by different operators using the same paint materials with different pigment/binder (P/BM) ratios (Tables 9 and 10, Experimental Section, grey part).

As an example for the quantification, the test samples G1 and GP2 (Table 9 and 10) were analysed by ATR-FTIR and Raman spectroscopies, and the integration values were calculated according to the method described before and quantified using the previously obtained straight line calibration. Figure 3 presents the values of the relative concentration of the test samples G1 and GP2, which are determined by the correspondence of the band area values via the linear regression. Hence, from the measured values of the band area (y-axis), the calculated concentration values (x-axis) are obtained, together with the uncertainty range given by the prediction bands (95 % probability) of the linear calibration best fit (red lines in Figure 3). To estimate the error made in the determination of the relative concentration of each component, the percentage values of discrepancy between the real value and the calculated one are determined (Table 6). They vary from 2 to 3 % for the binder and pigment of sample G1 for both ATR-FTIR and Raman measurements and for the pigment of sample GP2 for both techniques. This indicates a contained and well satisfactory dispersion of the data obtained.



**Figure 3.** Examples of the proposed quantitative method applied to test samples made of Plextol D498 acrylic binder + hydrated chromium oxide green pigment analysed by ATR-FTIR; the black lines represent the prediction bands. Each calculated value (P) presents a prediction interval with 95 % probability to contain the real value (V). The same evaluation for the Raman spectroscopy results can be found in Figure S10.



**Table 6:** Comparison of real and calculated concentration values of acrylic green G1 and GP2 test samples.

	P/BM ratio	Real relative concentration values (w/w)		Calculated relative concentration values (w/w)		Percentage discrepancy [%]			
		BM	P	BM	P	ATR-FTIR		Raman	
						BM	P	BM	P
G1	1:1.2	0.55	0.45	0.54	0.44	2.4	2.2	2.9	2.2
GP2	1:6	0.86	0.14	0.83	0.13	3.8	12.6	3.6	9.8

Table 7 summarizes the results obtained for the 12 test samples for the validation of the proposed evaluation method. The last column presents the average of the calculated pigment/binder (P/BM) ratio obtained from the calibration linear equation. The results clearly show that the calculated pigment-to-binder ratios match very well the ratios calculated in the preparation of the samples. The relative concentration values obtained for binder and pigment in the test samples and the percentage variation can be found in Tables S2,S3.

To further evaluate the accuracy of the quantification method proposed, one commercial paint sample was tested. The sample was produced by the manufacturer Schmincke® and is made of acrylic binder in a mixture of chromium hydrated oxide pigment PG18 (PRIMAcril, Schmincke) and unknown additives. The manufacturer indicated a P/BM ratio

**Table 7:** Quantitatively determined pigment and binder fractions of the test samples on the basis of the optimized straight line calibration for both ATR-FTIR and Raman spectroscopies. Pigment and sample acronyms are defined in Tables 9 and 10.

Sample name	Test samples		Prepared P/BM ratio	Calculated P/BM ratio
	Binder (B)	Pigment (P)		
GP2	Plextol	PG18	1:6.0	1:6.45
G1	Plextol	PG18	1:1.2	1:1.22
GA2	Alkyd	PG18	1:2	1:2.00
G2	Alkyd	PG18	1:1.5	1:1.51
BP2	Plextol	PB29	1:2	1:1.95
B1	Plextol	PB29	1:3	1:3.04
BA1	Alkyd	PB29	1:2	1:2.00
B2	Alkyd	PB29	1:0.7	1:0.70
YP2	Plextol	PY37	1:0.5	1:0.49
Y1	Plextol	PY37	1:0.4	1:0.38
YA1	Alkyd	PY37	1:2	1:2.00
Y2	Alkyd	PY37	1:0.7	1:0.68

**Table 8:** Comparison of the known and calculated relative concentration values of the Schmincke sample.

Sample	P/BM ratio	Method	Real con. values (w/w)		Calc. con. values (w/w)		Percentage discrepancy [%]	
			B	P	B	P	B	P
PRIMAcril, Schmincke	1:2.7	ATR-FTIR	0.73	0.27	0.708	0.287	3	−6.3
		Raman	0.73	0.27	0.714	0.286	2.2	−5.9

of 1:2.7. The experimental procedure performed was the same procedure used for the analysis of the previous test samples. The binder and pigment relative concentrations were calculated through the straight line calibration equation previously determined. The values obtained are shown in Table 8 (graphical evaluation: Supporting Information Figure S11). For the ATR-FTIR analysis, a ratio of P/BM 1:2.4 was calculated, and for Raman, 1:2.5 was calculated, which are very close to the values given by the manufacturer. The discrepancy from the real relative concentrations could be because commercial tube paints also contain additives and other organic constituents which were not considered in the test samples and are also not considered clearly in the description of the commercially available material. From these results, it is possible to confirm that the proposed quantitative approach is able to determine with good accuracy the relative concentrations of pigment and binder in commercial tube samples.

The results presented suggest that it is possible to use FTIR and Raman spectroscopies to obtain reasonable estimates of pigment/binder ratios, e.g., relative concentrations in a paint film, given a suitable set of reference spectra from the test samples prepared over the range of workable mixture compositions.

The first aim of this work was to carry out a qualitative analysis using non-invasive spectroscopic techniques, such as Raman and ATR-FTIR. The results of this first evaluation allowed identifying and characterizing the spectral features of the different binders and pigments used. This precise identification was of crucial importance to develop a fitting quantitative evaluation for different pigments and binders within paint mixtures. The results impressively show that the real and calculated concentration values have a limited discrepancy in percentages. Moreover, all of the concentration values calculated using the calibration equations fell within the prediction intervals. All these parameters indicate that the quantitative model used for FTIR and Raman spectroscopies is valid, reproducible, and reliable. These findings may extend the utility of IR and Raman measurements in the field of heritage science, by making it possible to characterize artists' paints in a quantitative way without sampling. While the proof-of-concept analyses were promising, more detailed studies will be done to estimate the effects of other variables such as surface texture, pigment particle size and layer thickness, which were not considered in the present study. However, from the promising results obtained, it is expected that the quantification method presented serves as a valuable tool for the investigation of cultural heritage

objects. Furthermore, these investigations may contribute to the finding of useful measures for specific conservation and restoration treatments of real art objects and also lead to a better understanding of the chemical degradation processes of such materials.<sup>[25]</sup>

## Experimental Section

The reference and test samples were prepared with different pigment-to-binder ratios (P/BM). After weighing the various amounts of binders and pigments (Supporting

Information Table S1), they were mixed with a muller and cast on glass slides. The wet film thickness of these paint samples was 150  $\mu\text{m}$ . In total, 36 samples were prepared, 18 with Plextol D498 mixed with the three different pigments, and the same for Alkyd Medium 4. 30 of these samples were used to represent the references useful for developing the quantitative method. A detailed description can be found in Table 9. To verify the precision and the accuracy of the straight line calibration developed, additional test samples (marked grey), prepared by different operators (Table 9, Table 10), were quantitatively analysed.

**Table 9:** Mixtures of reference and test samples (bold) indicating sample name, mixing ratio and addition of  $\text{H}_2\text{O}$ .

Mock-ups	Sample name	Ratio (P/BM) w/w [g]	$\text{H}_2\text{O}$
Plextol D498 + PG18	C7	1:2	10%
Plextol D498 + PG18	C8	1:3	12.5%
Plextol D498 + PG18	C9	1:6	14.3%
Plextol D498 + PG18	GP1	1:15	14.3%
Plextol D498 + PG18	GP3	1:1	10%
<b>Plextol D498 + PG18</b>	<b>GP2</b>	<b>1:6</b>	<b>12.5%</b>
Plextol D498 + PB29	C1	1:2	–
Plextol D498 + PB29	C2	1:3	–
Plextol D498 + PB29	C3	1:6	–
Plextol D498 + PB29	BP1	1:5	–
Plextol D498 + PB29	BP3	1:7	–
<b>Plextol D498 + PB29</b>	<b>BP2</b>	<b>1:2</b>	–
Plextol D498 + PY37	C13	1:2	10%
Plextol D498 + PY37	C14	1:3	12.5%
Plextol D498 + PY37	C15	1:6	14.3%
Plextol D498 + PY37	YP1	1:1	10%
Plextol D498 + PY37	YP3	1:10	14.3%
<b>Plextol D498 + PY37</b>	<b>YP2</b>	<b>1:0.5</b>	<b>12.5%</b>
Alkyd Medium 4 + PG18	NC10	1:2	–
Alkyd Medium 4 + PG18	NC11	1:3	–
Alkyd Medium 4 + PG18	NC12	1:6	–
Alkyd Medium 4 + PG18	GA1	1:1	–
Alkyd Medium 4 + PG18	GA3	1:5	–
<b>Alkyd Medium 4 + PG18</b>	<b>GA2</b>	<b>1:2</b>	–
Alkyd Medium 4 + PB29	NC4	1:2	–
Alkyd Medium 4 + PB29	NC5	1:3	–
Alkyd Medium 4 + PB29	NC6	1:6	–
Alkyd Medium 4 + PB29	BA2	1:1	–
Alkyd Medium 4 + PB29	BA3	1:5	–
<b>Alkyd Medium 4 + PB29</b>	<b>BA1</b>	<b>1:2</b>	–
Alkyd Medium 4 + PY37	NC16	1:2	–
Alkyd Medium 4 + PY37	NC17	1:3	–
Alkyd Medium 4 + PY37	NC18	1:6	–
Alkyd Medium 4 + PY37	YA2	1:1	–
Alkyd Medium 4 + PY37	YA3	1:0.5	–
<b>Alkyd Medium 4 + PY37</b>	<b>YA1</b>	<b>1:2</b>	–

**Table 10:** Additional prepared test samples.

Mock-ups	Sample name	Ratio (P/BM) w/w in g
Plextol D498 + PB29	B1	1:3
Alkyd Medium 4 + PB29	B2	1:0.7
Plextol D498 + PG18	G1	1:1.2
Alkyd Medium 4 + PG18	G2	1:1.5
Plextol D498 + PY37	Y1	1:0.4
Alkyd Medium 4 + PY37	Y2	1:0.7

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** acrylic and alkyd binders · FTIR spectroscopy · inorganic pigments · modern paints · Raman spectroscopy

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