Identification of synthetic organic pigments in contemporary artists’ paints by FT-IR and FT-Raman: an advanced analytical experiment.

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Identification of Synthetic Organic Pigments in Contemporary Artists’ Paints by FT-IR and FT-Raman: An Advanced Analytical Experiment

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ABSTRACT
The identification of coloring substances is a relevant task in the field of conservation and restoration, but it can be challenging as in real samples the target analytes are inserted in a very complex matrix made of binders and additives. Understanding this concept is fundamental for upper-division undergraduate students interested in conservation science; therefore, this laboratory experiment aims to make students aware of this problem and leads them to develop a simple protocol combining two spectroscopic techniques, FT-IR and FT-Raman, and basic chemical treatments to overcome this difficulty. The case of the two quinacridone pigments, PR122 and PV19, is presented and discussed, although the same approach can be extended to other commercially available organic pigments.

GRAPHICAL ABSTRACT

KEYWORDS

INTRODUCTION
The identification of coloring substances in works of arts represents an important task for conservation scientists, as it is relevant in the field of conservation itself and restoration.

The development of spectroscopic analytical techniques contributed substantially to gain this information, reducing time and sample amount required for the analyses. Anyway, the task can still be rather challenging as, in real samples taken from original paintings, the target analyte is inserted in a very complex matrix consisting of binders and additives. In this context, synthetic organic pigments, currently employed in contemporary art because of their excellent chromatic properties, pose a considerable problem. Recognizing them is in fact quite difficult because of their very low concentration in painting materials, due to their very high tinting strength. In addition, the number of synthetic organic pigments is significantly larger than that of pigments forming the palette of painters.
before the 20th century. Moreover, the application of those spectroscopic techniques commonly employed for the identification of traditional inorganic pigments suffers from some limitations when applied to organic compounds: indeed, X-ray fluorescence analysis is unable to detect light elements, Raman spectroscopy is affected by the problem of fluorescence background and Fourier-transform infrared (FT-IR) spectra are dominated by the signals due to binders and additives, which hide the weaker ones due to the pigment.

Other laboratory experiments that deal with chemistry for the characterization of coloring substances in art have been proposed. These include the use of visible reflectance spectroscopy for the identification of pigments1,2 and the application of Raman and SERS spectroscopy for the investigation of red natural colorants.3 Moreover, the synthesis of several inorganic pigments combined with different historical binders to create a paint has been proposed to give students the opportunity to learn what paints are made of and how, acquiring in the meantime simple chemical concepts such as stoichiometry, precipitation, and solubility.4-7

Starting from this scenario, this laboratory experiment for upper-division undergraduate students interested in the field of conservation science is designed not only for the identification of synthetic organic pigments, but also for making students aware of the complexity of their investigation in real artists’ paints. Beside applying two spectroscopic techniques commonly employed in analytical chemistry and already proposed in other experiments—IR and Raman spectroscopy3,8,9—students are led to develop a simple protocol based on spectroscopic techniques to overcome this difficulty. In this way, combining case studies and a critical approach (an already proven successful method10), this laboratory experience involves students in using chemistry and chemical instrumentation to solve problems. Moreover, a relatively recent category of pigments, synthetic organic pigments, has been proposed for the first time to the best of our knowledge for such an educational experiment.

In particular, students are presented with two synthetic organic pigments commonly employed by contemporary artists, quinacridone magenta PR122 and violet PV19, in three different forms: pure powder, commercial acrylic formulation, and oil formulation (only for PR122 in this example). Students are then faced with the challenge of identifying the two compounds responsible for color in each paint sample by means of two different vibrational spectroscopic techniques, FT-IR and FT-Raman, possibly combined with X-ray diffraction. The students first attempt measurements on the three samples as such. Thus, they observe that it is not possible to recognize directly the pigment in the commercial formulation but are able to identify the inorganic additives contained therein, as those signals are predominant in the obtained spectra. Afterwards, students are asked to experiment with chemical treatments aimed at removing such components that prevent the identification of the quinacridone pigments in the paints.

The procedure is designed for groups of 3 or 4 students within a 6 h period and it includes: (i) sample preparation; (ii) experimentation of chemical treatments suitable for removing the interfering substances; and (iii) FT-IR and FT-Raman analyses on the samples before and after treatment. A chemical laboratory equipped with a FT-IR and a FT-Raman spectrometer is obviously required.

**LEARNING OBJECTIVES**

The learning objectives of this laboratory experiment are multiple and all the levels of objectives reported in the new Bloom’s Taxonomy11 (remember, understand, apply, analyze, evaluate, create) are addressed, as will be detailed below. In particular, students gain confidence with two spectroscopic methods commonly employed in the field of conservation science and are called upon to experiment with a purpose-built chemical approach and solve the problem of analyzing a complex mock-up sample of a real artistic paint. Students are expected to use experimental observations to understand the situation, formulate hypotheses, propose a practical method, and finally optimize the experimental procedure in order to achieve their purpose. In this respect, the interpretation of FT-IR and FT-Raman spectra and the knowledge of some chemical concepts fundamental in the field of conservation science are the starting point to carry out the experiment. The comparison of the performances of the two vibrational spectroscopic techniques employed in the experiment is an additional outcome. Finally, the students are asked to present the obtained results in a detailed laboratory report.
THEORY

Quinacridone Pigments

Quinacridones are high-performance pigments that have been extensively since their introduction in 1950 in paints, in printing inks, and for the coloration of plastics and textiles. They are very stable to light, heat, acids, alkali, and solvents and, because of their brightness and high tinting strength, are really appreciated in the artistic field. They are very versatile pigments as methylation or halogenation of the quinacridone rings leads to different shades, from bluish-red to warm magenta. Pigment Violet 19 (PV19) and Pigment Red 122 (PR122) are among the most currently employed quinacridone pigments. The former, characterized by a red-violet shade, is the linear trans-quinacridone (QA); the latter is the 2,9-dimethylquinacridone (DMQA), whose color is shifted to reddish-magenta by the presence of two methyl groups. The chemical structures of the pigments are represented in Figure 1.

![Chemical structures of (a) PV19 (QA) and (b) PR122 (DMQA).](image)

Except for concentrated sulfuric acid, quinacridones are insoluble in most solvents. Moreover, the quinacridone pigments exhibit a significant fluorescence emission, thus limiting the use of conventional Raman spectroscopy for their identification.

**FT-IR and FT-Raman Spectroscopies**

FT-IR spectroscopy is based on the absorption of mid-IR radiation associated with transitions between vibrational energy levels. It is a reliable technique for the identification of organic as well as many inorganic compounds, owing to the fact that the spectrum is unique for a given compound. In addition, the possibility of fast and simple measurements on solid samples is surely one of the main advantages of the technique from the analytical point of view. Conversely, quite high detection limits (a few weight percentages points) and the overlapping of signals in the case of mixtures of different compounds should be considered as drawbacks. The latter is especially remarkable when mid-IR absorbing inorganic compounds (typically those containing polyatomic anions) are mixed with organic ones, as they have often broader and stronger bands that can hide the signals of the organic components. Indeed, this is the case of inorganic fillers such as gypsum, calcite, and silica contained in commercial paints whose bands usually dominate the IR spectrum of the paint.

Raman spectroscopy is based on molecular scattering of monochromatic visible, UV, or near-IR radiation. The components of the scattered radiation having lower frequency than the exciting one, and precisely with differences corresponding to vibrational frequencies, give rise to the Raman spectrum, which is again unique for organic and inorganic compounds. In comparison with IR spectroscopy, Raman spectra of organic molecules exhibit strong signals especially for polarizable bonds such as –C=O or –N=N–. This is the reason for the success of the technique in the identification of synthetic organic pigments, containing aromatic moieties and in many cases also the azo –N=N– group. Another significant advantage is the fact that sample treatment is not required to obtain a Raman spectrum. On the other hand, the Raman effect being quite weak, the detection limits are high and, moreover, fluorescence emission possibly due to the main components of the samples, but also to impurities, can partially or completely obscure the Raman signals. This is the case of the fluorescent quinacridone pigments and also of the organic binders, especially oil, contained in the paints. FT-Raman spectroscopy was developed as a possible solution to this problem. The use of near-IR exciting radiation, usually at the wavelength of 1064 nm emitted by a Nd:YAG laser, reduces fluorescence emission as its energy is lower than that of most electronic transitions. The weaker intensity of the
Raman scattering, due to the lower frequency of the exciting radiation, can be compensated by the accumulation of several spectra in a reasonable time with the use of an interferometer and Fourier transform (FT). Thus, FT-Raman spectroscopy is a suitable technique for the identification of the fluorescent quinacridone pigments.

**EXPERIMENTAL COMPONENTS**

**Preparation of the Samples**

Pure pigments are analyzed as powders. In the present example, PR122 and PV19 were purchased from Kremer Pigmente.

For analyses of the commercial paints, a small amount of them is spread on a glass slide and left to dry in the air. The use of an oven set at ~50 °C can help to speed-up the drying process. In the present example, the acrylic- and oil-based commercial paints—containing, respectively, PV19 and PR122—belong to the Maimeri brand. See the Supporting Information for details.

**FT-IR, FT-Raman, and XRD Measurements**

For the FT-IR analyses, all samples were ground and dispersed in KBr to obtain pellets. In the case of the commercial paints, a small amount of the paint film is scraped away from the glass slide by means of a scalpel. In the experiment described, FT-IR spectra were acquired by a Jasco FT-IR-620 spectrophotometer as a sum of 16 scans with 4 cm⁻¹ resolution. It is worth noticing that, if available, an attachment for attenuated total reflection (ATR) can be used, avoiding in this way the preparation of KBr pellets.

FT-Raman spectra are recorded directly on the samples (powders or pictorial layers), without any preparation, between 4000 and 200 cm⁻¹. In the present example, a RFT-600 Jasco FT-Raman spectrometer was employed, using for excitation the 1064 nm emission of a Nd:YAG laser. The output laser power was kept at 176 mW. A different number of scans according to the sample (between 100 and 300) was acquired. The resolution was 4 cm⁻¹.

Students can assign IR and Raman bands in the obtained spectra by comparison with a reference online database and research papers provided by the teachers and the experimental spectra they collect themselves on pure pigments.

XRD analyses were performed by means of a Philips PW 1820 diffractometer with vertical scan. The instrument was equipped with collimator plates (Soller’s slits), a single crystal graphite monochromator, and a Na(Tl)I scintillation counter with impulse height amplification. The incident radiation corresponded to Cu Kα (1.5418 Å) (settings HV: 40 KV and 40 mA), and the acquisition was run at room temperature in the angular range 5–65°.

**Chemical Treatments of the Commercial Paint Samples**

A first attempt to analyze the commercial paints as such shows that they need to be treated to partially eliminate the binders and the inorganic fillers that obscure the signals due to the pigments. The experimental procedure and the materials used are detailed in Supporting Information.

For binders:

- In the case of acrylic formulations, the paints are first washed twice (15 min at 6000 rpm in a laboratory centrifuge) with ethyl acetate in order to partially dissolve the acrylic resin. The solvent is chosen considering that acrylic binders are presently based on copolymers between methyl methacrylate and another acrylate such as the n-butyl one. Indeed, in a literature study on the solubility of poly(methyl methacrylate) ethyl acetate appeared to be one of the most effective solvents.

- For oil paint, a 2:1 CHCl₃: CH₃OH mixed solvent is used for the dissolution of the lipidic binder performing only once the same centrifugation procedure reported for the acrylic binder.

For inorganic fillers:

- After partial elimination of the binder, calcite is at least partly removed by dropping on the paint sample a 6% HCl aqueous solution.

- In the literature, the removal of silicate fillers from artistic paint samples is proposed by use of HF, but for safety reasons it is preferable to avoid it in an experiment intended for
undergraduate students. As it will be shown, a satisfying identification of the pigment is nevertheless possible because of the combination of the two vibrational spectroscopies.

HAZARDS
Contact with hydrochloric acid can cause burns and irritation to the skin and eyes. Ethyl acetate is flammable and can cause eye irritation. Trichloromethane is highly toxic and irritating. All the reagents must be used in a well-ventilated area, preferably under a laboratory hood, and safety goggles and gloves must be used at all times.

RESULTS AND DISCUSSION
Preliminarily, FT-IR and FT-Raman analyses are performed on all the samples as such. Apart from the pure powders, for which the typical spectral patterns of PR122 and PV19 are recognizable, at first both techniques fail in identifying the coloring molecules in paints.

For FT-IR analyses, in the case of acrylic formulations, both for QA and DMQA only calcite is detectable, while in the oil paint the spectrum is dominated by the bands due to amorphous silica. Other signals, in particular a band at about 1730–1740 cm\(^{-1}\), are assigned to the organic binders. Therefore, considering the interference of the inorganic components and/or of the binders, commercial paints require a treatment suitable for at least partial removal of them.

Concerning the two paints containing PR122, as shown in Figure 2, even after sample treatment the prevailing signals in the FT-IR spectrum are those due to calcite for the acrylic paint and to amorphous silica for the oil paint. In fact, CO\(_3^{2-}\) anions and Si–O bonds have very high absorption coefficients; thus, their bands are largely predominant in the IR spectrum in comparison with those of any organic component. Nevertheless, some very weak bands due to DMQA are recognizable between 830 and 520 cm\(^{-1}\) (see the box in Figure 2a and data in Table 1). In the same way, for the paint containing PV19, the main signals of QA can be observed as minor features between 1100 and 400 cm\(^{-1}\) (see the box in Figure 2b and data in Table 1).

Figure 2. FT-IR spectra of the analyzed PR122 and PV19 pure pigments and pre-treated paint samples: (a) Acrylic paint; (b) Pure powder; (c) Oil paint. The regions where the spectra of the paints show weak bands due to the pigments are enlarged in the boxes.

Table 1. FT-IR Bands of Pure PR122 and PV19, Acrylic and Oil Paint, after Treatment

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>PR122</th>
<th>PV19</th>
</tr>
</thead>
<tbody>
<tr>
<td>800–550</td>
<td>calcite</td>
<td></td>
</tr>
<tr>
<td>4000–500</td>
<td>silica</td>
<td>calcite</td>
</tr>
<tr>
<td>3500–2500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500–1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500–100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pigment</td>
<td>Analyzed Substance</td>
<td>FT-IR Bands (cm$^{-1}$)</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>PR122</td>
<td>Pure powder</td>
<td>3265, 3226, 3164, 2979, 2914, 2856, 1635, 1604, 1578, 1553, 1476, 1412, 1340, 1296, 1260, 1234, 1201, 1143, 1119, 1035, 976, 950, 915, 873, 808, 792, 771, 710, 700, 663, 612, 588, 555, 536</td>
</tr>
<tr>
<td></td>
<td>Acrylic paint</td>
<td>3272, 3231, 3170, 2963, 2915, 2874, 2514, 1797$^a$, 1741, 1424$^a$, 1242, 1144, 1021, 946, 875$^a$, 808, 792, 712$^a$, 604, 555, 537</td>
</tr>
<tr>
<td></td>
<td>Oil paint</td>
<td>3273, 3162, 2919, 2850, 1744, 1636, 1606, 1583, 1553, 1471, 1343, 1061$^b$, 792, 466$^b$</td>
</tr>
<tr>
<td>PV19</td>
<td>Pure powder</td>
<td>3258, 3219, 3150, 3097, 3058, 3015, 2973, 2941, 2919, 2842, 1626, 1604, 1582, 1554, 1523, 1498, 1469, 1448, 1407, 1341, 1313, 1264, 1235, 1193, 1155, 1138, 1107, 1023, 961, 894, 874, 851, 813, 749, 707, 690, 620, 607, 564, 527, 483, 447</td>
</tr>
<tr>
<td></td>
<td>Acrylic paint</td>
<td>2959, 2921, 2874, 2515, 2365, 2344, 1420$^a$, 1166, 875$^a$, 847, 712$^a$, 668, 617, 605, 564, 527</td>
</tr>
</tbody>
</table>

$^a$Bands due to calcite. $^b$Bands due to acrylic resin.

In addition, if available, XRD can be proposed to the students as a further method to analyze the paints$^{22}$ in order to identify the limitation of this technique.

In fact, apart from the pure powders where the typical diffraction pattern of the PR122 and PV19 crystalline structures are easily recognizable, the inorganic filler prevents the identification of the coloring molecules. In the case of acrylic formulations, in fact, both for QA and DMQA, only calcite is detected, while in the oil paint the spectrum is dominated by a broad peak due to an amorphous component. These results are in agreement with FT-IR analysis, that moreover allows the identification of the amorphous component as silica. The diffraction patterns of PR122 (pure powder and acrylic formulation) are reported as an example in Figure 3.

![Figure 3. XRD patterns of PR122: (a) Pure pigment; (b) Acrylic paint.](image)

Subsequently, FT-Raman analyses are performed. As explained above, the choice of this analytical technique is due to the fact that the excitation in the near-IR region (1064 nm), where most materials do not show electronic absorptions, quenches the fluorescence emission typical of organic materials.

Concerning the results of the measurements, in the case of PR122, the analyses performed directly on a paint layer detect only fluorescence for the oil paint and the presence of calcite in the case of the acrylic one. Small samples are thus taken from both paint layers and students have to treat them as described above to remove the oil binder in the first case and part of the acrylic binder and most of the calcite filler in the second one. In this way the signals due to DMQA become evident in the spectra of the commercial formulations, as evidenced by the comparison with the spectrum of the pure pigment (Figure 4 and Table 2). The same happens for the acrylic paint containing PV19. It is worth noting that...
in the same spectrum the presence of intense bands is due to the acrylic binder (Table 2), which was only partially dissolved by ethyl acetate.

![FT-Raman spectra of the analyzed PR122 and PV19 pure pigments and paints: (a) Untreated acrylic paint; (b) Treated acrylic paint; (c) Pure powder; (d) Treated oil paint.](image)

**Figure 4.** FT-Raman spectra of the analyzed PR122 and PV19 pure pigments and paints: (a) Untreated acrylic paint; (b) Treated acrylic paint; (c) Pure powder; (d) Treated oil paint.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Analyzed Substance</th>
<th>FT-Raman Bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR122</td>
<td>Pure powder</td>
<td>1647, 1593, 1567, 1536, 1513, 1379, 1348, 1334, 1314, 1231, 1198, 721, 677, 537</td>
</tr>
<tr>
<td></td>
<td>Acrylic paint</td>
<td>1648, 1593, 1567, 1511, 379, 1314, 1087ᵃ, 720</td>
</tr>
<tr>
<td></td>
<td>Oil paint</td>
<td>1648, 1593, 1567, 1511, 1314, 720</td>
</tr>
<tr>
<td>PV19</td>
<td>Pure powder</td>
<td>3060, 1660, 1651, 1628, 1598, 1563, 1514, 1481, 1440, 1243, 1208, 1162, 1137, 1023, 876, 739, 695, 558, 464</td>
</tr>
<tr>
<td></td>
<td>Acrylic paint</td>
<td>2935, 2876, 1731ᵇ, 1598, 1565, 1512, 1452ᵇ, 1311ᵇ, 1082ᵃ, 842ᵇ, 806ᵇ, 695</td>
</tr>
</tbody>
</table>

ᵃBands due to calcite. ᵇBands due to acrylic resin.

Finally, the students prepare the report of the experiment, with an introduction regarding the chemical formulation of paints and the problem of the identification of synthetic organic pigments in contemporary works of art. Then they present the spectral data obtained in each step. In particular, they provide the interpretation of the spectra, explaining on this basis and with reference to the binder declared by the manufacturer the choice of a given chemical treatment for each commercial paint and illustrating how spectroscopic analyses were used to monitor the efficiency of the selected treatment. See Supporting Information for more details about report guidelines. At the end of the report, students provide the data based on which pigments were identified for each paint. The experimental results can be summarized as suggested in Table 3.
Table 3. Summary of Results Comparing Substances Identified with Different Methods and Treatments

<table>
<thead>
<tr>
<th>Analyzed Paint/Pigment</th>
<th>Declared Binder</th>
<th>Substances Identified before Treatment, by Method</th>
<th>Chemical Treatment Performed</th>
<th>Substances Identified after Treatment, by Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FTIR</td>
<td>FT-Raman</td>
<td>XRD</td>
</tr>
<tr>
<td>PR122 powder</td>
<td>—</td>
<td>Pigment</td>
<td>Pigment</td>
<td>Amorphous component</td>
</tr>
<tr>
<td>PR122 oil</td>
<td>Oil</td>
<td>Silica</td>
<td>—</td>
<td>Amorphous component</td>
</tr>
<tr>
<td>PR122 acrylic</td>
<td>Acrylic</td>
<td>Calcite</td>
<td>Calcite</td>
<td>Calcite</td>
</tr>
<tr>
<td>PV19 powder</td>
<td>—</td>
<td>Pigment</td>
<td>Pigment</td>
<td>Pigment</td>
</tr>
<tr>
<td>PV19 acrylic</td>
<td>Acrylic</td>
<td>Calcite</td>
<td>Calcite</td>
<td>Calcite</td>
</tr>
</tbody>
</table>

STUDENT LEARNING OUTCOMES

The proposed experiment addresses all levels of the revised Bloom’s taxonomy. Indeed, first the students are asked to remember the basic notions of two vibrational spectroscopies FT-IR and Raman and the main differences between them (level 1). Then they must apply their knowledge to the acquisition of spectra, possibly with a satisfying S:N ratio (see Supporting Information for details), (level 3) and to the understanding of the spectral data (level 2). Subsequently, the students are required to analyze the obtained data in order to evaluate the best chemical treatment to emphasize bands due to the pigment (levels 4 and 5). Finally, students interpret the newly acquired data to identify the pigment and to produce a report in which the experiment and its results are critically described, especially from the point of view of the comparison of the employed techniques (levels 5 and 6).

Student learning is quantified based on the final report, where equal weight is given to the following items:

- Correct description with proper language of experimental conditions and parameters
- Correct choice of the best sample treatment supported by interpretation of spectral data
- (Correct identification of the pigments, supported by interpretation of spectral data
- Final discussion of pros and cons of each technique in the solution of the specific problem

The experiment has been performed five times by groups of three students. In the five repetitions, the final identification of the pigments was always successful. Dealing with vibrational spectroscopies, in fact, the obtained spectra are unique, and each peak can be reliably associated to the corresponding material. Therefore, in the case of FT-Raman, where no chemical treatments were necessary, the students always identified the pigments and the inorganic fillers. In the case of FT-IR the possibility of recognizing the pigment is strictly connected to the amount of binder and inorganic filler removed during the chemical treatment: when it was not very effective, the signals due to the pigment could not be distinguished in the spectrum. Repetition of the treatment led, in all cases, to the detection of at least weak FT-IR bands due to the pigment. At the end, combining the two spectroscopic methods, all the groups arrived at the correct conclusion of the experiment.

SUMMARY

This experiment, addressed to undergraduate students interested in the field of conservation science, aims to make students aware of the complexity of the identification of organic pigments in artistic mock-up samples and to lead them to develop a simple protocol based on spectroscopic techniques (FT-IR and FT-Raman) to overcome this difficulty. Of course when real paintings are
concerned, the situation is more challenging. Aging of the materials and the natural degradation connected to it can lead to the formation of by-products (i.e., oxalates and metal soaps), which can complicate the spectral response of the examined material. The chemical treatments presented in this experiment could allow for at least partial dissolution of the inorganic fillers and of such degradation products, making identification of the pigment possible. In this example, the quinacridone pigments PR122 and PV19 are chosen as analytes; it is worth noticing that the same experimental approach can be extended to other organic pigments.

At the end of the experiment, the students can successfully use FT-IR and FT-Raman instrumentation, make decisions based on the collected data, and perform simple chemical treatments on the samples.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX.

Detailed experimental procedure; Description of the instrumentation and the measurement conditions; Fillable summary table; Report guidelines to help students present their results (DOCX)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: margherita.longoni@unimi.it*

**REFERENCES**


Figure 1. Chemical structures of (a) PV19 (QA) and (b) PR122 (DMQA).

46x10mm (300 x 300 DPI)
Figure 2. FT-IR spectra of the analyzed PR122 and PV19 pure pigments and pre-treated paint samples: (a) Acrylic paint; (b) Pure powder; (c) Oil paint. The regions where the spectra of the paints show weak bands due to the pigments are enlarged in the boxes.

53x30mm (300 x 300 DPI)
Figure 3. XRD patterns of PR122: (a) Pure pigment; (b) Acrylic paint.
Figure 4. FT-Raman spectra of the analyzed PR122 and PV19 pure pigments and paints: (a) Untreated acrylic paint; (b) Treated acrylic paint; (c) Pure powder; (d) Treated oil paint.

49x31mm (300 x 300 DPI)