Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database

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Abstract
Pigments Checker is a collection of swatches of historical and modern pigments that offers art professionals, conservation scientists, conservators and fine art photographers, a tool to evaluate and test their imaging and spectroscopic methodologies for pigment identification. “Pigments Checker Free Spectra Database” is an ongoing project to thoroughly characterize each pigment in the collection with a series of spectroscopic and imaging techniques and to make the data open access. This paper presents the free and downloadable database of Raman spectra, adding to the reflectance spectral database already published. The Raman analysis is in agreement with the information provided by the pigments’ manufacturers since most of the pigments could be identified by their Raman spectra which were consistent with the expected content reported in literature.

1. Introduction

Museums, libraries, historical archives and conservation laboratories are in need of scientific examination performed on their art, archaeology and archival collections in order to gain information of their constituent materials. These data allow to understand how, when and where they were made, and they are of great interest to art historians and curators which can have unprecedented insights into their collections. Conservators use this information to devise more effective preservation procedures. There are plenty of scientific analytical techniques which have been tested on museums’ collections and among them non-invasive and non-destructive methods are particularly appreciated since they do not require any sampling and do not cause any damage to the objects. Conservation scientists are specialized in art and archaeology examination and they use both Spectroscopy (such as Raman spectroscopy [1], XRF spectroscopy [2], neutron spectroscopy [3]) and Imaging methods (such as Technical photography [4], Terahertz [5] and Multispectral Imaging (MSI) [6]). Raman Spectroscopy has proved to be one of the most valuable methods to determine provenance and authenticity of artefacts of artistic, archeological or historical significance. It is used to characterize very diverse objects, from biological materials to jewellery, and to comprehend their degradation processes. Its more popular application is for the identification of dyes and pigments. Raman spectroscopy is non-destructive, non-invasive and can be implemented as mobile and relatively lightweight equipment.

In the late 1990’s when Raman spectroscopy started to show its potential in art conservation, a major issue was the lack of databases of reference Raman spectra which are necessary to compare spectra of unknown materials and properly interpret spectral features. Spectral libraries where published on scientific journals since then [7–10] and even recently new libraries on more specific pigments and dyes collections have been presented [11].

Only in the early 2000’s the first Raman databases of pigments were available online. University College London [12] was among the first to upload on their website a collection of spectra acquired with dispersive Raman at 514 nm and 632 nm; IRUG (Infrared and Raman users group) [13] is certainly the most extensive database with a supporting community submitting new spectra acquired with different equipment from the numerous partner institutions; E-Visart [14] is a database developed by University of the Basque Country (Spain) and it covers pigments and archeological materials with FT-Raman and dispersive Raman with excitation at 780 nm. The Romanian Database of Raman Spectroscopy [15] uses a 532 nm laser. Some Institutions also published large databases of minerals including pigments, such as University of Arizona [16] and University of Parma [17].

This paper presents and discusses a new online Raman database of the pigments contained in Pigments Checker [18], a collection of swatches of standard historical and modern pigments (Fig. 1). The pigments are mulled into the binder (acrylic) which is added as needed for each pigment and applied with brush. Among all the pigments and their varieties ever used in art these selected pigments represent the most used ones from antiquity to early 1950’s. A swatch of just gum arabic is added as a reference. Pigments are painted over a cellulose and cotton
cardboard, which is acid and lignin free, not treated with optical brighteners, slightly fluorescent in the UV and reflects infrared radiation. Two cross-hairs (0.2 mm) are printed on each swatch of cardboard before paint application in order to evaluate each pigment’s transparency to infrared imaging.

Pigments Checker is an ongoing project which aims to select the best quality of the pigments and add new ones to the collection after careful research. Started in 2014, Pigments Checker has now reached version 3.0. Pigments Checker’s project is pursued by CHSOS (Cultural Heritage Science Open Source), an initiative to promote innovative, affordable and sustainable technologies for art examination for the art professional community.

“Pigments Checker Free Spectra Database” is a collaborative effort to develop a free and downloadable spectral database of the pigments contained in Pigments Checker: Reflectance, XRF and Raman. The Reflectance spectra database [19] is already available for download. This paper presents the new Raman database and discusses the results.

The goals of the “Pigments Checker Free Spectra Database” are:

1. Define a standard set of historical and modern pigments. All of the Raman databases introduced so far have been collected on samples of different origins. Some pigments belong to collections owned by some institutions, others are manufactured by companies specialized in historical pigments, while others are minerals collected over different geographical locations. Such a variety implies that the pigments’ chemical composition could be different due to a number of factors. For example, mineral pigments usually have specific impurities related to different origins and artificial pigments can have been produced with slightly different formulations, as often happened across their history. Pigments Checker provides a standard set of historical pigments that can be used by researchers and art professionals across different institutions and geographical locations to evaluate and practice their diagnostic methods.

2. Provide a complete characterization of Pigments Checker’s samples. The set of Reflectance, Raman and XRF spectra will provide deep understanding of the chemical composition of the set of standard pigments and will allow to confirm their composition.

3. Test different wavelength excitations. Pigments have been tested with 3 lasers and the database shows how each pigment responds to the 3 excitations. This information is useful to inform an actual analysis of the pigments on works of art.

2. Materials and methods

2.1. Pigments

Raman spectra were collected on the 54 pigments in Pigments Checker v.2 and on 4 pigments that have been added to v. 3. The 58 pigments are listed in Table 1.

2.2. Raman spectroscopy

The samples were analyzed in powder by means of the Xplora (Horiba) spectrometer (spectral resolution: 2 cm$^{-1}$) equipped with 532, 638 and 785 nm lasers and an Olympus microscope (spatial resolution 2 μm) using an Olympus objective 50× (N.A. = 0.75). All the spectra were acquired in the spectral range 100–3200 cm$^{-1}$ with all the 3 laser excitations. The excitation power was chosen depending on the wavelength used and the analyzed pigment, starting from very low values and increasing it gradually where possible. Time and accumulations were optimized for each sample. Calibration was performed using a Si wafer and a linear baseline was subtracted by means of the LabSpec6 software.

When the pigments are applied with a binder and a varnish, their identification becomes much more difficult than that achieved on pure powder samples, as done for this database. Indeed, these organic materials generate a strong fluorescence emission which covers the weak Raman peaks emitted by the pigments and often even the stronger ones, making it impossible their identification. However, it is possible to improve the signal-to-noise ratio by using a specific excitation wavelength which weakens the fluorescence emission or increase the Raman signal. The most effective wavelength depends on each combination of pigments and binders.

There are some Raman databases which report the spectra of the powder pigments acquired with different lasers [7,8,16] and it was also compiled a database of a collection of 99 pigments applied with different painting binders (fresco, egg tempera, casein tempera and linseed oil) and with 3 different excitation wavelengths [20]. That study
Table 1

Pigments Checker. Name (product name, color index, product code), chemical name, Raman peaks, and references. Pigments have been tested with all the 3 laser excitations and when one or more lasers were successful to provide peaks they are reported in the table. Suffix to the product code K, C, or Z indicate respectively Kremer, Cornelissen and Zecchi, pigment sellers.

<table>
<thead>
<tr>
<th>Name/product code</th>
<th>Composition</th>
<th>Principal Raman signals (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Black</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vine black (PBk8)</td>
<td>Amorphous C</td>
<td>532 nm: 1265, 1353, 1602</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>638 nm: 1265, 1353, 1514, 1602</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>785 nm: 1265, 1340, 1593</td>
<td></td>
</tr>
<tr>
<td>Lamp black (PBk7)</td>
<td>Amorphous C</td>
<td>532 nm: 630, 1348, 1585</td>
<td>[7,22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>638 nm: 1333, 1598</td>
<td></td>
</tr>
<tr>
<td>Ivory black (PBk9)</td>
<td>Amorphous C</td>
<td>532 nm: 1353, 1597</td>
<td>[7,22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>638 nm: 1344, 1514, 1602</td>
<td></td>
</tr>
<tr>
<td>Bone black (PBk9)</td>
<td>Amorphous C</td>
<td>532 nm: 462, 1354, 1603</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>638 nm: 1336, 1515, 1603</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>785 nm: 463, 1331, 1594</td>
<td></td>
</tr>
<tr>
<td><strong>Green</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt titanate green (K-44100)</td>
<td>Cobalt titanate green spinel</td>
<td>532 nm: 118, 173, 340, 480, 530, 720, 984, 1400</td>
<td>[23]</td>
</tr>
<tr>
<td>Viridian K-44250</td>
<td>Hydrated chromium oxide</td>
<td>532 nm: 262, 487, 584, 612</td>
<td>[7,24]</td>
</tr>
<tr>
<td>Cadmium green K-44510</td>
<td>Barium sulfate, cadmium yellow, phthalocyanine blue</td>
<td>532 nm: 231, 255, 298, 482, 597, 1034, 1341, 1447, 1527, 1595, 1672, 2870, 2974, 3056</td>
<td>[8,27]</td>
</tr>
<tr>
<td>Verdigris K-44450</td>
<td>Copper-II-acetate-1-hydrate</td>
<td>532 nm: 180, 228, 318, 477, 630, 702, 945, 1052, 1358, 1418, 1442, 1536, 2431, 2938, 2980</td>
<td>[42–44]</td>
</tr>
<tr>
<td>Chrome oxide green (K-44200)</td>
<td>Chromium(III)-oxide</td>
<td>532 nm: 301, 340, 388, 395, 1535</td>
<td>[14,26]</td>
</tr>
<tr>
<td>Green earth K-11000</td>
<td>Glauconite and celadonite</td>
<td>532 nm: 118, 173, 340, 480, 530, 720, 984, 1400</td>
<td>[45–47]</td>
</tr>
<tr>
<td><strong>Red</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lac dye K-36020</td>
<td>Laccic acid</td>
<td>638 nm: 367, 412, 454, 478, 661, 800, 967, 1012, 1102, 1183, 1231, 1318, 1384, 1466, 1579, 1642</td>
<td>[21,48]</td>
</tr>
<tr>
<td>Madder lake C-12061A</td>
<td>Rubic tintorum</td>
<td>No signal - fluorescence</td>
<td>[8,21,48,49]</td>
</tr>
<tr>
<td>Carmine lake K-42100</td>
<td>Carmine acid</td>
<td>532 nm: 1318, 1483</td>
<td>[21,48]</td>
</tr>
<tr>
<td>Vermilion K-10610</td>
<td>Mercury sulfide</td>
<td>532 nm: 153, 198, 253, 304, 353, 393, 443, 445, 474, 533, 577, 621, 686, 733, 754, 819, 901, 975, 1069, 1116, 1166, 1237, 1290, 1365, 1381, 1399, 1466, 1493, 1560, 1585</td>
<td>[26]</td>
</tr>
<tr>
<td>Vermilion red K-21120</td>
<td>Cadmium selenosulfide</td>
<td>532 nm: 153, 198, 253, 304, 353, 393, 443, 445, 474, 533, 577, 621, 686, 733, 754, 819, 901, 975, 1069, 1116, 1166, 1237, 1290, 1365, 1381, 1399, 1466, 1493, 1560, 1585</td>
<td>[26]</td>
</tr>
<tr>
<td>Red lead K-42500</td>
<td>Lead(I/II) oxide</td>
<td>532 nm: 120, 148, 225, 312, 388, 477, 548</td>
<td>[7,31,10,30]</td>
</tr>
<tr>
<td><strong>Brown</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Van dyke brown (NB5) K-41000</td>
<td>Humic acids, iron oxide</td>
<td>532 nm: 1358, 1600</td>
<td>[7]</td>
</tr>
<tr>
<td>Burnt umber (PBrb) K-40710</td>
<td>Manganese and iron oxides</td>
<td>532 nm: 209, 271, 590, 1267</td>
<td>[33]</td>
</tr>
<tr>
<td>Raw umber (PBrb) K-40610</td>
<td>Manganese and iron oxides</td>
<td>532 nm: 238, 300, 397, 575, 555, 681, 1240, 1284, 1470, 1505</td>
<td>[31,10,30]</td>
</tr>
<tr>
<td>Raw sienna (PY 43) K-17050</td>
<td>Iron oxides</td>
<td>532 nm: 238, 300, 397, 575, 555, 681</td>
<td>[31,10,30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>785 nm: 224, 293, 406, 465, 494, 607, 653, 810, 1307</td>
<td></td>
</tr>
<tr>
<td>Name/product code</td>
<td>Composition</td>
<td>Principal Raman signals [cm$^{-1}$]</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------</td>
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<td>------</td>
</tr>
<tr>
<td><strong>White</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalk (PW18) K-58000</td>
<td>Calcium carbonate</td>
<td>532 nm: 154, 278, 710, 1086</td>
<td>7,8,16</td>
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<tr>
<td></td>
<td></td>
<td>785 nm: 280, 1088</td>
<td></td>
</tr>
<tr>
<td>Zinc white (PW4) K-46300</td>
<td>Zinc oxide</td>
<td>532 nm: 201, 330, 381, 435, 584, 667, 1075, 1150</td>
<td>7,16</td>
</tr>
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<td>Titanium white (PW6) K-46200</td>
<td>Titanium dioxide</td>
<td>532 nm: 138, 230, 440, 609, 831</td>
<td>8,34,35</td>
</tr>
<tr>
<td>Lithopone (PW5) K-46100</td>
<td>Zinc sulfide and barium sulfate</td>
<td>532 nm: 215, 278, 344, 454, 460, 988, 1142</td>
<td>7</td>
</tr>
<tr>
<td>Lead white (PW1) K-46000</td>
<td>Basic lead carbonate</td>
<td>532 nm: 324, 410, 675, 965, 1050, 1372, 1477, 1731, 2847, 2879</td>
<td>7,16,51</td>
</tr>
<tr>
<td><strong>Blue</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smalt (PB32) K-10000</td>
<td>Cobalt potassium silicate glass</td>
<td>532 nm: 190, 310, 550, 1093</td>
<td>7</td>
</tr>
<tr>
<td>Cobalt cerulean blue (PB35) K-45730</td>
<td>Cobalt stannate</td>
<td>532 nm: 128, 176, 343, 513, 655, 985</td>
<td>7</td>
</tr>
<tr>
<td>Ultramarine nat. (PB29) K-10510</td>
<td>Sodium-aluminum-silicate</td>
<td>532 nm: 250, 547, 599, 668, 755, 945, 1104, 1149, 1251, 1318, 1362, 1463, 1493, 1576</td>
<td>7</td>
</tr>
<tr>
<td>Maya blue (N/A) K-36007</td>
<td>Indigo in silicic crystal matrix</td>
<td>532 nm: 181, 137, 162, 187, 230, 375, 430, 475, 570, 762, 782, 968, 1145, 1249, 1372, 1572, 1584, 1606</td>
<td>7,16</td>
</tr>
<tr>
<td>Prussian blue (PB27) K-45202</td>
<td>Iron-hexacyanoferrate</td>
<td>532 nm: 190, 310, 550, 1093</td>
<td>7</td>
</tr>
<tr>
<td><strong>Yellow</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gamboge (NY24) K-37050</td>
<td>Garcinia hanburyi tree</td>
<td>532 nm: 379, 459, 740, 1225, 1250, 1278, 1337, 1387, 1437, 1456, 1594, 1637, 1675, 1740</td>
<td>7</td>
</tr>
<tr>
<td>Naples yellow (PY41) K-10130</td>
<td>Lead antimonate</td>
<td>532 nm: 151, 175, 244, 272, 331, 397, 430, 500, 535, 712, 760, 832, 915, 1045, 1093, 1321, 1363, 1423, 1459, 1492, 1576</td>
<td>7</td>
</tr>
<tr>
<td>Lead tin yellow I (N/A) K-10100</td>
<td>Lead stannate</td>
<td>532 nm: 129, 194, 271, 290, 377, 454, 523, 546, 615, 1243, 1275</td>
<td>7</td>
</tr>
<tr>
<td>Cadmium yellow (PY35) K-21010</td>
<td>Cadmium zinc sulfide</td>
<td>532 nm: 131, 153, 179, 212, 257, 309, 353, 571, 615</td>
<td>7,41</td>
</tr>
<tr>
<td>Lead tin yellow II (N/A) K-10120</td>
<td>Lead and tin oxides</td>
<td>532 nm: 135, 260, 328, 451, 616, 916, 1050</td>
<td>7</td>
</tr>
<tr>
<td>**Cobalt violet (PV14) K-45800</td>
<td>Cobalt phosphates</td>
<td>532 nm: 181, 142, 227, 280, 328, 446, 473, 555, 608, 662, 953, 1003</td>
<td>53</td>
</tr>
<tr>
<td>**Yellow ochre (PY43) K-40010</td>
<td>Goethite</td>
<td>532 nm: 181, 194, 227, 280, 328, 446, 473, 555, 608, 662, 953, 1003</td>
<td>33,50</td>
</tr>
<tr>
<td>Realgar (PY39) K-10800</td>
<td>Arsenic sulfide</td>
<td>532 nm: 151, 175, 244, 272, 331, 397, 430, 500, 535, 712, 760, 832, 915, 1045, 1093, 1321, 1363, 1423, 1459, 1492, 1576</td>
<td>16,40</td>
</tr>
</tbody>
</table>
showed that a Raman system equipped with three lasers (532, 638 and 785 nm), allows the characterization of a larger number of pigments than it is possible with two or only one laser. Since the choice of the excitation wavelength is too pivotal to the success of a Raman examination, our database provides the spectra of each pigment acquired with the 3 most used lasers in Raman spectroscopy, 532, 638 and 785 nm.

3. Results and discussion

Pigments have been tested as dry powder. In this section the Raman spectra of the 58 pigments are discussed and compared with information in the literature regarding each pigment in order to evaluate how each one complies with the expected chemical composition. It was also acquired the spectrum of the gum arabic used as a binder for the swatches in Pigments Checker v.2. It shows only a broadband at 2930 cm\(^{-1}\), as previously found with FT-Raman [8]. This information is provided since it is necessary when the Pigments Checker swatches are analyzed by other users so they know what the contribution of the binder would be in their Raman spectra.

Table 2 shows a qualitative evaluation of the efficiency of each laser to identify the pigments. The 532 nm excitation laser is the most useful since it allows the characterization of 34 pigments, while excitation with the 785 nm laser permits to gather spectra only from 25 pigments. The 638 nm laser is the least effective allowing the identification of only 14 pigments. Table 2 summarizes which excitation provided the best spectrum for each pigment. Fig. 2 shows as an example, the spectra of Prussian blue acquired with the 3 lasers. The 532 nm excitation easily allows the identification of the pigment thanks to the peaks at 272, 528, 946, 1865, 2094, 2157 and 2431 cm\(^{-1}\) [7]. The same signals in a noisy spectrum can be read when the 638 nm laser is used, whilst that obtained with the 785 nm laser is of difficult interpretation.

Among the 58 pigments only 2: madder lake and yellow lake reseda did not provide any peaks. Indeed, we did not expect any signals with our system since, to overcome fluorescence, a far infrared excitation is required (see for example the results obtained on lakes [8,21]).

3.1. Black pigments

The Raman spectrum of amorphous carbon is characterized by broad bands around 1350 (D band) and 1550 (G band) cm\(^{-1}\) with a large variability in the actual positions of these two signals [22]. All the black pigments show these two bands and confirm to be carbon-based (Fig. 3).

3.2. Green pigments

Cobalt titanate green is a solid salts solution and the variation in manufacturing processes and composition is reflected in a slight variability in its spectra. It is characterized by its strongest peak centered at about 712 cm\(^{-1}\) and assigned to the symmetric stretching mode of CoO\(_6\) in Co\(_2\)TiO\(_4\) [23].

Viridian’s spectrum reveals peaks of chromium oxide hydrate (262, 487, 584 cm\(^{-1}\)) [24]. Malachite shows its four fundamental modes and OH stretching modes at 534, 430, 270 and 219 cm\(^{-1}\) [25]. Cadmium green is a mixture of barium sulfate, cadmium yellow and phthalocyanine blue but its Raman spectrum can reveal just the numerous peaks of the blue component. Verdigris is characterized by its \(\nu(CuO)\) (228 and 318 cm\(^{-1}\)) and \(\nu(CC)\) (950 cm\(^{-1}\)) bands. Chrome green proved to be a real chrome (III) oxide with bands around 340, 538 and 595 cm\(^{-1}\) and not the intimate mixture of chrome yellow and prussian blue, which is often called with the same name [26]. Phthalo green is a modern pigment whose numerous picks are in accordance with literature [27]. In the green earth the Raman peaks at 180, 275, 556 and 667 cm\(^{-1}\) indicate celadonite, its main mineral component.
3.3. Red pigments

The red organic colors are the most challenging to be analyzed with our system. Notwithstanding, lac dye and carmine lake, both from scale insects, provided peaks comparable to those collected with a 1064 excitation laser [21]. No signal could instead be detected for madder lake. Alizarin (organic synthetic monoazo, naphthol) spectrum shows numerous characterizing peaks among which 1290, 1365, and 1585 cm$^{-1}$ [28]. Vermilion has its strong peaks at 252, 283 and 343 cm$^{-1}$ [29]. The natural red ochre sample features the weak narrow doublet at 225 and 290 cm$^{-1}$ of hematite. For red lead the acquisitions gave useful results with the red and near-infrared exciting wavelengths, which gave the red lead spectrum according to literature with its characterizing peaks at 120, 148, 225, 388, and 548 cm$^{-1}$ [7,30]. On the other hand, the spectrum with the green excitation laser highlights that a transformation occurs in the pigment even if it does not show any burning or color change under visual inspection with the microscope. This degradation process is a well-known phenomenon [31]. Using the green laser, a spectrum from red lead was obtained only with an excitation power higher than 1.5 mW which already causes the degradation. The spectrum of the altered read lead is provided in the database since it is useful for its identification when the examination has to be performed with a green laser excitation (Fig. 4).

For cadmium red, the only useful Raman spectrum was obtained with the 638 nm laser and its spectrum (136, 200, 296, 361, 488 and
587 cm\(^{-1}\)) is in accordance with literature\([32]\) with no trace of the maximum at 988 cm\(^{-1}\) due to the barium sulfate filler found in other samples\([8]\).

3.4. Brown pigments

For van dyke brown and bitumen it was possible to see the broad bands around 1350 (D band) and 1550 (G band) cm\(^{-1}\)\([22]\) with the 532 nm laser. Raw umber shows peaks of hydrated ferric oxide at 304 and 400, and a band at 640 cm\(^{-1}\) that can be attributed to black MnO\(_2\)\([33]\). Burnt umber shows signals at 590 cm\(^{-1}\) resulting from MnO\(_2\) and the increased presence of anhydrous ferric oxide. As expected\([33]\) raw sienna’s spectrum resembles that of limonite, the yellow mineral of yellow ochre (peaks at 238, 300, 391, 477, 555, 681 cm\(^{-1}\)) while burnt sienna, due to the calcination of the pigment, has peaks of anhydrous iron oxides (224, 290, 406 cm\(^{-1}\))\([7]\) (Fig. 5).

3.5. White pigments

White pigments are the most easy to identify and their spectra obtained with the 532 nm excitation are shown in Fig. 6. Chalk is calcium carbonate (154, 278, 1086 cm\(^{-1}\))\([7]\) while gypsum is hydrated calcium sulfate (181, 415, 493, 617, 670, 1008, 1134 cm\(^{-1}\))\([7]\). Zinc white has its characterizing peaks at 330, 381 and 435 cm\(^{-1}\)\([7]\). Titanium white shows peaks of its two crystal forms of titanium oxide, anatase (143 cm\(^{-1}\)) and rutile (450, 615 cm\(^{-1}\))\([34,35]\). Lithopone is a mixture of zinc sulfide (peaks at 215, 460, 988 cm\(^{-1}\))\([16]\) and barium sulfate (peaks at 454, 460, 988 cm\(^{-1}\))\([16]\). Lead white shows peaks of its main component, hydrocerussite (965, 1050, 1372 cm\(^{-1}\))\([16]\).

3.6. Blue pigments

Four blue pigments and one violet are based on cobalt: cobalt cerulean blue has its characterizing peaks at 495, 533, and 670 cm\(^{-1}\) (excitation 785 nm)\([7]\); cobalt blue is identified (excitation at 532 nm) by its 2 peaks at 202 and 514 cm\(^{-1}\)\([36,37]\) while cerulean blue (cobalt chromite) by its peaks (excitation 532 nm) at 510 and 626 cm\(^{-1}\)\([28]\); the same cobalt violet pigment in Pigments Checker has been thoroughly characterized with XRD and FT-IR\([32]\) and has a characterizing peak at 953 cm\(^{-1}\); finally, the small’s signals shows the glass bands - this pigment being made of glass - centered at 550 and 1093 cm\(^{-1}\). Concerning ultramarine blue, the pigment results heterogeneous, mostly blue, with white and brown spots. The acquisitions on the blue parts gave better results for the analysis carried out with the resonant green laser. It is well known that, if a resonant wavelength is used, it is easy to obtain a resonant Raman spectrum of lazurite blue chromophores S\(_3\) (260 and 285 cm\(^{-1}\) (bending), 548 cm\(^{-1}\) (stretching)) and S\(_2\) (583 cm\(^{-1}\)) radical ions. The shoulders at ca. 285 and 583 cm\(^{-1}\) may be due to asymmetric bending and stretching modes; the Raman spectrum also shows harmonics (548 × 2 = 1096, 548 × 3 = 1644 cm\(^{-1}\), etc.) and combinations (260 + 548 = 808 cm\(^{-1}\), etc.), characteristic of the Raman resonance phenomenon. The analyses on the white and brown areas highlight the presence of diopside (136, 323, 390, 665, 1009 cm\(^{-1}\)) and hematite (217, 288, 401, 1330 cm\(^{-1}\)) respectively, other two minerals present in the rock lapis lazuli together with the blue lazurite (Fig. 7). Indigo is revealed by the 532 nm laser with peaks at 248, 547, 599, 1310, 1572, and 1584 cm\(^{-1}\)\([7]\) and Maya blue, made of indigo inserted in a silicic matrix, is unambiguously identified by its numerous peaks with the 532 nm excitation 548, 599, 668, 755, 1104, 1149, 1251, 1318, 1463, 1493, and 1576 cm\(^{-1}\))\([38]\). Egyptian blue has 4 characterizing peaks, 375, 430, 475 and 1084 cm\(^{-1}\)\([7]\). Phthalocyanine blue has numerous peaks, among the strongest: 590, 680, 1451 and 1527 cm\(^{-1}\)\([8]\). Strong peaks at 2094 and 2154 cm\(^{-1}\) identify prussian blue\([7]\). Excitation at 532 nm reveals the peaks of azurite at 247, 399, 762, 834, 1094, 1429, and 1577 cm\(^{-1}\) and signals in similar positions are found for blue bice, the artificial form of azurite.
3.7. Yellow pigments

Among the organic yellow colorants, the best results were obtained for gamboge which shows peaks (excitation at 785 nm) at 1250, 1437, 1594, and 1637 cm$^{-1}$ [7]; saffron (*Curcuma longa* root extract) does show its characteristic strong peaks at 1604 and 1630 cm$^{-1}$ attributed to the benzene ring [39]. Whilst, as expected, yellow lake reseda did not provide any peaks with our dispersive Raman system. Concerning inorganic pigments, three of the lead-based compounds: Naples yellow, lead tin yellow I and lead tin yellow II have very similar spectra (Fig. 8), especially for the maximum at around 135 cm$^{-1}$, but they can be distinguished for the minor signals with all the 3 lasers [7]. Also massicot, lead oxide, is clearly identifiable with all the 3 excitations thanks to its signals at 145, 287 and 383 cm$^{-1}$ [7]. Realgar and Orpiment, both arsenic

![Fig. 5. Baseline subtracted Raman spectra of the raw and burnt sienna and umber pigments and the respective lasers used to obtain the best spectra.](image1)

![Fig. 6. Baseline subtracted Raman spectra of the white pigments (lithopone, zinc white, titanium white, chalk, gypsum and lead white) acquired with the 532 nm laser.](image2)
sulfides, respectively As$_2$S$_3$ and As$_4$S$_5$, can be easily distinguished: the former has characterizing peaks (excitation at 785 nm) at 145, 172, 345 cm$^{-1}$ [40], the latter is identified by all the excitations at the bands at 134, 150, 178, 200, 288, 308, and 535 cm$^{-1}$ [40]. Cadmium yellow is identified by its two peaks at 309 and 615 cm$^{-1}$ (excitation: 532 nm) [41]. Cobalt yellow has (excitation: 532 nm) characterizing peaks at 179, 266, 296, 820, 835, and 1325 cm$^{-1}$ [7]. Chrome yellow shows its peaks (excitation 638 nm) at 336, 355, 372 cm$^{-1}$, and 134 (1) (2015) 1

4. Conclusions

This work provided the Raman spectroscopic characterization of the 58 pigments used in Pigments Checker. Only 2 pigments (madder lake and yellow lake reseda) did not provide any peaks, as it was expected for the used Raman dispersive system. The composition of the pigments was discussed and compared with known standards in literature and all the samples were found compatible with the compositions declared by the manufacturers.

This study contributes to the “Pigments Checker Free Spectra Database” project for the definition of a standard set of historical pigments for research and scientific education related to art conservation.

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