



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.

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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 were 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 milled 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

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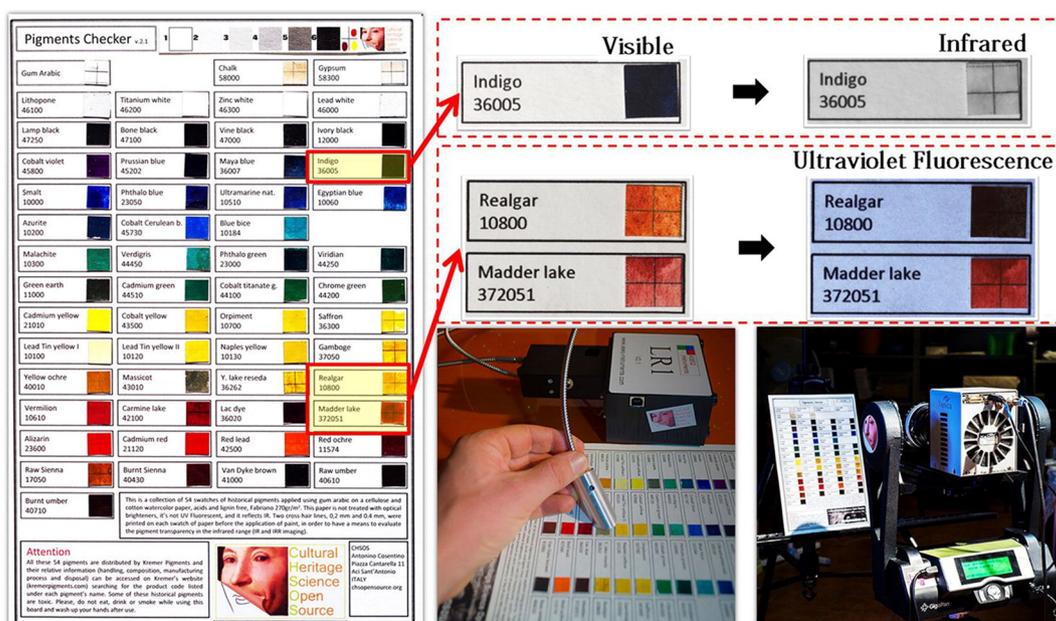


Fig. 1. Pigments Checker is a tool to evaluate and practice imaging and spectroscopic methods for pigments identification.

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 $2\text{ }\mu\text{m}$) using an Olympus objective $50\times$ (N.A. = 0.75). All the spectra were acquired in the spectral range $100\text{--}3200\text{ cm}^{-1}$ 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, pigments sellers.

Name/product code	Composition	Principal Raman signals [cm^{-1}]	Ref.
<i>Black</i>			
Vine black (PBk8) K-47000	Amorphous C	532 nm: 1265, 1353, 1602 638 nm: 1265, 1353, 1514, 1602 785 nm: 1265, 1340, 1593	[22]
Lamp black (PBk7) K-47250	Amorphous C	532 nm: 630, 1348, 1585 638 nm: 1333, 1598	[7,22]
Ivory black (PBk9) K-12000	Amorphous C	532 nm: 1353, 1597 638 nm: 1344, 1514, 1602 785 nm: 1348, 1496, 1585	[7,22]
Bone black (PBk9) K-47100	Amorphous C	532 nm: 463, 1354, 1603 638 nm: 1336, 1515, 1603 785 nm: 463, 1331, 1594	[22]
<i>Green</i>			
Cobalt titanate green. K-44100	Cobalt titanate green spinel	532 nm: 118, 173, 340, 480, 530, 712, 984, 1400 638 nm: 174, 705, 979, 1400 785 nm: 118, 173, 237, 338, 480, 530, 547, 608, 712, 984, 1400	[23]
Viridian K-44250	Hydrated chromium oxide	532 nm: 262, 487, 584, 618	[7,24]
Malachite K-10300	Basic copper(II) carbonate	532 nm: 153, 178, 219, 270, 350, 430, 508, 534, 564, 596, 717, 749, 1059, 1096, 1368, 1460, 1494	[7,16,25]
Cadmium green K-44510	Barium sulfate, cadmium yellow, phthalocyanine blue	532 nm: 231, 255, 598, 680, 842, 951, 1034, 1138, 1341, 1447, 1527, 1590, 2672, 2870, 2974, 3056 638 nm: 480, 588, 675, 747, 838, 951, 1139, 1202, 1335, 1443, 1527, 1610, 2006, 2198, 2265, 2661, 2862, 2966, 3046 785 nm: 258, 480, 594, 679, 752, 842, 950, 1143, 1338, 1447, 1526	
Verdigris K-44450	Copper-(II)-acetate-1-hydrate	532 nm: 180, 228, 318, 477, 630, 702, 945, 1052, 1358, 1418, 1442, 1536, 2431, 2938, 2980, 3022	[42-44]
Chrome oxide green K-44200	Chromium(III)-oxide	532 nm: 301, 340, 388, 538, 595, 1355	[14,26]
Phthalogreen K-23000	Copper-phthalocyanine	532 nm: 142, 162, 230, 505, 685, 770, 818, 978, 1080, 1200, 1284, 1340, 1388, 1503, 1536 638 nm: 199, 258, 282, 358, 683, 700, 738, 775, 817, 975, 1080, 1214, 1292, 1339, 1392, 1443, 1538, 1899, 2825, 2875, 3077 785 nm: 176, 350, 688, 744, 784, 1217, 1297, 1347, 1540	[8,27]
Green earth K-11000	Glauconite and celadonite	532 nm: 145, 180, 275, 345, 405, 556, 667	[45-47]
<i>Red</i>			
Lac dye K-36020	Laccaic acid	638 nm: 367, 412, 454, 478, 661, 800, 967, 1012, 1054, 1102, 1183, 1231, 1318, 1384, 1466, 1579, 1642	[21,48]
Madder lake C-LC12061A	<i>Rubia tinctorum</i>	No signal - fluorescence	[8,21,48,49]
Carmin lake K-42100	Carminic acid	532, 785 nm: 1318, 1483	[21,48]
Alizarin (naphthol red) K-23600	Organic synthetic monoazo. Naphthol	532 nm: 967, 1062, 1108, 1159, 1230, 1242, 1282, 1355, 1372, 1388, 1483, 1580, 1605 785 nm: 153, 198, 253, 304, 353, 395, 433, 445, 474, 533, 577, 621, 686, 733, 754, 819, 901, 975, 1069, 1116, 1166, 1237, 1290, 1365, 1381, 1399, 1466, 1493, 1560, 1585	[28]
Vermilion K-10610	Mercury sulfide	532, 638, 785 nm: 252, 283, 343	[7,29]
Cadmium red K-21120	Cadmium selenosulfide	638 nm: 136, 200, 296, 361, 488, 587	[41]
Red ochre K-11574	Iron oxides	532, 785 nm: 225, 290, 405	[7,33,50]
Red lead K-42500	Lead(II,IV) oxide	532 nm: 138, 279, 375, 541 638 nm: 120, 148, 225, 312, 388, 477, 548, 1098 785 nm: 120, 148, 225, 312, 388, 477, 548	[7,31,10,30]
<i>Brown</i>			
Van dyke brown (NBr8) K-41000	Humic acids, iron oxide	532 nm: 1358, 1600	[7]
Burnt umber (PBr8) K-40710	Manganese and iron oxides	532 nm: 209, 271, 590, 1267 638 nm: 224, 296, 410, 649, 1227, 1317	[33]
Raw umber (PBr8) K-40610	Manganese and iron oxides	532 nm: 298, 398, 635 785 nm: 175, 253, 304, 400, 640, 1233, 1312, 1585, 1730	[33]
Raw sienna (PY 43) K-17050	Iron oxides	532 nm: 238, 300, 391, 477, 555, 681, 1240, 1322, 1470, 1595 638 nm: 238, 300, 395, 477, 555, 681 785 nm: 302, 402	[33]
Burnt sienna (PR101) K-40430	Iron oxides	532 nm: 212, 273, 400, 465 785 nm: 224, 293, 406, 465, 494, 607, 653, 810, 1307	[33]

(continued on next page)

Table 1 (continued)

Name/product code	Composition	Principal Raman signals [cm^{-1}]	Ref.
<i>White</i>			
Chalk (PW18) K-58000	Calcium carbonate	532 nm: 154, 278, 710, 1086 785 nm: 280, 1088	[7,8,16]
Zinc white (PW4) K-46300	Zinc oxide	532 nm: 201, 330, 381, 435, 584, 667, 1075, 1150	[7]
Gypsum (PW25) K-58300	Hydrated calcium sulfate	532 nm: 181, 415, 493, 617, 670, 1008, 1134 785 nm: 1010	[7,16]
Titanium white (PW6) K-46200	Titanium dioxide	532 nm: 138, 230, 445, 609, 831 638 nm: 143, 238, 450, 615 785 nm: 142, 236, 449, 614	[8,34,35]
Lithopone (PW5) K-46100	Zinc sulfide and barium sulfate	532 nm: 215, 278, 344, 454, 460, 988, 1142 638 nm: 986 785 nm: 350, 454, 462, 992, 1145	[7]
Lead white (PW1) K-46000	Basic lead carbonate	532 nm: 324, 410, 675, 965, 1050, 1372, 1477, 1731, 2847, 2879 785 nm: 325, 413, 678, 969, 1050, 1372	[7,16,51]
<i>Blue</i>			
Smalt (PB32) K-10000	Cobalt potassium silicate glass	532 nm: 190, 310, 550, 1093	[7]
Cobalt cerulean blue (PB35) K-45730	Cobalt stannate	532 nm: 128, 176, 343, 513, 655, 985 785 nm: 132, 183, 254, 350, 419, 458, 495, 533, 621, 670, 990, 1144	[7]
Ultramarine nat. (PB29) K-10510	Sodium-aluminum-silicate	532, 638 nm: 260, 285, 548, 583, 808, 1096, 1358, 1644, 1904, 2192, 2452, 2740, 3000 785 nm: 364, 548, 583, 808, 1096, 1346	[7]
Maya blue (N/A) K-36007	Indigo in silicic crystal matrix	532 nm: 250, 547, 599, 668, 755, 945, 1104, 1149, 1251, 1318, 1362, 1463, 1493, 1576 638 nm: 546 785 nm: 254, 552, 758, 1317, 1574	[52]
Prussian blue (PB27) K-45202	Iron-hexacyanoferrate	532 nm: 272, 528, 946, 1865, 2094, 2154, 2431 638 nm: 276, 538, 956, 2157	[7]
Azurite (PB30) K-10200	Basic copper carbonate	532 nm: 110, 139, 174, 247, 282, 331, 399, 539, 738, 762, 834, 937, 1094, 1422, 1429, 1460, 1577, 1607	[7,16]
Indigo (NB1) K-36000	Indigotin	532 nm: 248, 280, 547, 599, 670, 755, 858, 937, 1009, 1096, 1145, 1249, 1310, 1362, 1460, 1483, 1572, 1584, 1606 785 nm: 254, 266, 279, 312, 547, 599, 675, 758, 1017, 1150, 1252, 1312, 1366, 1465, 1483, 1575, 1584	[8,48]
Egyptian blue (PB31) K-10060	Copper calcium silicate	532 nm: 114, 137, 162, 187, 230, 375, 430, 475, 570, 762, 782, 968, 985, 1011, 1084, 1140	[7]
Phthalo blue (PB15) K-23050	Copper phthalocyanine	532 nm: 231, 255, 590, 680, 747, 951, 1037, 1143, 1341, 1451, 1527, 1595, 2672, 2870, 2976, 3056 638 nm: 257, 488, 591, 682, 747, 954, 1105, 1140, 1212, 1305, 1341, 1454, 1534, 1612, 2205, 2274, 2670, 2870, 2978, 3056 785 nm: 257, 492, 596, 686, 752, 959, 1013, 1148, 1344, 1451, 1527	[8]
Cobalt violet (PV14) K-45800	Cobalt phosphates	532 nm: 141, 182, 227, 280, 328, 446, 473, 555, 608, 662, 953, 1003 638 nm: 187, 478, 612, 956 785 nm: 147, 169, 190, 963, 1014	[53]
Blue bice (PB30) K-10184	Basic copper carbonate	532 nm: 151, 175, 217, 244, 272, 331, 397, 430, 500, 535, 712, 760, 832, 935, 1045, 1093, 1321, 1363, 1423, 1459, 1492, 1576	
<i>Yellow</i>			
Gamboge (NY24) K-37050	<i>Garcinia hanburyi</i> tree	785 nm: 379, 459, 740, 1225, 1250, 1278, 1337, 1387, 1437, 1456, 1594, 1637, 1675, 1740	[7]
Naples yellow (PY41) K-10130	Lead antimonate	532 nm: 135, 257, 326, 446, 498, 588, 708 638 nm: 135, 257, 326, 446, 498, 588, 708, 1204, 1258 785 nm: 135, 257, 326, 446, 505, 594, 714	[7]
Lead tin yellow I (N/A) K-10100	Lead stannate	532 nm: 129, 194, 271, 290, 377, 454, 523, 546, 615 638 nm: 129, 194, 271, 290, 377, 454, 523, 546, 615, 1243, 1275 785 nm: 131, 198, 271, 290, 377, 454, 523, 546, 615	[7]
Cadmium yellow (PY35) K-21010	Cadmium zinc sulfide	532 nm: 131, 153, 179, 212, 257, 309, 353, 571, 615 785 nm: 131, 212, 309, 353, 571, 615	[7,41]
Lead tin yellow II (N/A) K-10120	Lead and tin oxides	532 nm: 135, 260, 328, 451, 826, 916, 1050 638 nm: 135, 260, 328, 451, 916, 1050 785 nm: 139, 260, 328, 916, 1050, 1276	[7]
Cobalt yellow (PY40) K-43500	Potassium cobaltinitrite	532 nm: 179, 266, 296, 474, 516, 680, 820, 835, 1095, 1237, 1325, 1392, 1798, 2142, 2327, 2431, 2645, 2851, 2938 785 nm: 112, 182, 274, 304, 820, 835, 1257, 1325, 1398, 2147, 2645	[7,8]
Massicot (PY46) K-43010	Lead(II) oxide	532, 638, 785 nm: 145, 287, 383	[7]
Yellow ochre (PY43) K-40010	Goethite	532, 785 nm: 205, 247, 300, 400, 487, 557, 681, 1332	[33,50]
Realgar (PY39) K-10800	Arsenic sulfide	532 nm: 182, 194, 224, 237, 270, 345, 355 638 nm: 136, 145, 155, 172, 185, 224, 237, 270, 345, 355	[16,40]

Orpiment (PY39) K-10700	Arsenic sulfide	785 nm: 136, 145, 155, 172, 186, 192, 224, 237, 270, 345, 355	[7,16,40]
Yellow lake reseda (NY2) K-36262	<i>Reseda luteola</i>	532, 638, 785 nm: 134, 150, 178, 200, 288, 308, 353, 378, 580, 644	
Saffron (<i>Curcuma longa</i>) (NY6) K-36300	Curcuma longa root extract	No signal - fluorescence	
		785 nm: 144, 516, 575, 640, 963, 1154, 1167, 1183, 1254, 1272, 1321, 1434, 1604, 1630	[39]
New			
Cobalt blue (PB28) Z-C0953	Cobalt aluminate	532 nm: 202, 410, 514, 650	[36,37]
Cerulean blue (PB36) Z-C0040	Cobalt chromite	785 nm: 204, 252, 410, 514, 616, 700, 762	
Chrome yellow (PY34) C-LC11053F	Lead chromate	532 nm: 162, 194, 510, 626, 735	[36]
		785 nm: 177, 202, 519, 631, 677, 730	
		532 nm: 351, 832	[7,31]
		638 nm: 336, 355, 372, 401, 843, 971	
		785 nm: 342, 359, 375, 405, 844, 972	
BITUMEN (NBK6) Z-0098	High-molecular hydrocarbons	532 nm: 1355, 1600	[22,54]

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 efficacy 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 less 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 four 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_2TiO_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 $\nu(\text{CuO})$ (228 and 318 cm^{-1}) and $\nu(\text{CC})$ (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]. Phthalocyanine 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.

Table 2

Laser excitation. Green indicates the best spectrum, yellow a noisy one, while red designates a spectrum difficult to interpret or no spectrum at all.

Pigments	532	638	785
Alizarin (naphthol red)	Yellow	Red	Green
Bitumen	Yellow	Red	Red
Azurite	Green	Red	Red
Blue bice	Green	Red	Red
Bone black	Green	Green	Yellow
Burnt sienna	Yellow	Red	Green
Burnt umber	Green	Yellow	Red
Cadmium green	Green	Yellow	Green
Cadmium red	Red	Yellow	Red
Cadmium yellow	Green	Red	Green
Carmine lake	Yellow	Red	Yellow
Chalk	Yellow	Red	Yellow
Chrome oxide green	Green	Red	Red
Chrome yellow	Green	Red	Red
Cobalt blue	Green	Red	Green
Cobalt cerulean blue	Green	Red	Green
Cerulean blue	Green	Red	Yellow
Cobalt titanate green	Green	Yellow	Green
Cobalt violet	Green	Yellow	Yellow
Cobalt yellow	Green	Red	Green
Egyptian blue	Green	Red	Red
Gamboge	Red	Red	Green
Green earth	Yellow	Red	Red
Gum arabic	Yellow	Red	Red
Gypsum	Green	Red	Yellow
Indigo	Green	Red	Yellow
Ivory black	Green	Green	Yellow
Lac dye	Red	Green	Red
Lamp black	Green	Yellow	Red
Lead tin yellow I	Green	Red	Red
Lead tin yellow II	Green	Red	Red
Lead white	Green	Red	Red
Lithopone	Green	Yellow	Red
Madder lake	Red	Red	Red
Malachite	Green	Red	Red
Massicot	Green	Red	Red
Maya blue	Green	Yellow	Red
Naples yellow	Green	Red	Red
Orpiment	Green	Red	Red
Phthalo green	Green	Red	Yellow
Phthalo blue	Green	Yellow	Red
Prussian blue	Green	Red	Red
Raw sienna	Yellow	Green	Yellow
Raw umber	Yellow	Red	Yellow
Realgar	Green	Red	Red
Red lead	Green	Red	Red
Red ochre	Yellow	Red	Yellow
Saffron (<i>Curcuma longa</i>)	Red	Red	Green
Smalt	Green	Red	Red
Titanium white	Green	Red	Red
Ultramarine nat	Green	Red	Red
Van dyke brown	Yellow	Red	Red
Verdigris	Green	Red	Red
Vermilion	Yellow	Green	Green
Vine black	Green	Red	Yellow
Viridian	Yellow	Red	Red
Yellow lake reseda	Red	Red	Red
Yellow ochre	Green	Red	Yellow
Zinc white	Green	Red	Red

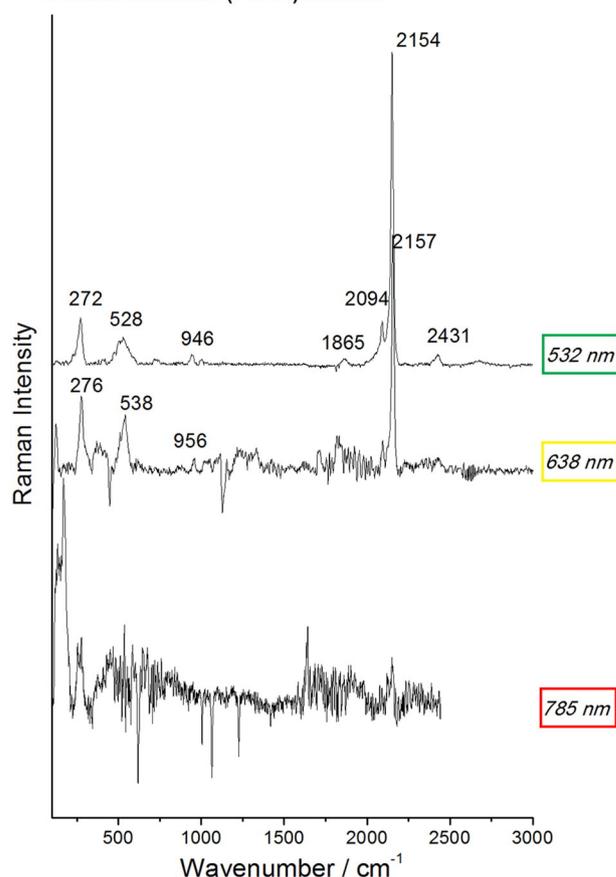
PRUSSIAN BLUE (PB 27) K-45202

Fig. 2. Baseline subtracted Raman spectra of the Prussian Blue (PB27) K-45202 standard acquired with the 532, 638 and 785 nm lasers. The color code is that followed in Table 2: green for the best spectrum, yellow for a noisy one, while red for a spectrum difficult to be interpreted or no spectrum at all. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 be instead 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 red 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

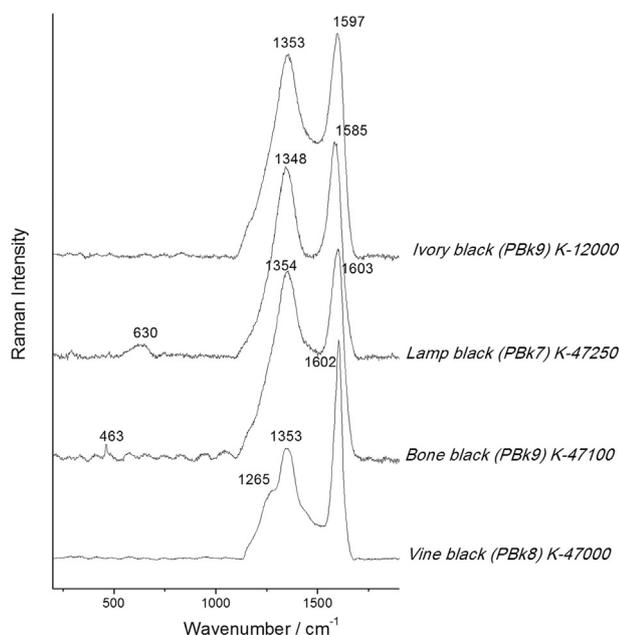


Fig. 3. Baseline subtracted Raman spectra of the four black carbon-based pigments showing the characterizing amorphous carbon D and G bands, acquired with the 532 nm excitation wavelength.

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 $238, 300, 391, 477, 555, 681\text{ cm}^{-1}$) while burnt sienna, due to the calcination of the pigment, has peaks of anhydrous iron oxides ($224, 290, 406\text{ cm}^{-1}$) (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 ($154, 278, 1086\text{ cm}^{-1}$) [7] while gypsum is hydrated calcium sulfate ($181, 415, 493, 617, 670, 1008, 1134\text{ cm}^{-1}$) [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 ($450, 615\text{ cm}^{-1}$) [34,35]. Lithopone is a mixture of zinc sulfide (peaks at 215 and 278 cm^{-1}) and barium sulfate (peaks at $454, 460, 988\text{ cm}^{-1}$) [16]. Lead white shows peaks of its main component, hydrocerussite ($965, 1050, 1372\text{ cm}^{-1}$) [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

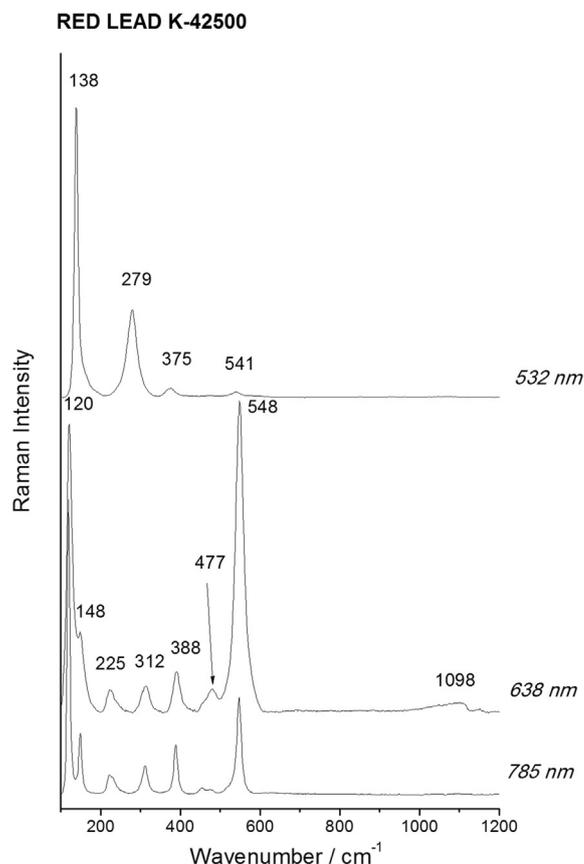


Fig. 4. Baseline subtracted Raman spectra of the Red Lead K-42500 standard acquired with the three lasers. The different spectrum obtained with the green, 532 nm, excitation must be noted.

has been thoroughly characterized with XRD and FT-IR [32] and has a characterizing peak at 953 cm^{-1} ; finally, the smalt'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_2^- (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 ($548 \times 2 = 1096, 548 \times 3 = 1644\text{ cm}^{-1}$, etc.) and combinations ($260 + 548 = 808\text{ cm}^{-1}$, etc.), characteristic of the Raman resonance phenomenon. The analyses on the white and brown areas highlight the presence of diopside ($136, 323, 390, 665, 1009\text{ cm}^{-1}$) and hematite ($217, 288, 401, 1330\text{ cm}^{-1}$) 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 $548, 599, 668, 755, 1104, 1149, 1251, 1318, 1362, 1463, 1493,$ 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.

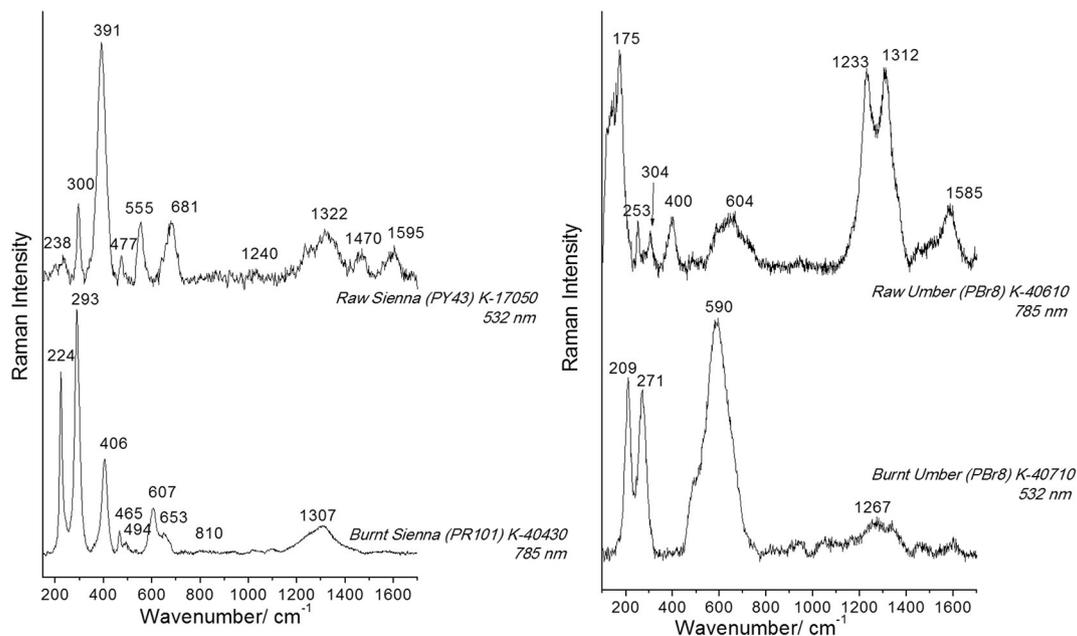


Fig. 5. Baseline subtracted Raman spectra of the raw and burnt sienna and umber pigments and the respective lasers used to obtain the best spectra.

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

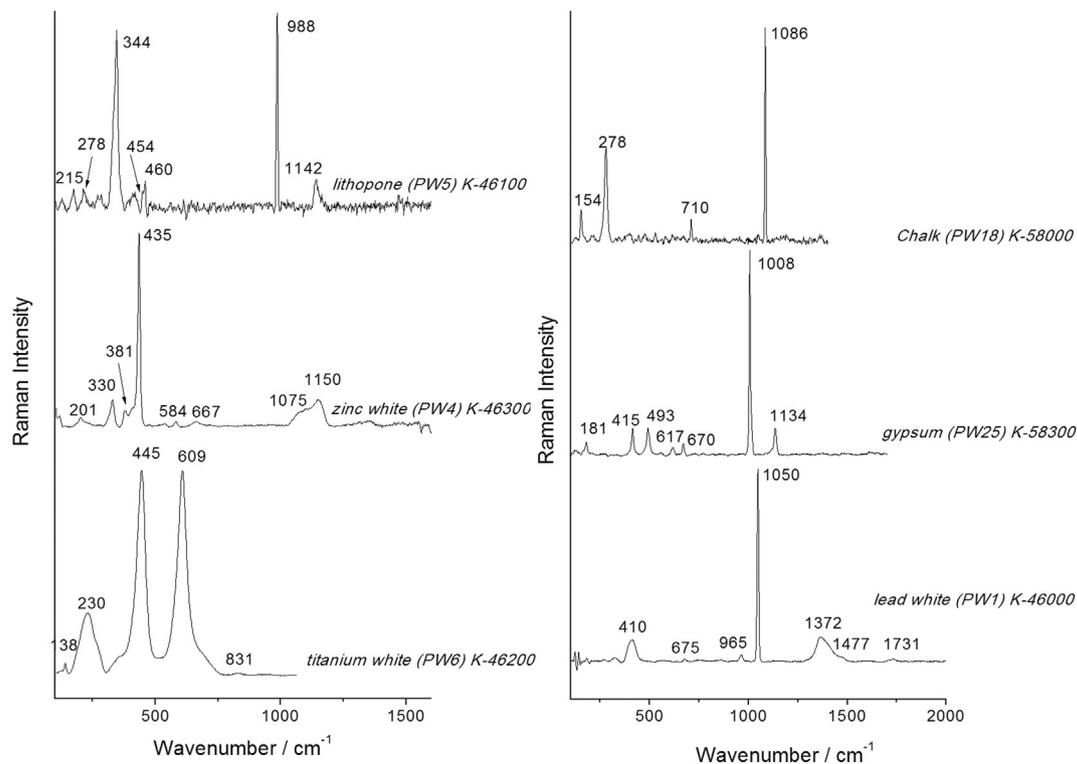


Fig. 6. Baseline subtracted Raman spectra of the white pigments (lithopone, zinc white, titanium white, chalk, gypsum and lead white) acquired with the 532 nm laser.

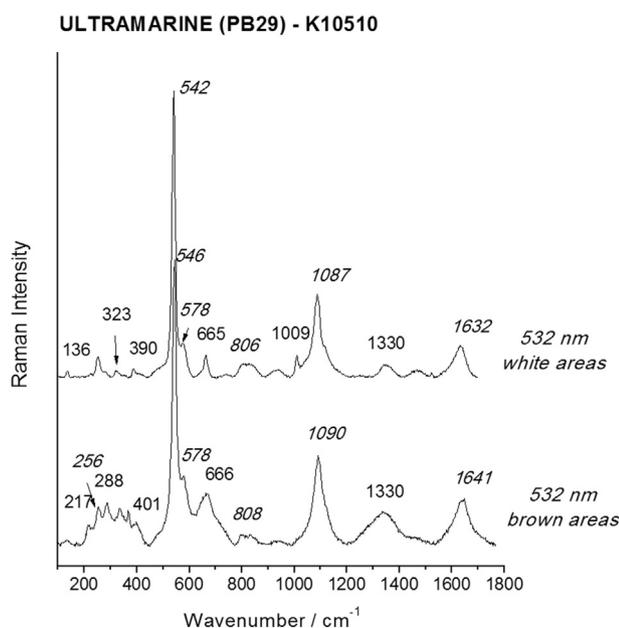


Fig. 7. Baseline subtracted Raman spectra acquired with the 532 nm laser on the white and brown areas found within the blue pigment ultramarine (peaks in italics), revealing respectively the presence of diopside (signals at 136, 323, 390, 665 and 1009 cm^{-1}) and hematite (signals at 217, 288, 401, 666, 1330 cm^{-1}).

sulfides, respectively As_4S_4 and As_2S_6 , can be easily distinguished: the former has characterizing peaks (excitation at 785 nm) at 145, 172, 185, 192, 224, 237, and 345 cm^{-1} [40], the latter is identified by all the excitations with the bands at 134, 150, 178, 200, 288, 308, and 353 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 and 401 cm^{-1} [7]. In the case of yellow ochre, the hydrated iron oxide (limonite) accounts for the bands at 205, 247, 300, 400, 487, 557, and 681 cm^{-1} [33].

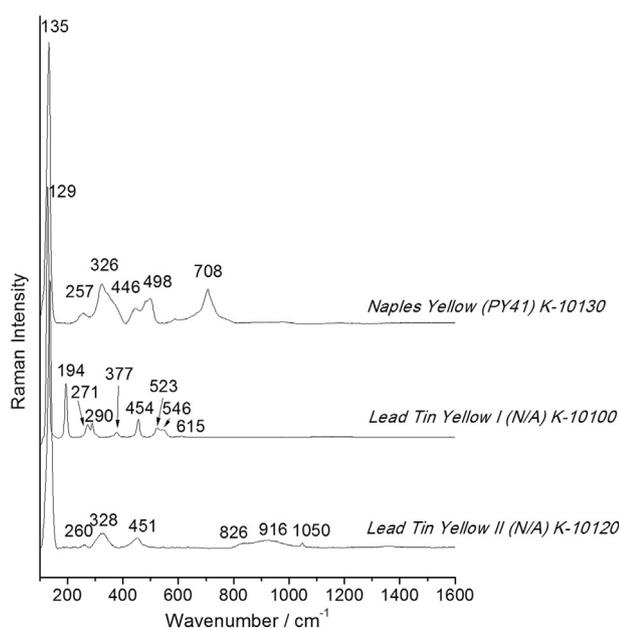


Fig. 8. Baseline subtracted Raman spectra of the lead-based yellow pigments: Naples yellow, lead tin yellow I and lead tin yellow II, acquired with the 532 nm laser.

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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