

ColoRaman project: Raman and fluorescence spectroscopy of oil, tempera and fresco paint pigments

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Received 25 February 2004; Accepted 28 April 2004

An on-line database was compiled for the Raman and fluorescence spectra, obtained using three different excitation wavelengths (531.5, 632.8 and 780 nm), of 99 pigments analysed dry and already applied with four painting techniques (egg tempera, casein tempera, oil and fresco). The database makes it possible to determine easily the most suitable excitation wavelength for the identification of pigments already applied with these painting techniques. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: fluorescence; pigments; tempera; fresco

INTRODUCTION

Raman spectroscopy has been used successfully in the investigation of the chemical composition of materials employed in various types of artefact of artistic–historical interest. In particular, good results have been obtained in the characterization of some fictile materials,¹ resins and organic materials,^{2–5} gemstones⁶ and metal artefacts.⁷ However, the results obtained from investigations of paint pigments seem, at present, by far the most promising. There are many publications on different types of coloured artefacts, such as manuscripts,^{8,9} frescoes,¹⁰ prehistoric wall paintings¹¹ and pottery.¹² The studies published to date confirm the validity of Raman spectroscopy as a non-destructive and *in situ* analysis methodology, appropriate in diagnostic investigations of artefacts of cultural heritage.

The present study was directed at providing detailed information for the identification of pigments already applied in paintings. In fact, the binding agents and ground material, almost always of organic origin, are responsible for fluorescence which in many cases is so intense that it covers the weak Raman signal emitted by the pigment, making it impossible to identify the latter. In many cases, however, it is possible to improve the signal-to-noise ratio (noise here consisting of the emission of fluorescence) by adopting an appropriate excitation wavelength. This must favour the weakening of the fluorescence while keeping the Raman signal measurable, or must stimulate a Raman

emission so great that it can be distinguished from the fluorescence. This wavelength will depend on the pigment and on the painting technique used because the different materials employed to produce binding agents and grounds can contribute in different ways to mask the Raman signal. From the above, it is clearly necessary to provide the spectra corresponding to each pigment and each painting technique, making it possible to evaluate, in each context, the most suitable excitation wavelength for the identification of the pigment.

EXPERIMENTAL

Instrumentation

Measurements were made using a combined system for Raman and fluorescence spectroscopy, the microSPEC produced by Jobin Yvon. This system uses a TRIAX 190 spectrometer carrying three diffraction gratings, of which one of 150 grooves mm⁻¹ is used for fluorescence measurements and one of 1800 grooves mm⁻¹ for Raman experiments. The signal is acquired by a SpectrumONE charge-coupled device (CCD) detector. The spectral resolution is 1–3 cm⁻¹, depending on the laser beam wavelength. The optical groups for the excitation and collection of the signal consist of an Olympus BX40 confocal microscope and a long working distance objective (50×). The system is equipped with three lasers: an Nd:YAG laser at 531.5 nm, an He–Ne laser at 632.8 nm and a diode laser at 780 nm, of 40, 30 and 20 mW power, respectively. Neutral density filters were used to reduce the intensity of the laser radiation on the specimen.

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Raman and fluorescence measurements were obtained using the same system, changing only the diffraction grating.

It should be noted that the results presented here depend on the particular characteristics of the system employed. More encouraging results could be obtained using a system with a better signal-to-noise ratio.

Specimen preparation

This paper presents a database of Raman and fluorescence spectra of pigments already painted using fresco, egg tempera, casein tempera and oil painting techniques.

The pigments were used in the laboratory according to documented recipes.^{13–16} It was then possible to perform measurements on a specimen produced using specifically selected materials and techniques. Recipes and products for the four painting techniques were as follows:

Pigments: 99 pigments were supplied by Kremer (Germany) and Zecchi (Italy).

Ground for oil and tempera; produced mixing Bologna chalk (calcium carbonate sulfate), rabbit glue and rock alum.

Binding agent for egg tempera: one teaspoon of vinegar, one teaspoon of honey, one teaspoon of rock alum and one egg albumen (for cool colours) or one egg yolk (for warm colours).

Fresco: quicklime, limestone sand.

Binding agent for casein tempera: casein binding agent is produced by Zecchi (Italy), art. 2050.

Binding agent for oil: clarified linseed oil from Lefranc et Bourgeois (France).

RESULTS AND DISCUSSION

The English name of the article, the supplier (K = Kremer, Germany; Z = Zecchi, Italy) and the product code are reported for each of the 99 pigments analysed (Table 1). For ease of identification, each pigment was assigned an identification number used hereafter in place of the pigment name. The presence of a letter indicates whether it was possible to obtain a Raman or fluorescence spectrum. For each of the three excitation wavelengths, the letters indicate in which painting techniques it was possible to identify the pigment. The following convention was adopted: P = dry pigment, F = fresco, C = casein tempera, E = egg tempera, O = oil. Upper-case letters refer to Raman spectra, the corresponding lower-case letters refer to fluorescence spectra. The table, with all the observable spectra, is also available on-line at <http://www.ct.infn.it/~arceo/>.

Raman spectroscopy

Pigments characterized with only one laser radiation wavelength

Some pigments could be characterized using Raman spectroscopy with only one of the three lasers tested. Using the other laser wavelengths, the Raman emission was too weak or the fluorescence of the pigment itself was too intense.

The pigments which could be characterized at only one of the three available excitation wavelengths are as follows: excitation at 531.5 nm, 8, 9, 12, 13, 35, 38, 45, 98; excitation at 632.8 nm, 17, 28, 29, 54, 59, 65, 69, 70, 77, 79, 80, 82, 89, 91, 94; and excitation at 780 nm, 56.

It is immediately clear that a system operating at these three wavelengths allows the characterization of more pigments than a system operating at only one or two excitation wavelengths. Even more important, as discussed below, this system often allows the identification of pigments already applied in paintings.

Resonance, fluorescence and painting techniques: choice of excitation radiation

As seen above, some pigments can be characterized using only one of the three wavelengths available. This alone is enough to indicate the use of Raman instrumentation with at least three lasers. This system is indispensable, however, for the identification of pigments used in paintings. From Table 1, it is evident that some pigments which can be characterized using all three excitation wavelengths can be identified using only one of the three laser radiation wavelengths once they have been painted on a ground. Some spectra illustrating these observations are reported below.

Except for the example referring to fresco painting, only those spectra with elements favouring the identification of the pigment are shown. It is understood, therefore, that if the spectrum obtained at a particular wavelength is not reported, it was not found to be useful for the identification of the pigment.

Fresco. Pigment 78, lead tin yellow, could be characterized with all three lasers; once applied on a fresco, it was identifiable only with the laser at 531.5 nm. Laser radiation at 780 nm was not able to generate a detectable Raman emission of the pigment; conversely, radiation at 632.8 nm excited fluorescence and Raman scattering of the ground (Fig. 1).

Oil. Pigment 81, cinnabar, was characterized, but only excitation at 780 nm allowed its identification after application to an oil painting (Fig. 2).

Egg tempera. Pigment 92, zinc yellow, could be characterized at several wavelengths, but only excitation at 632.8 nm allowed its identification after application with the egg tempera painting technique (Fig. 3).

Casein tempera. Pigment 97, white lead, was characterized with two laser wavelengths, but only excitation at 531.5 nm allowed its identification after application with the casein tempera painting technique (Fig. 4).

Table 1. ColoRaman project results^a

ID	Name ^b	Form	Code	532 nm	633 nm	780 nm
1	Cobalt yellow	K	43 500	P	C O	E E E E E E E E E E
2	Cobalt green	K	44 100	P	C C	E E E E E E E E E E
3	Nichel titanium yellow	K	43 200	P	F C	F F P P P P P P P P P P
4	Viridian green	K	44 250	P	C C	E E E E E E E E E E
5	Titanium orange	K	43 300	P	F C	F F P P P P P P P P P P
6	Chrome oxide opaque	K	44 200	P	F C	E E E E E E E E E E
7	Neples yellow	K	43 130	P	F C O	F C O E E E E E E E E E E
8	Verdigris	K	44 450	P	C C	E E E E E E E E E E
9	Cobalt blu light	K	45 720	P	P I C c o e	F F C C O E E E E E E E E E
10	Ultramarine blue	K	45 020	P	F C O	F F C C O E E E E E E E E E
11	Milon blue	K	45 200	P	C C	E E E E E E E E E E
12	Cobalt blue greenish	K	45 740	P	F C	E E E E E E E E E E
13	Cobalt cerulean blue	K	45 730	P	F I C c o e	E E E E E E E E E E
14	Cobalt violet dark	K	45 800	P	C C	E E E E E E E E E E
15	Manganese violet	K	45 350	P	C C	E E E E E E E E E E
16	Cobalt turquoise light	K	45 750	P	F I C o E e	E E E E E E E E E E
17	Chromium yellow	K	21 010	P	F C	E E E E E E E E E E
18	Cadmium orange	K	21 080	P	F O	E E E E E E E E E E
19	Cadmium red	K	21 120	P	C C	E E E E E E E E E E
20	Zinc white	K	46 300	P	C C	E E E E E E E E E E
21	Titanium white	K	46 200	P	F C O	E E E E E E E E E E
22	Iron oxide/mars red light	K	48 060	P	C C	E E E E E E E E E E
23	Iron oxide/mars red medium	K	48 120	P	C C	E E E E E E E E E E
24	Mars brown	K	48 300	P	F C	E E E E E E E E E E
25	Iron oxide/mars orange	K	48 060	P	F C	E E E E E E E E E E
26	Iron oxide/mars yellow	K	48 000	P	F C	E E E E E E E E E E
27	Iron oxide/mars black	K	48 400	P	C C	E E E E E E E E E E
28	Italian burnt senna	K	40 430	P	C C	E E E E E E E E E E
29	Terre ercolano	K	41 600	P	C C	E E E E E E E E E E
30	Terre pozzuoli	K	41 550	P	C C	E E E E E E E E E E
31	English red light	K	40 542	P	C C	E E E E E E E E E E
32	Red bole	K	40 500	P	C C	E E E E E E E E E E
33	Natural sienne	K	17 050	P	C C	E E E E E E E E E E
34	French ochre	K	40 040	P	C C	E E E E E E E E E E
35	Vine black	K	47 000	P	F C O	E E E E E E E E E E

(continued overleaf)

Table 1. (Continued)

ID	Name ^b	Form	Code	532 nm	633 nm	780 nm
36	Lamp black	K	47250			
37	Spinel black	K	47400			
38	Chrysocolla	K	10350	P		
39	Irgazine ruby	K	23182	P	F	P
40	Smalt	K	10000			
41	Phtalo blue	K	23060	P	F	P
42	Irgazine orange	K	23178			
43	Irgazine yellow	K	23330	P	F	P
44	Permanent yellow medium	K	23310	P	F	P
45	Thioindigo	K	23700	P	F	P
46	Hostaperm orange	K	23550	P	F	P
47	Dioxazine violet	K	23450	P	F	P
48	Quindo red	K	23410			
49	Bright yellow	K	23650	P	F	P
50	Indian yellow	K	23350	P	F	P
51	Phtalo green	K	29000	P	F	P
52	Hostaperm pink	K	23152			
53	Irgazine red	K	23180	P	F	P
54	Scarlat red	K	23200	P	F	P
55	indanthrone blue	K	23100	P	F	P
56	Dark red golo	K	23250			
57	Manenglas	K	11800	P	F	P
58	Isoindolorange	K	23800	P	F	P
59	Cinquasia violet	K	23710	P	F	P
60	Epidot	K	11150	P		
61	Elba brown ochre	K	11650			
62	Hostaperm red	K	23720			
63	Elba ochre	K	11510	C		
64	Sepia	K	12400			
65	Cote d'azur violet	K	11350			
66	Indigo	K	36000-C	P		
67	Celadonite	K	11250			
68	Ivory black	K	12000			
69	Red jasper	K	11300			
70	Green jasper	K	11200			

71	Azurite	K	10200	P	C		E	P	
72	Verona green	K	11000				E		
73	Maya blue	K	36000-M	P	C	O			
74	Malachite	K	10300	P	C		E		
75	Imperial purple	K	36010	P	F				
76	Verona green	K	11010	P			E		
77	Pink colour	K	10150	P	I	C c	O	P	O
78	Lead tin yellow	K	10110	P	F		E		
79	Egyptian blue	K	10060				E		
80	Purpurite	K	10960					P	
81	Natural cinnabar	K	10620	P	F		E	P	F C O E
82	Bavarian green earth	K	11100				E		
83	Spdarth	K	10420	P		O			
84	Aegerin	K	11140	P	C		E		
85	Lapis lazuli	K	10500	P	C		E	P	F O
86	Lime white powder	Z	0200P	P	F		E		
87	Bone white	Z	2400	P	C		E		
88	Asphaltum bitumen brown	Z	098						
89	Graphite in powder	Z	1300		C	O	E		O
90	Viridian standard	Z	607	P	F	I C c	O o	E e P	F C O
91	Red ochre	Z	008				E		
92	Zinc yellow	Z	2003	P	C		E	P	C
93	Roman black earth	Z	2803						
94	Flesh tint	Z	404						
95	Vermilian genuine	Z	0050		F	C	E	P	F C O E
96	Red lead	Z	0494	P	F	C	E	P	P C o E
97	White lead	Z	0110	P	C	O	E		O E

^a The table reports the identification number (ID), the English name of the item (Name), the supplier (K = Kremer, Germany; Z = Zecchi, Italy) (Firm) and the item code (Code) for each pigment. The presence of a letter indicates whether it was possible to obtain a characteristic Raman or fluorescence spectrum. Capital letters refer to Raman spectra and lower-case letters to fluorescence spectra. For each of the three excitation wavelengths, the letters indicate in which painting techniques it was possible to identify the pigment.

The following convention was adopted: P = dry pigment, F = fresco, C = casein tempera, E = egg tempera and O = oil.
^b Imperial purple was not applied in any of the four painting techniques because its use is not documented. Orpiment was not applied in any of the four painting techniques owing to its limited availability.

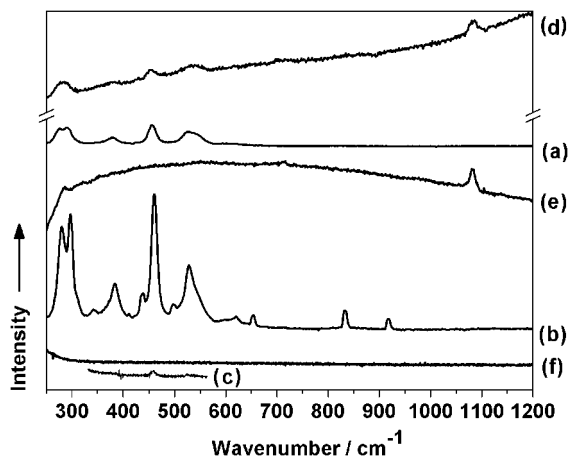


Figure 1. Raman spectra of pigment 78, lead tin yellow, acquired with excitation at (a) 531.5, (b) 632.8 and (c) 780 nm and of the pigment in a fresco painting with excitation at (d) 531.5, (e) 632.8 and (f) 780 nm.

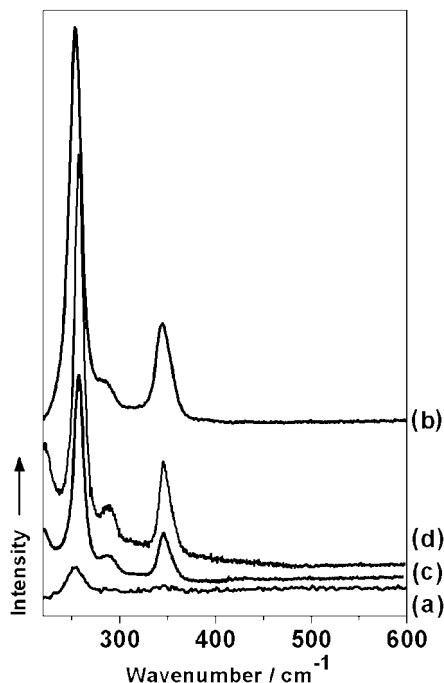


Figure 2. Raman spectra of pigment 81, cinnabar, acquired with excitation at (a) 531.5, (b) 632.8 and (c) 780 nm and of the pigment in oil painting with excitation at (d) 780 nm.

The pigment can be characterized only when already applied with one painting technique

Some pigments (14, 15, 22, 23, 30, 31, 33, 63, 72) gave characteristic Raman spectra only when analysed already applied with one of the painting techniques considered in this study. The spectra obtained from the painted pigments can, therefore, contribute to the completeness of the information contained in the databases, becoming

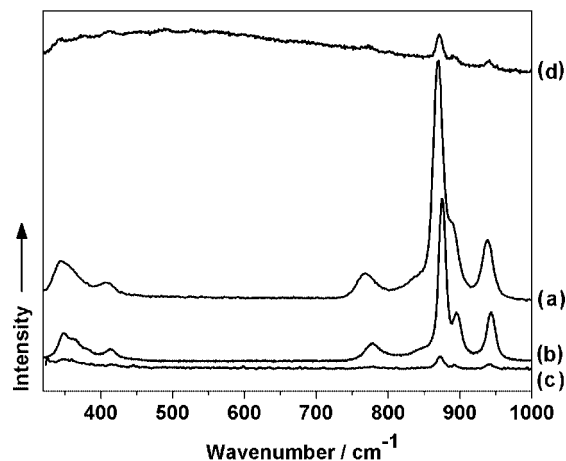


Figure 3. Raman spectra of pigment 92, zinc yellow, acquired with excitation at (a) 531.5, (b) 632.8 and (c) 780 nm and of the pigment in egg tempera painting with excitation at (d) 632.8 nm.

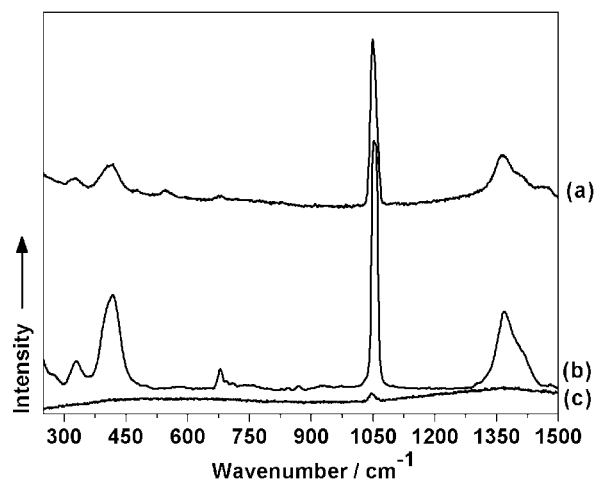


Figure 4. Raman spectra of pigment 97, white lead, acquired with excitation at (a) 531.5 and (b) 632.8 nm and of the pigment in casein tempera painting obtained with excitation at (c) 531.5 nm.

particularly important in the case of pigments which otherwise cannot be characterized. Clearly, it must be considered that the spectra of pigments applied to a painting include the contribution from the binding agent. As an example, pigment 55, indanthrone blue, could not be characterized with any of the three laser wavelengths, except after application in casein and egg tempera and fresco paintings with laser excitation at 632.8 nm (Fig. 5).

The pigment can be characterized only with laser radiation of 632.8 nm and, when painted, only with that of 531.5 nm

Pigment 42, irgazine orange, is only characterized with excitation at 632.8 nm. After application to a painting it

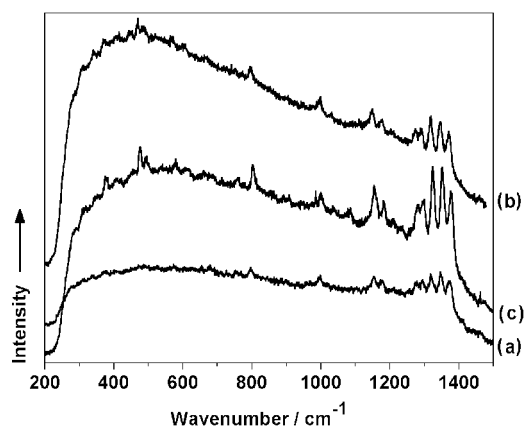


Figure 5. Raman spectra obtained with excitation at 632.8 nm of pigment 55, indanthrone blue, applied with (a) egg tempera, (b) casein tempera and (c) fresco painting techniques.

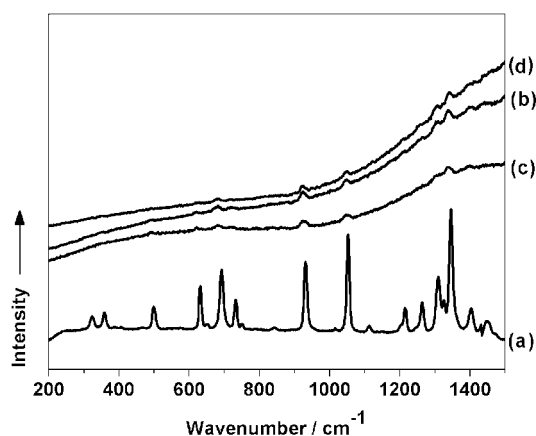


Figure 6. Raman spectra of pigment 42, irgazine orange, obtained at (a) 632.8 nm and of the same pigment applied with (b) egg tempera, (c) casein tempera and (d) oil painting techniques, obtained with excitation at 531.5 nm.

is only identifiable with excitation at 531.5 nm. Comparing it with the spectrum of the dry pigment obtained at 632.8 nm, it is possible to detect the weak peaks produced by excitation at 531.5 nm. Although the pigment can be characterized at 632.8 nm, this is no longer possible when it has been applied using any of the painting techniques studied. It is therefore necessary to use excitation at 531.5 nm, at least for its identification in egg and casein tempera and in oil paintings (Fig. 6).

Fluorescence spectroscopy

Although the fluorescence spectra are easily acquired, with practically the same system used for dispersive Raman spectroscopy, to date few workers have investigated the characterization of paint pigments using fluorescence spectroscopy.^{17,18} This paper shows that, although it allows the characterization of a modest number of pigments, its contribution can be decisive, in particular in cases where

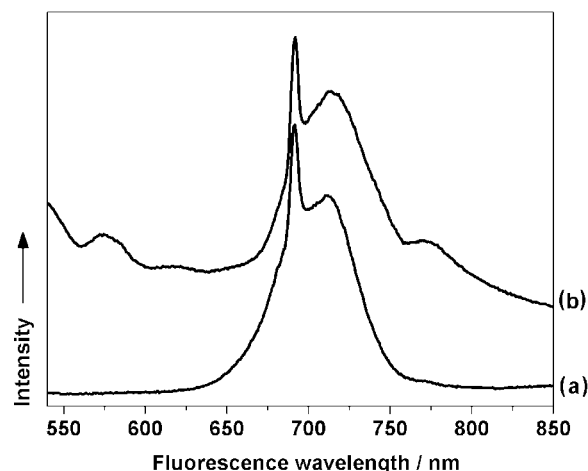


Figure 7. Fluorescence spectra of (a) pigment 13, cobalt cerulean blue, and (b) the pigment applied in oil painting, both obtained with excitation at 531.5 nm.

identification is not possible using Raman spectroscopy. For example, after application in oil painting, pigment 13, cobalt cerulean blue, can only be characterized based on the fluorescence obtained with excitation at 531.5 nm (Fig. 7). It should be noted that the database contains only those fluorescence spectra with peaks considered to be characteristic.

Painting grounds and binding agents

The correct attribution of the Raman and fluorescence peaks obtained in the analysis of an artefact requires their comparison with those in a database containing the spectra of the binding agents and painting grounds, given that any emissions of the latter will be found overlapping those of the pigment. Of the binding agents and grounds used in this study only the fresco, the binding agent for egg tempera and the ground gave Raman spectra with characteristic peaks. The spectra are shown in Fig. 8. It was not possible to characterize any of these grounds and binding agents using their fluorescence spectra.

CONCLUSIONS

A combined system for Raman and fluorescence spectroscopy, equipped with three laser wavelengths (531.5, 632.8 and 780 nm), allows the characterization of a larger number of pigments than is possible with two or worse, only one laser. However, given that even under these conditions it was not possible to characterize all 99 pigments examined, it would be advantageous to repeat the tests using other excitation wavelengths to obtain the characterization of the remaining pigments through the elimination of fluorescence or the excitation of resonance Raman emission.

The system was found particularly favourable for the identification of pigments applied with the painting

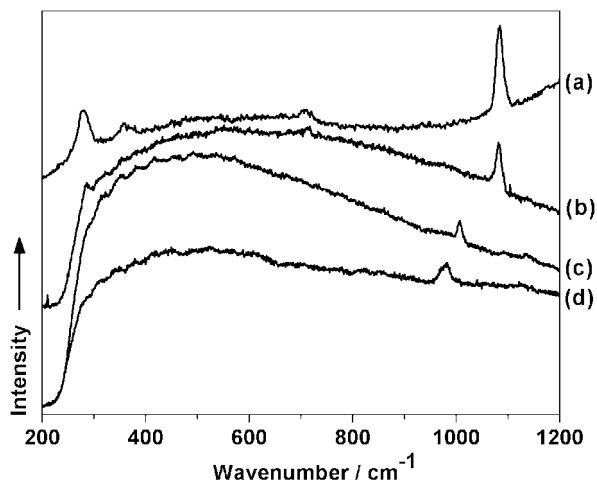


Figure 8. Raman spectra of the fresco ground obtained with excitation at (a) 531.5 and (b) 632.8 nm, of the egg tempera binding agent with excitation at (c) 632.8 nm and of the *preparazione* obtained with excitation at (d) 632.8 nm.

techniques studied. Nevertheless, even in this case, it would be advantageous to test other laser wavelengths which, as for the characterization of pigments, could increase the analytical range of the system.

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