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RAMAN VIBRATIONAL STUDY OF PIGMENTS WITH PATRIMONIAL INTEREST FOR THE CHILEAN CULTURAL HERITAGE

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ABSTRACT

Seven pigments of patrimonial interest for the Chilean artwork were analyzed by means of Raman spectroscopy by using the 632.8 nm excitation laser line. Samples were supplied by the National Center of Conservation and Restoration of Chile (CNCR) in a cooperative effort to determine the exact molecular composition of each pigment. In this contribution we propose to settle the use of the Raman spectroscopy as a method to contribute to the conservation and/or restoration procedures, and thus to the authentication of the works of art. Data collected were compared with published works confirming the reliability of Raman spectroscopy in this field of research.

1. INTRODUCTION

Molecular recognition of pigments, and other materials, in conservation arts is very important. The adequate identification of chemical species in a work of art ensures that the materials characterized will provide valuable information. The vibrational spectroscopy, a structural tool, with the infrared, Raman and surface enhanced Raman scattering (SERS) techniques along with new Raman performed instrumentation have been extensively used in conservation science [1-3].

The benefits of Raman spectroscopy are notorious, since samples needed are minimal in case that data could not be collected in-situ [4,5] or right in the object of study. The data collecting spectral process is also non-destructive [6] which is huge advantage among other methods for molecular recognition. The obtained information could avoid some unwanted visual effects due to undesired chemical reactions in the restoration process. Also can lead to choose the best method to remove a pollutant and/or consolidate the piece by knowing the degradation products of pigments [7-9]. Another usage of this technique is to determine authenticity and dating of objects by knowing the artist's palette and checking that the pigments found on it correspond to the date of first manufacture or usage. This aims to achieve a better understanding of the object studied in terms of its comprehension, conservation and also in the unique moment for the life of an object as the restoration.

The present work should contribute to give solid information on the different aspects of the work of professionals involved in the identification, restorations and preservation of cultural heritage art pieces using the vibrational knowledge and expertise. At present the spectral information here obtained is inserted in the study of the identification of pigments of a wall painting (unknown author) recently unveiled in the San Francisco church, in Santiago, Chile, and in the diagnosis of the wall painting Historia de Concepción, by Gregorio de la Fuente, in the ancient Concepción train station.

2. EXPERIMENTAL

2.1 Samples

Samples were provided by the CNCR and consisted in seven pigments from a Kremer standard set catalogued as displayed in Table 1. Samples are mostly common pigments used in contemporary art, excepting the magnetite.

Table 1. Pigment samples catalogued as received from CNCR.

Catalogue Number	Name	Color
PIG008	Zinc White (lead-free)	White
PIG028	Cadmium Yellow #9,5	Yellow
PIG047	Alizarin Crimson, dark	Red
PIG072	Chrome Green, dark	Green
PIG085	Ultramarine Blue, light	Blue
PIG138	Naples Yellow, light	Yellow
PIG169	Iron Oxide Black	Black

2.2 Raman measurements

All spectra were collected using a Renishaw Raman System 1000 equipped with a He-Ne laser (excitation wavelength 632.8 nm), an Ar^+ laser (excitation wavelength 514.5 nm) and a Leica microscope. The site for incident radiation was focused through a 50x objective. Spectra were recorded from 200 to 1800 cm^{-1} and the samples were exposed between 10 and 30 seconds taking from 1 to 5 accumulations. Radiation of 632.8 nm from the He-Ne laser was used as excitation source and the power was set from 1% to 100% as needed to obtain the best spectra.

3. RESULTS AND DISCUSSION

The first approach to the pigments composition was proposed on the basis of the names already published [10]. Results are summarized in Table 2 indicating the identification according to the Color Index (CI) name, the former catalogue number and the generic name (or the compound name in the case that there is not generic name); also the formula and the main Raman bands are displayed. The spectra are shown as obtained and are illustrated along with the discussion.

3.1 PIG008 Zinc White

Zinc White corresponds to Zinc (II) oxide, with wurtzite like crystal structure (w-ZnO), which was first produced as a white pigment in the 1780's. Because of its poor attributes when used in oil was not popular until 1834 [10] when it was sold under the name of Chinese White.

The w-ZnO belongs to the C_{6v} group of symmetry, and the symmetry species that show Raman activity (Fig. 1) are [11]: A_1 transverse optical phonon (A_1-TO) at 380 cm^{-1}; E_1-TO at 409 cm^{-1}; E_1-LO at 582 cm^{-1} and E_2 high (E_2h) at 437 cm^{-1}. These bands are consistent with previous works [12,13] for the w-ZnO. The bands at 330, 541 and 665 cm^{-1} are ascribed to possible multi-phonon scattering processes [12,14], and the bands at 1076 and 1150 cm^{-1} were assigned to multi-photon effects by Bouchard and Smith [15]. No contaminant products were found.

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Table 2. Results analysis.

CI name	Catalogue number	Name and composition formula	Raman bands cm^{-1}, relative intensities[1] and characteristic bands (bolded)	Fig.
PW4	PIG008	Zinc White, zinc (II) oxide ZnO	330w, 380w, 409vw, **437vs**, 541vw, 582vw, 665vw, 1076w(br), 1150w(br)	1
PY35	PIG028	Cadmium Yellow Lithopone, Cadmium sulphide with barium sulphate and zinc sulphide $CdS+BaSO_4+ZnS$	212vs, **298vs**, 341sh, 474w(br), **597s**, **987w**	2
PR83	PIG047	Alizarin, 1,2-dihydroxyanthraquinone $C_{14}H_8O_4$	485w, 656w, 841w, **1292m**, **1328m**, **1480m**	4
PB15	PIG072	Phthalocyanine (Pc) Blue, Copper Pc CuPc	233w, 259w, **482m**, 595w, **679s**, **746s**, 952m, 1132w, 1143w, 1215w, 1305w, **1341m**, 1450s, **1527s**, 2275w, 2674s, **2869s**, 2979m, 3054vs	5
PB29	PIG085	Ultramarine Blue, S_3^- and S_2^- in a sodium aluminosilicate matrix $Na_8[Al_6Si_6O_{24}]S_n$	255w, 286vw, **547s**, 583sh, 804w, 1096m, 1648w	7
-	PIG138	Massicot - Ternary Lead Tin Antimony oxide - Lead Antimonate mixture	**291s**, 318m, 345m, 456w, **510m**, 1367vs, 1398vs	9
PBk11	PIG169	Magnetite, iron (II/III) oxide $FeO{\cdot}Fe_2O_3$ (Fe_3O_4)	**668s**	10

[1] Relative intensity: v, very; w, weak; m, medium; s, strong; sh, shoulder; br, broad

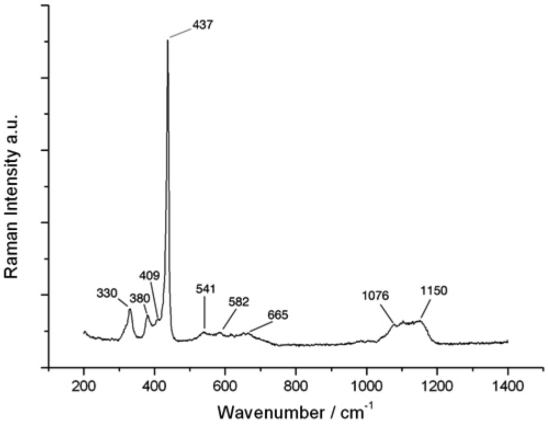

Figure 1. Raman spectrum of PIG008. 1 scan, 100% laser power.

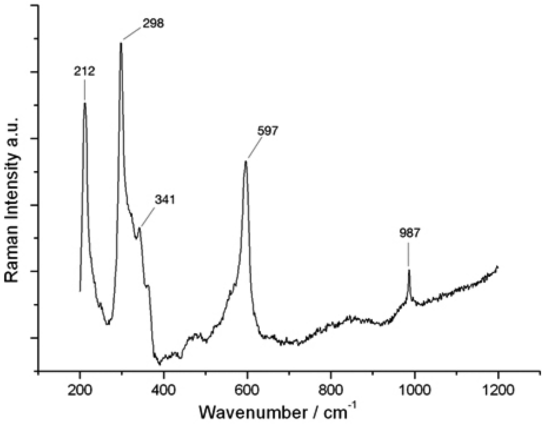

Figure 2. Raman spectrum of PIG028. 2 scans, 50% laser power.

3.2 PIG028 Cadmium Yellow Lithopone (former Cadmium Yellow #9.5)

Lithopone variant of Cadmium Yellow is formed by a co-precipitation of cadmium sulphide and barium sulphate; it was patented as a pigment in 1921 [10]. The bands at 298 and 597 cm^{-1}, (Fig. 2) assigned to the longitudinal optical phonon longitudinal optic (LO) and the overtone 2LO of the CdS crystal lattice [16] confirming the presence of CdS of the Greenockite type (Wurtzite like crystal structure) [17] in the sample. The band at 987 cm^{-1} is characteristic to recognize the barium sulphate presence [18,19]. Spectrum of PIG028 matches the spectrum shown as Cadmium Yellow Lithopone published by K. Castro et al. [20]; the sample measured by them was also studied by electrochemistry detecting the presence of an important amount of ZnS (25.2%) [21]. Bands at 212 and 341 cm^{-1} may be ascribed to the longitudinal acoustic (LA) and to the (LO) phonon modes of ZnS crystal lattice, respectively [22].

3.3 PIG047 Alizarin (former Alizarin Crimson)

Alizarin (Fig. 3) is a synthetic organic [23] madder-derived pigment characterized by the presence of anthraquinone which gives different colors according to its substituents [24].

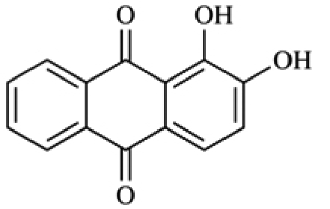

Figure 3. Alizarin structure

This pigment was originally extracted from the roots of various members of the Rubiaceae family [10]. The bands are assigned as it follows (Fig. 4): skeletal vibrations (485 cm^{-1}); C-H/C-O out-of-plane bending (841 cm^{-1}); CO/CC stretching and CCC out-of plane bending (1292 cm^{-1}); CC stretching (1328 cm^{-1}); and CO/CC stretching plus CH out-of plane bending (1480 cm^{-1}) [25]. The baseline observed in the alizarin spectrum (Fig. 4) is due to natural fluorescence of the alizarin molecule; it might be attenuated using Surface Enhanced Raman Spectroscopy (SERS) [25].

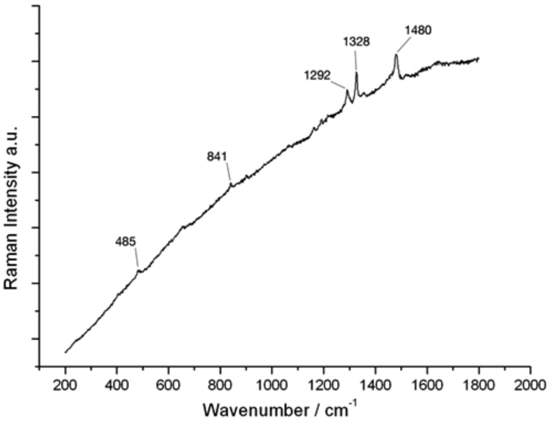

Figure 4. Raman spectrum of PIG047. 2 scans, 1% laser power.

3.4 PIG072 Chrome Green.

The case of this pigment in the present investigation is the most representative example of the usefulness of Raman spectroscopy in the field of pigment recognition. The sample provided was tagged under the name of Chrome Green which should correspond to a chrome (III) oxide [10], with expected bands around 350, 552 and 614 cm^{-1} [19,20], or to an intimate mixture of Chrome Yellow and Prussian Blue, with bands expected at 279, 360, 532, 845, 2092 and 2153 cm^{-1} [16], both with a strong inorganic character. However, these characteristic bands were not observed; a presumably organic spectrum, see figure 5, was obtained instead.

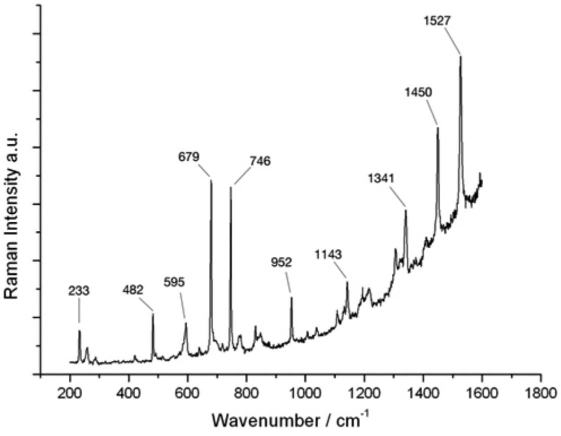

Figure 5. Raman spectrum of PIG072. 1 account, 1% laser power.

The pigment sample corresponds to a copper phthalocyanine (CuPc) [23] (Fig. 6). Phthalocyanines are macrocycles formed by four isoindole units that have the ability to coordinate different metal atoms [26]. The most intense bands shown on Fig. 6 at 482, 595, 679, 746, 952, 1143, 1341, 1450 and 1527 cm^{-1} are assigned to A_{2g}, B_{2g}, A_{1g}, B_{1g}, B_{2g}, B_{2g}, A_{1g}, B_{2g} and A_{1g} symmetry species, respectively [27,28]. Bovill et al carried out a complete band assignment [28].

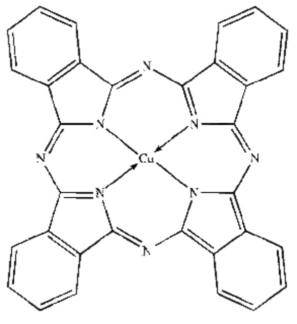

Figure 6. Copper phthalocyanine structure.

Phthalocyanines started to be used as pigment right after its discovery back in 1929 [10]. Thus, the Chrome Green pigment in the original sample is not chrome (III) oxide but copper phthalocyanine.

3.5 PIG085 Ultramarine Blue

According to published works [29,30] the Raman spectrum (Fig. 7) of the pigment corresponds rather to Ultramarine Blue, the synthetic equivalent of Lazurite. Lazurite is the main component in the precious stone called Lapis Lazuli. The use of Ultramarine Blue as a replacement of Lapis Lazuli began in 1787 in Italy [10]. The other components of Lapis Lazuli are calcite and pyrite, and since none of the main bands of those minerals [30] appears on the spectra taken for this sample, the synthetic origin is inferred.

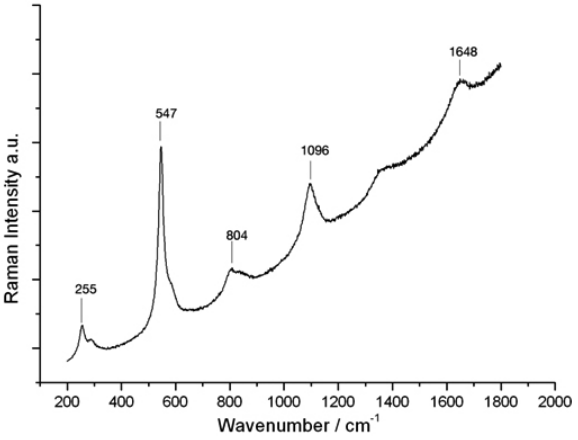

Figure 7. Raman spectrum of PIG085. 1 account, 10% laser power.

Synthetic Ultramarine Blue corresponds to a sodium aluminosilicate matrix with sulphur ions (S_3^-, S_2^-) in it; the generic formula for this kind of material is shown in Table 2.

On the microscope two types of crystals are distinguished, blue and white ones. The comparison between the spectra (Fig. 8) of both types suggests that they are the same compound.

The observed band at 547, 255 and 583 cm^{-1} correspond to the symmetric stretching mode ν_1, the bending mode ν_2 and to the anti-symmetric stretching mode ν_3 of the C_{2v} S_3^- ion (blue), respectively [31]; the other bands correspond to combination bands of the ν_1, ν_2 and ν_3, modes (e.g. 547 + 255= 802 cm^{-1}) [31,32]. The S_2^- ion (yellow) is characterized by a band (shoulder) observed ca. 590 cm^{-1} [32]; the S_2^- ion is responsible for the green hue of some of the Ultramarine pigments.

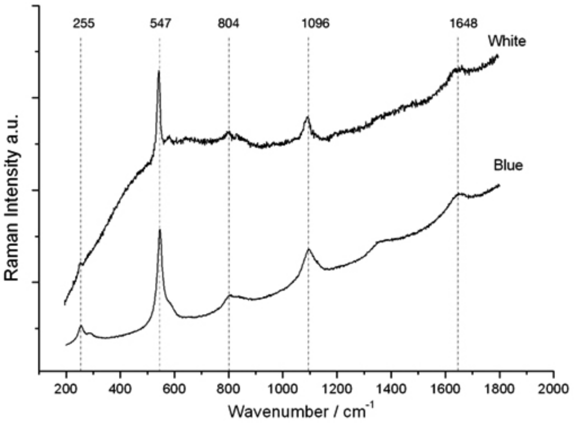

Figure 8. Comparison between the 2 types of crystals in the sample.

3.6 PIG138 Massicot - Ternary Lead Tin Antimony oxide - Lead Antimonate mixture (former Naples Yellow)

Lead based yellow pigments had been used since antiquity; they consist in lead oxides, lead-tin oxides (type I and II) and lead-antimony oxides (Naples Yellow being one of them), characterized by a strong band between 127 and 145 cm^{-1} (Fig. 9) attributed to νPb-O [33]. In particular, lead antimony oxides are synthetic analogues to the bindehimite that presents a pyrochlore crystal structure [10]. This type of crystal structure shows the ideal formula $A_2B_2O_7$ (Naples yellow most accepted formulation is $Pb_2Sb_2O_7$) where A and B can be replaced by cations such as Pb(II), Sb(II), Sn(II), Zn(II), Bi(II), getting octahedral coordination when they are in B position. In fact, the band at 510 cm^{-1} is assigned [34] to the symmetrical stretching of the octahedral formed by the Sb-O bonds when Sb occupies the B position; this situation can occur in more than one case in the context of yellow lead based pigments. Besides Naples Yellow, mentioned above, the band at 510 cm^{-1} can be observed in a Ternary oxide of Pb-Sn-Sb [35]. The other important bands could suggest the presence of Massicot, as it is present in the synthesis of both Naples Yellow and the Ternary Oxide [35,36], and a Lead-Tin Oxide (Pb_2SnO_4) [37]. As no information was obtained below 200 cm^{-1}, the species mentioned above are just proposed [16].

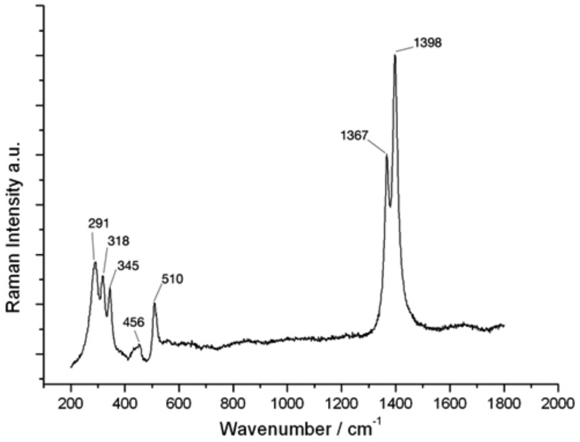

Figure 9. Raman spectrum of PIG138. 1 scan, 10% laser power.

3.7 PIG169 Magnetite (former Iron Oxide Black)

The A_{1g} band at 668 cm^{-1} (Fig. 10) identifies Magnetite [15,37], a magnetic mineral that consists in an Iron (II/III) Oxide observed mainly in igneous and metamorphic rocks [10]. The Raman spectrum of this sample (Fig. 10) was difficult to obtain because its black color. The observed slight asymmetry towards the high frequencies of the band centered at 668 cm^{-1} suggests the coexistence of the iron (II) and (III) oxidation states as it is in the original sample. The other bands at 538 and 306 cm^{-1} were also observed by Shebanova and Lazor [38]; these authors compared their results with other Raman studies indicating that discrepancies with the earlier data arise from photo-oxidation processes occurring during the Raman experiments. Under the spectral acquisition conditions here used no spectral modifications were observed by laser effect.

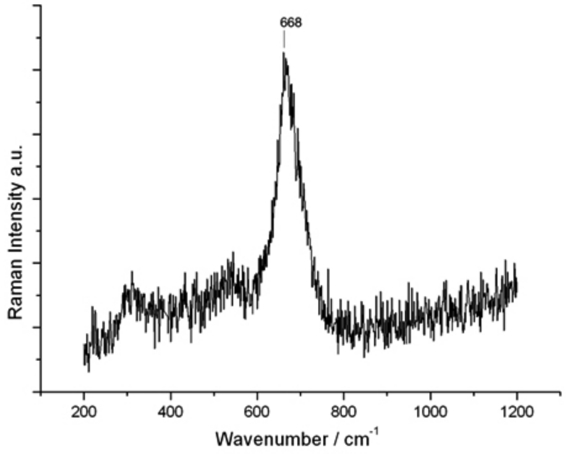

Figure 10. Raman spectrum of PIG169. 5 scans, 1% laser power.

4. CONCLUSION

Six of the seven pigments analyzed were successfully recognized and/or confirmed using Raman spectroscopy. This technique results to be useful in the fields of material characterization for cultural matters, namely conservation and restoration of artwork. Data bases available now days gathering Raman characterization for common materials used in art, whether they are published on journals or on-line, are widely accessible and reliable, increasing the importance of Raman spectroscopy as a complementary tool for comprehension, conservation and restoration of the works of art. Finally, recent published results concerning anthocyanin [39], a pigment extracted from copihue, will be extremely useful in the characterization of Chilean art pieces painted using that pigment.

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