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Vibrational spectroscopy for the study of Chilean cultural heritage

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Abstract

Background: Natural and synthetic colouring products along with its associated supporting materials have been studied in several expressions of the Chilean cultural heritage using vibrational spectroscopy. These expressions include archaeological remains as well as works of art.

Results: Among the materials studied so far we can count pigments found in archaeological sites from the north of Chile, in plaster (wall paintings) and in polychrome (beams), and dyes mainly related to added components on historic silk textiles. Identification of materials resulted to be relevant to know about Chilean culture through history.

Conclusions: The vibrational knowledge obtained contributes to give solid data as a complement to the different information aspects collected by conservation professionals involved in the characterization and conservation procedures of cultural heritage and also it gives us the opportunity to share knowledge and to give value to objects that not always are of the public domain.

Background

Techniques that involve micro-sampling or non-destructive are important aspects to consider when dealing with cultural heritage and unique objects while pursuing characterization through analyses of ancient samples [1–4]. Raman spectroscopy is a powerful technique for the analysis of different kinds of materials, showing advantages related to the specificity, sensitivity, reproducibility, applicability, mobility and resolution (spatial and spectral) [5]; moreover, it is a non-invasive and non-destructive technique by itself. These advantages, coupled with recent developments in instrumentation and techniques, particularly the surface enhanced Raman spectroscopy (SERS), have made it possible to extend its use in archaeometry and conservation [5–11]. Raman spectroscopy allowed identifying pigments and dyes used in the preparation of manuscripts, paintings, ceramics and textiles [12–17]. Its meaningful disadvantage lies in the formation of fluorescence, which is an accompanying phenomenon in the measurements of diverse materials; the nanostructured metal surfaces in the SERS technique, and the adequate use of specific lasers reduce, or totally quench the fluorescence.

Infrared spectroscopy (FTIR) has been widely present in the study of cultural heritage and it has become a permanent part of the instrumental techniques used in routine inspection of objects and materials related to the conservation of cultural objects. It is one of the most appropriate techniques to identify organic compounds presents in most several materials (e. g. binding media, varnishes, adhesives, etc.). It does, however, present some disadvantages (i.e. water absorption) related to the experimental procedures. Classically, a considerable amount of sample was required to disperse in an "IR transparent" material, such as KBr or NaCl, to form a pellet from where the information was obtained. This resulted, in most cases, in the sacrifice of the sample in order to obtain good quality results. Fortunately, instrumental advances have allowed obtaining the same information with fewer amounts of sample and practically without preparation. One of these advances is the use of attenuated total reflection (ATR-FTIR) sampling method, in which a small fragment of the sample is pressed against a crystal used as a medium to make the IR radiation to interact with the material. Despite this, in most of the cases the original form of the sample is modified somehow. FTIR besides being micro-destructive to the object is also destructive to the sample.

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The present work deals with our last results concerning the spectroscopic studies, mainly vibrational Raman and infrared, of different materials in the Chilean cultural heritage. The interest is focused on archaeological samples [18, 19], Diaguita pottery [20], mural painting [12], painted beams [21] and historical silks [22].

Results and discussion

Studied objects, selected to be presented in this work, represent a wide sample of the materials found in the Chilean cultural heritage. The findings allow us to show the versatility of the vibrational tools used, as well as to help improving the contexts in which the objects are/were in each case. Also it gives us the opportunity to share knowledge and to give value to objects that not always are of the public domain. The specific insights on each object are presented in the following sections.

Archaeological pigments

Samples of yellow pigment blocks from the archaeological site Playa Miller 7 (PLM7) of the Formative Period (3700–1500 years B.P.) on the northern coast of Chile were studied using micro-Raman data [see Additional file 1] [18]. Samples from complete blocks, detached fragments or powder were chosen. Yellow blocks (Fig. 1a, b), from the archaeological site consist mainly of a finely ground pigment. In some blocks finely grounded elongated structures (incorporated in the mixture) were identified as algae [23]. The yellow color is not often found in contexts of archaic hunter-gatherer groups. The yellow paint has been observed in the coating of a mummy of the Macarena Chinchorro site 38 and in rock art paintings of Andean foothills without further analyses. A spectral comparison between the archaeological samples and those from Andean geothermal areas of Arica and Parinacota: Jurasi (JU), located at 4000 m above sea level, was carried out. Until now in South America, yellow pigments has received little attention. Moreover yellow pigment such as natrojarosite, has only been reported in the cave paintings of Inca Cave 4 site in the region of Jujuy, Argentina [24], and in other sites in Argentinean Patagonia [25]. Jarosites are a large family of minerals that have a general formula $M_n(Fe^{3+})_6(SO_4)_4(OH)_{12}$, where M can be K^+, $(NH_4)^+$, Na^+, Ag^+ or Pb^{2+} and $n = 2$ for monovalent cations and 1 for the divalent cations [26]. The mineralogical characteristics and chemical properties of the jarosites have been widely studied [26–30]. The natrojarosite samples for the Raman study were extracted from the PLM7 Archaeological Sites 14 and 15, and from the Jurasi hydrothermal site 17 and 18. The band assignment was performed on the basis of published data [29, 30] and general spectral data [31]. These results indicate that most of the bands correspond to vibration normal modes associated to jarosite type compounds. The spectral comparison between the archaeological samples and those from the geothermal areas allowed us to infer that this hydrothermal source was probably used as source of yellow pigment by pre-Hispanic inhabitant of the Formative Period. Slight differences in wavenumbers are not enough information allowing differentiating jarosites. However, XRF results, and previous results obtained by SEM-EDX and XRD indicate that the main yellow pigments are natrojarosite and K-jarosite when compared with a database [32]. For the first time, results support the idea that minerals from the jarosite family have been used in Chile in ancient times (3700–1500 years B.P.).

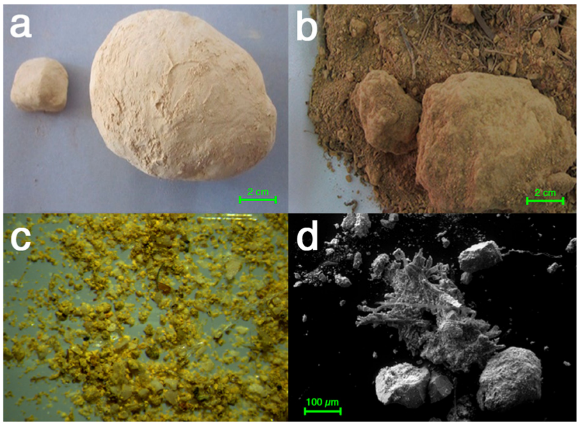

Fig. 1 Pigment samples. Pigment blocks from Playa Miller with (**a**) and without (**b**) the presence of algae. Pigment sample from Chorrillos, view under optical microscope (**c**) and under SEM (**d**)

Also, we show results on the analyses performed on an archaeological yellow pigment of an archaeological funerary site in Chorrillos, Calama city, in the north of Chile (Fig. 1c, d). The pigment sample was found in a mollusk shell making part of the grave goods related to a female individual (ca. 25–30 years old) dating to the Early Formative Period (800–200 B.P.). Here, we display and discuss results on the first study pointing to the identification of orpiment [19]. The identification of the toxic yellow arsenic sulfide mineral, orpiment, in archaeological mortuary contexts was performed by using optical microscopy, SEM, EDX, ^{1}H-RMN, ^{13}C-RMN, and IR and Raman spectroscopy. The microscopic images display amorphous yellowish granulates with heterogeneous chemical surfaces. Negative ^{1}H- RMN and ^{13}C-RMN results allowed conclude that the sample is free of organic matter. The SEM and EDX indicate the existence of arsenic and sulfur in the sample. Orpiment (As_2S_3) and pararealgar (β-As_4S_4) are yellow, while realgar (α-As_4S_4) is an orange to red mineral. All these pigments have different vibrational bands under structural analyses such as Raman or IR spectroscopy. The IR and Raman analyses confirm the presence of orpiment.

In fact, the IR spectrum of the archaeological sample shows the characteristic orpiment bands between 250 and 400 cm^{-1} due to the νAs-S mode [33–39]. The Raman spectrum (Fig. 2a) obtained shows the same spectral profile than the orpiment reference sample according to a spectrum database [32]. When comparing Fig. 2a, b, the eight bands appear at the same frequencies with similar relative intensities, indicating that they are likely the same compound. There are some minor shifts being the most noticeable the one at 359 cm^{-1}, which is actually a different band reported as a shoulder [33]. These kinds of intensity differences are often seen on anisotropic compounds such as crystals. The archaeological orpiment is an arsenic sulphide, toxic to humans [40]. Thus, it is remarkable that people of Calama, during the Formative Period, used this type of dangerous pigment as a funerary grave good. The present analysis opens the question of how this mineral was manipulated in ancient times.

Diaguita pottery

Four samples of ceramics fragments belonging to the Museum of Limarí [20] were investigated; samples display black, white, red and brown colors (Fig. 3). The tonality of these colors goes from intense to tenuous. Potteries belong to the Diaguita culture, one of the distinctive original people mainly settled during the pre-Columbian period in the III and IV region (18° to 31° south latitude) of the Chilean territory. The Diaguita culture was mainly developed in different stages between the 9th and 15th century; this culture is recognized in the pre-Columbian American territory because of the plastic richness of its pottery [41]. At least three development phases in the Diaguita culture have been identified; differences arise from the complexity in the manufacturing of pottery's artifacts. The last phase is associated to the Inca rule period [42]. The present results, to our knowledge, are the first related with ceramics from the Valle del Elqui investigated through micro-Raman spectroscopy. Some chemical components identified by Raman spectroscopy in the colored areas of the pottery were crystalline silicates, namely, quartz, and pigments such as kempite and tenorite; hematite and potentially goethite were also found. The characteristic sharp band of quartz at 464 cm^{-1} is attributed to the νSi-O vibration, showing some degree of shifting wavenumbers due to variations in the crystallinity of the sample. It was initially believed that the black pigment used to paint the ceramics was only a manganese salt ($Mn_2Cl(OH)_3$) or kempite [32]. Kempite displays a band at 293 cm^{-1}. Bands at 343, 632 and 1224 cm^{-1} belonging to copper oxide (II) or tenorite [32] were identified in deep black dashes of the samples [see Additional file 1]. Copper was already reported in the black pigments of Pre-Columbian Chilean potteries [43]. The copper content of the black color appears to be a particularity of Diaguitas; in fact, in other cultures of South America the black pigment contains iron, manganese and carbon [44–47] in their composition. The micro-Raman spectrum of sectors displaying red coloration shows characteristics bands of hematite at 223, 289, 411 and 613 cm^{-1}. Hematite has also been found in different red tonalities from orange to brown in the decoration of Viluco and Chilean Diaguita type ceramics [48]. Additionally, in the case of the brown color it is possible to interpret this tint either as a mix of different pigments or due to only one genuine pigment (goethite). Brown areas display bands of hematite as well as bands at 1228 and 1307 cm^{-1} from tenorite. Also it is possible to consider this spectrum as arising from a variety of hematite like FeO(OH) (goethite) [32], which color is described, among others, as a red-brownish or ochre [see Additional file 1] [49, 50].

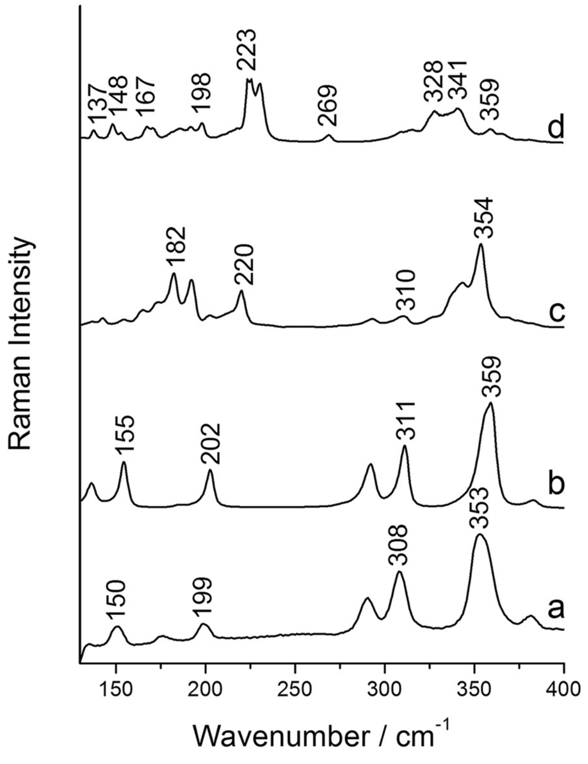

Fig. 2 Raman spectra of arsenic pigments Raman spectra from archaeological yellow pigment and library standard: (**a**) archeological sample, (**b**) orpiment reference, (**c**) realgar reference and (**d**) pararealgar reference

Mural painting

The wall painting *Historia de Concepción* (Fig. 4) built between 1943 and 1946, in the former Main Train Station of Concepción, Chile, is made of a mortar arrangement fixed to the wall. The total area of the painting is about 258 m^2. This wall painting is another subject of

Fig. 3 Diaguita pottery fragments. Diaguita ceramic fragments. Points where micro-Raman measurements were performed are marked on a square

interest in the present work [12]. This artwork displays intense deterioration originated mainly from earthquakes and permanent environmental humidity; efflorescence and pulverization are observed in some zones. Research projects dealing with the diagnosis of the current conservation state of the wall painting considered the Raman microscopy to identify pigments and fresco-related materials. Samples were collected with a brush and scalpel from the wall painting; samples of dimensions 0.5-1 mm^2 were selected according to the main colors displayed in the artwork and from zones where apparently they were altered after its creation.

The pigments found in the wall painting *Historia de Concepción* are mostly in agreement with those expected for a fresco [see Additional file 1], except for toluidine red and minium. Some mixtures of hematite and minium, Pb(II,IV) oxide were observed; they are identified from the characteristic Raman bands of hematite and the νPb(IV)-O mode at 548 cm^{-1}, and the O-Pb(IV)-O deformation mode at 119 cm^{-1}. The νPb(II)–O is ascribed to the band at 147 cm^{-1} [51]. The organic red pigment [52], toluidine red, displays bands at 1629, 1503, 1452, 1402, 1338, 1325, 1221, 1190, 1131 1080, 844, 797, 723, 379 and 337 cm^{-1}. Bands at 988, 616, and 453 cm^{-1} are ascribed to $BaSO_4$ used as filler in this pigment [53]. Spectral information concerning mainly pigments and composition on the surface decidedly corresponds to the fresco technique and helps confirming historical data. The blue color is ultramarine blue ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$), a matrix composed by sodium aluminosilicate salts and sulfur anions; this corresponds to the synthetic lazurite, the substitute of natural lapis lazuli. The band at 547 cm^{-1} is ascribed to S_3^-; this molecular fragment defines the blue color [54]. The very low concentration of the S_2^- anion (yellow) with a Raman band at 580 cm^{-1} in the blue pigments, gives rise to the green tones associated with some ultramarine pigments. The yellow color pigments with bands at 299, 387, 481 and 550 cm^{-1} are mainly due to goethite α-FeO(OH) [55, 56]. The intensity of some blue and yellow zones on the wall painting and the exact coincidence with the pigments analyzed from the studio allowed to infer that at least these two colors were repainted. Samples containing the black pigment display bands at about 1595 and 1319 cm^{-1} certainly ascribed to amorphous carbon. This pigment is known as

Fig. 4 Wall painting detail. Detail of the central character on the wall painting *Historia de Concepción*

carbon black [52]; the absence of the band at 960 cm^{-1}, of the phosphate moiety in calcium phosphate [57], suggests the vegetal origin of the coal in the fresco. The white color is due to $CaCO_3$ (band at 1090 cm^{-1}), which is the binder used in this painting technique; gypsum ($CaSO_4 \cdot 2H_2O$) displays a characteristic band at 1011 cm^{-1}. The green color is due to the chromium(III) oxide (Cr_2O_3), the main green chromophore in the mural painting, with bands at ca. 554 and 349 cm^{-1} [58, 59]. The identified pollutants suggest that the strong pulverization observed in this wall painting is probably due to the successive transformation of calcite into gypsum. Large gypsum crystals detach sand from the calcite matrix. The pulverization in different degrees of the painting layer produced by this phenomenon appears on the whole surface. This suggests that sulfate impurities were probably present in the original materials used by the artist. It is probable that external pollutants are acting on some areas that appear more affected today. Pulverization continues due to the high humidity in Concepción, Chile.

Painted beams

Structural painted beams (Fig. 5) and a wall painting were recently discovered in the San Francisco church, Santiago, Chile [21]. Information dealing with the origin of these artworks that belong to the same time period, between the end of the 17th and the 19th century is rather inexistent. In this section we discussed the painting technique used in the beams from the identification of their materiality, in particular pigments, ground layers, supports and ultimately agglutinants. Besides micro-Raman spectroscopy, materials were studied by using complementary techniques as microchemistry and optical microscopy.

Five different designs painted on the beams, arranged in 2 of the 5 different rooms, and a single beam in the San Diego room of the Franciscan museum, in the architectonic complex of the San Francisco church were selected for the spectral study. The museum is installed in the ancient convent built between 1800 and 1850. Samples selected from the different beams were carefully extracted following international procedures [60]. The paint layer was analyzed separately from the wood and the supporting material. The microscopic analysis of samples of wood from the beams was carried out following Richter et al. [61].

The cross section of the painted beams of the San Francisco church indicates the existence of four different layers; from the outside the pigments, then the preparation layer, a cotton rag paper [62], and the wood. Cotton rag paper is made from cotton linters or cotton from rags as the main material source [62]; cotton was identified using optical microscopy. Microscopic observation indicated that the wood samples correspond to the conifer, genus cupressus. The Franciscan congregation in 1779 ordered cypress beams to be prepared from trees cut in La Dehesa forest, in the foothills of Santiago [63]; this agrees with the species identified, thus confirming the uniqueness of the beams. The fuchsine test was positive for the rag paper and the preparation layers, suggesting that the rag paper was imbibed with a protein component, as the binding media to apply pigments. IR bands of protein were observed at 1623 and 1553 cm^{-1} corresponding to the amide I and II vibrations, respectively [64]. The micro-chemical analysis of the preparation layer indicates the presence of gypsum ($CaSO_4 \cdot 2H_2O$). The white color from the beams containing pigment and preparation layer, is gypsum for the base layer, and calcite ($CaCO_3$) band at 1087 cm^{-1} for the pigment. The green color resulted from a mixture of orpiment and ultramarine blue. The intense Raman signal at 838 cm^{-1} of the yellow color is characteristic of chrome yellow [see Additional file 1] ($2PbSO_4 \cdot PbCrO_4$ or $PbCrO_4$) [65, 66].

Historical silks

Two sets of samples were selected from the costume collection of the Museo Histórico Nacional of Chile [22]; these samples belong to a group of textiles exhibiting

Fig. 5 Polychrome beams examples. Structural polychrome beams found in the San Francisco church in Santiago

worrying levels of deterioration. The first group includes light color weighted silk samples highly friable; its degradation has continued over time despite being stored under controlled conditions. A second group includes samples of dark silk belonging to the same period as the light samples, but differentiated by a lesser degradation with respect to the stability of the textiles. Samples of Bombyx mori silk fibroin, and its motif peptide component (GAGAGS) were also studied by using mainly Raman and surface enhanced Raman scattering (SERS) techniques [67]. Silk degumming, weighting and dyeing processes effects on the degradation of Bombyx mori silk fibroin were investigated through the ATR-IR and Raman techniques along with SEM/EDS microscopy.

The Raman spectrum of the raw Bombyx mori silk (CS), has many similarities with the spectral profile of the peptide GAGAGS, the crystal fraction dominating the spectrum [67]. The ATR-IR spectrum of the raw silk shows two strong bands at 1617 and 1511 cm^{-1}. The ATR-IR spectra of the degummed silks samples using the same method [68] but different pH, temperature and time conditions DS1 (pH 10, at constant boiling temperature for 1 h.) and DS2 (pH 8.5, at constant 85 °C for 2 h.), display the same profile except for the intensity variation of the bands at 1617, 1440 and 1403 cm^{-1}. Relative to the spectrum of CS, the intensity of the first band decreases in the sample DS1 and displays the same relative intensity in sample DS2. In both degummed samples the band at 1063 cm^{-1} reduces drastically its intensity when compared with the spectrum of CS. The spectral variation of the sericin bands [69] at 1403 and 1063 cm^{-1} is consistent with the degumming process used. Raman spectral modifications between the CS and degummed samples were also observed. In general, no protein conformational changes can be inferred from Raman spectral variations observed for amide I (1650–1670 cm^{-1}) and amide III (1230–1280 cm^{-1}) vibrations, and skeletal modes in the 900–960 cm^{-1} spectral region [70]. The pH, time and temperature parameter modifications of degumming methods could produce the observed spectral changes. Thus, the degumming process exposes the single fibroin protein.

No historical information on the weighting process type used in the case of cream color lining, lining of a pink dress and a purse samples has been reported. ATR-IR bands at about 969 and 995 cm^{-1}, and 955 and 993 cm^{-1} are ascribed to silicate and phosphate fragments, respectively (Fig. 6). The bands of the fibroin are displayed with the same spectral profile as in the case of the isolated fibroin. The relative intensity of the amide I and II bands allows differentiating the dynamite and pink weighting processes, this is, when the intensity of the amide bands is similar to the group of bands at about 970 cm^{-1} it is possible to propose that the pink process was used. A strong intensity of the amide bands is characteristic of a dynamite weighting process [71]. The spectral shift of the band at 1617–1623 cm^{-1} gives account of the chemical effects of metal atoms on the fibroin component induced by different weighting processes in the series of the historical weighted silks as concluded by Taddei et al. [72].

On the other hand, and in order to investigate about the weighting process used in the historical samples we have prepared tannin-weighted silks from the un-weighted white silk sample. Two tannin weighted samples TWS1 and TWS2 were obtained by using a first and a second charge procedure, respectively. The samples display identical ATR spectra and both similar to the un-weighted sample. The expected IR bands of the gallic acid [73] or the iron gallic complex [74] are

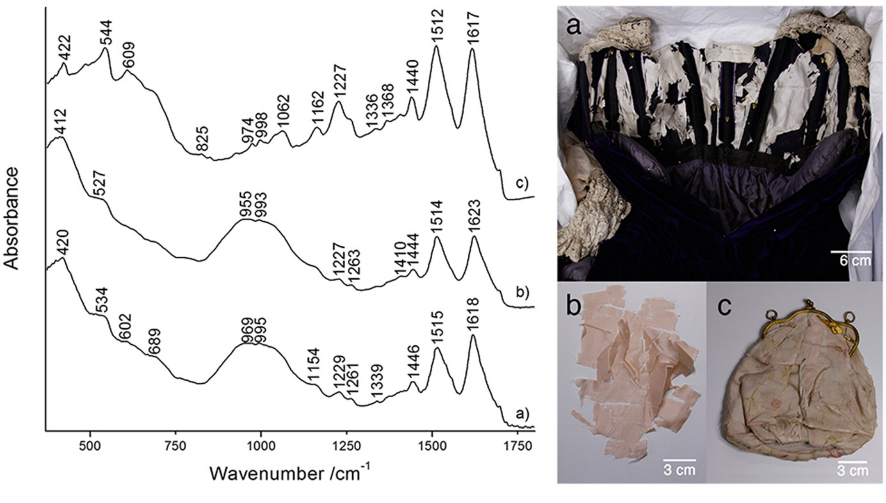

Fig. 6 ATR of historic weighted silk. ATR-IR spectra of weighted historic silk samples obtained over a diamond window: **a**) cream color lining, **b**) lining of a pink dress and **c**) a purse

probably masked by the fibroin bands. The Raman spectra of the samples are very similar and dominated by the iron (II)/gallic acid complex; this is also similar to the Raman spectrum of the iron gall inks. The most intense bands of the metal complex are located at 1473, 1318, 960, 813, 582 and 535 cm^{-1}, and the spectrum of the complex has the same spectral profile of that reported by Lee et al. [75]. The present Raman results are highly consistent with the fact that the tannin weighting processes does not modify the silk fibroin structure; the weighting agent dominates the Raman spectrum. On the basis of the above results we recognize the formation of the iron-gallic acid complex and thus we propose that the iron atom could act as a molecular assembler between the fibroin and the gallic moiety.

In a recent publication concerning the RB5 dyed silk we observed that the Raman signals are mainly due to the dye [41]. In the case of some historic samples of dyed silks analyzed, the ATR spectrum of one of them dated the beginning of the 20th century, displays bands easily ascribed to silk fibroin and two intense bands at 2073 and 492 cm^{-1}. In another sample black weft and pink warp fibers were identified. The Raman spectrum of the black warp fiber displays bands at 2166, 530 and 273 cm^{-1}, corresponding to Prussian blue; then, the warp fiber was stained with Prussian blue. According to Hacke [76] the stannous and iron chloride solutions were used as mordant of the Napoleon blue a modification of the Prussian blue pigments. The SEM-EDS data indicate the presence of tin and iron confirming that these mordant were used in this sample. The spectral analysis of the pink warp allows identifying silk bands. In the case of the Manila mantle dated to the late nineteenth or early twentieth century showing a black to brown fading, no Raman spectra of the silk were obtained; the laser excitation probably induced the sample degradation. To avoid the degradation we used the SERS methodology and the 785 nm laser line for the study. The SERS signals correspond to the dye Sudan Black B following Geiman et al. [77] and the Raman data [see Additional file 1].

Conclusions

Raman results of the yellow blocks from the archaeological site Playa Miller 7 (PLM7), on the coast of Atacama Desert in northern Chile, allowed identify natrojarosite and K-jarosite type compounds as the main components. A spectral comparison between the archaeological samples and those collected in Andean geothermal areas of Arica and Parinacota: Jurasi (JU), located at 4000 m above the sea level, permitted propose that this hydrothermal source was probably used as obtaining source of yellow pigment by pre-Hispanic inhabitant of the Formative Period (3700–1500 years B.P.).

Sources of pigments such as arsenic sulfides could be interesting to trace and identify their hidden dangers in ancient populations, Formative Period, of northern Chile [78]. Colorful pigments (manganese, iron) and funerary behavior have been reported for the Chinchorro Culture and for rock art in northern Chile [79]. The use of orpiment allows infer that ancient populations were familiar with several pigments that are beautiful but some dangerous to human health [80]. Future studies could focus on the sources of origin, extraction and management of this dangerous mineral.

Red, black, brown and white colors were identified in ceramic fragments from the unknown contexts of the Diaguita culture. The Raman data allowed distinguish the use of the pigments such as quartz and manganese (kempite) salts, as well as different types of oxide pigments, hematite, tenorite and possibly goethite.

The Raman microscopy was used to identify pigments and fresco-related materials from the wall painting Historia de Concepción by Gregorio de la Fuente in Concepción. Subsequent interventions were recognized when pigments were compared with those originals obtained from the artist’s studio. Salt efflorescence materials were identified. The results contribute to the diagnosis of the current conservation state of the wall painting and consequently its future restoration.

Structural painted beams in the San Francisco church were analyzed by using different techniques including the micro-Raman spectroscopy. Animal protein was identified in the ground layer. The supporting material of the beams was identified as cypress wood, and a rag paper layer was used as a base for the paint layer, mainly composed by a white ground layer on which the color was then added; the yellow pigments are orpiment and chrome yellow. The green color probably arises from a mixture of orpiment, red lead, ultramarine blue and calcite.

A set of degummed and weighted silks was prepared in order to recognize the vibrational profile associated with the processes used. On this basis, the Raman and ATR-IR spectral information allowed the identification of the weighting process and also the dyes used in some of the different historic silk objects studied. The different spectra also allowed infer about the deterioration observed in the samples. The silk fibroin displays slight conformational modifications by the weighting process. The degumming process seems to have no chemical effect on the fibroin stability.

Vibrational spectroscopy are hereby shown as a versatile group of techniques, suitable to the study of the widespread materials found in the Chilean cultural heritage giving valuable information that allowed in each case to increase the knowledge about objects, contexts, etc.

Several objects belonging to the Chilean cultural heritage have been studied using vibrational techniques besides those here exposed. No data are at present available in the form of technical reports from the associated institutions of our cooperation network. This information is important, as those institutions are reference centers for Conservation of Cultural Heritage in Chile.

Methods

Raman and SERS

Raman and SERS spectra were recorded on a Raman Renishaw Microscope System RM1000 apparatus with an electrically cooled charge-coupled device (CCD) detector, equipped with 514, 633 and 785 nm laser lines for excitation, coupled to a Leica microscope. The 785 nm laser line was the most used in the different objects since is the less energetic and thus it is less probable to induce resonance or fluorescence than with the other laser lines. The instrument was calibrated using the 520 cm^{-1} line of a Si wafer and the spectral scanning conditions are chosen to avoid sample degradation and photodecomposition or photo-bleaching. The chosen conditions involved the laser line used, the laser power on the samples, which is usually set in the range 1-10 % (maximum power on the sample not higher than 5 mW on every wavelength), spectral resolution, accumulations and time of exposure. The parameters mentioned above are usually set in each case to obtain the best spectral quality using the softer conditions possible. SERS measurements were performed by depositing a drop of the colloidal solution over the sample in a clean quartz slide and letting it dry at room temperature. The spectrum was then acquired as described above. Data are collected and analyzed using the programs WIRE 2.0 and GRAMS 8.0. Raman spectra of samples, which were impossible to be accommodated in the area of bench instrumentation, were obtained by using an i-Raman portable instrument from B&W Tek equipped with the 785 nm laser line, a thermoelectrically cooled CCD detector and a 1 m optical fiber probe. Before each measurement a dark scan is acquired to improve the S/N ratio. No spectral corrections (i.e. smoothing, baseline, etc.) were performed.

Infrared

The infrared spectra are measured on a FT-IR Bruker Vector 22 and on a Perkin-Elmer series 2000 apparatus both equipped with a DTGS detector. The spectral resolution was 4 cm^{-1} and 16 scans, spectral scanning conditions generally used, were performed. A KBr or polyethylene pellets are used according the spectral region scanned. FT-IR attenuated total reflectance (ATR-IR) spectra were acquired over a diamond window with a Bruker alpha FT-IR spectrometer over the range 4000–370 cm^{-1}, accumulating 128 scans at a spectral resolution of 4 cm^{-1}, and over a Ge ATR window on a Thermo Nicolet iZ10 apparatus.

Nanoparticles synthesis and characterization

Silver nanoparticles to be used in the SERS experiments were prepared by chemical reduction of silver nitrate with hydroxylamine [81]. The size distribution of the nanoparticles is in the range 60–150 nm, with the most probable size around 80 nm; the FWHM of the plasmon absorption of silver colloids is 90 nm. The aqueous solutions utilized for the Ag-NPs formation were prepared by using deionized (18MΩ) water. A diode array spectrophotometer Hewlett Packard 8452 A is used to scan the extinction spectra. The colloid shows an extinction spectrum showing a maximum ca. 411 nm. A control of the colloidal solution is carried out by measuring the Raman spectrum from aggregates dried at room temperature.

Scanning electron microscope measurements

The morphological characterization of the weighted silks samples and their elemental composition were analyzed in a scanning electron microscope coupled with an energy dispersive spectroscopy device (SEM/EDS) from Electron Microscopy Ltd, England LEO 1420 variable pressure VP. Morphological observations were made using high magnified images (100X-1000X) and an electron dispersive analyzer at 10–15 KeV accelerating voltage.

Additional file

Additional file 1: Complementary Raman spectra for the article "Vibrational Spectroscopy for the Study of Chilean Cultural Heritage".

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

All authors contributed to data analyses and to finalizing the manuscript. All authors have read and approved the final version. All authors read and approved the final manuscript.

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