Colors and dyes of archaeological textiles from Tarapacá in the Atacama Desert (South Central Andes)

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Research Article

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Abstract

This work concerns the study of colors and dyes identified on archaeological textiles from the Atacama Desert. The different garments and ornaments come from the excavation of two important pre-Columbian cemeteries of the Tarapacá region: Tarapacá-40 attributed to the Formative period (1100 BC - 660 AD) and Pica-8 to the Late Intermediate period (900 - 1450 AD). For the first time, a multi-analytical approach with non-invasive techniques using Fiber Optics Reflectance Spectroscopy (FORS), Attenuated Total Reflection Infrared Spectroscopy (FT-IR) and Surface-enhanced Raman Scattering (SERS) were applied on samples of less than 2 cm of length for physicochemical characterization of the raw materials and the dyes employed in the textile production of northern Chile. The fibers are from animal origin. Blue, green, and yellow are identified as indigo, but we cannot discard a mixture with other dyes to vary hue and shade; while carminic acid and alizarin - to a lesser extent - are found on red, orange and brown samples. This research provides new elements for the discussion about the textile technology developed in this desertic region, its changes and continuities along with the history. Our results are compared to recent findings on neighbouring regions from northern Chile, to improve the current knowledge and discuss the existence of dyeing textile cultural traditions.

Introduction

In South America, Andean textiles are recognized as a major art of the pre-Columbian societies that inhabited these territories. This tradition is still preserved. These textiles stand out for the variety of techniques and materials employed, their rich iconography and their ample chromatic palette. In the words of John Murra, one of the main scholars of the Andean world: “No political, military, social, or religious event was complete without textiles being volunteered or bestowed, burned, exchanged, or sacrificed” [1]. And even if Murra is referring in this case to the Inca State, from the XIV-XVI centuries, we can easily imagine that a similar situation may have befallen in previous periods. Textile testimonies of this production are exhibited in famous museums around the world, acting as evidence of the great achievement of the textile artisans. For their production, they used different types of fibers (animals, vegetal and human hair), spun and knitted with a variety of structural techniques, using naturally colored threads or others painted and dyed, with eventual incrustations of beads, colored minerals, metals, and feathers. The textile production in the Andes involved the gradual development of a technological system, which began in the Late Pleistocene [2]. The use of dyes also evidences a long historic tradition, as recently proven by the identification of indigo on 5000-year-old textiles, the oldest record of the use of this type of dye in the world so far [3].

Today, the techniques, materials and polychromy recognized on certain objects raise the textile production to a prominent position among the handcrafts of Andean pre-Columbian communities [1,4-10]. The knowledge related to the acquisition of the diverse raw materials, the knitting and structure of textiles, as well as the mathematical logic applied to the elaboration of the textile structures is widely recognized [11-12]. The chromatic attributes of these structures have also attracted great interest since it
has been demonstrated that numerous plants and insects were used and prepared to achieve the wide chromatic palette observed in textile dyeing [1,13-22].

Textile production involves several technological procedures related, on one side, with the procurement of the fibers and the preparation of the yarns, made from animal (mainly camelids and other mammals on a minor proportion), plants (cotton, totora and junquillo, among others) or human hair, which will become part of the textile structure. Such procedures are also related to the incorporation or application of color on the yarns, to accomplish the design of the textiles. The color was incorporated through dyeing, imprinting, or painting, using organic dyestuffs or mineral pigments, collected, and prepared using other compounds that served as mordants or post-mordants, for ensuring a better adherence of the color on the fibers [9,10,19,20]. A third element are the skills associated with the knitting or the construction of the textile structure [5,23-25]. Moreover, the incorporation of symbols or figures through color constitute a true semiotic device. The final form of the textiles, as well as the choice of colors, the structures that shape the design, figures and elements elaborated on each textile, contribute to defining diverse styles and manufacturing traditions, often related to socio-cultural distinctions of status, gender or role, as well as ethnic or cultural identities, among others [26-35].

In the Andes, the color in archaeological textiles have been interpreted in terms of the prestige and power of certain social entities, but also as an expression of gender identity [1, 29, 36-43]. However, until now the color materiality is poorly understood, i.e. regarding the materials and immaterial knowledge involved in the making of textile production. The interpretation of their materiality requires an interdisciplinary approach and the implementation of multiple analytical techniques.

A review of the available published literature shows that analytical studies applied to historic Andean textiles are still scarce [3, 44-73], more so for colonial and republican periods [47]. In synthesis, for the pre-Columbian period, studies usually involve the analysis of a few samples, commonly reds or blues, with little information about other colors or shade variations [3,48-55,57-67,70]. Other colors like yellow, green, white, or brown are less studied [49,50,53,56,64,66,67,69,70]. Only a few of them have widened the analyses of the dyes and focused on the mordants [50,51,54,67,68,70]. Other investigations have approached the painted textiles, a rarely addressed subject [71,72]. From an analytical point of view, they have been applied chromatographic or spectrometric techniques (CG-MS; HPLC; LC-DAD-MS; DART-MS, between others), which albeit sensitive are destructive methods [3, 48-50,53,54,56-60,62-64,66,70]. SERS spectroscopy analysis was applied in just four cases to analyze in two studies the archaeological textiles from Peru and, in the other two, samples from northern Chile [55,61,65,69]. Finally, the available literature shows a particular emphasis on the analysis of polychrome textiles from the Paracas and Nazca cultures (700 BC- 800AD), on South - Central Perú [51-53,59-61,66,67,70]. For northern Chile, only two studies have
been published addressing the physicochemical analysis of textile dyes: one related to textiles from San Pedro de Atacama, almost 500 km to the south of our region of study, and one for Arica textiles, 270 km to the north [63,69]. Other results were just announced at a congress and are still unpublished [55]. Finally, and in general, those studies and other have demonstrated the use of indigo from plants of the genera Indigofera for the blue shades, carminic acid obtained from cochineal (Dactylopius coccus coccus), purpurin and alizarin from plants of the Rubiaceae family (Galium or Rebulinium) for the reds and other plants mixed in complex recipes with several dyes and mordants to obtain other colors and tones [13-22,55,67,73,74].

Every garment or ornament textile is unique; hence its study must privilege the use of non-invasive (or minimally invasive) and non-destructive analytical techniques. The identification of the fibers and the colorant raw materials used for dyeing constitutes one of the routes for achieving a better comprehension of textile technology and production [10,51,66-68,70]. Although multiple analyses are available, a better understanding of the technological processes involved can be reached through the combination of multiple analytical techniques. In this work, we present the analysis of dyed fibers from different textiles from the Atacama Desert in northern Chile, specifically from the Tarapacá region (Fig. 1). Each sample was first observed by Optical Microscopy. The fibers were identified by Fourier-Transform Infrared Spectroscopy (FTIR). Then colorimetry was used for preliminary identification of colors. Finally, dye identifications were performed by Fiber-Optics Reflectance Spectroscopy (FORS) and Surface-Enhanced Raman Scattering (SERS).

**Materials And Methods**

**Archaeological samples**

The analyzed textiles belong to two important cemeteries from the Tarapacá region, ascribed to two different periods of the pre-Columbian chronological sequence of the Atacama Desert in northern Chile: Tarapacá 40 and Pica 8 (Fig. 1).

Tarapacá-40 is in the desert, about 60 km from the Pacific coast; the site corresponds to an extensive cemetery, placed at the north slope of the Tarapacá ravine (Fig. 1). Excavations began in the 1960s and continued until the 2000s [75-79] and now its collections are deposited in different institutions (museums and universities) throughout the country [80]. C14-AMS dating of different burial contexts on the site allowed proposing it was occupied during the Formative period (+/- cal. 1.110-1.100 B.C.- 410-550 A.D.) [26,79]. The cemetery’s configuration is associated with the occupation of its contemporary village Caserones-1, composed of more than 350 structures [77,78,81,82]. This period is characterized by the consolidation of the villages with more sedentary dwellers and a food-producing economy [83]. Previous studies on the textiles from Tarapacá-40 have focused on the collections available on museums from
northern Chile [26,41,75]. In the present study, a total of 163 textiles from this cemetery were studied. Five samples were taken from five textiles including two blankets, two headdresses, and a bracelet. They all belong to the Early and Late Formative periods (Fig. 2a to 2e; Table 1).

Pica-8 is a vast cemetery located in the Pica oasis, at the south from Tarapacá valley and 90 km from the Pacific coast (Fig. 1). The site was excavated since the 1960s [84-87], and as in the case of Tarapacá-40, the collections are also dispersed in several institutions [80]. Dating studies placed the occupation in the Late Intermediate Period (+/- cal. 769-969 to 1301-1414 A.D. [88]. Pica-8 belongs to the Pica-Tarapacá cultural complex, a set of communities settled in the driest area of the Atacama Desert, which established colonies for exploiting resources from other ecological regions and at the same time articulated the exchange of resources with other neighboring cultural traditions. Deep social differences and inequalities, with a higher level of economic specializations, are characteristics of this considered segmentary society Intermediate Late cultural complex [87]. Textile analyses from this same cemetery were also previously published [28,89]. During our project, a group of 258 textiles were studied, and a total of 17 samples were collected from 8 textiles (Fig. 2f to 2m). The textile pieces correspond to seven tunics and a loincloth associated with the Late Intermediate period [87] (Table 1).

Sampling was performed at the Collection Deposit of the Anthropology Department of Universidad de Chile after the dry cleaning and packing in new boxes to replace previous and original plastic bags from the excavation. The study included a material-technical analysis and an assessment of their state of conservation, which in turn contributed to the identification of functional and typological characteristics. The first description of textiles techniques and colors was carried out. Colors were preliminarily reported with the Munsell Table. Quantitative colorimetric measurements were also performed with a CR-10 colorimeter (Konica Minolta) to complete the Munsell description. Samples consist of a textile fiber fragment of less than 2 cm of length. At the laboratory, optical microscopy analyses were performed using a B-600TiFL microscope (Optika) to acquire morphological information of the yarns and fibers of the archaeological textiles, the state of conservation, the color and possible salt adhered coming from the sand and the original archaeological context (Fig. 3).

**Infrared Spectroscopy analysis**

Infrared reflectance spectra of the archaeological textiles studied in this work were acquired using a Bruker Alpha FTIR spectrometer equipped with an external Attenuated Total Reflection module (ATR-FTIR). The IR spectra have a resolution of 4 cm⁻¹ and are measured in the mid-IR spectral range, namely from 400 to 4000 cm. Textiles samples were placed in contact with the focal point.
**Fiber-optics Reflectance Spectroscopy (FORS)**

A portable FieldSpect-4 (ASD Inc., Colorado, USA) was used to acquire visible, NIR and shortwave near-infrared (SWNIR) reflectance and absorbance (log[1/R]) spectra. A non-contact probe was used, which is placed at 8 cm of the sample. A D65 illuminant provides illumination over the whole spectral range. The analysis area is about 1 cm$^2$ and spectra were obtained with a 0.2 s integration time. In absorbance mode, data is processed with the Kubelka-Munk theory [90,91]. Calibration was performed using a certified reflectance standard (AS-02035-000CSTM-SRM-990-362, ASD Inc).

For analysis purposes, the visible and NIR regions are presented together in a zone named visible-near infrared (VNIR). VNIR ranges from 300 nm to 1000 nm and SWNIR ranges from 1000 nm to 2500 nm. Inflection points in all spectra were determined using the first derivative of the spectrum, generated using the Origin Software (OriginLab Corporation, Northampton, USA).

**SERS Analysis**

A washing protocol was developed to avoid particles adhered to the surface of the fiber from interfering with the dye-substrate interaction during SERS analysis. Textile samples of approximately 0.5 cm were placed on vials containing 0.01% v/v solutions of Triton™ X-100, a mild non-ionic detergent, and then stirred in a vortex. After washing, the samples were repeatedly rinsed with water under vortex stirring to remove the detergent. The effectiveness of the washing procedure was verified by optical microscopy and Scanning Electron Microscopy (data not shown).

Gold nanoparticles substrates for microSERS measurements were prepared by chemical reduction with sodium citrate using the method described previously [92,93]. In particular, 0.1 mL of HAuCl$_4$ solution (4%, w/v) is added to 40 mL of triply distilled water, then 1 mL of trisodium citrate solution (1%, w/v) is added dropwise with stirring. The resulting mixture is boiled for 5 min.

SERS spectra of samples were recorded with a Raman Renishaw InVia Reflex apparatus, equipped with the 532, 633, and 785 nm laser lines, a Leica microscope, and an electrically cooled CCD detector. The instrument was calibrated using the 520 cm$^{-1}$ line of a Si wafer and a 50× objective. Its resolution was set to 4 cm$^{-1}$ and 1-10 scans of 10-50 s each were averaged. Spectra were recorded in the 200-1800 cm$^{-1}$ region. The laser power was set between 10 and 100 mW. Spectral scanning conditions were chosen to avoid sample degradation and photodecomposition; the 785 nm laser line was used. Data were collected and plotted using the programs WIRE 3.4, GRAMS 9.0, and OriginLab Pro 2016.
Results

Fiber Characterization

All analyses performed on fiber samples present similar characteristics, one case illustrates our results (Fig. 4). The spectral profile shows a set of characteristic bands corresponding to animal keratin [94] and was interpreted based on published data [94,95]. The band centered at 3272 cm$^{-1}$ is assigned to the NH vibrational mode, namely amide A. A strongly absorbent band at 1622 cm$^{-1}$ is associated with the amide I mode, corresponding to a CO stretching vibration with a small contribution from the NH in-plane bending mode [95]. The band at 1516 cm$^{-1}$ is attributed to the combined CN stretching and NH bending (amide II) modes. The weak 1263 cm$^{-1}$ band, assigned to the amide III mode, is the result of bending of NH and a CN stretching of the peptide chain [95].

Colors characterization

The colorimetric analysis revealed the use of a wide range of colors and hue variations: red, red-orange, yellow, brown, green, and blue, combined with naturally colored bers (Table 1), highlighting the great polychromy of Tarapacá textiles.

FORS analysis of the bers suggested the presence of anthraquinones of both vegetal and animal origin for the red bers, as well as indigo on the green ones. The FORS spectral features of alizarin and cochineal, among other red dyes, have been previously reported [96-99]. Alizarin shows apparent absorbance maxima at 505-510 and 540 nm, while for cochineal those apparent absorbance maxima are red shifted towards 520-525 and 555-560 nm, leading to differentiating both anthraquinones (Fig. 5a and 5b). In our case, those apparent absorbance maxima are barely present on the spectra of the red samples, probably due to the combination of two factors: the degradation of the dye over time and the small sample size. The non-contact FORS probe used has an analysis area of 3 mm in diameter and the bers studied are only about 1 mm thick, hence, part of the signal acquired originated on the sample support, instead of the fiber itself. However, the first derivative of the reflectance has proven to be more sensitive for the identification of madder and cochineal-based dyes [100], due to the presence of inflection points at 496–503 nm and 533–545 nm for cochineal, while for alizarin they are at 486–490 nm and 520–524 nm.

With the information from the reflectance and the first derivative spectra, it can be suggested that cochineal was used to dye the Samples 1 and 2, while a plant from the genus *Galium* is the plant-based dye present on Sample 4 (Fig. 5a and 5b, respectively; Table 1). However, other animal-based anthraquinone dyes, such as kermes or Armenian cochineal, cannot be discriminated from the American
cochineal by FORS alone [97,98] and the assumption that the animal-based anthraquinone dye found on the analyzed fibers is in fact cochineal is supported by historical information, since this is the only red anthraquinone of animal origin found on previous studies on the Andean area for pre-Hispanic collections [15,17,18,21] and that continued being used during colonial times [101,102].

In the case of the green samples (Samples 12 and 18), FORS results suggest the presence of indigo (Fig. 5c), from the apparent absorption maxima at 648 nm and the inflection point at 717 nm, in agreement with the spectra of indigo references and the results of FORS analysis of Mexican codices [103], and polychrome ceilings [104].

SERS has proven to be a powerful technique for the analysis of colorants in textiles [61,65,105-109]. Most of these works used silver nanoparticles, while gold nanoparticles are equally useful [110,111]. In our analyses, the best results were obtained using gold nanoparticles and a 785 nm excitation laser. The optical microscopy images of the fibers, covered with nanoparticles and later dried, showed that the textile samples have an adherence to the nanoparticles as previously described [108]. In our case, using fibers already washed with Triton™ X-100, we observed areas with agglomerates of the nanoparticles, while others showed a thin and uniform layer of AuNPs. The latter led to better-defined spectra, with a low noise to signal ratio, while photodegradation and/or photodecomposition were avoided.

Alizarin, carminic acid and indigo were identified on the samples (Table 1). In the case of alizarin, Cañamares and collaborators carried out a complete theoretical analysis and SERS experiments [112], while the results reported by Chen and co-authors were registered after the extraction of the dye from the textile by acid hydrolysis [106]. In our case, the spectra were acquired directly from the dye adhered to the fiber.

The SERS measurement obtained for Sample 13 (Fig. 6a) shows a complex spectrum of the Dye-Mordant-Fiber (DMF) molecular system where groups of bands are consistent with signals reported for alizarin [113,114]. The SERS spectra provide additional information regarding shifts in wavenumbers, changes on their relative intensities are fundamentally the presence of new bands that cannot be observed when analyzing isolated molecules. These spectral features may be related to a certain arrangement and orientation of the dyes due to the interaction's NPs/fibers or NPs/dyed fibers. According to SERS selection rules, the intensity increases or decreases when the $\alpha_{zz}$ component of the polarizability of the analyzed vibrational mode is parallel or perpendicular to the excitation beam, respectively. Band shifts are related to the electronic redistribution in the vicinity of the atoms involved in the interaction.
This concept supports the chemical or charge transfer contribution to the mechanism of enhancement of the Raman signals [115].

The spectral changes discussed above are present in the spectrum of Fig. 6a. The weak band around 1647 cm\(^{-1}\) can be attributed to the coupled \(\nu\text{CO}/\nu\text{CC}\) vibrational modes. The coupled vibrational mode \(\text{ipdCH}_3/\text{ipdCOH}/\nu\text{CC}\) is observed at 1475 cm\(^{-1}\) as a shoulder and with medium intensity, although it has been described before as a high-intensity mode [112,113]. This difference may be because this molecular moiety is vibrating inclined in relation to the surface.

A commonly reported high-intensity characteristic band is present at 1258 cm\(^{-1}\) [116,117]. It is associated with coupled \(\nu\text{(CO)}/\nu\text{(CC)}/\delta\text{(CCC)}\) modes and is included among a group of high-intensity bands in the 1460 - 1200 cm\(^{-1}\) interval. The signal at 1078 cm\(^{-1}\), attributed to a CC stretching in proteins, is not reported for alizarin [112-114]. Owing to our experience in the vibrational analysis of proteins and according to the literature [118-121], this band may be related to the protein structure of the animal fiber. Vibrations of the peptide backbone in proteins are usually associated with three main regions of the Raman spectrum [122]. We expect to find the vibrations of the backbone skeletal stretch region at 870–1150 cm\(^{-1}\), which arose from the Ca-C, Ca-C\(\beta\), and Ca-N stretching coordinates. The extended amide III region, expected at 1230–1340 cm\(^{-1}\), is mainly involved in the in-phase combination of the N–H in-plane deformation with the Ca-N stretch, with mixing among the N–H and the Ca-H deformations. Finally, the C=O stretch gives rise to the amide I region in the range of ~ 1630–1700 cm\(^{-1}\) [122]. In our case, a broad low-intensity band is observed around 1700 cm\(^{-1}\). Some amino acid bands were also observed in the spectrum of the DMF complex, as is the case for the proline bands at 956 or 858 cm\(^{-1}\). A complete vibrational assignment is given in Table 2.

The SERS vibrational analysis of carminic acid was performed based on our own SERS data and those reported for the pure dye, isolated from cultural heritage samples or as part of a more complex molecular system [112,114,123]. As in the case of alizarin, Cañamares et al. carried out a complete theoretical and experimental analysis using analytical grade carminic acid [112], while the results published by Pozzi et al. account for the effect of sample pretreatment with vapours of fluorhydric acid, before the SERS analysis [107].

Cochineal was identified in Sample 4 and its SERS spectra (Fig. 6b) show bands of both carminic acid and protein [112,114,123]. The intense band at 1582 cm\(^{-1}\) is attributed to \(\nu\text{CC}\) of an aromatic ring, while Cañamares found this band to be of medium intensity and assigned it to a coupled \(\nu\text{(CC)}/\delta\text{(COH)}/\delta\text{(CH)}\)
mode. As discussed for alizarin, the differences in the intensity may be related to the orientation of this vibrational mode, parallel to the excitation beam. It is also described that this signal is accompanied by the bands at 1472 and 1322 cm\(^{-1}\), associated with modes ipdCH\(_3\)/ipdCOH/\(\nu\)CC and \(\delta\)COH/\(\delta\)CC, respectively. The band at 1322 cm\(^{-1}\) is particularly interesting since it has been reported as a strong band by Garrido et al. [124], while Cañamares and collaborators reported it as a medium intensity band [112]. In both cases is broadband that encloses a group of bands in the 1380 - 1300 cm\(^{-1}\) interval. Moreover, this band can be influenced by the amide III vibration described for proteins [119,120]. Bands near 1397, 1076, 956 and 858 cm\(^{-1}\) suggest the presence of the proteinic structure of the animal fiber, as reported before by our group in the study of isolated proteins or as part of a complex matrix [118-120]. Other bands that can be attributed to the dye are located at 505 and 456 cm\(^{-1}\). A complete vibrational assignment is given in Table 2.

For the vibrational analysis of indigo, found in Sample 11 (Fig. 6c), we used our SERS data and the results obtained from other researchers [61,100,125-127]. A strong band is observed at 1573 cm\(^{-1}\) (ring stretching mode), with a shoulder at 1591 cm\(^{-1}\) related with \(\nu\)CC, \(\nu\)CO and in-plane NH deformations (\(\delta\)NH) modes (Fig. 6c). The bands at 1345 and 896 cm\(^{-1}\) cans are assigned to coupled vibrations involving the stretching and bending vibrations of the six-member ring. C-H deformations are responsible for the bands at 1463 and 1257 cm\(^{-1}\), and the five- and six-member ring vibrations produce bands at 762 and 644 cm\(^{-1}\). A complete vibrational assignment is given in Table 2.

**Discussion**

All colors identified in our study suffered numerous alterations during the years, which undoubtedly modified their original hue and shade. The variation in shade, saturation, and shine in the same and/or different yarn can also be related to the degradation of the dye, since all the analyzed textiles belong to burial contexts (Table 1), where they were used as mortuary clothing and/or deposited as burial offerings. Several variations on the shade (Sample 22) and color saturation for a single yarn (Sample 10) can be attributed to changes that took place after the chemical interaction of the dye with the body fluids, during the decomposition of the buried individual. However, we cannot rule out the occurrence of different initial preparations for dyeing, associated with the use of varied aqueous media and/or the inclusion of mordants looking for better fixation of the color on the fibers [10,54,66,67,68,70]. Thus, the observed differences can be the consequence of technological factors inherent to the dyeing process (fermentation time, length of the exposure of the yarn to the mordants, temperature and humidity during the process, among others), which yield numerous alternatives and combinations amid them, as well as provoked by external agents and factors following the use of the textiles as burial offerings.
We were able to demonstrate the usefulness and expeditiousness of the simultaneous application of different non-destructive analytical techniques to the study of Andean textiles. FORS was just recently applied to textiles from this region [65] but has proven very suitable for preliminary characterization of the dyes if the proper references are available. In our case, the analysis was hampered by the fact that they were performed on small fragments of the dyed fibers, after sampling. When possible, it is always advisable to carry out the FORS measurements directly on the textile, using the non-contact probe when possible. In this way, one may take advantage of both the portability and non-destructive character of the technique and acquire multiple spectra from different areas of the same textile, looking for more precise identification of the dyes present. On the contrary, SERS is a potent tool for the characterization of textile dyes on small fragments of fibers and with relatively short analysis times, for a big number of samples. At this stage, we decided not to pursue the identification of mordants, in part, due to a cleaning and fumigation protocol applied to the textiles in 2015, which could interfere with the results. Also as indicated by Wallert and Boytner soil and body remains can contaminate textile, and results obtained by elemental analysis for example can be ambiguous [54].

FTIR results confirmed that all the fibers are of proteic origin, more probably animals from the Camelidae subfamily (*Lama* or *Vicugna*) as previously interpreted by macroscopic identification [28,41]. In general terms, FORS and SERS allowed the identification of the red, orange, yellow, blue, and green dyes. For a set of samples, the identification of alizarin using both techniques were very precise, while for others, although the FORS signals are very weak, it was possible to identify the presence of alizarin or carminic acid (Table 1: Samples 3 and 20). For this second group of samples, the dyes identification by SERS is troublesome, due to the complexity of the spectra acquired. Some of the SERS bands observed can be assigned to alizarin or carminic acid, indistinctly, as opposed to FORS. However, the observed bands are characteristic of anthraquinones, the common molecular structure of both alizarin and carminic acid (Table 1: Sample 4).

Our colorimetric, FORS and SERS results show that the different colors and their shade variations can be achieved from natural extracts, both from animal and vegetal origin. For the reds and its varied shades, including a few orange and brown fibers, we detected the use of anthraquinones from animal origin, carminic acid, from an extract of the cochineal insect (*Dactylopius coccus coccus*), as well as alizarin, commonly found on the roots of a plant from the family of Rubiaceae, *Gallium* or *Relbunium*, depending on the taxonomic classification, used [14,18,21,66]. In the blue, green and one yellow (Sample 19) samples, we found indigo or indigo-like molecules, known as indigoids, obtained from Indigofera plants [13,16,18,21,66]. However, we cannot discard that other dyes were mixed with indigo to modify hue and shade as observed in Paracas textiles [53,66].
The *Galium* genre plants used as a source of the dyestuffs are common along the coast of the Atacama Desert, principally the species *G. corymbosum* and *G. aparine* (distributed along the whole coastline of northern Chile), *G. diffusoramosum* (Taltal) and *G. hypocarpium* (Paposo) [128-137]. The main sources of indigo in South America are plants from the genres *Indigofera* (Fabaceae), *Eupatorium* (Asteraceae) and *Yangua* (Bignoniaceae) [49]. Although *Indigofera* species are typically found on Perú and Northwestern of Argentina [49,138], there are also records of *I. suffruticosa* specimens in the Azapa Valley, near Arica, as well as in the Chaca area on the Vitor ravine, to the north of Tarapacá region [119,140]. Specimens of *I. Truxillensis* have also been found in regions north of Arica, and Tarapacá [129,141]. In the Atacama Desert, the only native *Eupatorium* species are *E. glechonophyla* (also known as *Ageratina glechonophyll*) and *E. Salvia*. The first is distributed in the coast (0 - 200 m.a.s.l.) from Antofagasta to the south, almost 400 km of distance from Tarapacá locality [136], mainly in Paposo locality [134]. *E. Salvia* is also found along the coast further to the south, with a northernmost limit in the Coquimbo region, more than 1.000 km to the south of our region study [136].

Niemeyer and Agüero (2015) supposed that *Relbunium* supply for San Pedro de Atacama textiles came from northeast Argentina, based on the strong trade relationship between the localities in the area. Nevertheless, the authors arbitrarily and with no basis, ruled out the possibility that the raw materials may also have its origin on the Pacific coast, where specimens of *R. corybosum* have been registered, locally identified as *G. corybosum* [49,134,136,137], as well as other Galium species (*G. aparine, G. diffusoramosum, G. hypocarpium*) [128-137].

It is a fact that pre-Colombian communities in the Atacama coast were in close contact with this inland oasis, as well as with other groups that inhabited the inland valleys territories since remote times [142-147]. The traditional Andean model has placed in a prominent position the trade with foreign regions and the products and technologies from abroad, from territories beyond the Andes mountain to the east, while to the coastal gatherer-hunters have been assigned a passive role in the regional economies. In that sense, given the abundance of plants of Galium species along the northern Chile coastline, this could have been also a possible source of direct supply or by an exchange of dyestuffs, for the textile production. This possible hypothetical link with the coast becomes even more plausible when we consider that several vegetable sources of indigo are also found on the littoral, including *E. glechonophyla* and *A. glechonophylla*. Also, we cannot forget that indigo can be extracted from an extremely popular marine mollusc from the coast of the Atacama Desert, the *Concholepas concholepas* [21], a potential animal source of dye supply that has not yet been considered in archaeological studies of the region. Hence, there is a need for a proper botanical characterization of the available local plants, according to the information provided by ethnohistorical and ethnographic studies, together with further efforts for the elaboration of local references, to enhance the discussion regarding the foreign origin of the dyes.
Archaeological studies on textile dyes in the Atacama Desert have scarcely considered the available ethnohistorical and ethnographic information, looking rather for substances and species popular in other neighbouring regions. This trend generates a hiatus in local information, since not all Andean or South American communities opted for the same technical solutions when it came to coloring their fabrics.

As an example, for the San Pedro de Atacama area, the naturalist Rodolfo Philippi pointed out in 1854 that “for the blue, you can use añil [or indigo], for the red grana, for the yellow and indigenous plant, called fique, which I have not seen. Grana is a kind of cochineal that is brought from the Otra Banda provinces [Northwestern Argentina], mainly from Santiago del Estero”[148]. In an ethnographic study from the mid-XX century, Grete Mostny and co-workers recorded that the people from Peine village used alum as a mordant for dyeing textiles, and the color came from different local plants, such as monte verde, chilca and mocaraca for the green, ticara for the brown, algarrobo for mustard hues and sacha-uva for purples [149]. Munizaga and Gunckel, in a similar contemporary study, carried out at the Socaire village, also acknowledged the use of ticara (Krameria iluca), romasa (Rumex patientia) and monte verde for dyeing yellow textiles [150]. Finally, Villagrán and Castro, on a research with an ample geographic scale, identified the use of molle (Schinus molle), algarrobo (Prosopis alba), monte verde (Krameria lappacea), pingopingo (Ephedra andina), kopa (Artemisia kopa), Siput’olas or pulikas (Parastrephia species, including P. lepidophylla, P. quadrangularis and P. teretiuscula) and male tikara (Ambrosia artemisoides) for dyeing purposes, each one of them with a particular color and shade, depending on their preparation and combination [151]. We need to broaden our knowledge about the use of local plants for the production of dyes, to later generate useful references for chemical analysis as it has been done in different regions of the Central Andes [17-19, 21,152].

Finally, the results reached for textiles from the Tarapacá region associated with the Formative period allowed detecting the use of carminic acid and alizarin, dyestuffs that will continue to be used during Later Intermediate period (Table 1). In chronological terms, it is interesting to confirm that the same dyes technology was preserved for almost 2.400 years. It is also interesting to observe that the same colorants can be used for different types of textile garments and ornaments. When comparing our results with previous molecular identification of red dyes in neighbouring regions, we found to the north in southern Peru that purpurin from a plant from Relbunium species and carminic acid from cochineal were reported for the Late Intermediate period (1000 - 1450 A.D.) [54]; while only purpurin was identified at San Pedro de Atacama (300 km to the south from Tarapacá), in the Atacama Desert, for the Middle (600 - 1000 A.D.) and Late Intermediate periods (1000 - 1450 A.D.) [63]. In the case of the Tarapacá region, only alizarin and carminic acid have been continuously used for a long time. If this can be confirmed we could identify some specific and different knowledge concerning the dye manufacturing process, as each region demonstrates the use of different dye molecules (alizarin and purpurin) probably from different plant origins. Also and until now, for all the Atacama Desert the carminic acid has only been identified in our region, but more analyses are still required.

Conclusions
The results presented here show that the textiles offered at the Tarapacá 40 and Pica 8 cemeteries from the Atacama Desert were dyed with substances that until now were not found in the vicinity of the settlements. Its closest supply is, on the other hand, at approximately 100 km, both on the Pacific coast and in the valleys to the north and the Argentine Northwest to the southeast. However, the local populations of the Pica and Tarapacá valleys lived in close social and economic ties with those inhabitants settled in the supply areas of these plants and insects with potential for dyeing [83,87]. Thus, the technology of color in the pre-Hispanic textiles of Tarapacá must have depended above all on social networks and an association with these different communities, and not just for dyes procurement but also for the other raw materials needed such as fibers. The identification of cotton was also confirmed in our preliminary recognition of the complete textile collection studied. Unfortunately, the advancement of regional archaeology does not yet make it possible to confirm how and where textiles were produced and how dyed fibers were obtained. At this moment, we cannot precisely if they obtained just dyes and complete locally the process of dyeing fibers, ball of dyed yarns and they wove the different textile garments or finally the complete woven textile pieces by exchange from other localities.

In addition, archaeological studies dealing with textile dyes in the Atacama Desert have paid little attention to the available ethnohistorical and ethnographic information, looking instead for substances and species popular in neighboring regions. This has led to a lack of information about local dyeing technologies since not all the Andean or South American communities had probably chosen the same technical solutions when it comes to textile dyeing. The brief ethnohistoric and ethnographic review presented in the discussion section demonstrates the local availability of a wide variety of plants with dyeing capabilities in the Atacama Desert. However, very few of them have been studied to identify chemical markers that can be traced to pre-Columbian objects. Meanwhile, archaeology continues to look for the most popular dyeing plants used outside the region.

Considering these shortcomings concerning the reference samples, the textiles from the Tarapacá region are an excellent evidence of deep knowledge regarding dyes and dyeing techniques, about botanical and insect species available for these purposes, as well as a particular dexterity for the construction of complex polychrome textiles, conceived before the fabrication. The number and size of the textiles deposited as offerings, their shapes, and designs points to the existence of specialists, committed not only to the fabrication of the textiles but also to the previous stages of acquisition and conditioning of the fibers, in addition to the procurement and elaboration of the materials used to prepare the solutions or dyestuffs where the fibers were immersed.

So, to conclude these results need to be complemented and reviewed regarding the production processes: on the one side to precise the nature of the fiber raw materials and their possible provenance (wool, cotton, etc.) and hence their domestication and exploitation; and on the other side, the nature and localization of the vegetable and animal resources from where the dyes were extracted and produced. This paper constitutes just a first approach to this topic in the Atacama Desert.

Declarations
Availability of data and materials

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Authors’ contributions

MS: conceptualization, investigation, in situ analyses, formal analysis, writing original draft, editing, funding acquisition, project administration; CL: investigation, in situ analysis, funding acquisition, project administration; JC-V: laboratory analyses, formal analysis, visualization, writing; EC-G: formal analysis, visualization, writing original draft, editing; SG: in situ analyses, laboratory analyses; MAM-R: in situ analyses, laboratory analyses; BB: investigation, formal analysis, writing original draft; JLRS: investigation, supervision, editing original draft, funding acquisition, project administration; All authors read and approved the final manuscript.

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Tables

Tables 1-2 are available in the Supplementary Files