Journal of Archaeological Science: Reports 4 (2015) 23–31

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: http://ees.elsevier.com/jasrep

Applications of Raman spectroscopy in archaeometry: An investigation of pre-Columbian Peruvian textiles

N.D. Bernardino [a], D.L.A. de Faria [a,*], A.C.V. Negrón [b]

[a] Laboratory of Molecular Spectroscopy, Institute of Chemistry, University of São Paulo, C.P. 26077, 05513-970 São Paulo, Brazil
[b] Laboratory of Biopolymers and Metallopharmaceuticals, Professional School of Chemistry, Faculty of Sciences, National University of Engineering, PO Box 31-139, Lima, Peru

ARTICLE INFO

Article history:
Received 6 April 2015
Accepted 19 August 2015
Available online xxxx

Keywords:
Pre-Columbian textile
Dye
Archaeometry
SERS
Nitric acid etched copper

ABSTRACT

In this work fibers from pre-Columbian Peruvian textiles and synthetic analogs of the natural dyes previously found in Andean historical textiles (indigo, carmine, indigo carmine, purpurin, alizarin and luteolin) were analyzed using a Raman microscope which was also used as a microspectrofluorimeter. SEM-EDS and FTIR were used as complimentary techniques. The efficiency of HNO_3 etched copper surface as SERS substrates was investigated aiming at its application in archaeometry; in this particular case, the capability of such SERS active substrate to cope with luminescence presented by the dyed textile was evaluated.
The archaeological fibers were identified as dyed wool by FTIR, FT-Raman and SEM; the red dye (carmine) was identified by resonance Raman and SERS, however, the blue dyed fiber presented a strong fluorescent background in the visible and, in the NIR, the FT-Raman spectrum was not conclusive, therefore the identification was performed using SERS through the dye in-situ reduction on a Cu etched disk.
Specifically in the case of synthetic dyes, although all of them had already their SERS spectra reported in the literature, it is here shown that the copper etched surfaces provide SERS and SERRS information that are in full agreement with previously reported data, with the advantage of a much simpler and faster preparation.

1. Introduction

Textiles are among the most impressive contributions from ancient Andean cultures, particularly the Paracas and Huari cultures, who inhabited the south coast of Peru in the 1000 B.C.–200 A.D. and 700–1100 A.D. periods, respectively (Macedo, 2005). Made of wool or cotton fibers, the textiles from such cultures are characterized by intricate and colorful weaving patterns that survived degradation for centuries. In previous investigations on Paracas textiles Wouters et al. (Wouters and Rosario-Chirinos, 1992) used HPLC to identify indigo, luteolin, carminic acid, alizarin and purpurin; some of these dyes had already been identified by Martoglio et al. (1990) using spectroscopic methods such as FTIR and UV–VIS absorption. The procedure used in such studies are, however, either destructive, as in the case of Wouters's work (Wouters and Rosario-Chirinos, 1992), or rely on spectral subtraction, making the dye identification susceptible to artifacts due to the spectra manipulation.

The textiles color fastness is assigned to climatic factors since the archaeological sites where they were found are located in arid zones; furthermore, the textiles were buried and thus protected from light for several centuries (Dutton, 1992). Whether the dyeing process used plays any role in such stability is still an open question as the Andean pre-Columbian cultures neither develop writing language nor the procedure was preserved in the oral tradition. To get some insight on the dyeing procedure it is therefore necessary to investigate not only the colorants employed but also the substrate and its interaction with the dye, what includes the identification of compounds possibly used as mordant.

According to the International Union of Pure and Applied Chemistry (IUPAC), mordant is a "substance that fixes a dyestuff in or on a material by combining with the dye to form an insoluble compound" (Burkinshaw and Kumar, 2009), typical mordants are polyvalent metal cations and tannic acid. In some cases, as with alizarin, purpurin and carminic acid, the use of such mordants is mandatory due to the small affinity between dye and fiber, whereas in others – indigo is the best example – mordants are not necessary and the dye is covalently bound to the fibers or linked through van der Waals forces; in spite of this, studies trying to reproduce indigo textile dyeing using alum, $FeCl_3$ and others mordants can be found in the literature (Zarkogianni et al., 2011).

Raman spectroscopy is a very important and powerful touchless technique in archaeometry, considering its noninvasive and nondestructive nature and it's capability of providing a wealth of information on chemical composition and structure of archaeological artifacts (Smith and Clark, 2004). The major drawback in this case is the

* Corresponding author at: Laboratório de Espectroscopia Molecular, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748—Butantã, 05508-000, São Paulo, SP, Brazil.
E-mail address: dlafaria@iq.usp.br (D.L.A. de Faria).

http://dx.doi.org/10.1016/j.jasrep.2015.08.029
2352-409X/

luminescence generally observed in degraded objects or in those that were buried or exposed to the environment for centuries. (Kavkler and Demšar, 2011) Particularly in the case of pigments and dyes, the right choice of the exciting laser line can cope with this problem by providing selective enhancement in the intensity of the Raman bands associated with the chromophoric groups in a spectral region which is not substantially affected by light emission (Efremov et al., 2008). This is not, however, the most common situation and Surface Enhanced Raman Scattering (SERS) lies as the only reliable option. SERS effect corresponds to an expressive selective enhancement (up to 6 orders of magnitude) in the Raman spectrum of chemical species that are adsorbed on or close to some specific metal surfaces or nanoparticles Another important feature in the SERS spectra is that luminescence is frequently quenched by the surface, allowing the observation of the Raman bands that were swamped by the emission background. (Aroca, 2006) Despite these positive aspects of SERS, some amount of sample or area in the object is irreversibly affected by the presence of silver particles (frequently a silver sol) or is consumed in the sampling procedure. These facts motivated investigations aiming at the preparation of detachable SERS substrates, designed to minimize such deleterious effect (Doherty et al., 2011).

Nonetheless, SERS is being increasingly used in cultural heritage investigations, (Casadio et al., 2010) for two main reasons: the luminescence background is quenched generally by energy transfer to the silver nanoparticles and the Raman bands are selectively enhanced by several orders of magnitude, which ranges from 3 to 6, depending on the nature of the investigated material and on the metal nanoparticles or surface morphology (Haynes et al., 2005). When combined with resonance Raman, in the so called Surface Enhanced Resonance Raman Scattering effect (SERRS), both effects add up their contributions, thus making such enhancement even larger (from 5 to 9 orders of magnitude in general) (Campion and Kambhampati, 1998).

One of the major drawbacks of the technique, however, is the fact that the SERS substrates are generally not easy to prepare and present poor repeatability and reproducibility. In this work, a cheap and easy procedure to prepare SERS substrates, made through nitric acid etching of a Cu surface (Xue et al., 1991) followed by treatment with a silver nitrate solution (Nie and Feng, 2002), was tested using the dyed fibers and the synthetic dyes. Such surfaces can be prepared in less than 5 min and are at least as efficient as silver sols.

Even considering that SERS is a virtually nondestructive technique, taking into account the minor amount of sample used, when cultural heritage objects are considered all the efforts must be directed towards truly nondestructive and noninvasive procedures, as discussed above. Confocal microspectrofluorimetry is an alternative which is being successfully applied in pigments and dyes identification (Claro et al., 2008, 2010). Raman microscopes can also be used as microspectrofluorimeters (Oakley et al., 2011, Dyer and Smith, 1995; Choi et al., 2014), benefiting from a much better spatial resolution and confocality than dedicated equipment (Turrell and Corset, 1996), however, to our knowledge it was never used with this purpose in archaeometry. Thus, even when fluorescence or other type of luminescence cannot be avoided and precludes the detection of Raman bands, a Raman microscope can still be used to obtain the emission spectrum from specific spots.

This work thus aims at to highlight some features of Raman spectroscopy that can be explored in archaeometry, when severely degraded samples are investigated as in the case of the Peruvian archaeological fibers which were here studied using non-destructive or virtually nondestructive spectroscopic methodologies.

2. Material and methods

Red and blue dyed fibers were 5 and 8 cm long strands (Fig. S1 — supplementary materials), respectively, from the local site of Uquira, Asia valley localized ca. 100 km in the South of Lima. They were studied exactly as received and the only precaution was to avoid dirties on their surface, what was easily achieved when selecting the areas to investigate by Raman microscopy.

Synthetic alizarin, purpurin, carmine, luteolin, indigo and indigo carmine (Fig. S2 — supplementary materials), all from Sigma-Aldrich, were used as received, as were the non-processed natural cotton (*Gossypium hirsutum*) and wool fibers, which were from local suppliers.

Copper disks (12 mm diameter and 1 mm thick) were used to prepare the active surfaces and were etched by a 1:1 HNO_3 (67% in mass, Synth) aqueous solution. Ag coated copper surfaces were used in the investigation of the red archaeological fiber and carmine and were prepared by dropping a $AgNO_3$ (Sigma-Aldrich) aqueous solution on the Cu surface. $Na_2S_2O_4$ (87%, Lafan) and NaOH (P.A, Synth) were used to obtain the leuco form of indigo. Methanol (Merck, UVASOL) and dimethyl sulfoxide (DMSO, Reagen) were used as solvents.

Archaeological and contemporary fibers were analyzed by Raman Microscopy, Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). For the SEM micrographies, the fibers were Au coated (ca. 2 nm) by sputtering (Edwards Scancoat Six Sputter), fitted with a quartz microbalance (Edwards FTM6).

In order to understand the role of the fiber in the dye luminescence, contemporary alpaca wool fibers were dyed with synthetic indigo using the well-known vat dyeing procedure, (McKee and Zanger, 1991) carried out in thermostatic bath (Quimis, Q214M2) at 30 °C: approximately 10 mg of wool was immersed in a saturated NaCl water solution and after 5 min indigo was added to the solution and homogenized during 30 min. After that time, sodium dithionite 10% (m/v) and sodium hydroxide 0.8 mol/L aqueous solutions were added to the suspension. The final mixture was kept under continuous shaking at a constant temperature of 30 °C by 1 h. The fibers were dried in air to allow the dye re-oxidation.

SERS (and SERRS) measurements on the synthetic dyes were carried with nitric acid copper etched disks; (Xue et al., 1991) the disks were initially sanded (silicon carbide 600 grit sandpaper), rinsed and immersed in a HNO_3 aqueous solution (1:1 in volume) till Cu^{2+} ions rendered the solution light blue. The copper disks were then removed from the acidic solution and thoroughly rinsed with deionized water, dried with nitrogen and some of them were treated in one side with one drop of a $AgNO_3$ 1 10^{-3} mol/L solution for 1 or 2 min and then extensively rinsed with deionized water. The so prepared SERS substrates were immersed for ca. 20 min in the dye solution made with appropriate solvent: methanol was used with alizarin, indigo carmine, luteolin and purpurin, whereas DMSO was used to prepare the carmine and indigo solutions. In all the cases the dye concentration was ca. 1 10^{-3} mol/L and after exposure to the dye solution the metal disks were thoroughly rinsed with deionized water, dried under a N_2 flow and immediately placed at the Raman microscope stage.

Concerning the archaeological fibers, a very small fragment was taken from each fiber and placed on the SERS active copper surface (blue fiber) or on the Ag coated surface (red fiber); in the latter, a drop of chloroform was applied to the fragment in order to extract the dye and the disk was left to dry naturally; the fiber was then removed and the spectra were obtained from the metal surface. Such solvent extraction was not efficient with the blue fiber and, considering the evidences from FT-Raman that the dye was indigo, the fiber on the Cu substrate was simultaneously treated with a sodium dithionite and NaOH solutions (10% *v*/*v* and saturated, respectively) to produce the water soluble leuco form ($Na_2C_{16}H_{10}N_2O_2$), which is readily re-oxidized to indigo by air. A blank disk (without dye) was prepared exactly under the same conditions to identify contributions other than from the dye to the SERS spectrum.

Raman spectra were obtained with the lines at 632.8 nm (He–Ne laser) and 785 nm (diode laser) in a Renishaw inVia Reflex Microscope, fitted with a CCD Peltier cooled detector (Renishaw, 600 × 400 pixels) and a Leica optical microscope (DM2500 M). A Leica objective (×50, N.A. 0.75) was used in all the measurements. For excitation at 488 nm