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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1720680> since 2019-12-27T20:38:08Z

Publisher:

IMEKO TC4

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Surface enhanced Raman spectroscopy for detecting dyes in micro-samples

M. Gulmini¹, A. Idone¹, P. Davit¹, C. Petiti¹, F. Natale¹, E. Diana¹, E. Calà², M. Aceto^{2,3}

¹ *Dipartimento di Chimica, Università di Torino, Via Giuria, 7 - 10125 Torino, Italy*

(monica.gulmini@unito.it, ambra.idone@unito.it, patrizia.davit@unito.it, eliano.diana@unito.it)

² *Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale, Viale Michel, 11 - 15121 Alessandria, Italy*

(maurizio.aceto@uniupo.it, elisa.cala@uniupo.it)

³ *Centro Interdisciplinare per lo Studio e la Conservazione dei Beni Culturali (CenISCo), via Manzoni, 8 - 13100 Vercelli, Italy.*

Abstract – The need of fully preserving our tangible cultural heritage influences the availability of samples for diagnostic purposes. For precious or fragile ancient objects such as ancient manuscripts or finely decorated archaeological textiles, only micro samples are normally (if ever) available. Dyes can be detected in these samples by Surface Enhanced Raman Spectroscopy (SERS), which has recently emerged as a powerful diagnostic technique for facing this task. Because of the large variety of materials that can be found when investigating objects from the cultural heritage, ongoing research aims at developing tailored procedures to enhance selectivity. Examples of tasks faced by our team to detect natural dyes in ancient manuscripts and archaeological textiles are reported here.

Keywords: Surface enhanced Raman spectroscopy, SERS, natural dyes, ancient manuscripts, archaeological textiles

I. INTRODUCTION

During the last years, Surface Enhanced Raman Spectroscopy (SERS) has emerged as a valuable tool for revealing dyes in samples from the cultural heritage. To enable the SER effect, the molecule of interest has to be placed in the vicinity of (or deposited on) a plasmonic surface. Metallic nanostructures, normally of Au or Ag, can act as SER substrates and enable the detection of fluorescent natural dyes, as the interaction with the noble metal substrate highly enhances the Raman signals of the dyes while quenching luminescence.

For precious or fragile artefacts, only very small samples can be available for the scientific investigation. These micro-samples can be tested by SERS as the analysis is performed by focusing the excitation laser beam by a microscope. This enables the highly sensitive and selective detection of the dyes, normally present in a very low concentration on a variety of supports [1, 2].

Two main approaches have been proposed to perform the analysis:

“Extractive” approaches carry out solvent/acid extractions of the dyes, or use active hydrogels to remove the dyes from the support.

“In situ” analysis are performed directly on the sample by means of: i) non-extractive hydrolysis, ii) laser photo-reduction of the SERS substrate, iii) hydrogels doped with silver nanoparticles or iv) silver colloidal pastes as SER substrates.

Our research team has considered silver colloidal pastes [3] to develop tailored procedures aimed at detecting dyes in a number of situations, with particular attention to ancient manuscripts and archaeological textiles.

In particular, two aspects have been considered:

- the detection of the dyes that have been employed in Late Antiquity and Middle ages to produce precious “purple codices”;
- the detection of yellow dyes in archaeological textiles.

In both instances, the SERS approach overcomes the diagnostic limits of a non-invasive investigation by other spectroscopic techniques such as fibre optics diffuse reflectance spectroscopy (FORS) or X-ray fluorescence spectrometry (XRF). The detection of SER signals form the target molecules allows us to identify the natural materials (plants or animals) which have been employed to obtain the colour. This information is relevant for historical studies of artistic practice, and may support the establishment of provenance, enables the reconstruction of the original appearance, and informs restorers on proper conservation intervention.

II. EXPERIMENTAL

The silver colloidal paste employed as SER substrate was prepared by reducing silver nitrate with sodium citrate and then by concentrating the nanoparticles by a centrifuge [3].

For developing a procedure for the detection of dyes in purple codices, model samples of purple parchment were prepared according to historical procedures using *orchil* (obtained from lichens), *folium* (obtained from *Chrozophora tinctoria*) and mixtures of the two dyes. They were then extracted from the parchment with formic acid and the solution was analyzed by SERS.

As for yellow textiles, samples dyed with weld were considered. They were both reference samples and a few yellow fibers obtained from an archaeological textile. The fibers were treated directly with the silver colloidal paste without pre-treatment.

SERS measurements were carried out with a Renishaw InVia spectrometer coupled with a Leica DM2500 M optical microscope, using an excitation wavelength of 633 nm for orchil and folium and of 532 nm for weld, with a magnification objective of 100X.

III. RESULTS

SERS analysis of purple parchment allowed us to define the specific SER response for orchil and folium (Figure 1) in a formic acid extract.

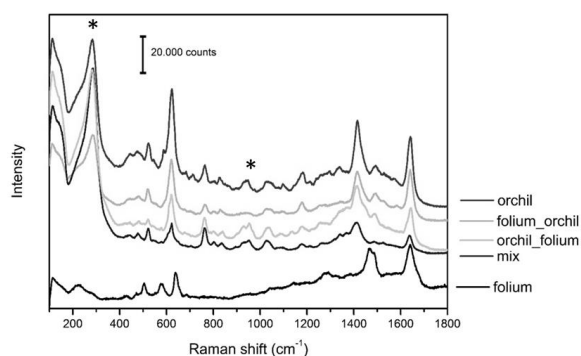


Fig.1: SER spectra of extracts obtained from parchments dyed with orchil, folium and both of them. Asterisks indicate signals from the substrate. $\lambda_{ex}= 633 \text{ nm}$

Experiments also highlighted that orchil inhibits the response of folium. When the two colourants are present in the same solution, only the signals of orchil are evident (Figure 1) and the signals of folium are not detected even if the dye is present in a great excess (19:1 w/w) with respect to orchil.

It is therefore evident that we need to separate orchil and folium if we want to succeed in revealing them both when they have been used together to impart the purple colour. Thin layer chromatography (TLC) is being tested to overcome this issue.

The development of the procedure to detect weld on archaeological samples was performed at first on reference materials, in order to select the signals that can

be robustly attributed to the main colouring species obtained from the plant: i.e.: luteolin and apigenin. After that, the analysis of the archaeological sample was performed (Figure 2). Some signals from apigenin can be detected, in addition to signals from unknown contaminants.

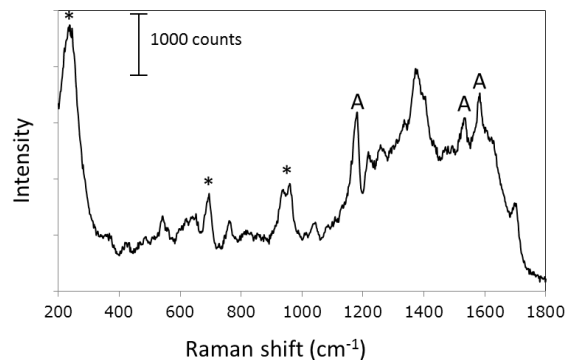


Fig.2: SER spectrum of an archaeological textile dyed with weld. Peaks related to apigenin are marked with A. Asterisks indicate signals from the substrate. $\lambda_{ex}= 532 \text{ nm}$

IV. CONCLUSION

The corpus of the analytical data on dyes detected on micro-samples taken from historical or archaeological objects is increasing, as the research is very active in the field. Some intriguing challenges are presented here. In particular, issues were highlighted when analysing samples in which both folium and orchil were employed to obtain the colour in purple codices. The detection of weld in heavily degraded samples, as in the case of archaeological textiles, is complex due to signals from contaminants that can mask those of the analytes.

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