

## Dry-state SERS for the “in-situ” identification of natural textile dyes

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Vibrational spectroscopies are currently and successfully employed for the non-invasive identification of colouring substances directly on works of art, especially when inorganic pigments are concerned, while the investigation of natural organic dyes represents a challenging task.

Surface-Enhanced Raman Spectroscopy (SERS) has been currently adopted to recognise dyes extracted from textiles, as well as applied to extractionless analysis directly on fibres. Nevertheless, there is still a demand for a method based on SERS and thus exploiting the molecule-specific response of the technique, allowing the identification of the dyes on intact fabrics in museums or exhibitions. Until now, some analyses performed directly on artistic objects were reported, but all of them require a close contact with the SERS substrate in wet conditions [1].

Of the two different mechanisms responsible for the SERS effect, i.e. the electromagnetic and the chemical one, the former contributes to the enhancement in an order of magnitude of  $10^{10}$ , while the second one of  $10^2$ . Therefore, in principle, the intensification of the Raman signal in SERS can be observed also in the absence of a chemisorption of the analyte on the substrate, thanks to the electromagnetic component of the effect itself. Thus, a dry-state analysis leading to a completely non-invasive approach should be possible and highly recommended in the field of cultural heritage.

In this context, we are studying the possibility of using thin films obtained by deposition of silver colloids on an optically transparent support, such as a glass slide, in order to prepare in an easy way SERS probes suitable for “in situ” analysis by means of portable Raman instrumentation, with no need of complex procedures as those already reported in the literature [2,3]. Silver nanospheres obtained by different methods [4,5] or, alternatively, silver nanostars [6] were deposited on glass slides functionalised with (3-aminopropyl)trimethoxysilane, in order to promote the adherence and prevent the so-called “coffee ring” effect. The obtained films were tested for the non-invasive identification of anthraquinonic dyes by a portable Raman micro-probe in mock-up samples of dyed textile fibres.

Finally, to the best of our knowledge, we exploited for the first time commercial electrochemically-deposited substrates (SERSitive) to observe dry-state SERS, obtaining positive results that encourage in perspective to experiment the electrochemical path to produce suitable substrates for our purposes.

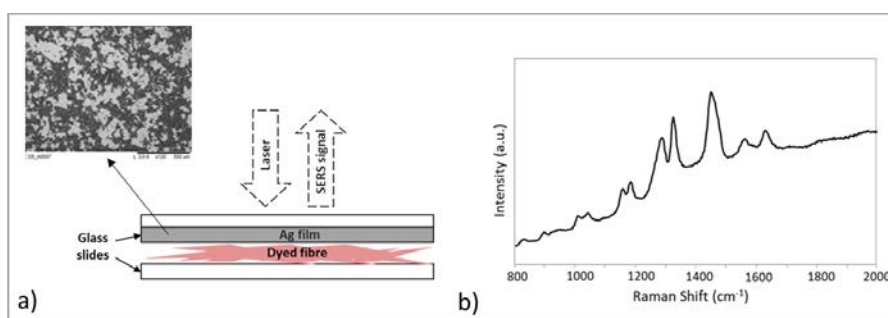


Figure. (a) Scheme of the dry-state SERS probe with a detail of the SEM image of the deposited silver film and (b) SERS spectrum obtained from a wool thread dyed with alizarin.

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