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Reproducibility and stability over time of silver colloidal pastes for Surface Enhanced Raman Spectroscopy (SERS) of natural dyes in ancient artworks

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Surface-Enhanced Raman Scattering (SERS) using noble metal nanometric surfaces represents an ideal analytical technique to detect and identify dyes in artworks (1), due to the dramatic enhancement of the Raman signals together with fluorescence quenching with respect to traditional Raman spectroscopies. Ag colloids are among the most popular SERS substrates employed in the detection of dyes in samples from the cultural heritage domain. One of the procedures to synthesize Ag substrates was proposed by Lee and Meisel and uses silver nitrate as Ag precursor and sodium citrate as reducing agent. The synthesis can be followed by an aggregation of the Ag nanoparticles through centrifugation of the colloid, obtaining the so-called 'silver colloidal pastes'. These pastes have been successfully used to obtain direct SER spectra of dyes from a number of materials, with the advantage of being effective in obtaining signals from very small samples without the need of complex preliminary treatments.

An inherent characteristics of the SERS technique is the variable intensity of the SER signals. Accordingly, the recent research activities of our group in the field of SERS analysis of dyes in archaeological and historical samples (2,3) evidenced a certain variability of the SERS response for different Ag paste batches. Moreover, for a same Ag paste batch, it has been highlighted that the SERS behavior is not constant over time. Furthermore, the synthesis procedure is relatively time consuming and cannot be realized on a very small scale. Thus, following the behavior of the Ag pastes over time would be very helpful in obtaining more controlled and reproducible results and in reducing any possible wastefulness. Considering all these factors, the synthesis of different Ag paste batches was carried out to evaluate: 1) the aging effect on the SER spectroscopic response of the pastes, by acquiring spectra on the same batch at different times (up to 10 weeks), 2) the reproducibility of the SER spectroscopic response of the pastes within the same batch (*intra-batch*) and among different batches (*inter-batch*) at the same aging time, 3) the use of an alternative synthesis procedure (by using ice at the end of the chemical reduction thermal step) and 4) the comparison of the spectroscopic response obtained on samples prepared with the same Ag paste at different aging times with those on the same sample prepared with the newly synthesized paste and acquired at different times.

For considering the above reported points, we evaluated the spectroscopic response of the Ag pastes - as signals of Ag and citrate are normally obtained - and of a wool sample dyed with cochineal.

The overall results suggest that it is not possible to obtain a completely predictable enhancement and this is quite consistent with the inherent characteristics of the SERS technique.

Notwithstanding, the obtained results allow drawing some important conclusions. First of all they indicate that the paste efficiency reaches a maximum after some time from its synthesis. Moreover, they give precious indications on the optimal sample preparation procedure and guarantee the analysis of the samples even after several weeks from the preparation.

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