SERS analysis of red lakes paints: coated glass slides and cross sections

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The SERS technique has already been applied in the field of Cultural Heritage to study organic dyes using different samples (solid micro-samples, fibers) taken from several artistic objects (paintings, pottery, statues, textiles). However, little has been studied about the application on cross sections mounted on different supports (resins or inorganic salts) [1]. It is well known that only the cross section can reveal the precise stratigraphy and the spatial collocations of all the layers composing a work of art.
This work focuses on the formulation of a protocol for the application of the SERS technique directly on cross sections using metal nanoparticles (NPs). Analysed organic colorants are anthraquinone-based red lakes: pure purpurin, carminio estratto (mainly composed by carminic acid complexed with aluminum) and lacca rubia (made of alizarin complexed with Al^{3+}). Samples were studied as paint layers on glass slides and cross sections.
Various types of silver NPs were employed as SERS substrates: Ag spherical NPs prepared by chemical reduction with citrate (AgCt) [2] and hydroxylamine (AgHx) [3], Ag nanostars (AgNS) [4], Au NPs with different sizes [5] and Ag NPs prepared by photo reduction [6].
Regarding the analysed dye, purpurin is the easiest to detect because it is not a lake. Between the two lakes, carminium and lacca rubia, the first one is more detectable. Considering the type of SERS substrate, AgCt colloid shows the best performance. AgNS, in spite of being slightly less effective, are valuable as well because they do not need to be aggregated, decreasing the level of the interfering species on the sample and increasing the reproducibility of the measurements. The AuCt colloid has the great advantage that its analysis is performed at 785 nm, laser that lowers consistently the fluorescence but the size of its NPs must be at least of 70 nm to be effective. Concluding, the AgHx one, although free from the highly interfering citrate, does not work well in the detection of colorants.

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