USE OF NANO GOLD OBTAINED BY LASER ABLATION FOR SEIRA ANALYSES OF COLORANTS

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SEIRA (surface- enhanced infrared absorption) is based on the effect of enhancement when the sample is absorbed onto islands produced by the deposition or electric deposition of a noble metal [1]. Since the enhancement factors (about 10-1000 times) of SEIRA is not competitive when compared with those of SERS, few attention has been paid on its possible applications [2-5]. However, the cross sections for absorption in the infrared are order of magnitude higher than the corresponding Raman cross sections. Thus, even if SEIRA enhancement is modest, it can have effect in practical applications [6].

In the present study, an advanced and alternative SEIRA based analytical protocol for the analysis of small quantities of colorants, have been proposed.

In more details, Acid Orange 7 - a synthetic colorant used for dyeing - has been selected. Moreover, gold nanoparticles obtained by laser ablation in solution (LASiS), which allows to synthesize stable colloidal solution without interfering molecules (such as stabilizing agents), has been used for the development of the method.

Two different protocols were studied and tested in different modes as summarized in table 1.

The first foresaw the deposition of 5 µl aliquots of aggregated or not aggregated colloidal solutions over a slide obtaining a circle of almost 2 mm diameter. 5 µl of the colloidal solutions were deposited for 3, 5 or 8 times in order to produce a more homogeneous distribution. The dried drops were applied on a gold coated glass slide characterized by RAS (Reflection Absorption Spectroscopy) to define the presence of polluting species. Afterwards, 0.5 µl of 10^{-3}M AO7 solution were deposited on the gold coated slide and used as reference for peak attribution, whereas 0.5 µL of 10^{-4}M AO7 solution were deposited both on the naked support and over the different types of colloidal depositions in order to compare the spectra and to verify the presence of surface enhancement effects.

In the second protocol the interaction of the colorant with the nanoparticles (aggregated and not aggregated) was obtained in solution. In this case 10 µl of 10^{-4} M AO7 solution were dried and 10 µl of aggregated or not aggregated gold colloid solutions were added. After sonication, 1 µl of the obtained solutions was spotted on the gold coated glass slide for RAS analyses. The most effective way to analyze small quantities of colorants has been resulted the second approach proponed, which was based on the mixture of the not aggregated particles with analytes; in all the enhanced spectra an enlargement of peaks can be noted and the definition of bands is worse than in the normal spectra. Nevertheless, the identification of the colorant absorption bands was not compromised. Indeed, the analyses performed in RAS mode on the borders of the spot, which contain the highest quantity of colloid and colorant, allowed to analyze solution down to $5*10^{-5}$M.

Consequently, the method has been applied for the analyses of dyed wool. To define the proper micro-extraction procedures for analysis a few pieces of fiber, different extraction procedures were tested and compared.

The formic acid (HCOOH) method appeared to be the less effective in extracting Acid Orange 7.

The ethylenediaminetetraacetic acid(EDTA) method showed an optimal extraction capability. Intense and well resolved spectra were obtained without the presence of spurious peaks. However, reducing the amount of wool, spurious peaks connected to EDTA appeared in the spectrum.

The methanol (MeOH) method provided results similar than EDTA with the advantage to be completely eliminated when the sample is dried and therefore it was selected for SEIRA analyses.

Indeed, the extraction with MeOH provided the most effective results, among three extraction methods tested, and it was applied for the analysis of a few pieces of fiber. SEIRA spectra obtained mixing the extract with not aggregated AuNP allowed to recognize bands of the colorant, even if present in low concentration.

Further efforts will be devoted to the optimization of the micro extraction procedure in order to improve the limit of detection and the method will be applied for the analyses of several types of colorants, in order to understand the limits of the proposed methodology to discriminate among different compounds.

Tab. 1: Analytical protocols employed for SEIRA analyses of a solution 10^{-4}M AO7

COLLOIDAL SOLUTION	METHOD OF DEPOSITION	RESULTS
Aggregated	3 deposition 5 µL + 0,5 µL AO7 10^{-4}M	Medium enhancement, variable intensity, band enlargement
Aggregated	5 deposition 5 µL + 0,5 µL AO7 10^{-4}M	Modest enhancement, variable intensity, band enlargement
Aggregated	8 deposition 5 µL + 0,5 µL AO7 10^{-4}M	Modest enhancement, variable intensity, band enlargement
Not aggregated	3 deposition 5 µL + 0,5 µL AO7 10^{-4}M	Modest enhancement, variable intensity, band enlargement
Not aggregated	5 deposition 5 µL + 0,5 µL AO7 10^{-4}M	Modest enhancement, variable intensity, band enlargement
Not aggregated	8 deposition 5 µL + 0,5 µL AO7 10^{-4}M	Modest enhancement, variable intensity, band enlargement
Aggregated	1 µL mixture AO7 10^{-4}M - aggregated AuNP	Medium enhancement, band enlargement
Not aggregated	1 µL mixture AO7 10^{-4}M - aggregated AuNP	High enhancement, variable intensity, improved spectral resolution

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