The Micro-sampling with Gel Matrix Associated with SERS Analysis for the Identification of Organic Compound in Polychrome Works of Art

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Abstract

The present paper shows the results obtained through the micro-sampling with gel matrix associated with SERS analysis (Surface Enhanced Raman Spectroscopy), for the first time applied to the study of organic dyes in polychrome works of art.

The obtained results allow us to affirm that the micro-samples taken with the technique developed are much lower than a millimeter, size commonly taken for chromatographic investigations currently employed for the identification of organic compounds in polychrome works.

In addition, from the colorimetric investigations conducted, it is clear that there is no visible change in the optical properties of the painted surfaces after the micro-sampling.

Introduction

SERS is a spectroscopic technique that combines the laser spectroscopy with the particular optical properties of metallic nanostructures, which produce the amplification of the Raman signal and the reduction of background fluorescence, upon resonance interaction between the molecules of the dye and the nanostructures of Ag.

As regards the field of Cultural Heritage, the interest arises from the fact that the non-invasive analytical techniques, commonly used in the identification of inorganic pigments, may not enable a secure recognition of organic dyes. So in general, it is necessary to take millimetrical samples for the execution of destructive and invasive techniques such as HPLC. The introduction of the micro-sampling associated with SERS analysis is this a turning point for the identification of organic compounds in the field of Cultural Heritage, filling an important gap in the framework of the techniques available to the diagnostician.

In particular, attention has focused on the use of solid matrices, and among those subject of the most recent publications, was particularly interesting matrix Ag-Agar, which was introduced by C. Lofrumento et al. [1] for the extraction of dyes from textiles and their subsequent identification by SERS.

Materials & Methods

The first step of the research was the preparation of specimens for the execution of the micro-sampling tests. The main organic lakes used in polychrome works were prepared, following the recipes contained in the ancient and medieval recipes manuals [1], both from animal and vegetable raw materials, both for shearing, by extraction of the dye from dyed wool (preparation technique typical of the medieval period). In order to test the applicability of the gel micro-sampling to the various artistic techniques, specimens of panel paintings, using the egg as a binder, of paintings on paper, using gum arabic, and of wall paintings, using animal glue (rabbit glue), were made for a total of 18 specimens.

Results

Based on the experience gained and the problems found in the use of the matrix Ag-agar was introduced a new type of gel which, due to its transparency, the lower gelling temperature and the greater rigidity is better compared to the agar and was designed a kit for micro-sampling associated with SERS analysis (patent pending), which contains devices specifically designed and everything necessary for the execution of the protocol and aimed to make it simple, rapid and reproducible.

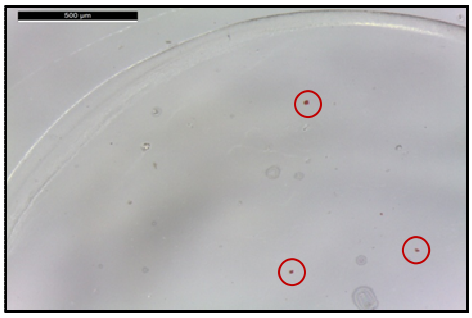

Fig. 1 - Example of micro-sampling with gel matrix

The specimens produced were used for the execution of the micro-sampling tests, conducted using devices designed, for a total of 162 micro-samplings.

The evaluation of invasiveness of micro-sampling was carried out through photographic documentation of all 162 micro-samples with a Leica 3D microscope (example in fig. 1) and through the use of video-colorimeter
(MHT SpectroShade), making colorimetric measurements before and after the micro-sampling.

Conclusions

The obtained results allow us to affirm that the micro-samples, taken with the technique developed, are much lower than a millimetre, size common taken for the execution of the techniques currently used for the identification of organic compounds in polychrome works (HPLC).

Furthermore, the colorimetric investigations conducted shows that there is no visible change in the optical properties of the painted surfaces after the micro-sampling (the results are summarized in tab.1).

Tab. 1 - Result of colorimetric analysis on specimens of paper paintings, panel paintings and wall paintings

PAPER	
ZONE	<ΔE>(± 0.5)
rob rad 1	2.3
rob rad 2	2.3
rob rad 3	1.6
rob cim 1	0.3
rob cim 2	2.3
rob cim 3	3.4
cocc 1	2.0
cocc 2	0.7
cocc 3	3.2
cocc cim 1	1.4
cocc cim 2	1.1
cocc cim 3	3.1
cocc sn 1	1.5
cocc sn 2	2.0
cocc sn 3	4.7
gom lac 1	0.4
gom lac 2	2.8
gom lac 3	1.4

PANEL	
ZONE	<ΔE> (± 0.5)
rob rad 1	1.0
rob rad 2	1.1
rob rad 3	0.7
rob cim 1	3.1
rob cim 2	2.5
rob cim 3	1.7
cocc 1	0.7
cocc 2	0.6
cocc 3	0.8
cocc cim 1	0.8
cocc cim 2	0.4
cocc cim 3	1.0
cocc sn 1	1.8
cocc sn 2	1.1
cocc sn 3	0.9
gom lac 1	0.6
gom lac 2	0.7
gom lac 3	0.6

WALL	
ZONE	<ΔE> (± 0.5)
rob rad 1	1.0
rob rad 2	1.4
rob rad 3	2.1
rob cim 1	0.9
rob cim 2	2.2
rob cim 3	1.1
cocc 1	1.1
cocc 2	2.0
cocc 3	1.0
cocc cim 1	1.8
cocc cim 2	0.9
cocc cim 3	1.2
cocc sn 1	4.0
cocc sn 2	0.9
cocc sn 3	1.6
gom lac 1	0.8
gom lac 2	2.4
gom lac 3	4.3

References

1) C. Lofrumento, M. Ricci, E. Platania, M. Becucci, E. Castellucci, SERS detection of red organic dyes in Ag-Agar gel. *J. Raman Spectroscopy* 44, (2012) 47-54

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