Nanostructured substrates for application of SERS to cultural heritage studies

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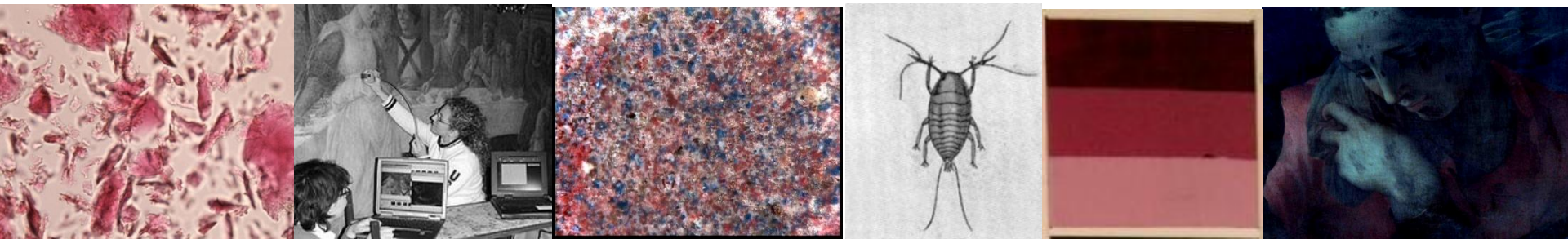

MOLAB (Mobile Laboratory)

CHARISMA
Cultural Heritage Advanced Research Infrastructures
Synergy for a Multidisciplinary Approach to Conservation/Restoration

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- -fiber-optic FT-IR
- -micro-Raman
- -fiber-optic Vis-NIR
- -fiber-optic fluorescence
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- -IR-colour scanner reflectography
- -laser micro-prophilometry
- -NMR relaxometry (MOUSE)
- -drilling resistance
- -fiber optic NIR
- -video-microscopy
- -AFM
- -....

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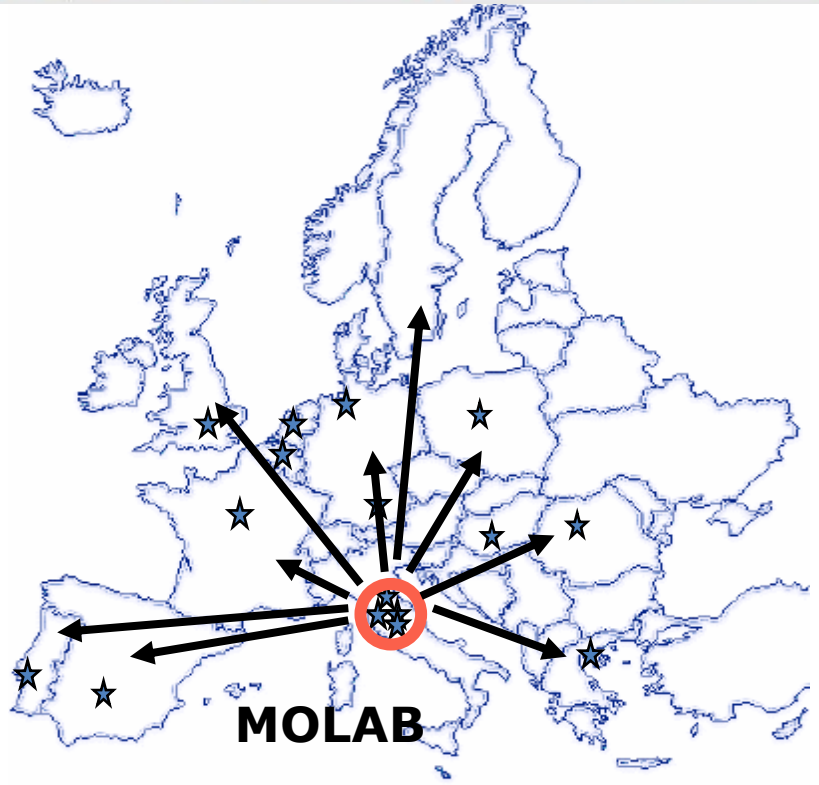
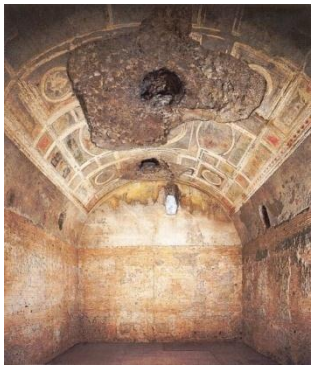


Lake pigments **since antiquity** have been prized by painters for their rich colours.

occurrence



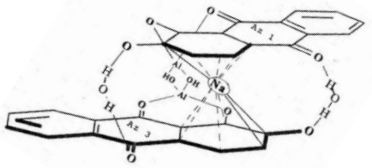
*Wall painting decoration of the Domus Aurea, Rome (***64 a.C.***).*

Raphael, *Pala Baglioni,* Galleria Borghese, Rome. *(***1507**).

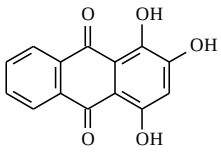
A. Renoir, woman tying her shoe, Courtauld Institute Art Gallery, London *(***1893***).*

preparation

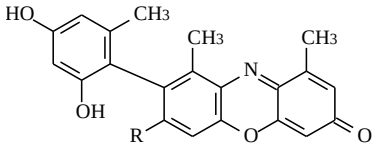
Natural organic dyestuffs obtained from various plant and insect sources can be used as artists' pigments if they are **co-precipitated with an inorganic substrate**. The reaction between potash alum ($AlK(SO_4)_2.12H_2O$) and an alkali forms hydrated alumina which precipitates from solution.



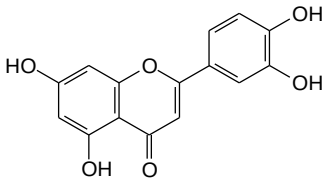
P. Soubayrol, G. Dana, G. Bolbach, *Analysis,* 24, 7 (1996) 34-36



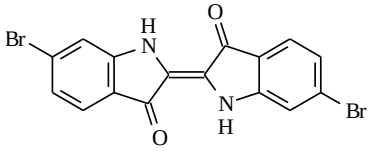
Hydroxy-anthraquinones

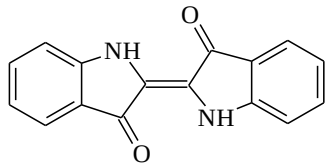


Phenoxazones



Hydroxy-flavonoids

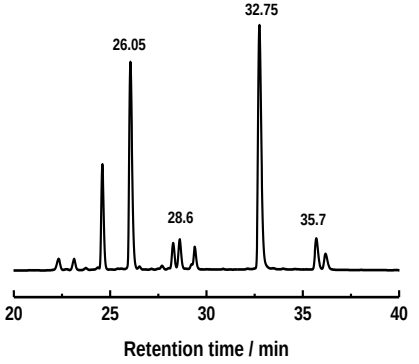




indigoids

How to identify dyes and lakes non-invasively?

UV-*vis* reflectance and fluorescence (steady state and time resolved)

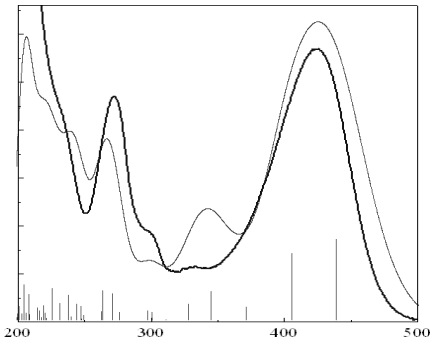


Clementi C., Miliani C., Romani A., Favaro G., *In situ fluorimetry: a powerful non-invasive diagnostic technique for natural dyes used in artefacts. Part I: Spectral characterization of orcein in solution, on silk and wool laboratory-standards and a fragment of Renaissance tapestry*, ***Spectrochimica Acta part A***, 64 (2006) 906-912;

Clementi C., Miliani C., Romani A., Favaro G. **Account of Chemical Research**, in press.

High sensitivity but poor specificity

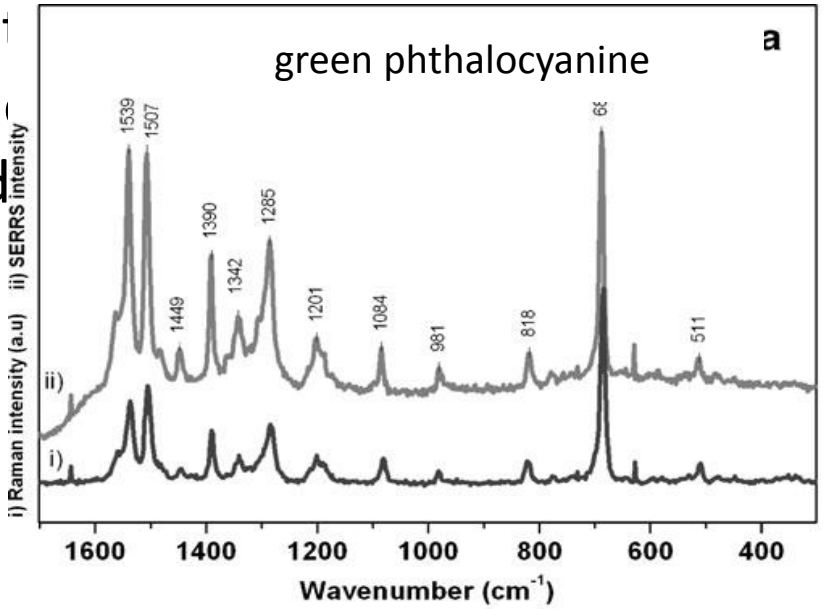
fiber optic Resonance Raman spectroscopy



F. Rosi[1], M. Paolantoni[2], C. Clementi[2], B. Doherty[3], C. Miliani[3], B. G.Brunetti[1], A. Sgamellotti[1,3] *Fluorescence suppression in resonance Raman spectroscopy of organic dyes and lakes by Subtracted Shifted Raman Spectroscopy-SSRS* **Journal of Raman Spectroscopy, 2010**

SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS)

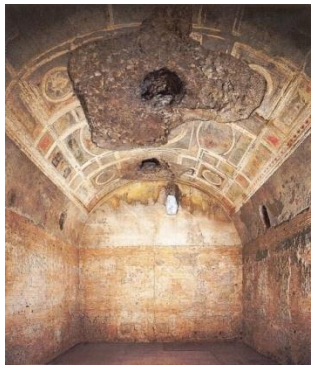
Based on the huge enhancement of
molecules when they are placed in th
metallic surfaces through chemical and

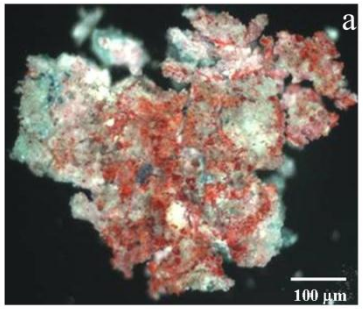


Ancient lakes

Non invasive and micro-destructive investigation of the *Domus Aurea* wall painting decorative materials

C. Miliani et al. Anal Bioanal Chem, 2012

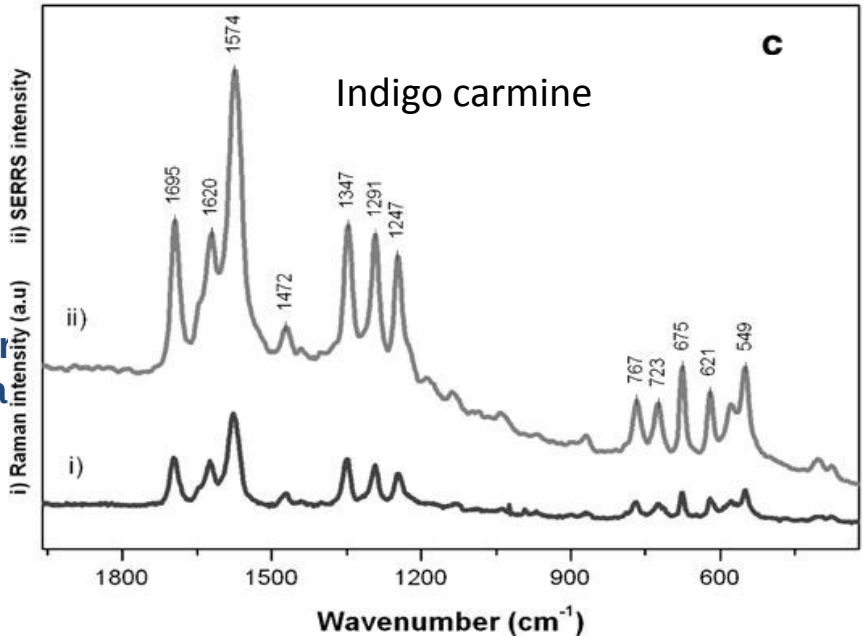




Modern synthetic lakes

Unilateral NMR, 13C CPMAS NMR spectroscopy and micr materials and state of conservation of an ancient Egyptia

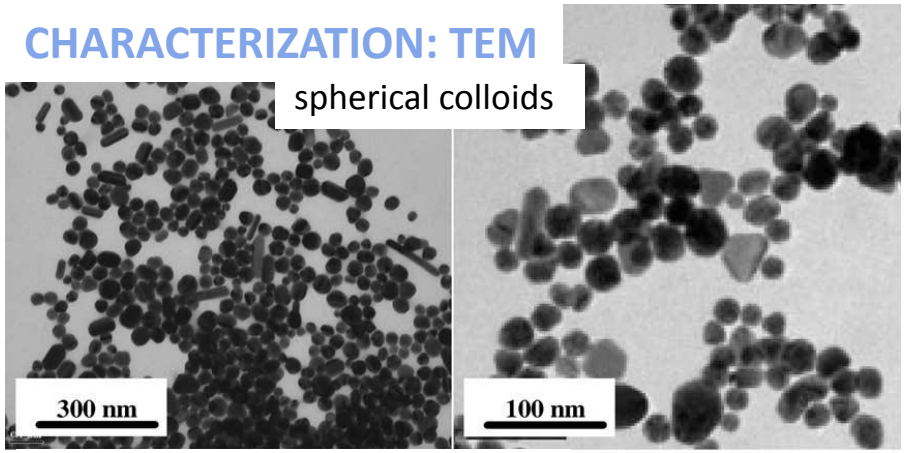
N.Proietti , et al Anal Bioanal Chem 2012



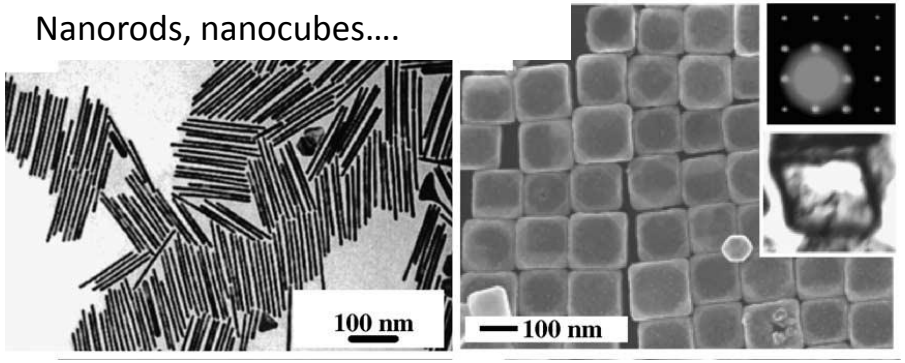
SERS substrate: NANOPARTICLES

CHARACTERIZATION: TEM

spherical colloids



Nanorods, nanocubes….



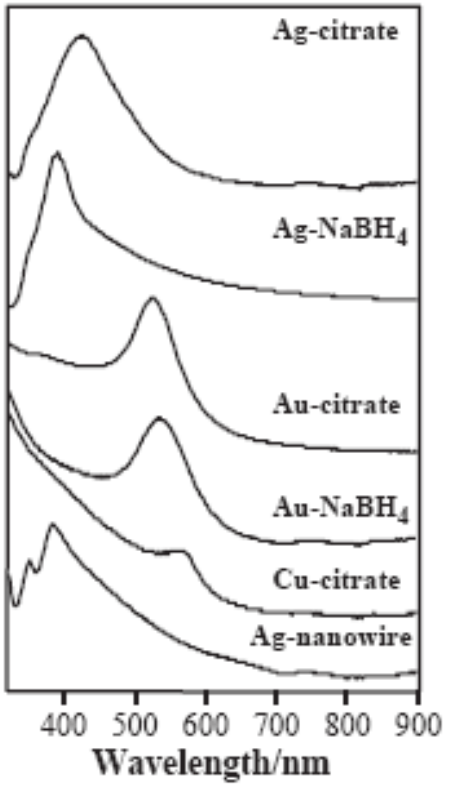
COLLOID SYNTHESIS[

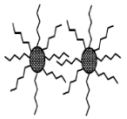
1. Chemical reduction
2. Photo-reduction
3. Laser-ablation

CHARACTERIZATION: UV-Vis absorption

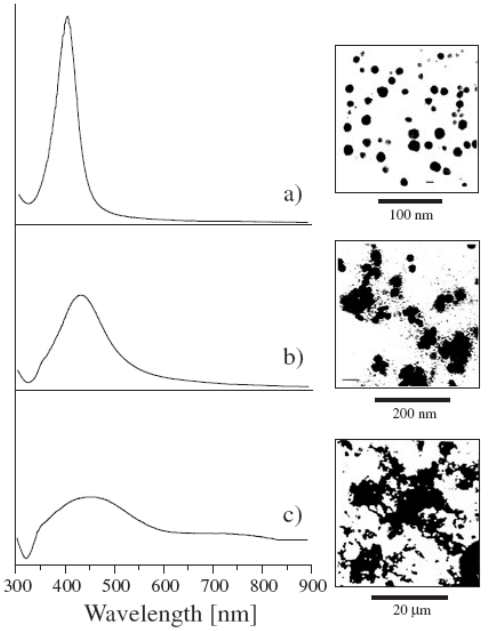
Characteristic surface plasmon resonance (SPR):

- Abs. max. gives information on average particle size
- FWHM, estimation of particle size distribution
- Shifts attributed to morphological differences

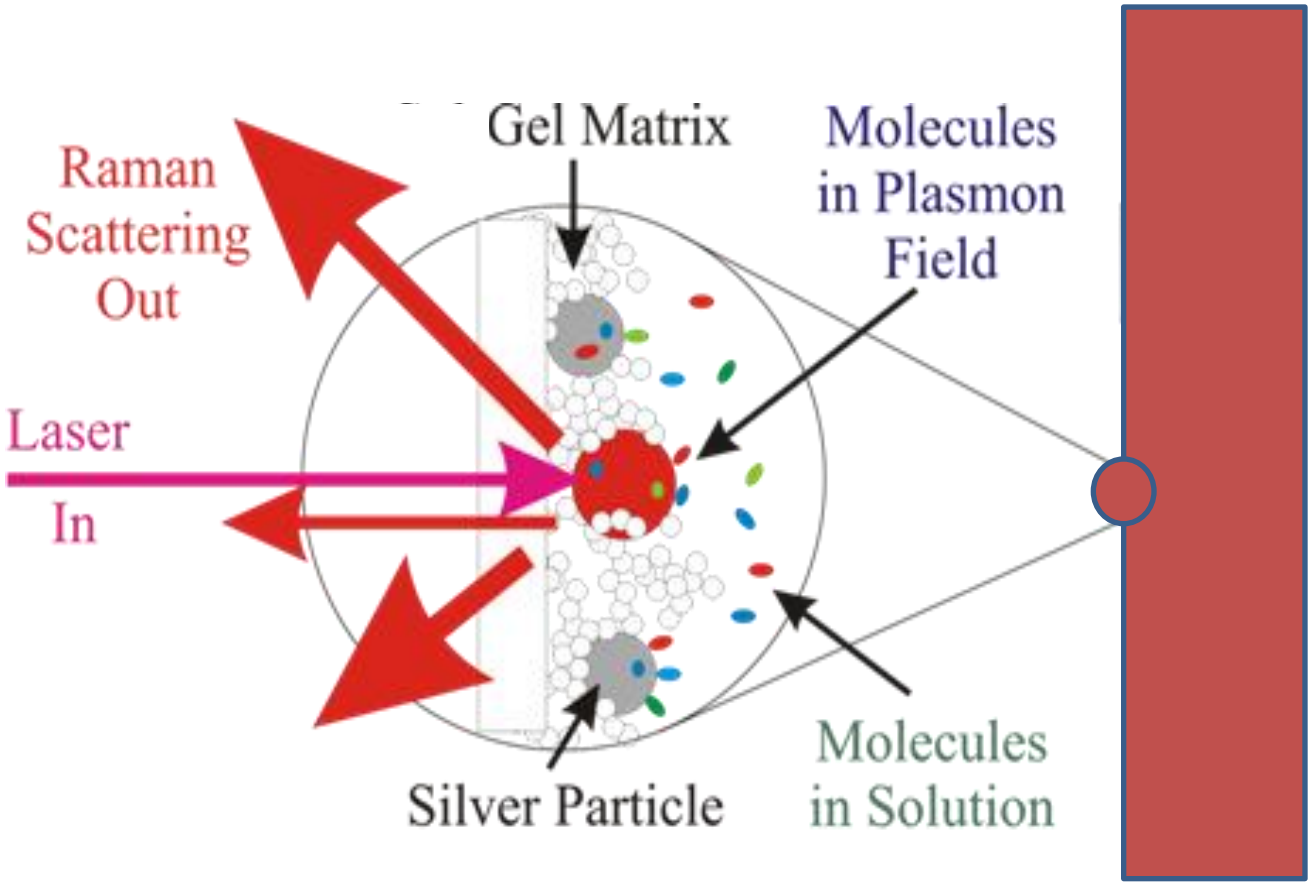




- Aggregation leads to an increase in SERS activity



In situ non-invasive SERS measurements ?



1. **Metal nanoparticles colloid applied directly on the artwork surface by means of a detachable gel substrate.**
2. **Portable fiber optic Raman spectrometer (exc. 532 nm).**

In situ non-invasive SERS measurements ?

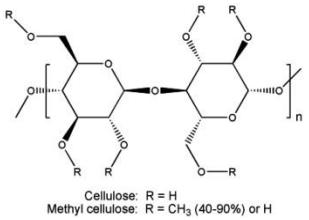
A **gel doped with the AgNPs** has been specifically designed:

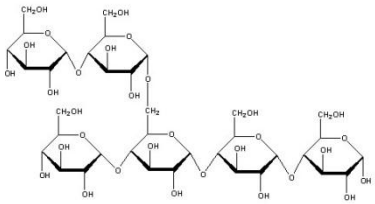
1. **Suitable average SERS enhancement**
2. **Good stability and reproducibility**
3. **Neutral pH**
4. **Transparency**
5. **Removability**

Methylcellulose

&

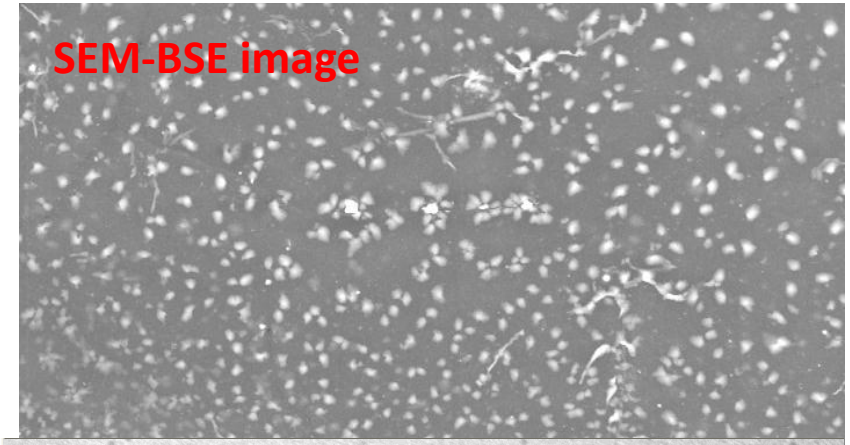
AgNP starch colloid

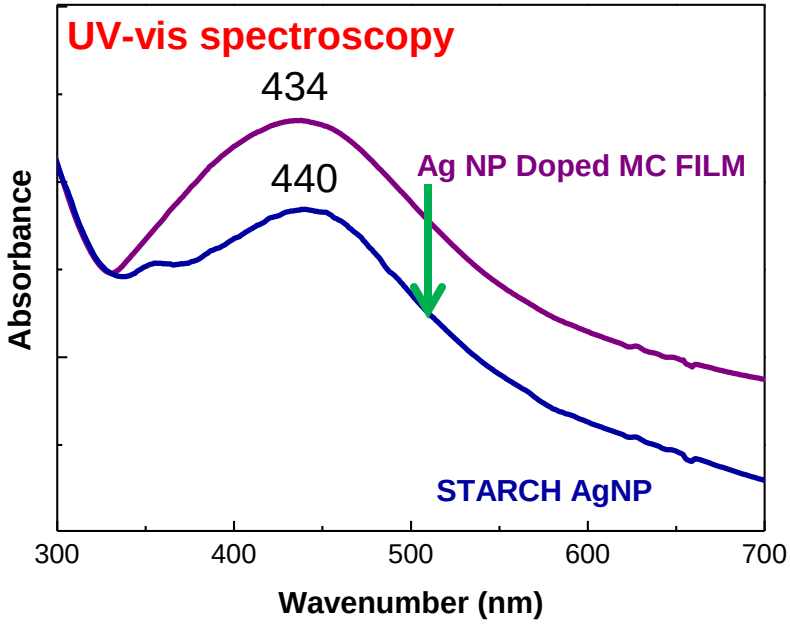


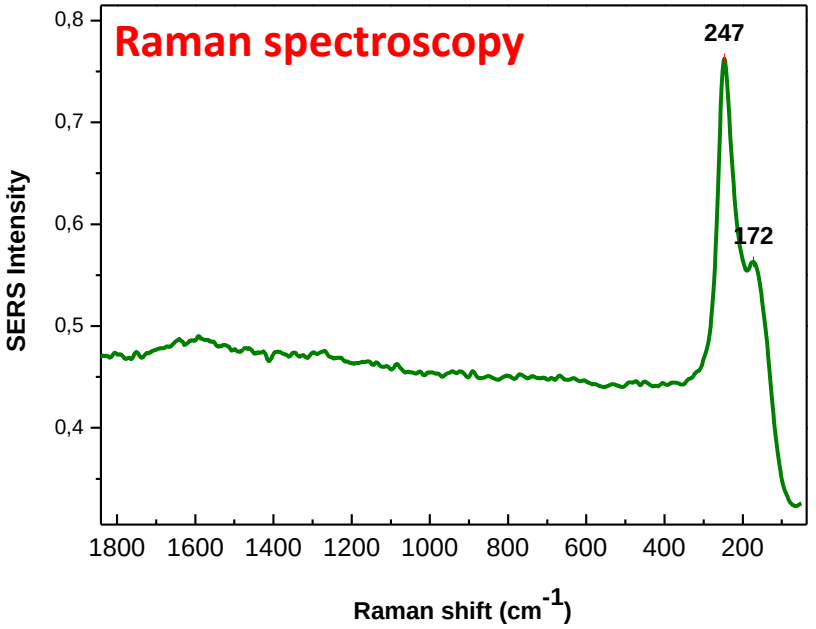


It is shown that silver nanoparticles prepared by green chemical reduction can be effectively doped into a methylcellulose matrix for the formation of a **gel that can be applied to a minute area of an artwork to be studied and that after SERS measurements can be safely removed.**

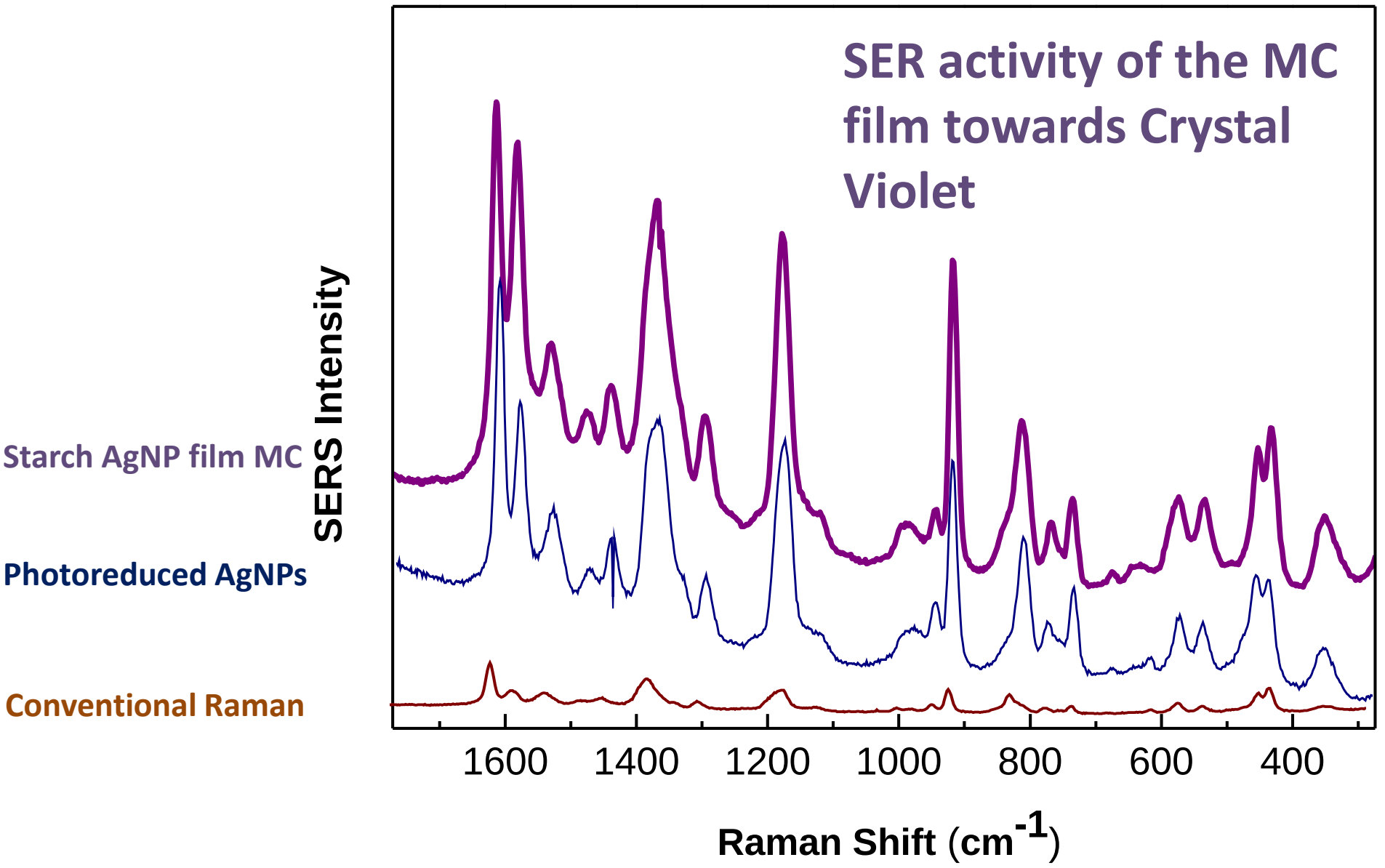
1. Characterization of the detachable SERS active substrate



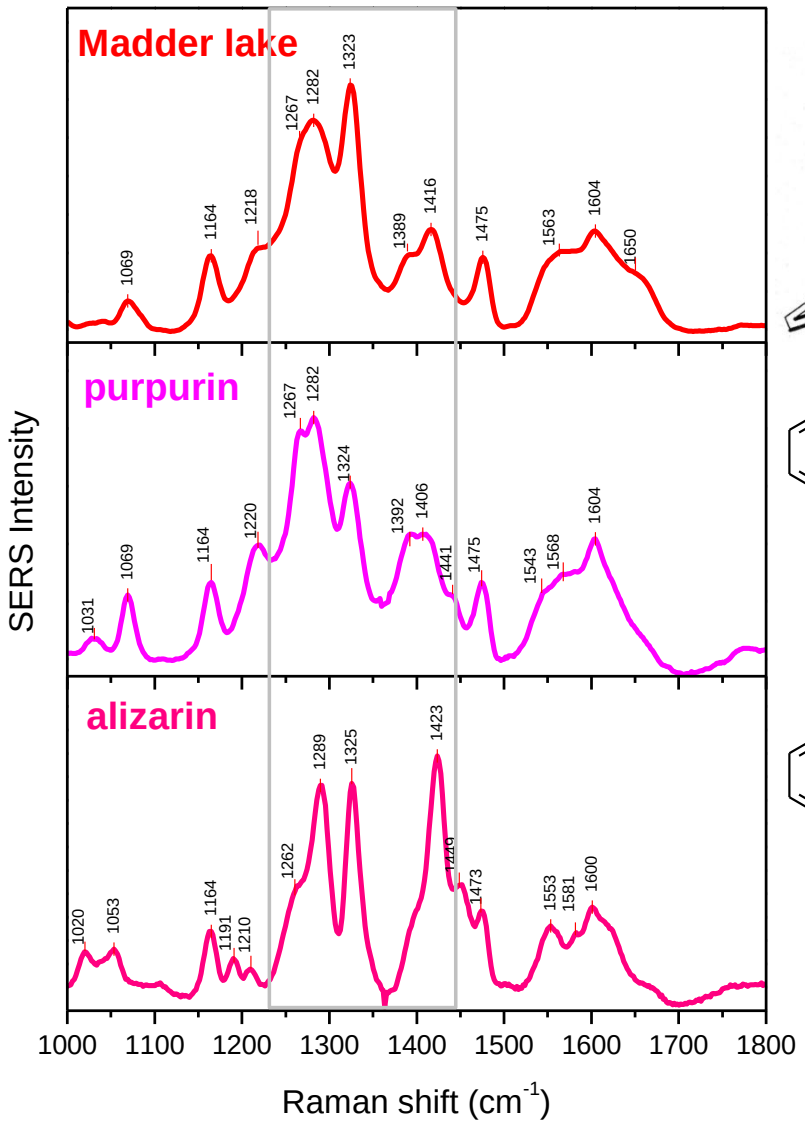


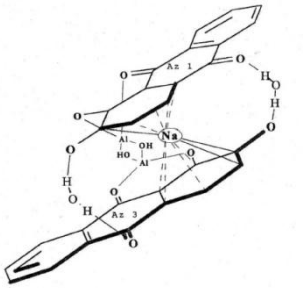


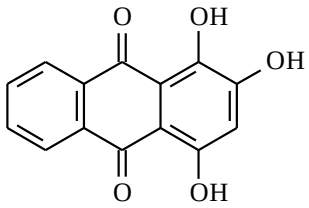
1. Characterization of the detachable SERS active substrate

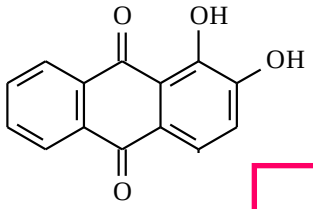


Study of madder lake powder by SERS active substrate





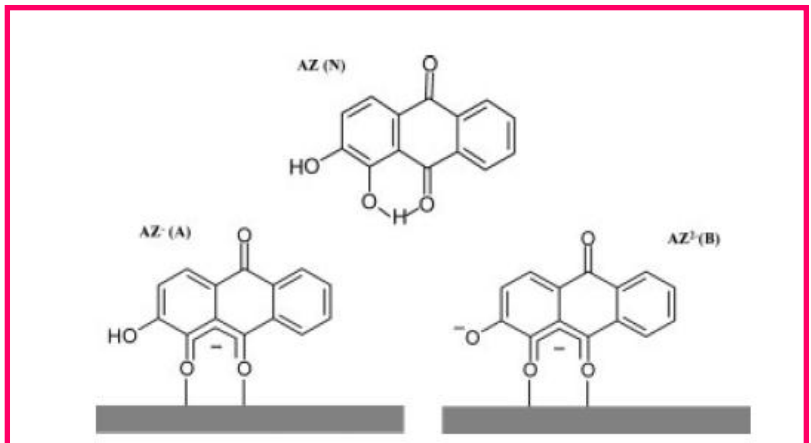




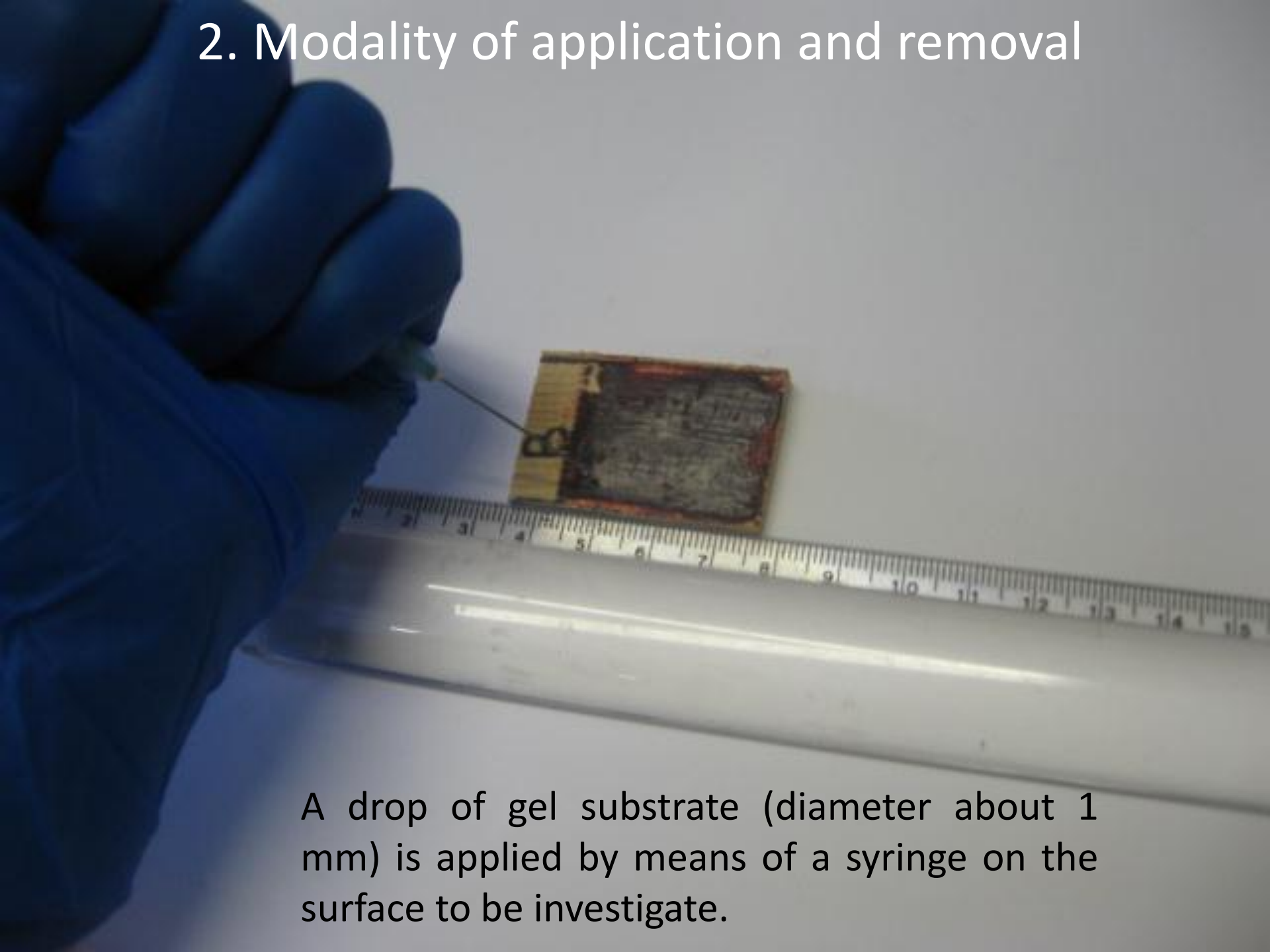
SER spectra of madder lake is similar to SER spectra of purpurin:

-interaction with free purpurin (incomplete complexation)

-higher interaction with the complexed form of the purpurin component due to the greater number of hydroxyl sites in purpurin

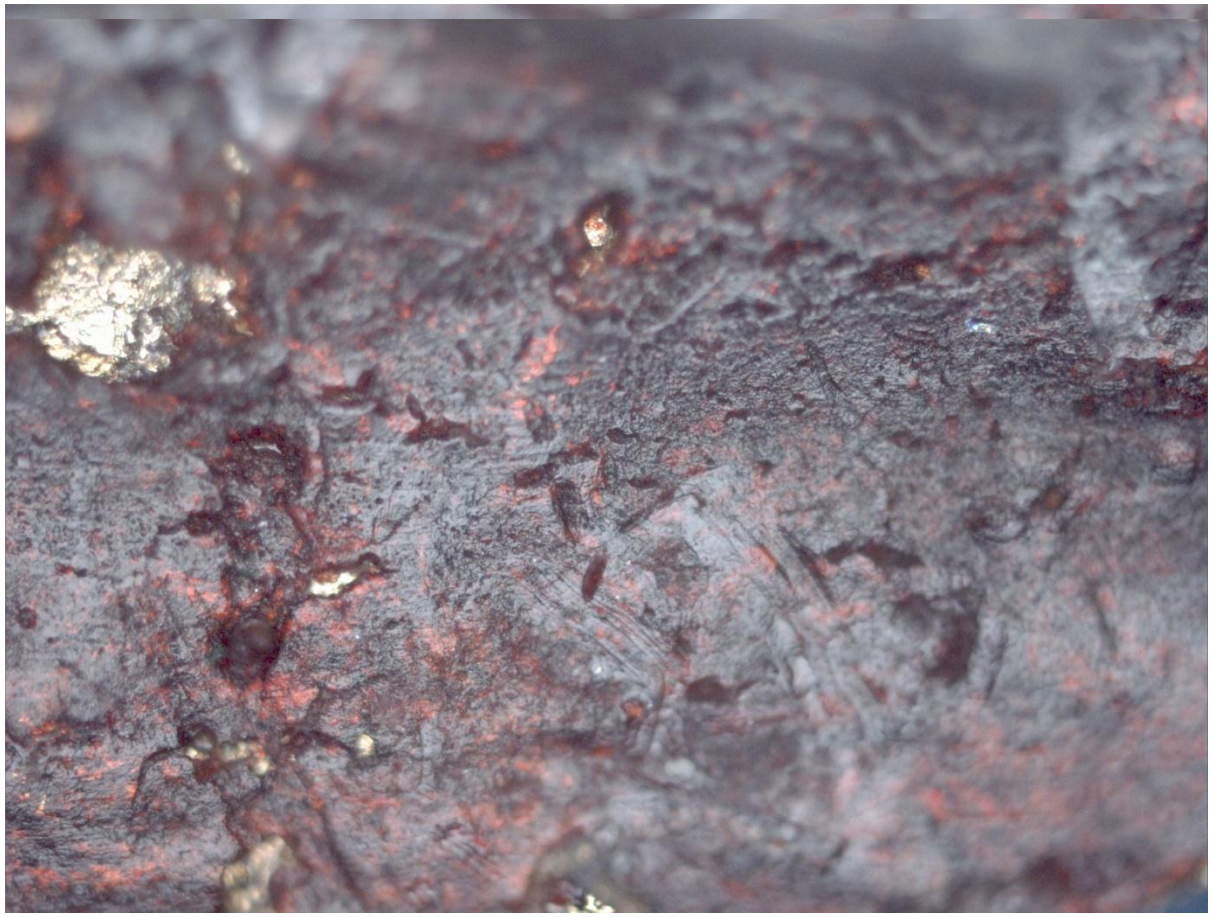


2. Modality of application and removal



A drop of gel substrate (diameter about 1 mm) is applied by means of a syringe on the surface to be investigate.

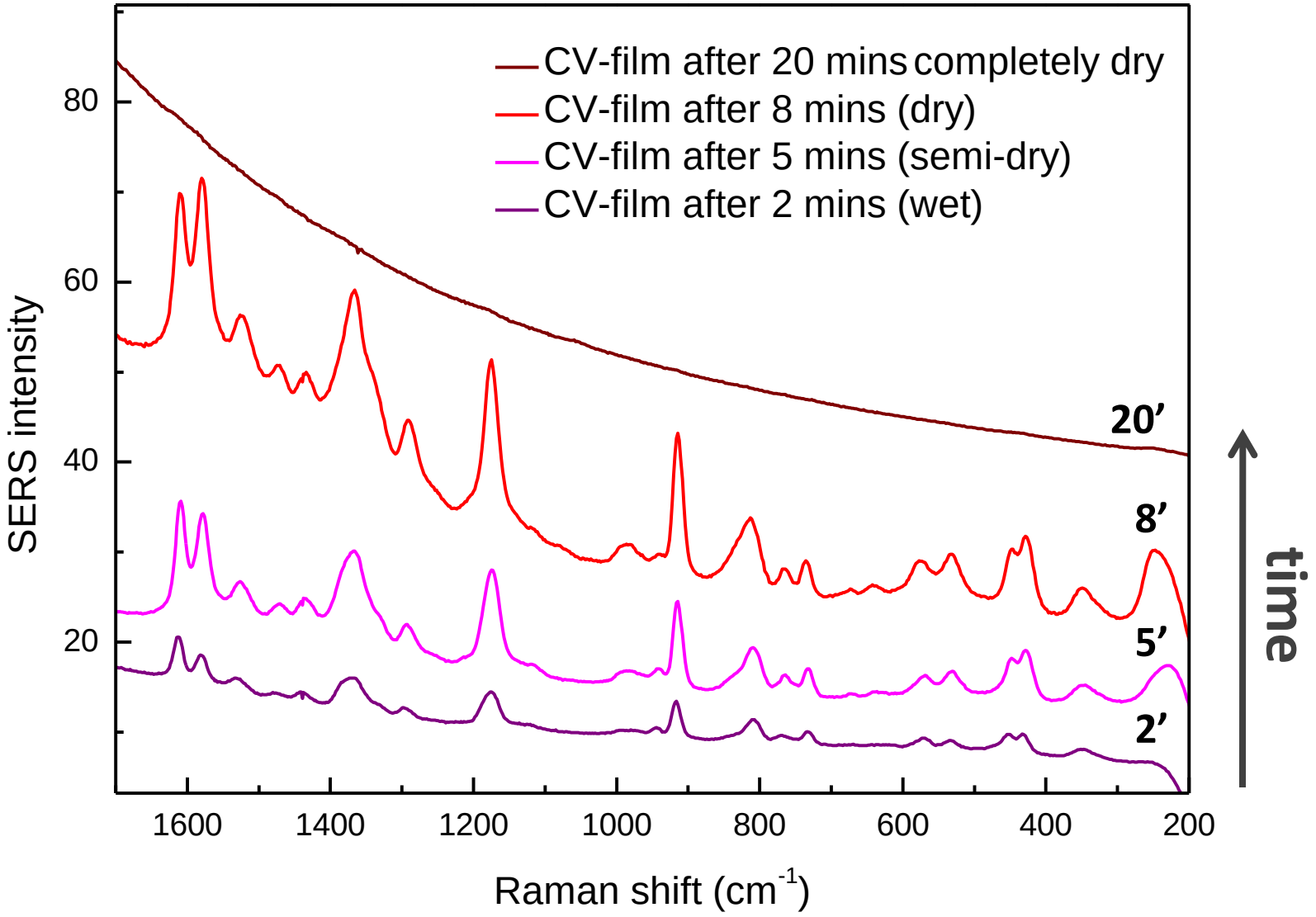
2. Modality of application and removal



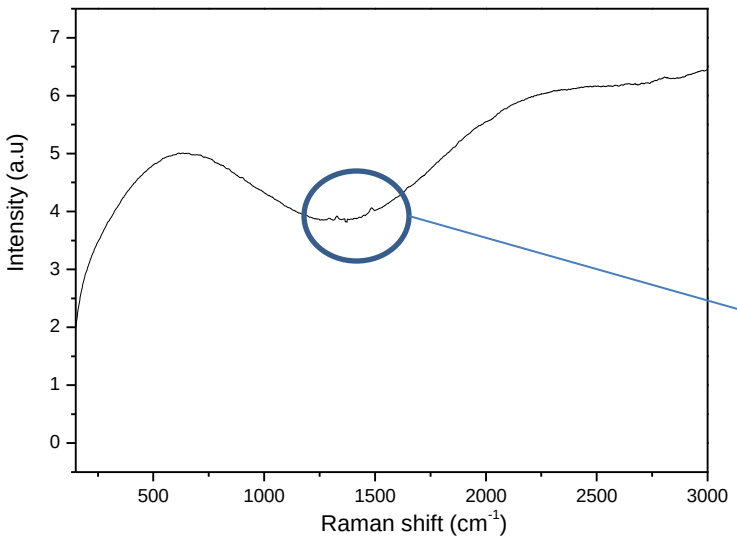
On complete drying the film can then be peeled off the studied surface leaving no visible trace.

2. Modality of application and removal

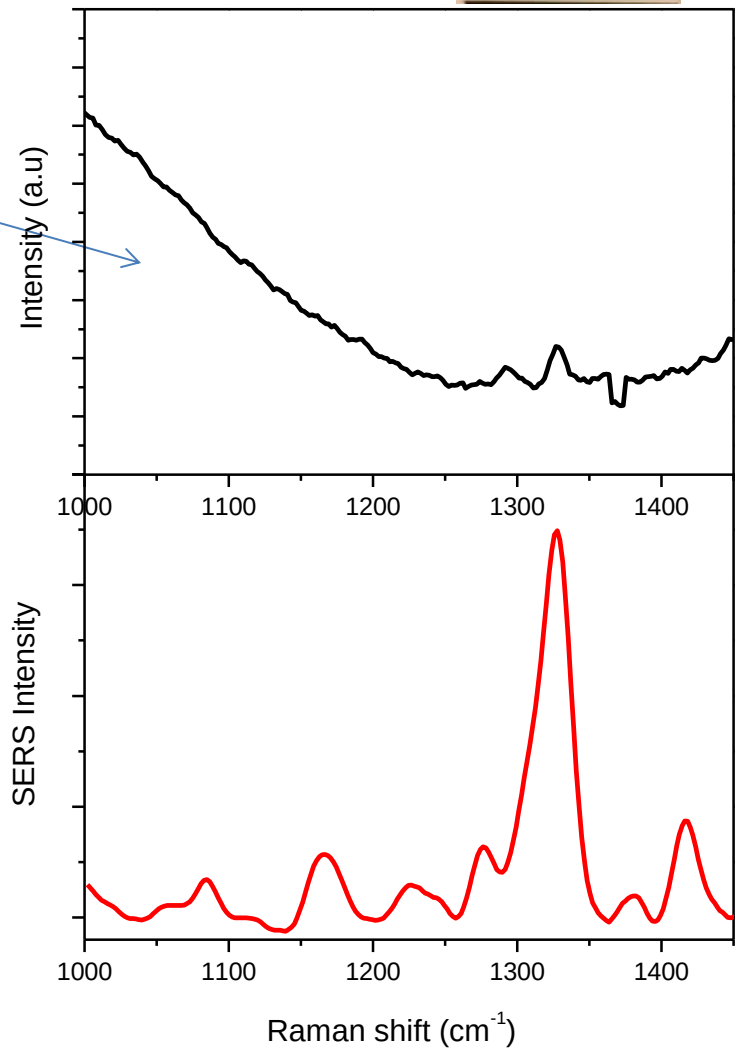
SER activity of the MC film towards Crystal Violet as a function of time



3. Study of madder lake painting mock-ups



Conventional Raman spectrum collected from the surface of mock-up made by madder lake and linseed oil (exc. 532 nm)

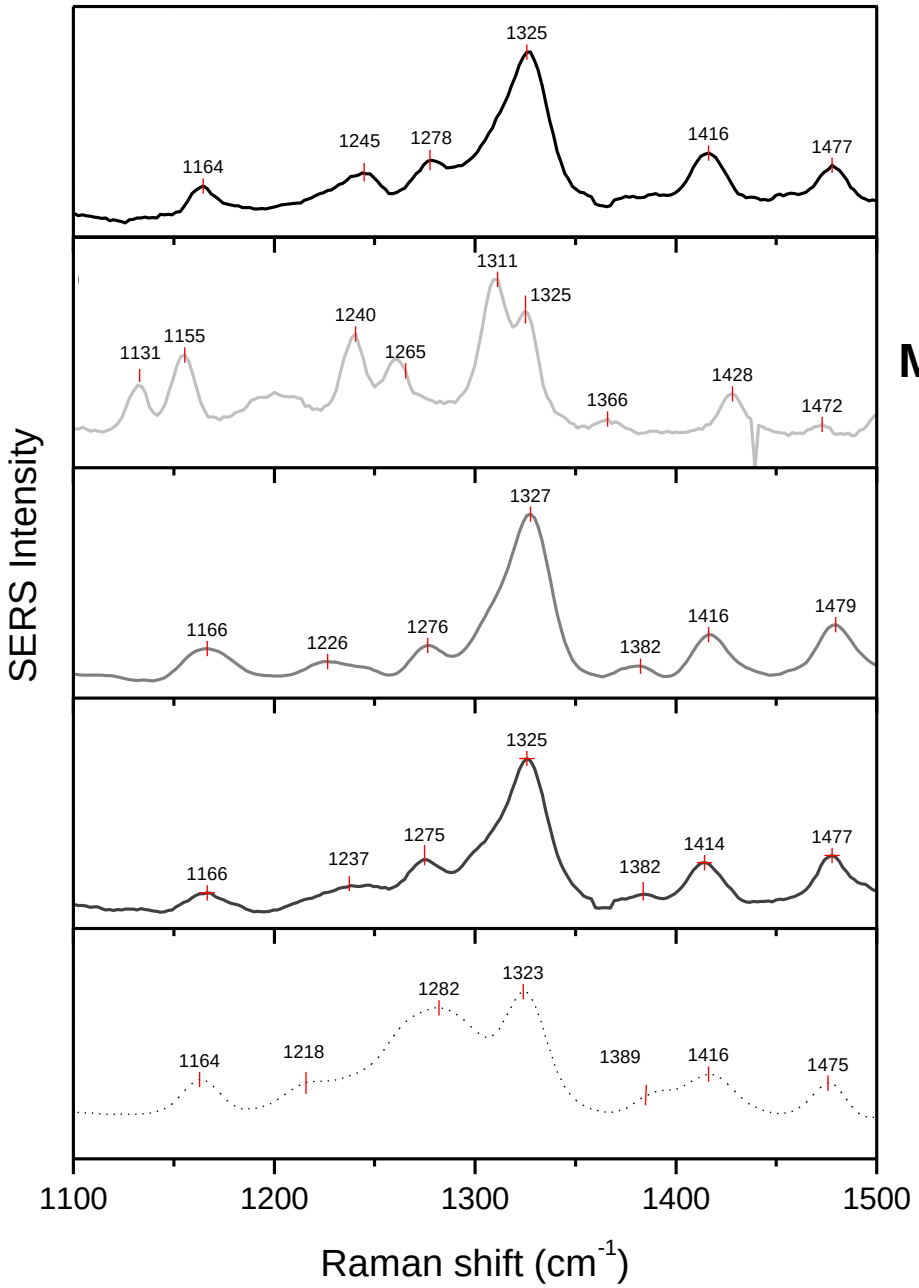


Qualitative Enhancement Factor (EF) of roughly **10^3 -10^4** , given by:

$EF = I_{SER}/I_{RS}$ (@ 1325 cm^{-1})

SER spectrum collected from the surface of mock-up made by madder lake and linseed oil (exc. 532 nm)

3. Study of madder lake painting mock-ups



Madder & Casein

Madder & Wax (encaustic)

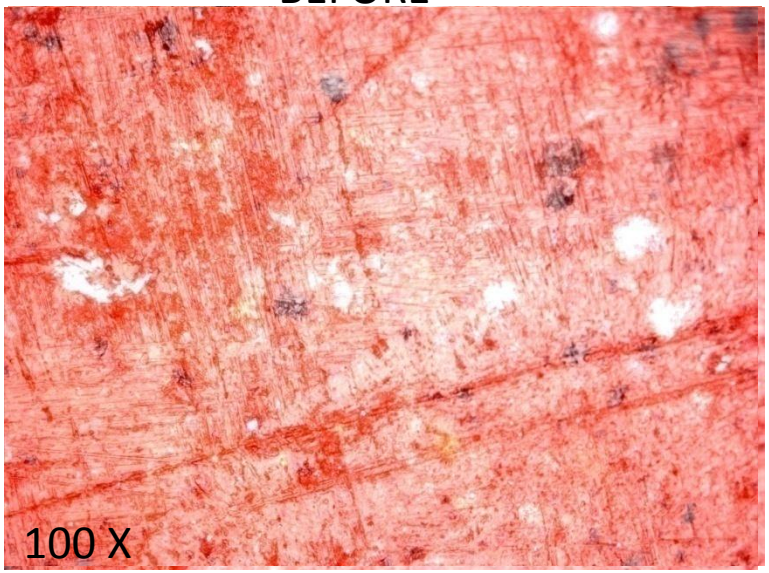
Madder & Linseed oil

Madder & Egg tempera

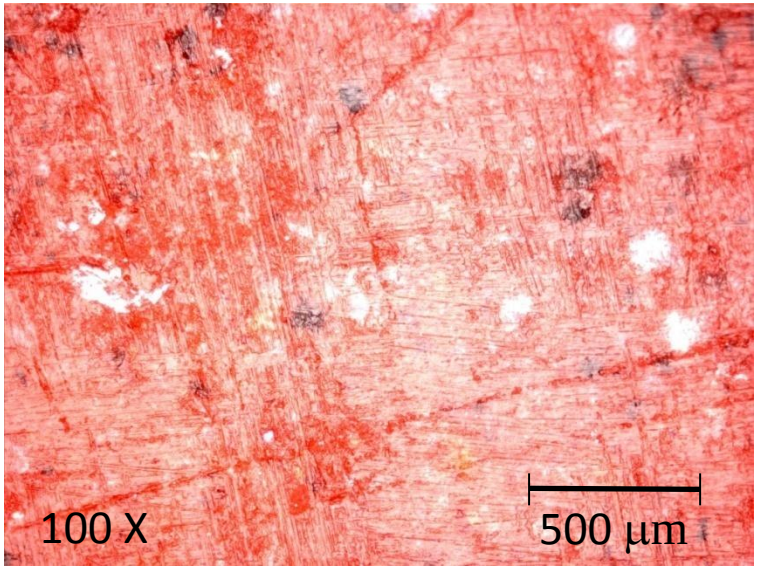
Madder

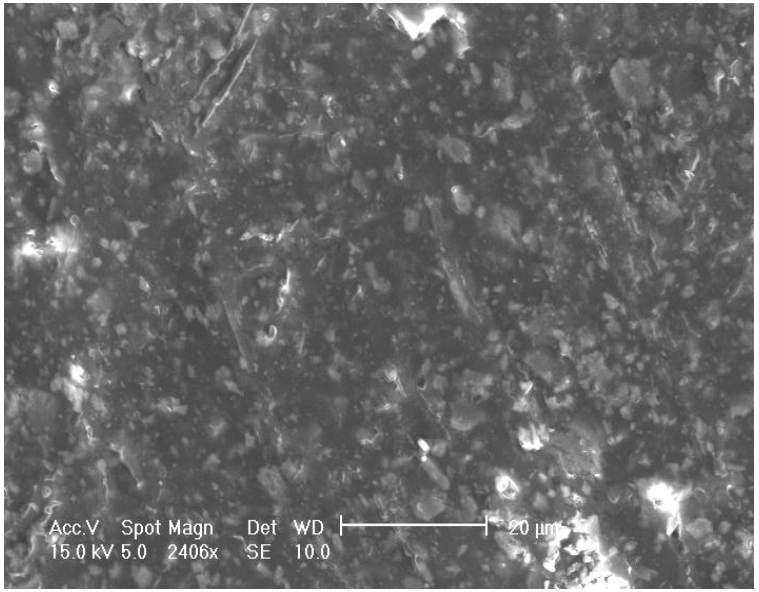
4. Verification of the non-invasivity

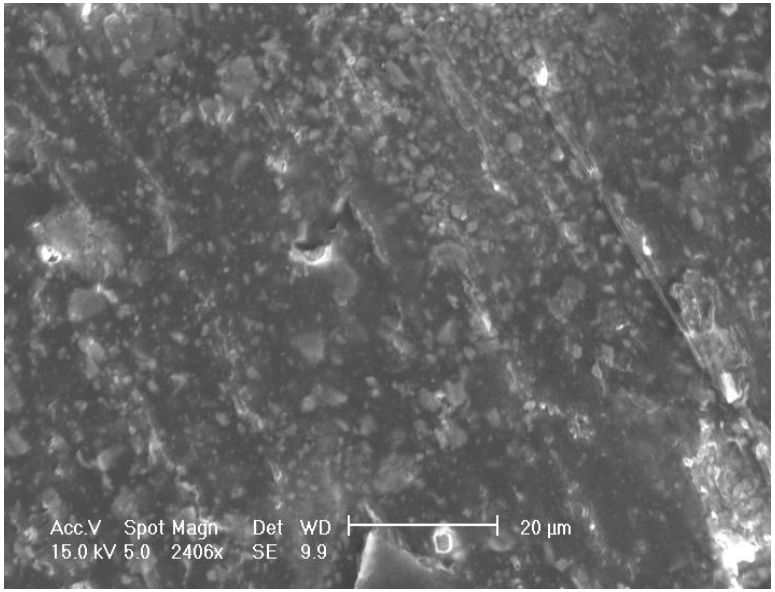
BEFORE

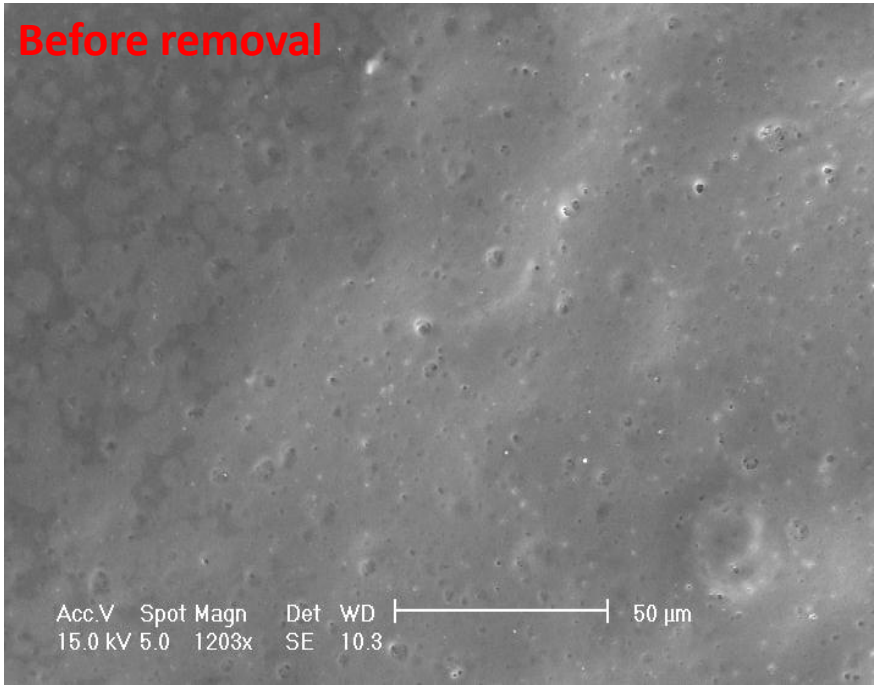


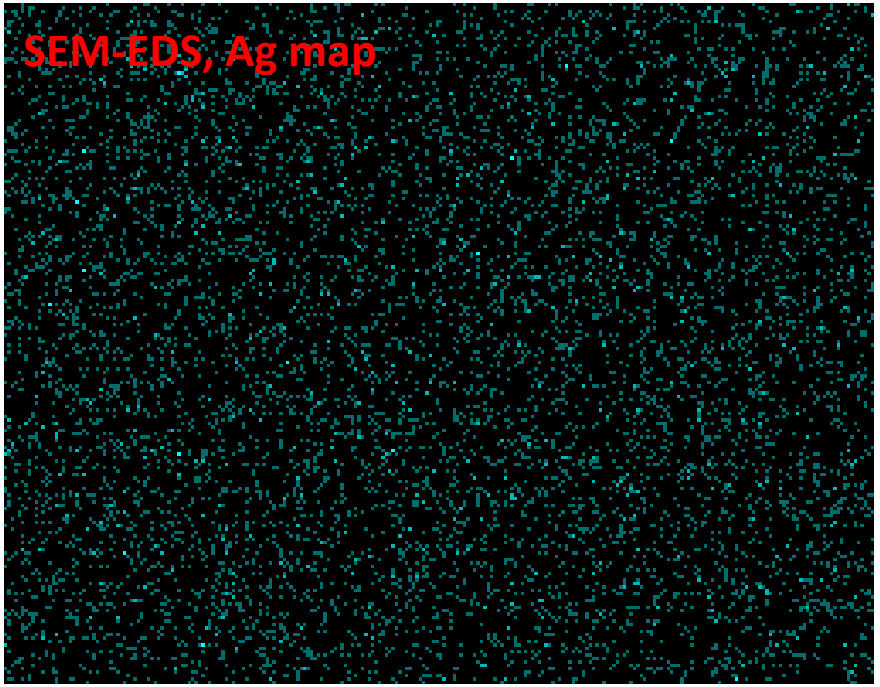
AFTER

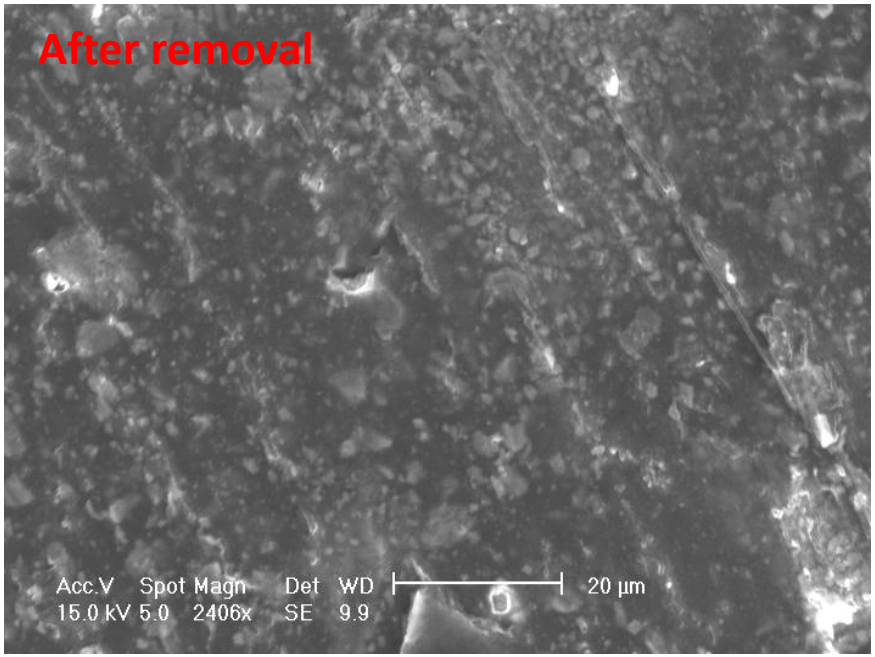






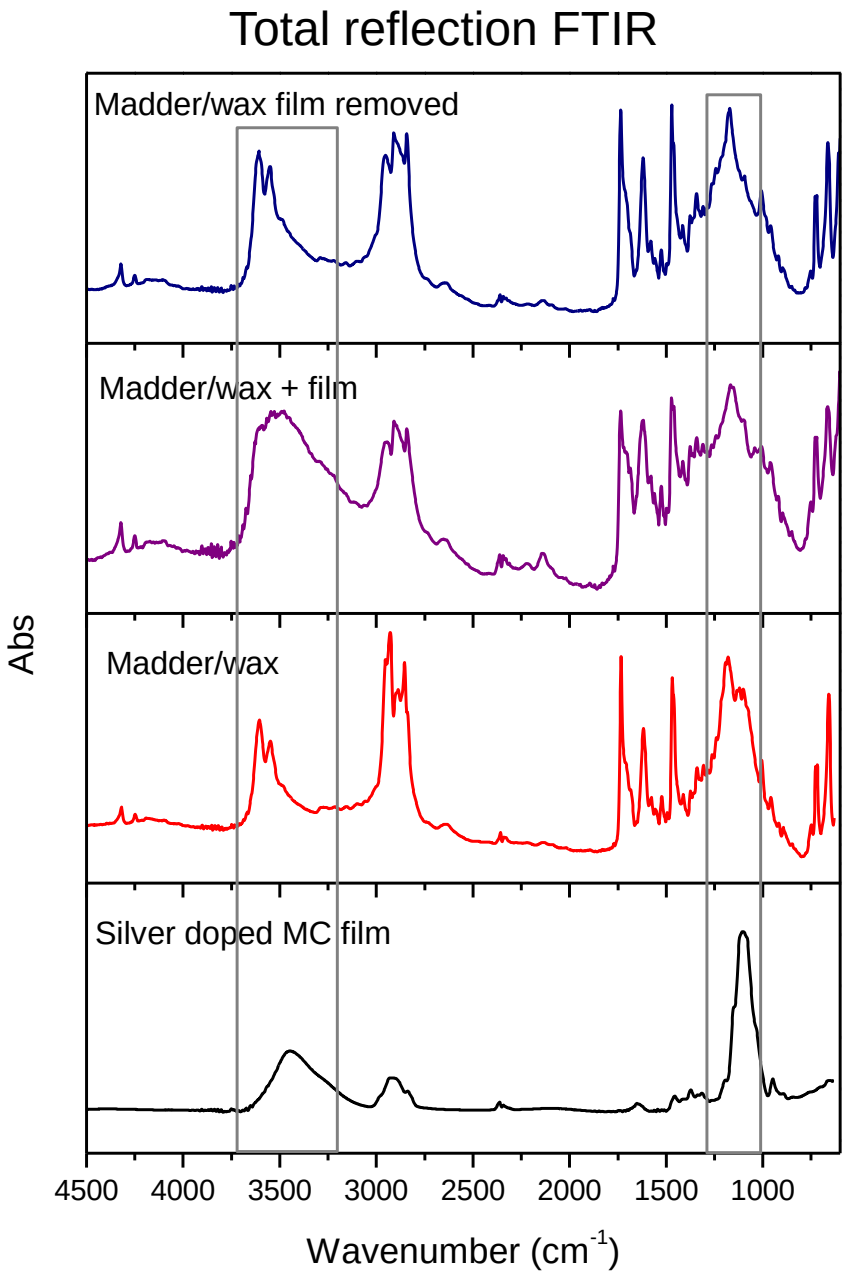

Before removal
Acc.V Spot Magn Det WD
15.0 kV 5.0 1203x SE 10.3
50 µm


SEM-EDS, Ag map


After removal
Acc.V Spot Magn Det WD
15.0 kV 5.0 2406x SE 9.9
20 µm


SEM-EDS, Ag map

4. Verification of the non-invasivity



3500 cm^{-1} ν (OH) MC/starch

2892 cm^{-1} ν (CH)

1374 cm^{-1} δ (CH)

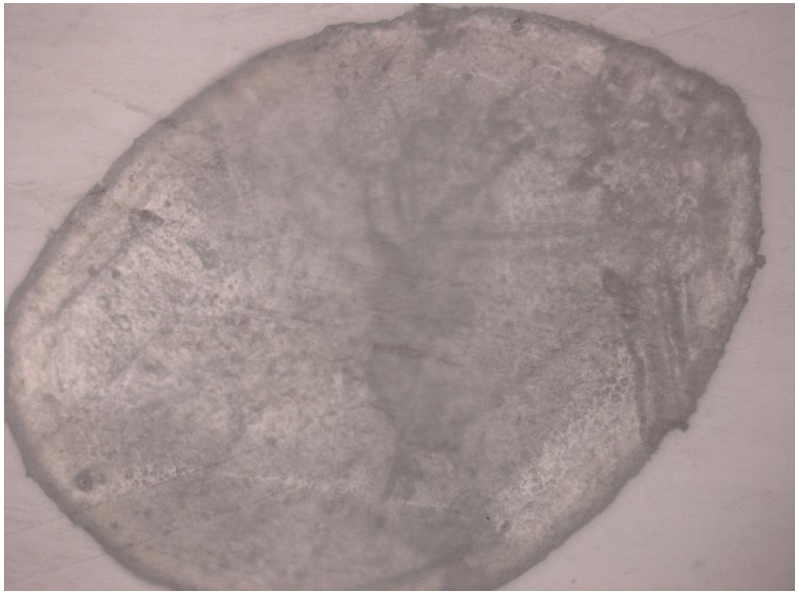
1159 cm^{-1} ν (C-O-C)

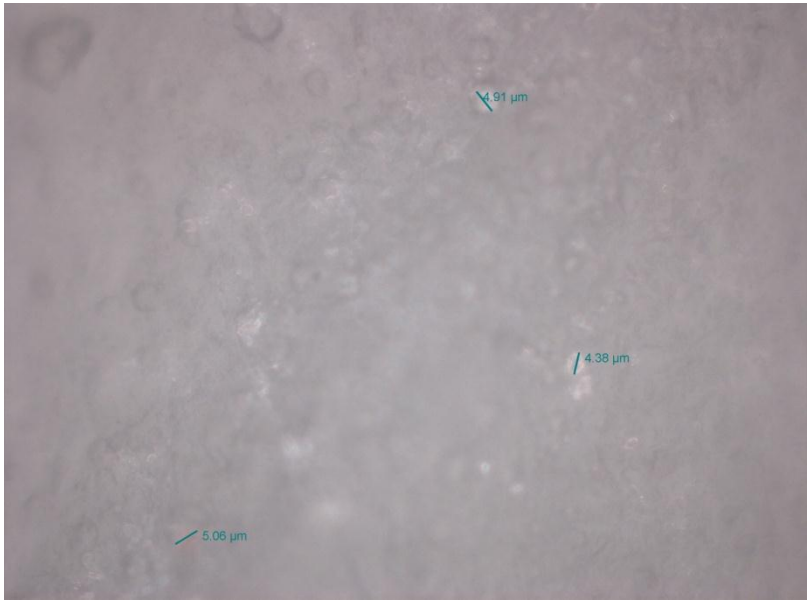
1090 cm^{-1} ν(O-C) anhydro-glucose ring

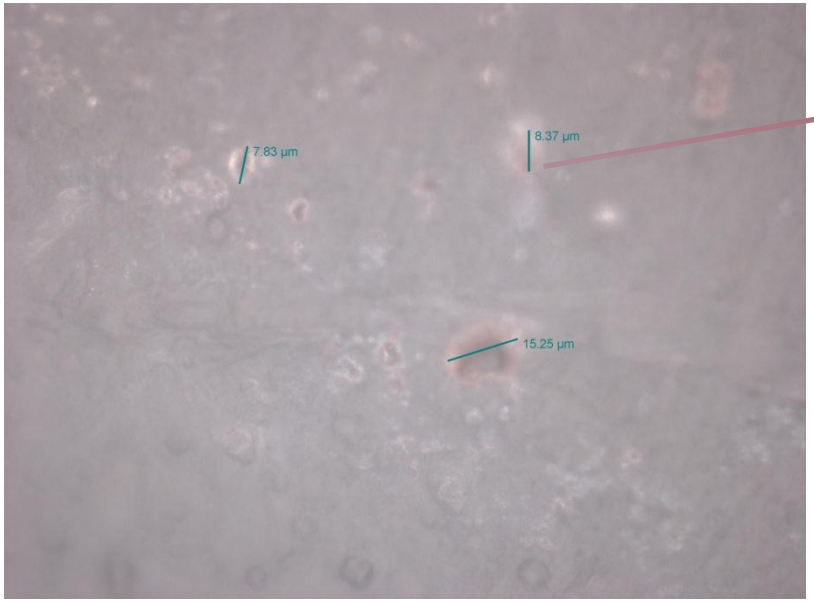
1070 cm^{-1} ν (C-O) MC

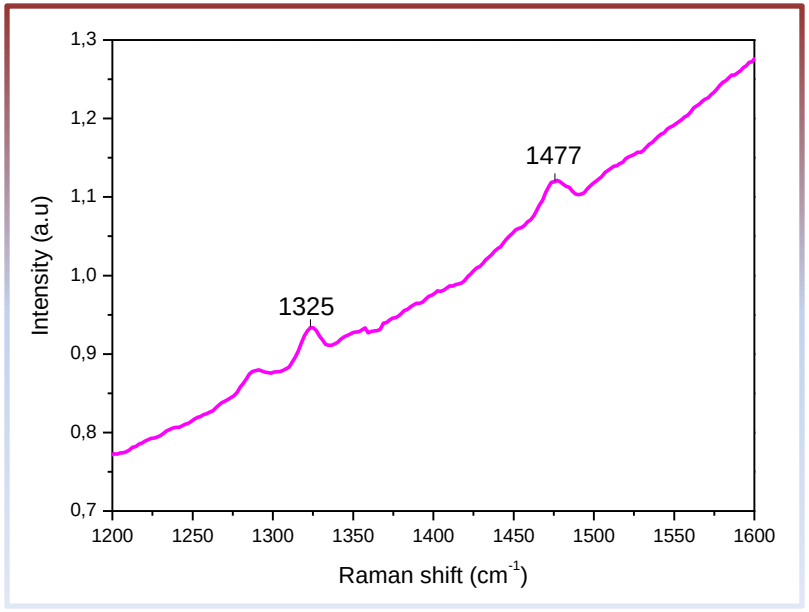
Absence of band at 1384 cm^{-1} indicating a complete reduction of Ag^{+} to Ag^{0}

4. Verification of the non-invasivity









Conclusions and perspectives

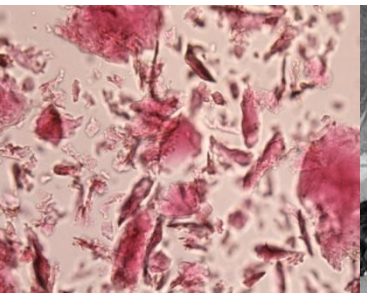
The novel SERS nanoscructured substrate:

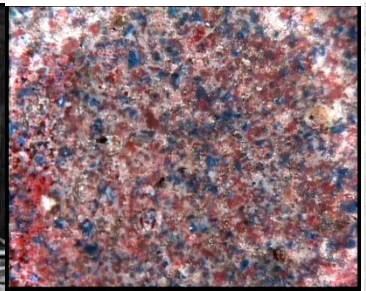
1. is detachable;
2. does not leave residues (nor AgNPs , $AgNO_3$, or MC);
3. gives an enhancement factor of 10^3-10^4 for madder lake in several binders;

→ Lakes showing higher fluorescence quantum yield will be tested. Effect of pH of the gel.

4. causes the loses of small grain of lake for egg and casein.

→ The rheological property of MC gel has to be further optimized (PEG, gelatin, cfr. Agar-gel by Castellucci JRS 2012). Use of innovative cleaning gels. Effect different NP shape and dimension.






Non-invasive SERS

2001

THE ANALYST COMMUNICATION
www.rsc.org/analyst

Disposable, stable media for reproducible surface-enhanced Raman spectroscopy

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2009

Anal. Chem. **2009**, *81*, 9233–9238

Recyclable Molecular Trapping and SERS Detection in Silver-Loaded Agarose Gels with Dynamic Hot Spots

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A detachable SERS active cellulose film: a minimally invasive approach to the study of painting lakes

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2011

analytical chemistry
pubs.a

Nondestructive Identification of Natural and Synthetic Organic Colorants in Works of Art by Surface Enhanced Raman Scattering

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2012

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SERS detection of red organic dyes in Ag-agar gel

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JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2004; **35**: 800–807
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jrs.1199

JRS

Semi-quantitative analysis of alizarin and purpurin by surface-enhanced resonance Raman spectroscopy (SERRS) using silver colloids

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Table 1. Analytical parameters obtained for the semi-quantitative analysis of alizarin by SERRS

Excitation wavelength /nm	Band/ cm^{-1}	pH	Slope[a]	Intercept[a]	Correlation coefficient[a]	Concentration range[a] mol dm^{-3}[a]	χ^2	LOD ppm[b]	Orders of magnitude[a]
632.8	1071	1.73	0.9	8.6	0.935	10^{-7}–10^{-6}	0.035	14	1
	1265	1.73	1.1	10.2	0.988	10^{-7}–10^{-5}	0.014	4	2
514.5	1274	1.34	1.6	11.0	0.995	10^{-5}–10^{-4}	0.002	83	1
	1334	1.34	1.5	10.1	0.997	10^{-5}–10^{-4}	0.015	39	1

SERS measureme

Current literature and reviews
problems posed when working
through the use of:

1. **HF gels for non-extractive**
   pigment complexes[3];

   M. Leona, PNAS (2009)

2. **minimum quantities of sil**
   (non-exctractive and non-hy

   C.L. Brosseau, K.S. Rayn
   (2009) *Anal Chem* 81:74

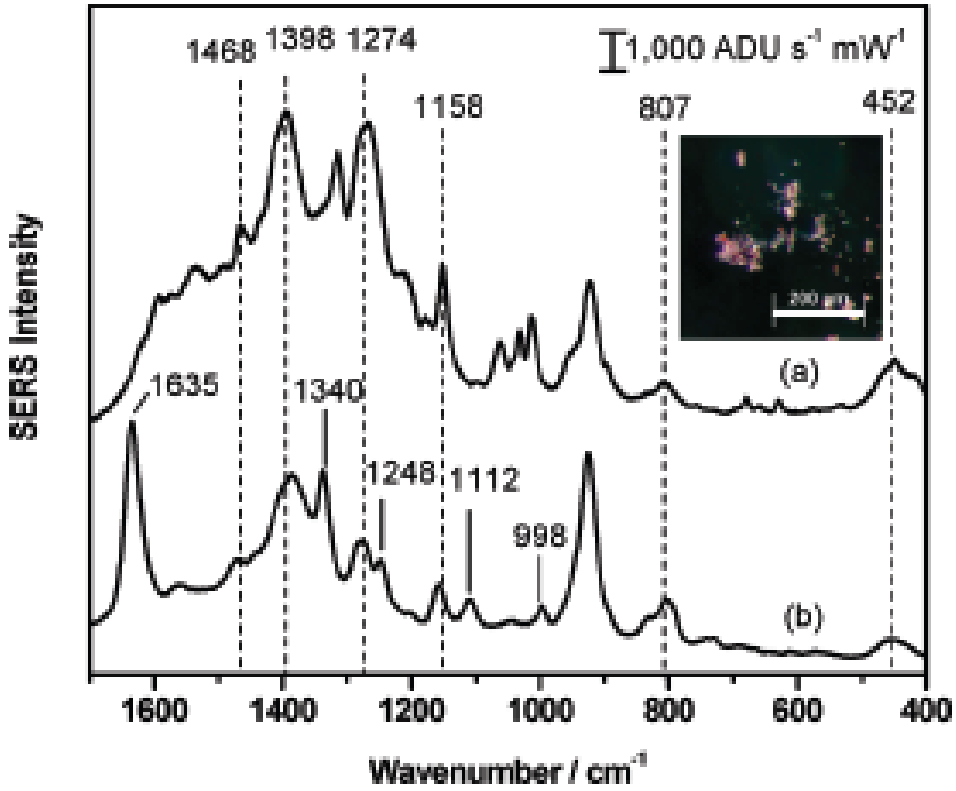

Figure 8. SER spectra of (a) madder root (*Rubia tinctorum L.*) and (b) sample no. 12 "mauve" from Mary Cassatt's "Sketch of Margaret Sloane, Looking Right". Dashed lines indicate peaks that are consistent with madder root dye. Solid lines indicate unidentified bands due to a second component in the sample. In the inset is a photomicrograph of sample no. 12.

Ag nanoparticles generated *in situ*

3. **in-situ photo-reduction studies with the production of silver nanoparticles directly on dyed textiles.**

   Z. Jurasekova, C. Domingo, J. V. Garcia-Ramos and S. Sanchez-Cortes,
   J. Raman Spectrosc. 2008; 39: 1309–1312.