SERS on “tapa”: detecting dyes and pigments on a Polynesian cloth through a multi-technical approach

Alessandro Ciccola[a], Claudia Colantonio[b], Francesca Ripanti[c],

Ilaria Serafini[a], Claudia Fasolato[d], Roberta Curini[a],

Claudia Pelosi[b], Paolo Postorino[c]

[a]Dipartimento di Chimica, [b]Dipartimento di Fisica, **Sapienza Università di Roma**

[c]Dipartimento di Economia, Ingegneria, Società e Impresa, **Università degli studi della Tuscia**

[d]Dipartimento di Fisica e Geologia, **Università degli Studi di Perugia**

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SAPIENZA UNIVERSITÀ DI ROMA

UNIVERSITÀ DEGLI STUDI DELLA TUSCIA

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The Issue

- Relevance of diagnostics in Cultural Heritage
  - Historical information
  - Restoration treatment
  - Conservation conditions
- Micro-invasivity and conservation principles
- Difficulty in identifying materials from other cultures (lack of reference materials)

The Case Study

- Object of diagnostics: *tapa* stored in the **Museum of the Congregation of the Sacred Hearts of Jesus and Mary (Picpus)** in Rome (French Polynesia and other places ethnographic objects)
- Function: decoration of homes, clothes for important rituals such as weddings or funerals, etc.
- Collection: original objects of the Island of Tahiti (Archipelago of the Society Islands); but possibility of other archipelagos provenance not excluded (**Samoa Islands**)
- Conservation: **not exhibited** but rather folded several times on itself and placed inside a drawer of the central cabinet in the Museum

The Case Study

The tapa (front and back) before the restoration, performed by Erminia Censorii (student of the LMR/02 master course of University of Tuscia) under the supervision of Federica Moretti (restorer and conservator) and Paola Pogliani (Professor of L-ART/04)

The Case Study

- The artifact (inventory Nr. Ta 262): large rectangular tapa measuring 135x150 cm
- Layers of light-colored barks beaten with wooden tools
- Use of vegetable starch binders (from tapioca or taro roots) or process of felting
- Dried support for the decoration
- Geometric decorative motifs with alternating hourglasses
- Preparatory drawing with yellow contours
- Red-brown color background
- Not uniform glossy finish, red-brown opaque portions
- Other black decorations are made in black
- Inscription that reads "TOVIA"

The Approach

- Multispectral imaging through **Hypercolorimetric Multispectral Imaging (HMI)** developed by Profilocolore Srl (Rome, Italy)
- **XRF** spectroscopy (atomic number > 15)
- **Fourier Transformed InfraRed** (FTIR) spectroscopy (possible vegetable binders)
- **Microstratigraphic analysis** on cross-sections (morphology and thickness of layers)
- **SERS** analysis (organic dyes)

The Techniques

Hypercolorimetric Multispectral Imaging

Journal of Cultural Heritage 40 (2019) 1–16

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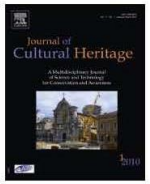


Original article

Development of integrated innovative techniques for paintings examination: The case studies of *The Resurrection of Christ* attributed to Andrea Mantegna and the *Crucifixion* of Viterbo attributed to Michelangelo's workshop

Stefano Laureti[a], Claudia Colantonio[*,b], Pietro Burrascano[a], Marcello Melis[c], Giuseppe Calabrò[b], Hamed Malekmohammadi[a], Stefano Sfarra[d], Marco Ricci[e], Claudia Pelosi[b]

[a] *Department of Engineering, Polo Scientifico Didattico di Terni, University of Perugia, Terni, Italy*
[b] *Department of Economics, Engineering, Society and Business Organization (DEIm), Tuscia University, Viterbo, Italy*
[c] *Profilocolore S.r.l., Rome, Italy*
[d] *Department of Industrial and Information Engineering and Economics, University of L'Aquila, L'Aquila, Italy*
[e] *Department of Informatics, Modeling, Electronics and Systems Engineering, University of Calabria, Rende (CS), Italy*

SERS on "tapa": detecting dyes and pigments on a Polynesian cloth through a multi-technical approach

The Techniques

Hypercolorimetric Multispectral Imaging

Acquisition of images

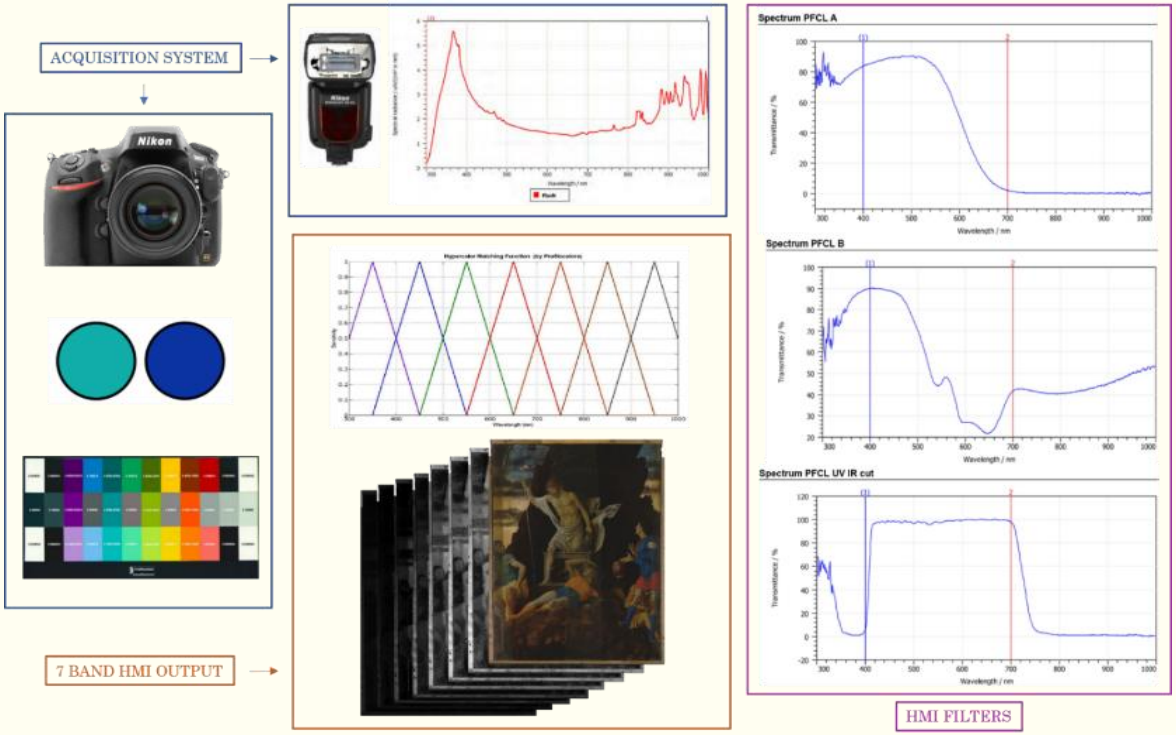
- Nikon D810FR 36 Megapixel camera, modified to obtain **full-range spectral reflectance** measurements
- Nikon SB910 xenon flashes after removing their front plastic lenses -> **UV emission**
- **UV induced fluorescence** (UVF) was then obtained by filtering the flashes light with a UV band pass filter with a cut at 380 nm, and UV-IR cut filter (400-700 nm) in front of the camera
- Various white patches and a sample with 36 patches of colour-checkers built using colour samples from the **NCS – Natural Colour System®© catalog** were placed next to the object

Calibration was performed through **SpectraPick**, a software developed by Profilocolore srl.

Image processing was then performed by **PickViewer®.**

The Techniques

Hypercolorimetric Multispectral Imaging



- Nikon digital camera modified in full range (300-1000nm)
- Flash units modified in FR
- 2 bandpass filters + 1 IR-CUT filter
- radiometric calibration target
- UV lamp or Flashes with UV filters for UVF photography

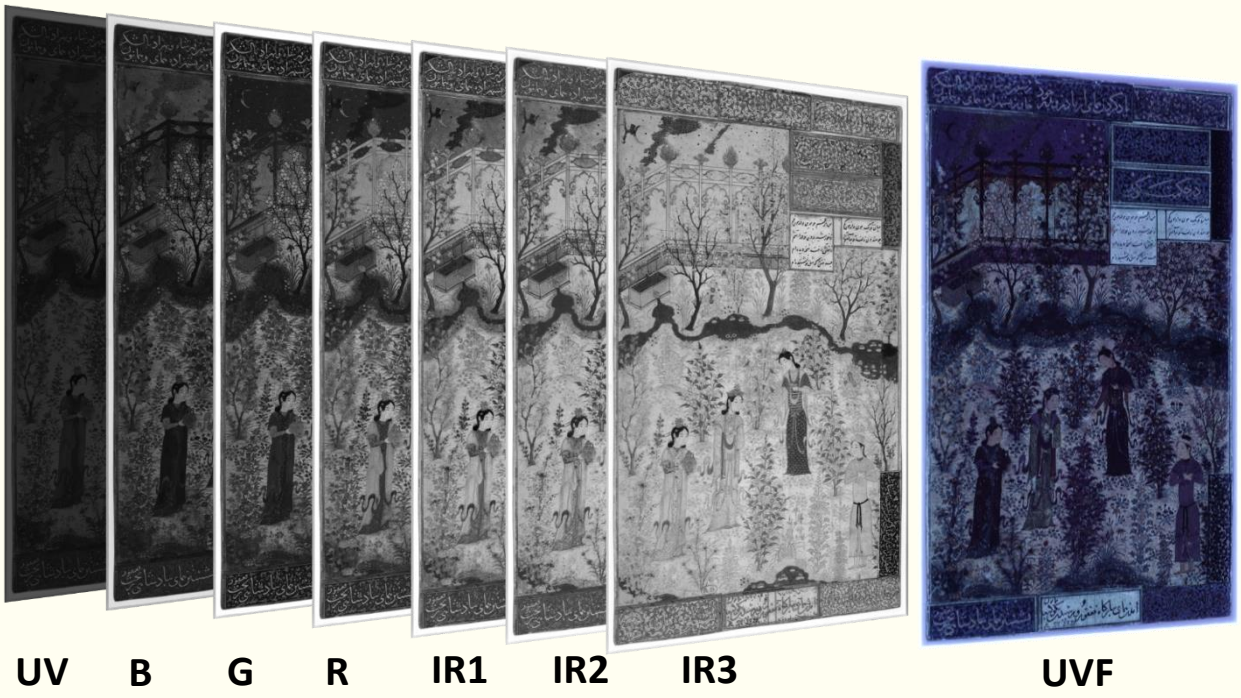
HMI software for Digital Image Processing AI-based calibration software, two shoots enable to obtain 7 spectral reflectance images

- **radiometric precision** > **95%**
- **1 CIELAB image**, with **36 megapixels resolution** and **ΔE <2**
- **statistical processing** tools (PCA, cluster analysis) + **spectral database** to support pigment identification

http://www.profilocolore.com/

The Techniques

Hypercolorimetric Multispectral Imaging



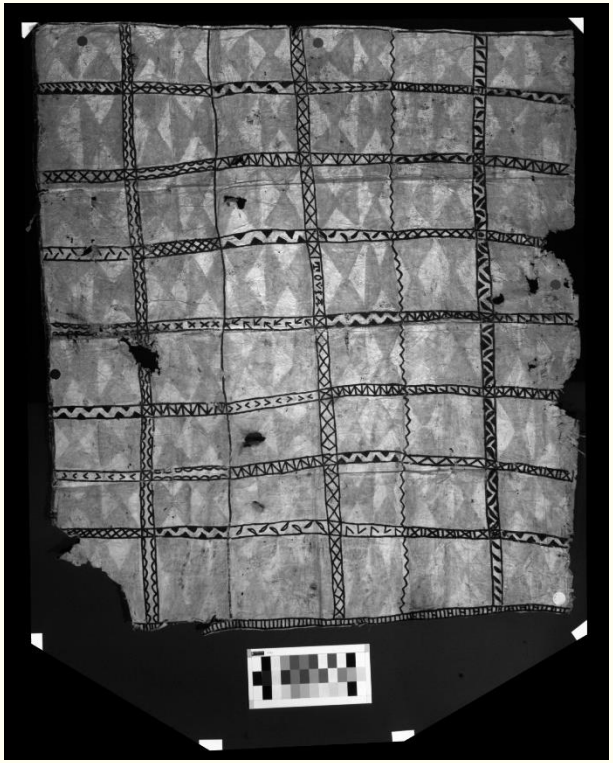
Every pixel contains:
L*a*b* colorimetric coordinates
7 radiometric values centered at
350, 450, 550, 650, 750, 850, 950 nm

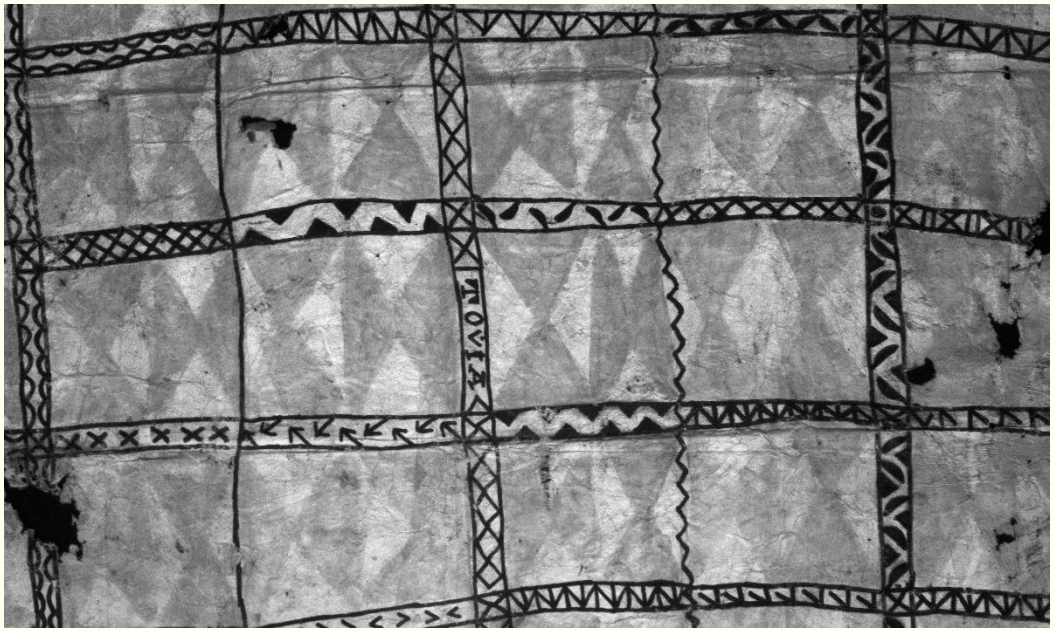
With a **third shoot**:
RGB colour image of the
UV-induced fluorescence

MAIN ADVANTAGES

- rapid, easy, affordable, non-invasive, reproducible
- in situ analysis (no power supply)
- system adaptable to different commercial cameras + specific professional cameras (Hasselblad, Phase One)
- integration of multi-source imaging data to MSI

The Results





- **First PC from PCA on the three IR channels:** enhancement of linear geometric black decoration and lacunae.
- **Painting technique** and **state of conservation**

The Dyes

UV false color image

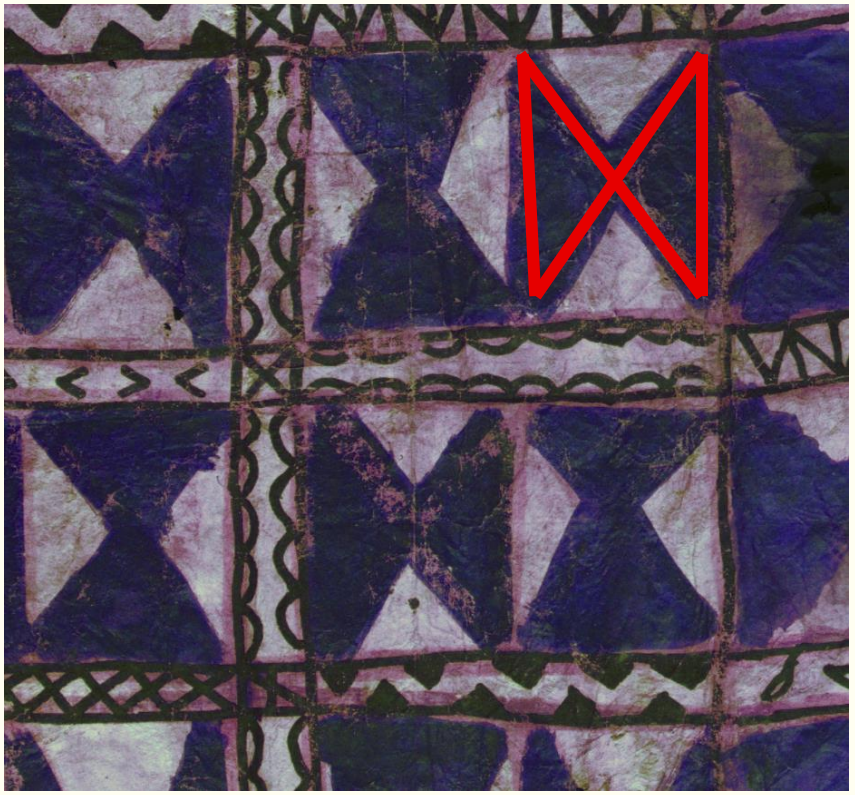
- Different spectral behaviour -> different painting materials

- Reconstruction of painted hourglass figures (two different red pigments, not remarkable in the VIS image)

The Results

UVF image, detail

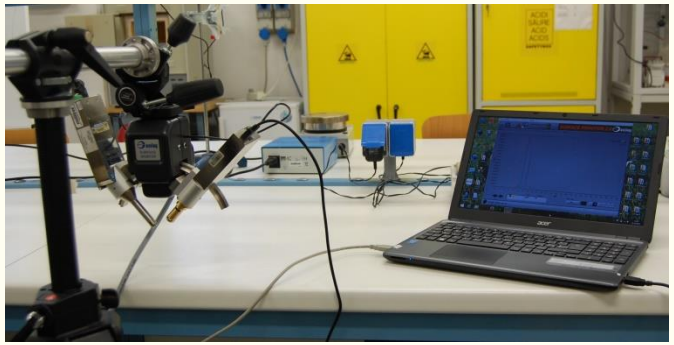
UV FC image, detail

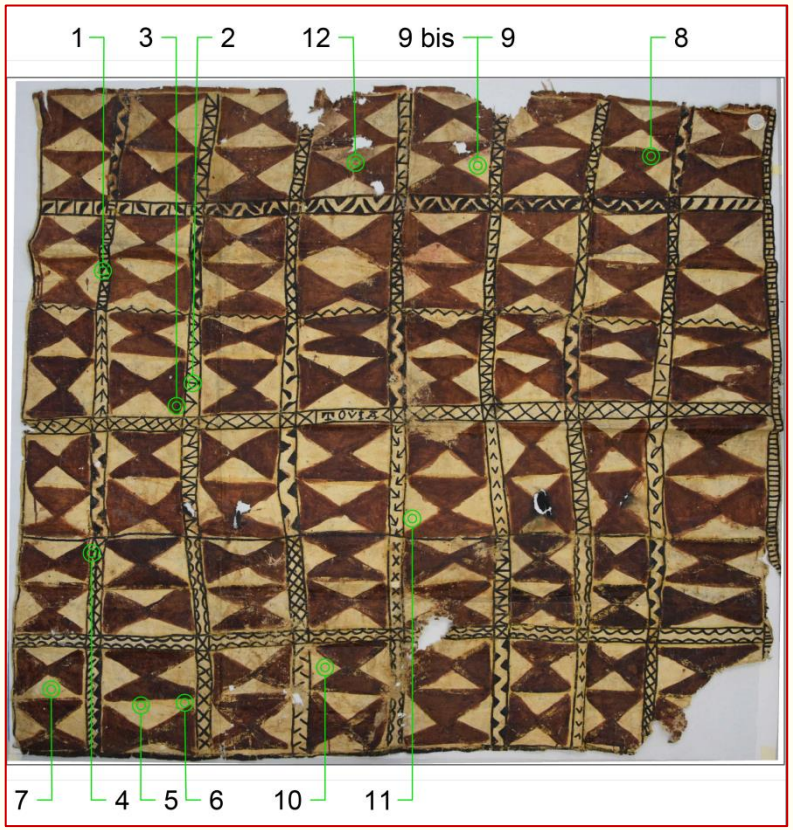


The Techniques

X-Ray Fluorescence

- Portable XRF spectrometer (Surface Monitor II, Assing, Rome, Italy)
- Silver anode as the excitation source
- Detector X-123 Si Pin (elements from 16S to 92U, energy resolution of 146 eV)
- Spot diameter for collimation: about 2.0 mm in
- Experimental conditions were employed: tube voltage 40 kV; tube anode current 76 µA, acquisition time 60 s
- 11 points





The Results

X-Ray Fluorescence

	K	Ca	Cl	Fe
Points	**Kα**	**Kα**	**Kα**	**Kα**
X 1 - black	258	254	59	156
X 2 - black	131	260	46	141
X 3 - brown	240	205	56	116
X 4 - black/brown/yellow	244	201	71	182
X 5 - yellow	134	128	50	100
X 6 - yellow	493	604	150	344
X 7 - fibers	397	491	165	335
X 8 - red	680	746	297	420
X 9/9bis - fibers	354	396	812	313
X 10 - fibers	99	123	200	73
X 11 - fibers	180	177	74	95

XRF results. Table with the counts per second (cps) of the detected chemical elements

Fe, Ca and K: inorganic pigments based on earths mixed with the organic dyes (Flowers et al. Herit. Sci., 7:2, 2019).

Cl: sea water residues (washing or shipping)

No information about organic dyes -> **SERS**

The Results

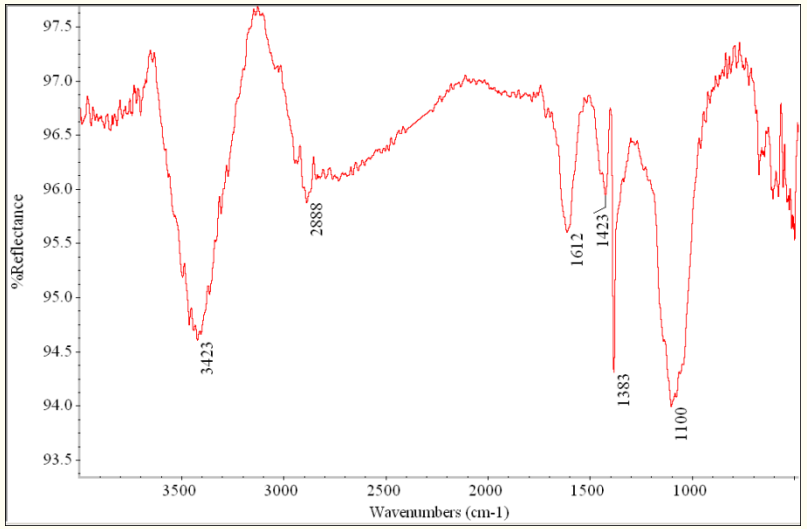
FTIR spectroscopy:

- Nicolet Avatar 360 instrument equipped with a DTGS detector
- Sample powders were grounded in agate mortar with potassium bromide (KBr) used also as background material.
- 128 scans for each sample
- Diffuse reflectance modality (DRIFT)

Micro-stratigraphy:

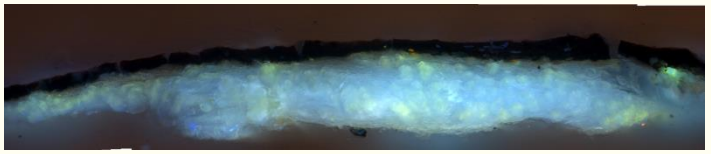
- Examination under a polarizing microscope Zeiss Axioskop equipped with a digital Zeiss AxioCAM and a mercury-arc lamp for UV fluorescence detection.

Use of starch for joining the fibers



FTIR spectrum of a sample of adhesive from the bark fibers

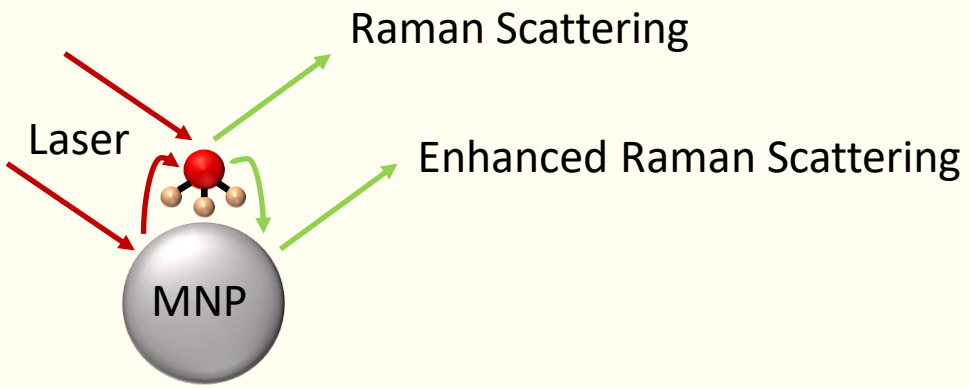
Cross-section 20x reflected light



Cross-section 20x UV fluorescence

The SERS effect

- SERS: Surface Enhanced Raman Scattering
  - Strong amplification of Raman signal from molecules in close proximity to a nanostructured metal surface / nanoparticle
  - Enhancement factors: $10^6 – 10^9$
  - Combination of Electromagnetic and Chemical mechanisms



The SERS effect

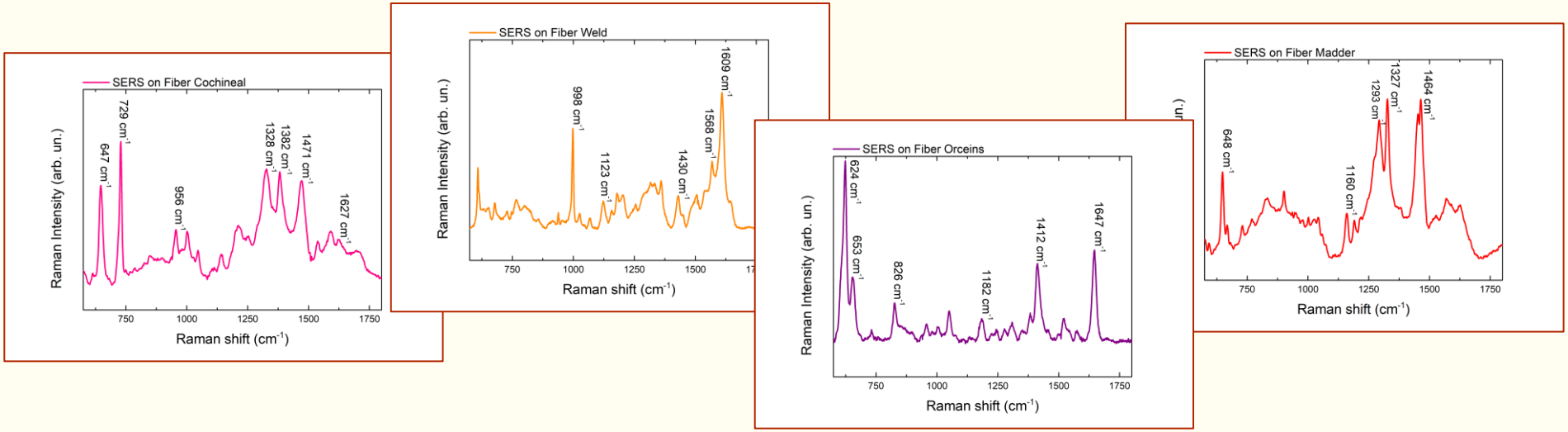
- SERS for Cultural Heritage:
  - Guineau e Guichard, 1987
  - Remarkable application after 2004

PROs	CONs
• Organic materials • Micro-invasivity • Micro-samples • No pre-treatment • Comparability	• Low reproducibility • Matrix variations • Literature

PERSPECTIVES
• New sampling methods • New analytical protocols • Maximinzing reproducibility

The Database

- ADAMO: **Development of a SERS Database for organic dyes**

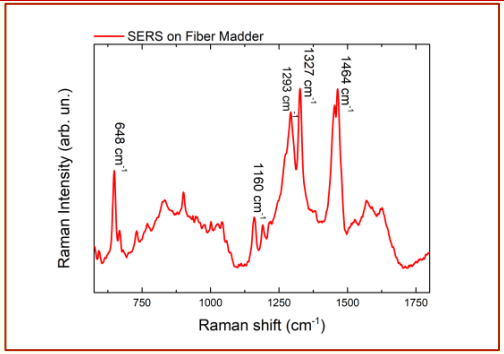


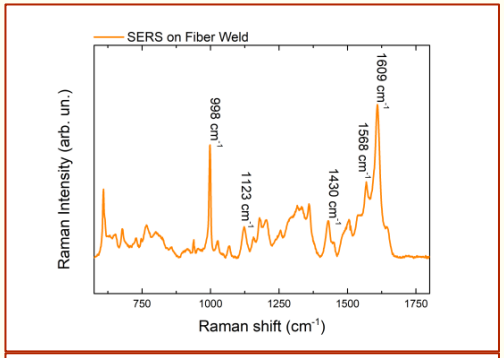
- SERS approach:
  - SERS *on fiber*
  - SERS of extracted dyes

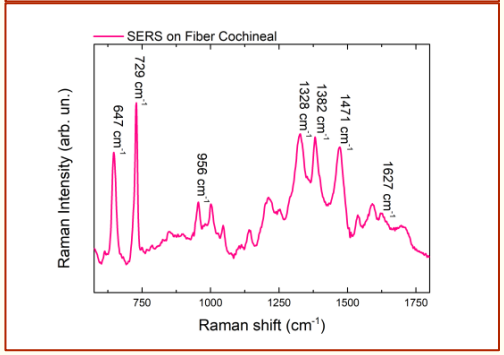
The Database

- SERS approach:

- SERS on fiber
  - Leopold and Lendl colloid
  - Aggregating agent: $MgSO_4$
  - Raman measurement close to the fiber







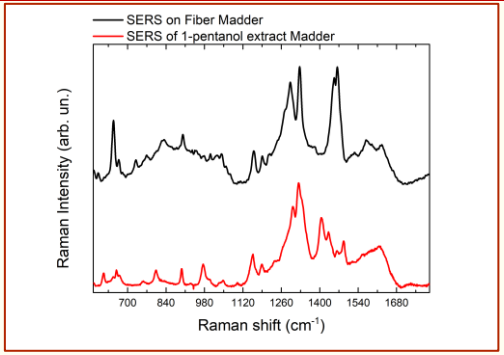
N. Leopold et al., Journal of Phyiscal Chemistry B, 107 (2003), 5723-5727

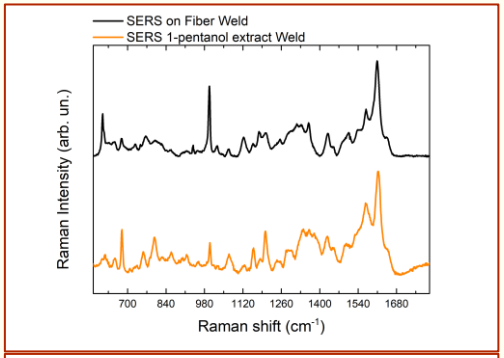
The Database

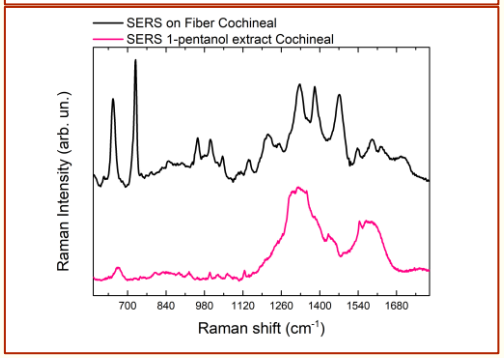
- SERS approach:

- SERS of extracted dyes
  - Leopold and Lendl colloid
  - Aggregating agent: $MgSO_4$
  - Extraction: ammonia «mild» protocol
    - Extracting solution: NH_3 + EDTA + NaCl
    - Neutralization of extracting solution
    - DLMME protocol
    - Organic phase: isopropanol/pentanol 1 : 2

  - Raman measurement at several extraction steps





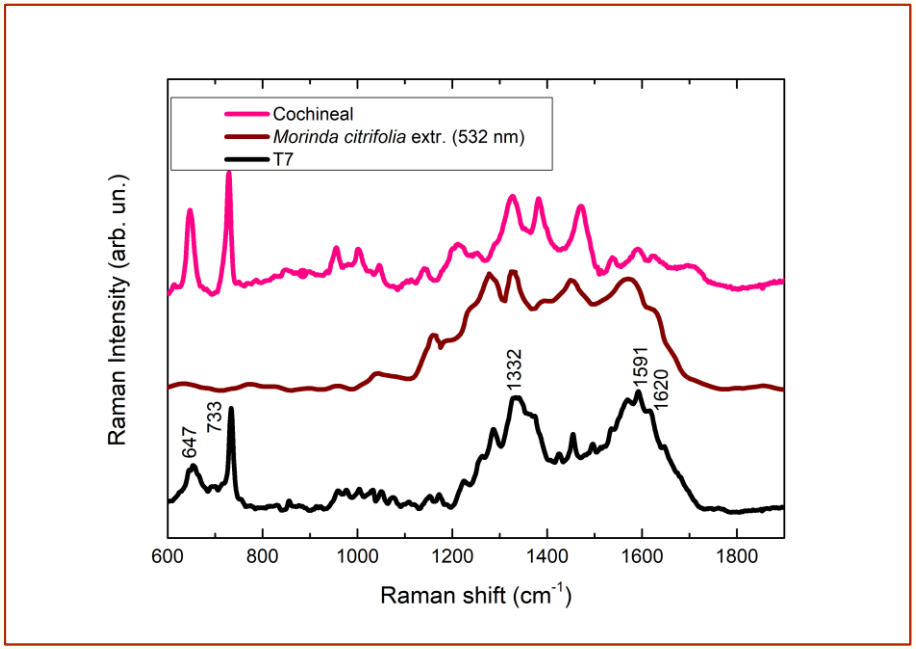


I. Serafini et al., Microchemical Journal, 134 (2017), 237–245

The Application

- SERS on *tapa* samples:
- SERS on fiber
- Samples from the cloth (T5, T7, T8)

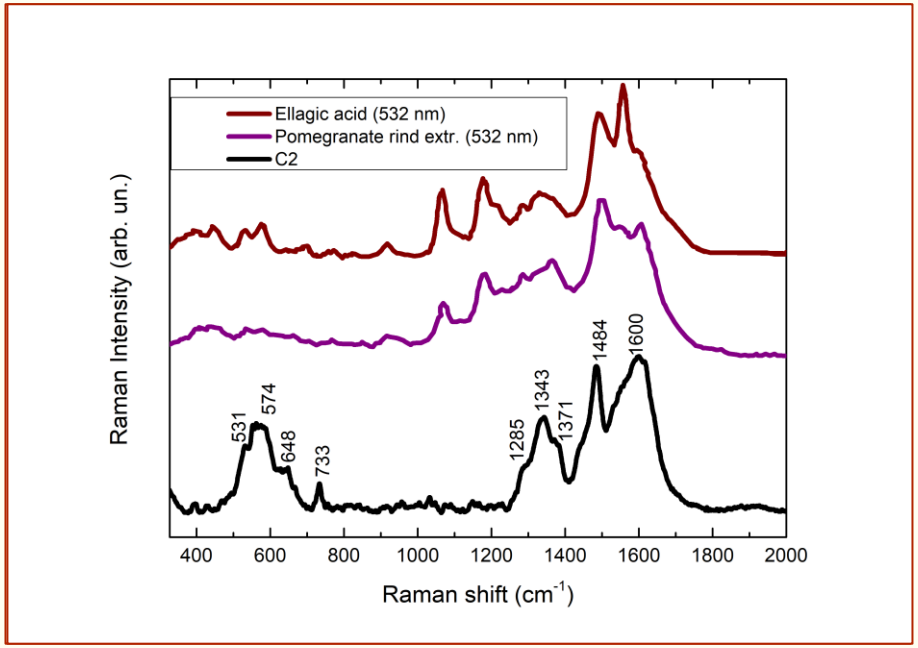
  - No main colloid background
  - Anthraquinone signals
  - Mixtures of dyes



E. De Luca et al., Vibrational Spectroscopy, 95 (2018), 62-67

The Perspective

- Analysis of extracted dyes
- Chromatographic analysis (HPLC-MS)
- Database extension
- Application to other matrices:
  - High reproducibility
  - No database matching
  - Presence of ellagiotannins



S. Bruni et al., Journal of Raman Spectroscopy, 42 (2011), 465-473

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