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Laser remote and in situ spectroscopic diagnostics to CH surfaces results of case studies in recent regional projects: COBRA and ADAMO in Latium

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The needs for *in situ* and remote surface diagnostics on CH



The preservation of CH surfaces requires suitable **material diagnostics**. CH surfaces have been produced on very different substrates, some of them very fragile, and often at a monumental scale (large size) with limitation of access (remote view). CH surfaces can be located in hostile environments (underwater) or must be examined in dangerous situations (after earthquakes, wars) which ask for complex interventions.

<u>The laser break-through</u>: Laser scanners for non invasive or microdestructive interrogation of the surface

- Optical measurements: collection of sets of monochromatic images by multiple visible laser scanners to reconstruct 3D model with native color information. Laser reflectance (backscattered and diffused signals). Data relevant to surface appearance and morphology.
- Spectroscopic measurements: space resolved collection of spectra containing information on surface layers. Laser spectroscopies (LIF, Raman, LIBS, with possibilities of time resolved detection). Data relevant to surface elemental and aggregate composition. Possibilities of subsurface analysis and stratigraphy.
- Joint application of different remote and in-situ diagnostics (thermography, XRF, PIXE), with point detection or imaging capabilities.



Laser surface interactions: Remote surface characterization

The monochromatic laser beam interaction with a surface may cause different phenomena, with a probability depending on the incoming power for surface unit (irradiance), which determines the final energy balance.

- Together with partial radiation absorption, at growing irradiance, we may have:
 - Back Scattering (BS) at the same wavelength as the exciting beam;
 - Laser induced Fluorescence (LIF) at wavelengths larger than the incoming one, with shifts related to energy differences between electronic states, eventually coupled through internal relaxations processes in species at the surface;
 - Stokes Raman Scattering (SRS) at wavelengths larger than the incoming one, with shift related to vibrational modes in species at the surface;
 - Laser Induced Breakdown (LIBS) with atomic emission from the plasma generated at the surface, during an ablation/ionization process occurring above the threshold (~1 GW/cm²).





Multilayered

High resolution laser scanners for remote imaging and analysis

Advantages

- Nondestructive and non invasive / micro-destructive (LIBS)
- Self illuminating
- Not affected by external light sources (at low or moderate irradiance)
- Additional geometrical requirements are taken into account
- Automatic software handling/processing of very large data sets
- Reference data for digital archiving (after calibration)

Novelty

- Integrated use of more than one single prototype, in hardware or software
- Integration with different kinds of in situ sensors
- Surface diagnostics coupled to possibility of virtual fruition
- Suitable to development of augmented reality algorithms for restorers



High resolution laser scanner for 3D modeling with color images





Color calibration of remote imaging prototypes



Angular corrections are included to take into account different efficiency of BS.

The possibility to inspect both colour and structure information permits to study pigments and structure modifications, to give an early warning for possible efflorescence outcrops or micro-cracking outcomes.



Pietro da Cortona's vault at Barberini Palace in Rome An application of RGB-ITR high resolution laser scanner



The average operating distance of 18 meters allowed to obtain a spatial point-to-point resolution of about 1mm, on the entire surface (14 x 24 m

in total **530** m²⁾.

A small portion of the vault (60x45 cm) in which a post-processing was carried out to enhance the contours of the figure of the skeleton-soldier



High resolution laser scanner for subsurface monochromatic imaging



A new prototype operating in the near infrared (IR-ITR) at 1.5 μ m has been realized for subsurface-imaging and modeling

	5m Distance	10m Distance
Scanned size	418x452mm	489x558mm
Angular resolution	0.002x0.002 gradi	0.002x0.002 gradi
Pixel resolution	2400x2600	1400x1600
Space resolution	0.174x0.174mm	0.349x0.349mm
Acquisition time	1h45min	39min
Spot size at the surface	1.5-2mm	3-4mm

Application in retrieving former paintings or background drawings





Line scanner for hyperspectral fluorescence imaging

Collection of both reflectance and fluorescence spectra (LIF and TR-LIF)





LIF (Laser Induced Fluorescence) scanning systems were designed and built in order to obtain analytical information on 2D images of the outermost layers on CH surfaces. A fast, non invasive, remote (up to 25 m), sensitive and selective technique was developed. After automatic preprocessing data are released as false color reflectance and fluorescence images suitable to the identification of original and added materials.



The laser beam is shaped as a light blade, thus there is no need to vary in-plane θ angle, the scan system controls only the bending φ . The entire line profile is imaged on the monochromator slit, which spreads the entire spectrum collected at each point on the squared ICCD at 90°. **Time Resolved** data are obtained collecting **LIF spectra** at different delays, by gating the camera.

Large Area LIF imaging

Apparatus

- KrF laser at 248 nm
- repetition rate of 500 Hz
- pulse duration of 10 ns
- Energy max 20 mJ
- ICCD + filter wheel (8 filters)











Labview program

- To define area in the scene
- To set experimental parameters
- To control different components
- To acquire data
- Preliminary data processing

System advantages

- Reduced acquisition time (Scan time 60s/band for 10 m x 10 m area)
- Reduced data processing (selected spectral bands)
- Compact
- Remote (up to 30m)



LIF compact fluorescence point scanner CALIFFO





ExcitationLaser (@405nm)



Micro spectrometer +collecting optics

CALIFFO (Compact Advanced Laser Induced Fluorescence Friendly Operating system) is a prototype developed at ENEA for laser induced fluorescence measurements, with violet excitation and visible detection. It is a scanning system of reduced size, weight and power consumption developed for *in situ* applications at short distances (2 - 5 m).

Its main application field is the detection and characterization of **bio-attack** on CH surfaces. The post-processing of acquired data allows to create maps able to highlight the presence of degradation forms.

CALIFFO can be completely controlled in remote way by tablet or smartphone.

Integrate Laser Scanner for remote surface analysis and stratigraphy

ILS: An Integrate instrument for remote LIBS (exc. @1064 nm), Raman (exc. @ 355 nm) and LIF (exc. @ 355 nm).

Developed for security applications, successfully tested on CH surfaces: Ceramics, coins.



Characteristics in LIBS measurements

- Measurement distance: 10.5 m (range 8- 30 m)
- Two color cameras: to collect large scene and details
- Choice of the scanning area
- Wi-Fi remote control of the instrument
- Single shot LIBS spectrum 200-850 nm
- Samples depth profiling: 20 laser shots in 6 points per sample or coating type.



Ceramic fragments remotely examined in a lab. demonstration





Post processing of spectra and spectroscopic data Needs to handle large amount of data in multispectral images

	acronym	Processing technique				
	PCA	Principal Component Analysis Linear transformation of the input variables: maximize the variance explained by each output variable.				
	SAM	Spectral Angle Mapper Spectral projection operator that geometers the "distance" between the spectra.				
	MCR	Multi Curve Resolution Analysis Decomposition of a large number of spectra into simple components using appropriate constraints which allows to obtain physical meaning to decomposition (non-negativity of spectra and concentrations, mono mode,)				
	PARAFAC	Parallel Factor Analysis Allows to identify all the components with direct physical meaning.				
	$\alpha = \cos^{-1}(\hat{u}, \hat{w}) =$	$\frac{\sum_{i=1}^{N} u_{i} w_{i}}{\sqrt{\sum_{i=1}^{N} u_{i}^{2} \sum_{j=1}^{N} w_{i}^{2}}} \qquad x_{ik} = \overline{x}_{k} + \sum_{\ell=1}^{N} p_{\ell k} t_{i\ell} + e_{ik} \qquad e_{ij} = 1 - \frac{\sqrt{\int (s_{i}(x) - s_{j}(x))^{2} dx}}{\sqrt{\frac{1}{N} \int \sum_{j}^{N} s_{j}^{2}(x) dx}} \qquad $				
	ENEL	13				

COBRA Project – Spectroscopic laser scanners applications

Main objective

To develop and disseminate methods, technologies and advanced tools for the conservation of cultural heritage, based on the application of radiation and Enabling Technologies.

Selected case studies in field campaigns carried out upon conservators' request:

- 1. The blue demon tomb in Tarquinia Etruscan necropolis
- 2. The greek chapel in Priscilla catacombs Rome
- 3. Roman fresco's in S. Alessandro catacomb near Rome.
- 4. Marble statues in Palazzo Altemps Museum, Rome
- 5. The Orants marble sarcophagus in S. Sebastian Catacomb, Rome
- 6. Egyptian sarcophagi from Milan, under restoration in Rome



Sviluppo e diffusione di metodi, tecnologie e strumenti avanzati per la COnservazione dei Beni culturali, basati sull'applicazione di Radiazioni e di tecnologie Abilitanti

> A Latium regional project entirely dedicated to <u>technology transfer</u> and <u>innovation</u> in the CH conservation (Jul. 21,2015 – Dec. 20, 2017) ENEA

Needs of integrate application of spectroscopic techniques



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1. The Blue demon Etruscan tomb in Tarquinia RGB-ITR reflectance and color analysis

Questions: original pigments – 1. *were the demons really blue?* modern consolidants – 2. *are they still there?* how the murales was realized – 3. *is it a true "fresco"?*



Normalized reflectivity distribution from the RGB calibrated channels



Colorimetric answer #1: now they currently look greysh – what was the original color?





Raman in situ analyses of pigments

Red pigment identification: hematite from red ochre





«Blue» pigment identification: impossible due to the intense fluorescence upon excitation @785 nm (*)





Commercial Raman probe operating @ 785 nm – GaAs diode laser



Blue pigment fluorescence

(*) see also P. Westlake et al. Anal. Bioanal. Chem. (2012) 402: 1413-1432

White pigment identification: calcite, used as preparatory layer.

Absence of carbonatation in mineral pigments.

Answer #3 it is not a true fresco.



Overlap of LiF image on the 3D color model





LIF data analysis line scanner with excitation @266 nm





Statistic analysis: PCA and MCR

Blind PCA shows that most variance is accounted for in the first 3 components, associated respectively to the intense UV emission, the broad visible band and a few weak features. No spectral assignment is possible.





In situ X ray Fluorescence point analyses Cross confirmations



- «Blue pigment» analysis: the presence of Ca/Cu/Si supports the assignment as cuprorivaite (CaCuSi₄O₁₀ or CaO·CuO·4SiO₂), known as Egyptian Blue.
- Red and brown pigments: the presence of iron confirmed the use of ochres, i.e. iron oxides (red - hematite, yellow - goethite).
- Black pigments: no characteristic elemental emission, C-based pigments of organic origin.
- Consolidants: no information from XRF, as expected for paraloids.

Answer #1 The demons were meant to look blue

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Università di Roma

Frescoes in Priscilla's Catacombs in Rome Laser scanners for biodegradation analysis



P1 - subarea where the
biomass appears more
denseP3 - subarea where the
bio-deterioration is not
evident naked-eyeP2 - subarea where the
biomass is less denseP4 - far away from the
biomass area

<u>Question</u>: Is it possible an early detection of bio-attack? <u>Answer</u>: YES by remote LIF

Contribution to bio-attack monitoring by means of biofilm area's circumscription by the post processing analysis of the RGB-ITR 3D model



P1 - intense emission band at 340 nm, identifying the biological material present in that area

P2 - the emission in intensity band at 340 decreases and a large band at 500 nm appears P3 - Band at 340 nm still present, low intensity, and band at 500 nm increased in intensity P4 - Band at 500 nm is the only band present

Persistence of the fluorescence band at 340 nm in P3 possibility of early detection by LIF of areas attacked by microorganisms not visible in this stage



New successive colonization of other areas is visible 4 and 8 months after the first observation, due to spread of microorganisms

2. Fresco's in S. Alessandro Catacomb: G6 and G15 Reflectance and fluorescence imaging

Needs for spectroscopic diagnostics during the fresco's restoration





False color fluorescence image

Is it possible by spectroscopic imaging to read the lost part of the inscription? **YES by LIF**

picture

LIF imaging on G6 – the lost inscription

Questions: Possibility to clean 1. Is the painted layer still present? Efficiency of cleaning 2. What consolidant was used? Original materials and dating 3. Which pigments were used?





False color LIF image @560, 420, 330nm



Result: a peculiar spectral signature @340 nm from a consolidant on the missing letters and other decorations.

Answer #1. **YES** The efflorescence is covering the missing letters where the consolidant was used.

Attempt of consolidant assignment by LIF



Discrimination among consolidants with significant emission near 340 nm has been attempted by SAM, projecting spectra collected at S. Alessandro onto each reference spectrum.

0,34 EVA Vinyls 0,42 **PVA PVA+PVAC** 0,43 SiEt **ESTEL 1000** 0.29

Best matching minimizes θ angle.

Nevertheless LIF was able to detect the presence of a consolidant and determine its surface distribution, alone it could not clearly identify the consolidant.

The latter information is needed for its efficient removal and successive surface treatments.

Consolidant assignment after integration of all spectroscopic data

Summary of results from different spectroscopic investigations on consolidants with emission near 340 nm (upon excitation @266 nm)

	S. Alessandro	SiEt	Vinyls	Acrilics
LIF	340 nm band: Intense	340 nm band: Intense	340nm band: Intense (in most cases)	340nm band: Present in some cases (AC35)
Time Resolved LIF	340nm band: Prompt	340nm band: Prompt	340nm band: Delayed	340nm band AC35 D elayed
RAMAN	Peak at 1291cm ⁻¹ (No vinyl band at 630cm ⁻¹)	Peak at 1295 cm ⁻¹	Peak at 630 cm ⁻¹ (No peak at 1296 cm ⁻¹)	Peak at 1296 cm ⁻¹ Primal AC35 Plextol D492

Answer #2. Combined analysis confirms the identification of SiEt: Estel 1000 - A nasty consolidant responsible for localized saline efflorescence when used in humid environment, its incomplete removal was verified by LIF one year later.



Time Resolved LIF analyses Red pigments assignment confirmed by in situ Raman and XRF



- They are characterized by the same decay time at about 8-12 ns.
- Raman analysis confirmed red ochre (G6) and a mixture of red ocher and minium (G15).

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3. The same pigments were utilized, fresco's are contemporary



Ares



Palazzo Altemps Ludovisi collection of classic marbles

Starting from the *FORLAB* fluorescence images, the application of the data processing developed

permitted us to discriminate different stone materials.





LIF spectra collected in the areas pointed by red arrow (LIF scanning prototype was used)

The Roman statue was restored by Bernini - <u>Question</u>: Is it possible to trace this old intervention?



Evidence of reintegration of missing material

False colors LIF image

wavelength (nm) 27 Laser remote and in situ spectroscopic diagnostics to CH surfaces, Seville, March 26-30, 2019

JF Intensity (a.u.

2000

300

400

500

White marble type identification on LIF images

Development of an automatic algorithm to discriminate Greek marble (penthelic) from Italian marble (Carrara)





The algorithm is based on fluorescence intensity ratio at selected couples of detection channel



Greek marble in the statue (yellow)

<u>Answer</u>: Automatic recognition of «original» Greek marble from Italian marble added during the «renaissance restoration» is possible



LIF imaging on white marble statues

Additional Information on materials supporting art historians and conservators



Raman bands revealed at:				
1084 cm ⁻¹	calcite CaCO ₃			
1007 cm ⁻¹	gypsum CaSO ₄			

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- Different marbles used for integration in historic restorations (XVI century)
 Identification of white pigments on junctions.
- Detection and distribution of degradation products (in combination with Raman)
- Search for waxes and other historical coatings, detected also on other statues of the collection.



Sarcophagus of "Orants"- San Sebastian Catacombs Marble identification



400

300

The sarcophagus is a marble sculpture made between the 3rd and 4th centuries AD and preserved in the Sarcophagi Museum of the catacomb of San Sebastian in Roma.

Question:

> geographical origin of the three pieces (left, central, right) constituting the sarcophagus

Processed 900 fluorescence images 800 with application of the 700 recognition algorithm. 600 Small yellow areas 500

correspond to encrustations.

Answer:

> It is all Italian marble

Additionally the presence of natural waxes was revealed in images collected at 415 nm

Characterization of painted wood artifacts Egyptian Sarcophagi under restoration in Rome



Peftjauyauyaset (XXVI din. -VII-VI century BC) sarcophagus from Archaeological Museum of Milan

The Case containing the anthropoid sarcophagus where the mummy was accommodated and the sarcophagus itself were investigated.

Polychrome decorations are present inside the sarcophagus and on the external surfaces of the case.

<u>Question</u>: is it possible to map former interventions at the wood surfaces?







LIF imaging on sarcophagus



Slice of the long side LIF image obtained by 340/380nm spectral ratio

Casket

The areas highlighted in the image correspond to areas which were restored by means of acrylic materials.

Winged goddess Nefti on the short side of the casket and LIF image filtered at 340 nm





Intense fluorescence emissions in correspondence of fissures and cracks suggest presence of the acrylic product used as consolidation material for the ancient wood.

<u>Answers</u>: > LIF maps of formerly used acrylic consolidant are obtained > Its use is demonstrated both on painted surface and on cracks ₃₂

Remote LIBS on ceramic samples

Fragments from a «butto» near Tarquinia (XIII-XIX century)





Why remote LIBS on ceramics? For their extensive use as coating on monumental walls in Mediterranean area.

Glaze	White	Blue	Yellow	Light brown
Cu, Ag, Al, Ca, Mg, Mn, Fe, Sr, Na, Li, K	Cu, Ag, Pb, Sn	Co, Pb, Si, Al, Mg, Fe	Cu, Ag, Mg, Mn, Li, K, Rb	Cu, Ag

Picture of a fragment taken by the on-line camera; LIBS craters marked by arrows

<u>Results</u>: Blue pigment is a cobalt based smalt, probably saffre.

The copper/silver rich glaze in the first layer and in the yellow luster suggest possible dating to this fragment in the XVI century*, according to Piccolpasso receipt for pottery. *F. Colao et al. Spectrochim.

Acta (2002): B57 1219-1234

Remote LIBS stratigraphy on a white area



and XRF data for different CH samples*

ADAMO Technologies of Analysis,

Diagnostics and Monitoring for the preservation and restoration of

Cultural Heritage

A Research project in the Center of Excellence of the District of Technologies for Culture of Lazio Region

Participants: ENEA, INFN, CNR, Uni. Rome Sapienza, Uni. Rome Tor Vergata, Uni. Roma Tre, Uni. Tuscia (Viterbo)

Project objectives

- 1. Technology transfer on relevant themes
- 2. Services to enterprises based on facilities offered by DTC partners
- 3. Demonstrations in selected cases studies
- 4. Development of prototypes and test of innovative products



ADAMO

TECNOLOGIE DI ANALISI, DIAGNOSTICA E MONITORAGGIO PER LA CONSERVAZIONE E IL RESTAURO DI BENI CULTURALI

Oct. 2, 2018 – Jan 1, 2020 Progettoadamo.enea.it

Integrate applications of remote, in-situ and laboratory instruments for spectroscopic diagnostics



Contest analysis and choice of demonstration sites







Bishop's Palace In Frascati: Hall of Landscapes RGB-ITR 3D digitalization

 Image: select select

The Hall of Landscapes appears as a colorful room fully decorated with tempera painted canvas covering all the walls, where painted areas and wood frames create the illusion of an architectonic structure.



Ceiling detail where the restored areas (repaints) after discoloration) are detected

Questions:

Location of residual damage from former water infiltration

Location of current damages on canvas and other painted surfaces 36

Bishop's Palace In Frascati: Hall of Landscapes RGB-ITR 3D digitalization and LIF imaging



LIF investigation of the wooden cover at fireplace in the same room.

A carefully repainted crack is evident in the 380/450 nm LIF image.



Answers:



 Residual damages are detected by both techniques as discoloration, morphology changes, repainted cracks

Bishop's Palace In Frascati: "Stufette" room **TR-LIF spectroscopy and imaging**





Two decorated small bathrooms belonging to the pope niece Lucretia Della Rovere, recently restored.

Question: Can we detect early damage?

Reference reflectance image collected by the LIF scanning system

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Marble busts gallery of Chigi Palace at Ariccia LIF imaging by FORLAB prototype

An important Baroque collection



Question: > Was the marble surface treated for aesthetic purposes?







LIF spectral image reconstruced in false colors (400-500-600nm)





The emission bands are centerd at different wavelength on face and hair:

- No presence of acryl (original surfaces)
- Presence of wax on the hair

Processed FORLAB images

ENER <u>Answer</u>: YES added material is present on the hair (assignment in progress)

Picture-gallery of Chigi Palace at Ariccia High resolution IR-ITR laser scanner



Chigi Palace in Ariccia represents a unique example of baroque home remained intact over the centuries. The palace was transformed into a magnificent baroque residence by Gian Lorenzo Bernini in the XVIIth century.

The picture-gallery contains paints from Mario de Fiori and other Roman baroque artists (The Four Seasons), sometimes working together on the same canvas.

Question:

> Is it possible to remotely reveal changes of mind of the last author?



3D IR-ITR image

Revealing artist's changes of mind «Ripensamenti» Remote high resolution IR-ITR sub-surface inspections



Hidden details not seen in the visible spectrum

from IR-ITR image







IR-ITR features

Maximum working range: 15-20m Maximum spatial resolution at 10m: 1mm No shadows No ambient illumination interference

Answer:

> Yes, with high sensitivity and high resolution, without any image post-processing

Conclusions and Future Work plan for laser diagnostics on CH surfaces

 Spectroscopic techniques (LIF and TR-LIF, Raman, XRF) allowed to obtain remotely and in situ unique information on different CH surfaces. • Image processing algorithms suitably developed for semi-automatic applications were applied to obtain space distribution of different surface features. • 3D high resolution color models are useful to precisely locate spectroscopic Conclusions data collected on different points and 2D fluorescence images. • The integration of different remote optical and spectroscopic techniques is often the only way to solve complex real challenges from case studies in CH samples in order to effectively answer conservators questions. • RGB-ITR wavelength extension: the additional near IR 1.5 μm channel for subsurface investigation will be integrated in short; a further UV source (@355 nm) will be added for UV imaging; implementation of up to 8 wavelengths is planned in the IR - to UV range. Addition of Raman imaging in the ILS prototype, already integrating Future LIF/LIBS and Raman; its operation up to 30 m on real CH surfaces. Work plan • Addition of a short pulse (ps) laser source on LIF imaging prototype to fast acquisition of time resolved images has been proposed (E-RIHS.it Lazio). Laser remote and in situ spectroscopic diagnostics to CH surfaces, Seville, March 26-30, 2019

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