

Supplementary materials: Comparative bibliography analysis tables (2020–2022)

Detecting recent research trends and applications of some molecular archaeometric analysis techniques: a review

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Table S1: RAMAN SPECTROSCOPY

YEAR	AUTHORS	AIMS	MATERIALS and RESEARCH PROBLEMS	METHODS AND INSTRUMENT S	RESULTS and/or CRITICISMS	APPLICATION FIELDS and NEW PERSPECTIVES
2020	Perini et al.	<ul style="list-style-type: none"> - Detect the traces of the microorganism and microbial pigments in ancient documents - Biodeterioration of parchment 	semi-solid collagen matrix - verify the DNA for Bacteria, mainly Actinobacteria (e.g., <i>Saccharopolyspora spp.</i>) and fungi (<i>Penicillium</i> and <i>Aspergillus</i> among others)	Review and synthesis of different methods, such as: RAMAN spectroscopy, performed both directly and on chemically extracted pigments	Detection of bacterioruberin and other pigments, blaming the halophilic archaea as the unequivocal culprit of the purple spot deterioration	preservation of many ancient documents
2020	Couthino L. et al.	Detect the applicability of protective coatings on glazed tiles to prevent biological colonization, for inactivate and mitigate microorganisms	<ul style="list-style-type: none"> - Glazed wall tiles, that are ceramic plates covered with a vitreous glaze applied as revetment on buildings. - Research coatings that applied on outdoor glazed tile are meant to improve deterioration processes. The anti-biofouling properties of the TiO₂ treatment were evaluated by inoculating the fungus <i>Cladosporium</i> sp. on the glazed tiles. 	micro Raman spectroscopy supported by SEM, XRD analysis	-The coating did not prevent fungal growth, although a slight reduction in the proliferation was observed for most of the samples. The bioreceptivity experiment also showed that the cracks on the glaze's surface influenced fungal growth, probably due to the different amounts of nutrients that remained on the surface	<ul style="list-style-type: none"> - Prevent Biological Colonization of glazed tiles - Research must focus on coatings with a less aggressive pH, a lower thermal treatment and presenting better aesthetical properties. Future work also needs to address the reversibility and durability of the coatings.
2020	Retko K. et al	Material characterization of a painted beehive panel	The panel depicting the theme of "A fight over a pair of men's trousers" from the collection of the Slovene Ethnographic Museum	Te spectra (785 nm and 514 nm laser excitation lines) Horiba Jobin Yvon LabRAMHR800 Raman spectrometer	Detection of several different particulate materials such as cinnabar/vermillion (cinabro / vermiglio), iron oxide, lead oxide, iron hydroxide, carbon-based black, Prussian blue, ultramarine, lead white, calcium	comprehensive material characterization

				Olympus BXFM optical microscope.	carbonate, anatase, and barium sulphate. - The investigated object was degraded, likely as a consequence of outdoor weathering. As such it represented a complex analytical problem requiring complementary analytical techniques	
2020	Legane L. et al.	Investigation of proteinaceous paint layers to study effects of exposure to the overall impacts of the fire	Paint layers of egg yolk adhesive and lead white tempera that were exposed to fire-related impacts	- cone calorimeter: was used as a device for the exposure of egg tempera model samples to controlled burning conditions or for an investigation into the degradation of paint layers. - Raman spectroscopy, infrared spectroscopy and GC-MS can offer detailed information for material characterization as well as about the degradation and degradation products	changes in the molecular structures for the exposed samples of egg yolk adhesive and lead white tempera that was caused to fire-related effects	-restoration - the results can be very helpful for planning successful conservation and restoration treatments of egg yolk based paint damaged by fire
2020	Zoleo et al.	SERS (Surface enhanced Raman spectroscopy) is exploited to study the signals of degraded of aged dyes and inks on two different type of paper	sample preparation: Two type of paper and a Bic Crystal Blue ballpoint pen were used for. The chromaticity of the samples is significantly altered by artificial ageing	- A Renishaw in Via m-Raman spectrometer equipped with a Leica DM-LM microscope was used to record all the Raman spectra. - SERS measurements: were carried out by depositing a microdrop of 2 mL of AuNP colloid on the sample surface. Once the solvent dried up, the SERS spectra were recorded using the same instrumental procedure used for the Raman measurements	strong change in the color of the commercial ballpoint pen ink on paper, which changes from blue to gray	Nanomaterials for Conservation and Diagnostics in Cultural Heritage
2020	Dong et al.	combined investigation on the material, chemical composition, phase, fluxing	glass-making process of an ancient multicolored stratified glass	Optical coherent tomography, μ -XRF and μ -Raman Spectroscopy can obtain information on both microscopic	Chemical Composition of the Eye Glass	comprehensive material characterisation

		agent, colorant, cross-sectional structure, craftsmanship, and provenance of an ancient multicolored glass	eye bead (perline)	morphology and the phase at the same time; especially, for ancient material, it can also identify pigments and opacifiers, as well as provide further information on the type of glassy matrix.		
2020	Botteon et al.	characterise the penetration of a polymer into a gypsum substrate,	<ul style="list-style-type: none"> - A matrix made of gypsum blocks for the application of the two organic conservation gels reconstruction of the diffusion of the cleaning products into the matrix 	<ul style="list-style-type: none"> - Micro-spatial offset Raman spectroscopy (micro-SORS) is an analytical technique developed for the non-destructive study of non-transparent micro-layered materials - The spectra were collected using a laser power of 100 mW and an acquisition time ranging from 100 to 300 s. 	These results suggest the possibility of estimating the absolute penetration depth of an agent into matrix after a calibration set is prepared and quantitative calibration established	Evaluation of cleaning and recovery methods
2020	Cappa F. et al.	Raman spectral imaging was applied for the analysis of three different types of materials widely used in the field of cultural heritage from the middle ages to nowadays	<ul style="list-style-type: none"> - the pigments used for the triptych "The Last Judgement" by Hieronymus Bosch - laboratory prepared parchment and ink for the identification of the type of ink used on parchment of Glagolitic, Greek and Latin manuscripts - stability of synthetic ultramarine blue used in modern and contemporary paints. 	<ul style="list-style-type: none"> - Samples taken from the painting were embedded in synthetic resin and cross-sectioned in order to study the stratigraphy of the paint layers - The calf parchment were applied with fountain-pen on the calf parchment the black/brown carbon and iron-gall inks and the red inks such as vermilion and lead red - Commercial acrylic and alkyd colors containing synthetic ultramarine blue. - Witec alpha300 RSA+ Raman-Imaging-System -LabRam 800HR Raman spectrometer 	<ul style="list-style-type: none"> - This type of elaboration has identified copper resinate and lead tin yellow, mixed with azurite crystals -degradation due to the corrosive nature of the inks applied, such as iron-gall inks. • The iron-tannin complex which gives iron-gall ink its black/brown color is obtained from the reaction of gallic acid with iron sulfate - The distribution of the S2 - and S3 - radical anions is strictly related to the variation in the content of the chromophores in the solalite cage. • S3 - radical anions are mainly responsible for the blue color of the pigment while S2 - radical anions represent the yellow chromophores 	Conservation of 3 different type of cultural heritage's materials

2021	Quintero Balbas D. et al.	Dye identification in historical textiles to understand their original colour, supports informed preventive conservation strategies	<ul style="list-style-type: none"> - turmeric and saffron dyes in silk and wool Fibres - identification, authentication and quality evaluation. 	<ul style="list-style-type: none"> - the analysis was carried out on an artificially aged sample and on a real sample - colorimetric measurement (to measure the colour difference between natural and artificially aged) - μ-Raman measurements (using a Renishaw inVia Raman confocal microscope equipped with a Leica DM2700 optical microscope and a solid-state 785-nm excitation source) - FT-Raman measurements (using a Bruker FT-Raman spectrometer with a 1064-nm Nd:YAG laser and a Ge diode detector cooled with liquid nitrogen). 	FT-Raman offered a more intense contribution from the fibre, and this allowed studying the substrate, whereas μ -Raman gave more information regarding the colourant	Identification of dyes in proteinaceous textile
2021	Fierascu I. et al.	Non-invasive microanalysis of a written page from the Romanian heritage which can help the restorers to recognize the materials, as well as their state of conservation, facilitating the selection of the appropriate method of conservation and/or restoration	<ul style="list-style-type: none"> - historical document (Romanian old books collection) - analysis of ink present on the samples, as well as evaluation of degraded zones 	<ul style="list-style-type: none"> - X-ray fluorescence (XRF), - Infrared microscopy - Raman spectroscopy 	Identification of the used inks for the printing of the Book and information were also obtained on paper support and the nature of the stains present on the document.	research method of conservation and/or restoration
2021	Ogalde J. Et al.	Chemical characterization of 13 ceramic shreds	Cabuza ceramic objects	<ul style="list-style-type: none"> - SEM-EDX with emission-diffusive - X-ray detector - Raman Microscope System RM1000 (laser diode at 785 nm), a Leica microscope, a CCD detector cooled electrically, and a notch filter to eliminate elastic scattering 	In this decorative pottery, it was identified the red chromophore as hematite, while the black pigment was jacobsite. It was also identified important secondary chemical elements, including arsenic. The discussion of all this evidence allowed to reflect on the relationship between	study of material composition

					the individual and the environment, using the ceramics as cultural material.	
2021	Eisnor et al.	EC-SERS (electrochemical surface-enhanced Raman spectroscopy) as a useful technique for the identification of complex natural dyes which may find potential use in the cultural heritage realm	<ul style="list-style-type: none"> - Polyphenols in yellow lake Pigments, Reseda Lake and Stil de Grain - develop a spectrometric tool for detection of polyphenols in yellow lake pigments 	- DXR Smart Raman spectrometer equipped with 780 nm excitation wavelength (Thermo Fisher Scientific, Mississauga, ON, Canada). The spectrometer resolution is 3 cm ⁻¹ and it is equipped with an air-cooled charge coupled device (CCD) detector.	- Eight polyphenols which included caffeic acid, chlorogenic acid, apigenin, luteolin, emodin, kaempferol, quercetin, rhamnetin were chosen, and EC-SERS spectra were obtained for all.	<ul style="list-style-type: none"> - study of material composition - Future work will seek to extend this work to art historical samples and will focus on the extent to which EC-SERS can be used for pigment fingerprinting
2022	Giuffrida D. et al.	<p>This study was aimed:</p> <ul style="list-style-type: none"> • To acquire a detailed 3D model of the building • To analyze the 1600s wall painting preserved inside the church • To realize a web-based virtual tour able to stimulate visitors' interest • To create a database-based informative model 	- church of Santa Maria delle Palate, (Messina)	<ul style="list-style-type: none"> -3D survey for digitalization - Raman and XRF analysis for material characterization and diagnostic and thermal analysis for digitalization 	The result of the work is a combined "digital archive" useful not only for the purposes of conservation, monitoring and dissemination, but as a container of information enjoyable at different levels of depth	Study, evaluation and recovery of archaeological sites
2022	Botti S. et al.	obtain aging markers based on variations of Raman and fluorescence spectral features. analyze precious and ancient samples degradation processes and to evaluate the performance and effectiveness of	It was studied differently degraded paper samples, dated from 1873 to 2021	IR, Raman, and luminescence spectroscopy were employed to study paper ageing, because all these techniques are able to identify degradation effects on paper exposed to artificial and natural ageing treatments.	The obtained results confirmed that the applied method can be used to compare degradation processes of different paper samples in a quick and reliable way.	<ul style="list-style-type: none"> - study the state of aging of paper samples -The possibility to successfully apply this method for evaluating the effectiveness of cleaning and restoration treatment on paper artifacts

		restoration treatments.				
2022	Kavkler et al.	- determine the extent of the damage and the main reasons for deterioration of 17th century painting	<p>- 17th century Celje Ceiling, tempera painting in a wooden frame, covering 143 m2 of the ceiling</p> <p>- build a predictive model of potential further biodeterioration and consequent damage to the paintings</p>	<p>- The study was divided into three parts:</p> <p>1) long term environmental monitoring in the room where Celje ceiling is located in order to estimate if conditions are enabling microbial growth</p> <p>2) analysis of the painting's constituents to predict which materials and positions enable fungal growth,</p> <p>3) determination of biodeterioration agents</p> <p>- LabRAM HR800 spectrometer (Horiba Scientific, France), connected to a microscope Olympus BXFM (Japan) under the laser of 785 nm wavelength. CCD detector with spectral resolution of about 1 cm⁻¹</p>	- original ground is made from a mixture of calcite and dolomite, with the addition of some aluminosilicates and some other minerals, bound with a protein binder, which sometimes shows carbonyl vibrations of fatty materials. Several different decay products were mainly different oxalates (calcium, copper), carboxylates, platnerite and possibly sulphate salts	- identification of tempera paints' biodeterioration

Table S2: FLUORESCENCE

YEAR	AUTHORS	AIMS	MATERIALS and RESEARCH PROBLEMS	METHODS AND INSTRUMENTS	RESULTS and/or CRITICISMS	APPLICATION FIELDS and NEW PERSPECTIVES
2020	Agua F. et al.	The goals of the study consisted in determining the average chemical composition of the ceramic body, its textural and microstructural characteristics, the crystalline phases to establish firing temperatures, also in studying these aspects in the enamel or glaze layer, as well as in identifying the	19 ceramic fragments and encompasses examples from the 16th and 17th century, either from Talavera or Toledo provenances, and was mainly selected according to stylistic and decorative criteria (17 tiles and 2 earthenware shreds.	X-ray fluorescence (XRF) spectrometry with a PANalytical Axios wavelength dispersion X-ray spectrometer, equipped with a tube of rhodium of 4 kW and 60 kV, using pressed samples.	<p>- The tiles were produced from highly calcareous ceramic materials which were mainly fired at a temperature between approximately 950 and 1050 °C</p> <p>- All the glazes can be classified as lead/alkaline-earth base enamels which have been opacified by using tin oxide probably</p>	study of ceramic products composition

		chromophores for the coloring of the decorations.	Most of the tile samples come from dependencies of the Habsburg Palace, while others come from the refectory of the monastery		added from cassiterite grains. - They also show varied amounts of spherical bubbles, which means that the cooling process was not suited enough since the enamel prolonged its viscosity during cooling, not allowing gases to scape, and thereby producing bubbles.	
2020	Michałowski et al.	studies of archaeological ceramic materials from two sites located in Poland	The experiment was conducted on a selection of 100 fragments of vessels from two sites	<ul style="list-style-type: none"> - the surface of the samples had been cleaned with a soft brush and dust had been removed using a vacuum cleaner. - The handheld X-ray Tracer III ED-XRF spectrometer (Bruker AXS, USA): the voltage range 4–45 kV; current 1–45 mA and the Silicon Drift Detectors (SDD) were used 	chemical composition of the group of the pottery from the pre-Roman Iron Age shared rather similar features	archaeometric analysis for determining the origin of ceramics
2021	Andric et al.	An efficient procedure was developed for the attribution of artwork origin, based solely on XRF spectral data	<ul style="list-style-type: none"> - icons from the iconostasis of the Krusedol Monastery in Serbia (16th to 19th century) - employ different pattern recognition techniques as a support to pXRF analysis of colored layers on a wood (icons from four different centuries) and cardboard (paintings from the 20th century) 	<ul style="list-style-type: none"> - A representative set of 10 icons was selected to cover the development of icon painting over 300 years - side-window X-ray tube as an excitation source (Oxford Instruments, Rh anode, max. voltage 50 kV, max. current 1 mA, with forced air cooling) and a compact X-ray spectrometer 	- icons and paintings were classified by select pattern recognition techniques using two different types of XRF data (peak areas and spectral intensities)	- characterization of icons and paintings

2021	Badica et al.	Investigation of pottery vessels made of kaolin clay from the Roman Period found in Romula from Dacia Inferior	kaolin vessels from sites located in the Lower Danube region	<p>- Selection of the samples, apart from the archaeological context, was based on criteria such as visual general aspect, texture, and identified minerals in the paste trying to cover as much as possible the entire diversity</p> <p>- X-ray fluorescence spectrometry (Bruker S8 Tiger with two detectors, one proportional flow counter and one scintillation counter)</p>	The geographical context of these pottery was determined: local kaolin ware production at Romula and with raw materials from unknown deposits that are possibly located north of the Danube	determination of the origin of archaeological pottery
2022	Favero Luongo et al.	evaluate the biocidal potency of a commercial mixture of essential oils of clove, wild Sicilian thyme and cinnamon against lichen species responsible for biodeterioration in two heritage sites	<p>- TEST SITE1: a non decorated wall of the northern basement of the Tachara Palace in Persepolis (Iran)</p> <p>- TEST SITE 2: non decorated surfaces, ornamentations and statues (gargoyles) of the external walls and the court of the Marquis Chapel of the gothic church of Saint John in Saluzzo (Italy)</p>	<p>- essentials oils were applied as 1.5% (SITE 1) and 1.4% (SITE 1) water solutions of Biotersus, product distributed for the removal of biological patinas from stone</p> <p>- HandyPEA fluorimeter using red light (peak at 650 nm) and data recorded after a saturating light pulse of 1 s</p>	essential oils exert a biocidal effect against lichens which is similar to that observed for traditional biocides	recovery of sites contaminated by lichen patinas
2022	Es Sebar L. et al.	Characterization of the Santa Maria del Fiore cupola construction tools using X-ray fluorescence . This study is the first one that investigates their alloys composition to find the best	<p>- two turnbuckles, eight pulleys, two three-legged lewises and a pincer.</p> <p>- investigate the composition of the</p>	- The instrument is equipped with a 20 mm ² silicon drift detector and a Rhodium (Rh) anode. The Ti-Al filter was used in order to reduce the intensity of peaks related to Rhodium and Palladium	- It was possible to discriminate between the different iron alloys employed for the pulleys, which can be discriminated in two typologies belonging	- analysis on alloys of historical objects

		conservation strategies and to have new insights on the production techniques typical of the Renaissance.	constituent materials	<p>(Pd)</p> <p>- Measurements were performed using a Brucker Tracer 5i analyser, which allowed to perform non-invasive measurements without moving the tools from their collocation in the Museum</p>	<p>to different historical times. The use of PCA allowed also to highlight the presence of two bronze alloys and two iron alloys used for the turnbuckles</p> <p>- The use of XRF analysis does not allow to draw univocal conclusions on dating of these objects, as this technique is not even specifically intended for this purpose. Anyway, these findings, if supported also by historical sources and by the work of curators, can give new insights on the world of technology in the Renaissance era.</p>	
2022	Cadena-Caicedo A. et al.	Time-resolved fluorescence and anisotropy studies of red pigments present in acrylic formulations	<p>- set of four representative acrylics of red pigments, including quinacridones and diimides of the perylene tetracarboxylic acid contained in acrylic formulations frequently used in modern paintings</p> <p>- detection of acrylic formulations to guide investigations about cultural heritage and for restoration efforts</p>	<p>- the pure forms of the pigments were obtained by isolation from the commercial samples. The molecules were purified by column chromatography using dichloromethane and methanol for the elution procedure.</p> <p>- fluorescence anisotropy experiments: The 485 nm excitation beam was sent through a film polarizer placed before dichroic separator. The emission was split into its parallel and perpendicular components with a polarizing beam splitter cube</p>	<p>- It was obtained the effects of sample concentration, sample nature and dimensions, and acquisition method, to serve as the basis of a comprehensive study with a much broader set of pigments and mixtures.</p>	characterization of acrylic pigments for painting

Table S3: LIBS

YEAR	AUTHORS	AIMS	MATERIALS and RESEARCH PROBLEMS	METHODS AND INSTRUMENTS	RESULTS and/or CRITICISMS	APPLICATION FIELDS and NEW PERSPECTIVES
2020	Fortes F. J. et al.	use of an advanced statistical algorithm for the recognition and classification of a set of 30 archaeological metallic objects from the Museum of Malaga	<ul style="list-style-type: none"> - A set of archaeological metallic objects was analyzed in situ by LIBS in the Museum of Malaga (penknife, axe, bottom, chisel, arrow, fibulae, stick etc) - chemical characterization and chronocultural study 	The LIBS system consists of (i) a hand-held probe that encloses the laser head, the focusing lens, and the fiber-optic cable, (ii) a main unit containing the spectrometer, a miniaturized PC motherboard, and electronics, and (iii) the laser power supply	The recognition of the sample's constituents	Characterization of metallic objects
2020	Izzo F. et al.	identification of relevant mineralogical phases forming Cultural Heritage materials on which to create a dataset	<ul style="list-style-type: none"> - different typologies of materials, from gemstones to mono- and poly-phasic rocks, also including some organic materials commonly used in restoration works. 	- Bruker Optics Alpha-R portable FTIR spectrometer with an External Reflectance (ER) head for contactless and non-destructive analyses	- This dataset represents an advantageous tool for the identification of single crystal specimens and ornamental stones, as well as organic compounds normally used as protective or consolidant of geomaterials in the field of Cultural Heritage	- identification of mineralogical phase of cultural heritage materials
2020	Meng Z. et al.	provides complete information of the historical relics (color, surface reliefs, and chemical composition)	Naxi mural fragments found on the walls of buildings in Yunnan province, Southwestern China.	The combined use of LIBS with 3D laser scanners provides data that may be converted to a digital image	Naxi paintings gives information about the pigments, the binder, and individual chemical elements involved in the creation of the Naxi art	<ul style="list-style-type: none"> - detect the composition of dyes. - This approach will be tested with larger objects in the future studies.
2020	Pagnin L. et al.	identification of modern paints composed of inorganic pigments and	- 27 paint mixtures made of all combinations of pigments	comparison the LIBS spectra of the acrylic, alkyd, and styrene-acrylic binder in	It was obtained PCA (Principal component analysis)	study of material composition

		organic binders, such as acrylics, alkyds, and styrene acrylics	and binders were prepared by mixing pure Plextol® D498 (Kremer Pigmente, Germany), Alkyd Medium 4 (Lukas®, Germany), and Acronal S790 (BASF, Germany) in combination with 9 inorganic pigments (Kremer Pigmente, Germany) - characterizati on of contemporary art materials was carried out	the range of 450–660 nm	evaluation of pure materials	
2020	Malloy A. et al.	investigate the usefulness of LIBS and digital imaging for the analysis of oil paint pigments for indirect dating, authentication, and identification.	pigments in oil medium are analyzed individually, as well as in mixtures. Samples for LIBS were prepared using 4"x4" canvas boards. Samples for digital imaging were prepared on 1"x1" canvas boards and 1"x1" artists paper. All paints were professionally mixed by RGH Artist Oil Paints.	- Digital image processing technology and algorithms were used to analyze pure and mixed pigments in single and multi-layer samples. - In LIBS was used these Experimental Parameters: # Laser energy: 90 mJ #Time delay: 1 s, ICCD gain: 150 #0.25 second gate width: 20 s; exposure; operating in either single shot mode or single shot mode with 10 accumulations	LIBS and Digital Imaging allowed to determinate pigments either pure or in binary mixtures	Determination of authenticity and dating artwork
2021	Oujja M. et al.	chemical and physical characterization of grisaille paint layers on historical stained glasses, from different chronologies and provenance in Spain	four representative samples of historical stained-glass windows with grisaille paint decorations that come from different Spanish sites	LIBS analyses were performed using laser excitation at 266 nm (4th harmonic of a Q-switched Nd:YAG laser, 6 ns pulses, 10 Hz repetition rate) and a 0.30 m spectrograph with a 1200	The spectrum reveals the elemental composition by virtue of the emission lines of the major and minor components.	characterization of the composition of grisaille materials

			and chronology, encompassing a wide period from the 13th to the 20th century	grooves/mm grating (TMc300 Bentham) coupled to an intensified charged coupled detector (ICCD, 2151 Andor Technologies)		
2021	Ruan et al.	LIBS experiments were performed using 35 archaeological ceramic samples, treasure of Chinese culture	<p>- 35 ceramic samples provided by China Waves Art identification Co Ltd in the form of fragments</p> <p>- investigate the origins of the ceramic samples</p>	An X-Y-Z manual micrometric stage was used to directly place the ceramic samples and the measurement was carried out at atmospheric pressure. A 532 nm Q-switched Nd:YAG laser (Dawa 300, Beamtech Optronics, USA) was used for obtaining the LIBS spectra of ceramic sample	Ceramic samples are complex samples with a variety of chemical elements, and the spectral lines of Fe, Ca, Si, Al and Mg were identified based on the NIST database.	identification and classification of ancient artefacts
2021	Senese et al.	Analyze exhibited surface degradation of Castello Svevo di Bari	a limestone fragment from a masonry block at the Castello Svevo in Bari that exhibited surface degradation in the form of a black crust.	Three measurements of about 6-s duration were made at each sample point to acquire a total of 150 spectra, corresponding to 1800 laser pulses that were then averaged	C, Mg and Ca were the major constituents of the unaltered limestone, whereas the altered surface layer was characterized by the presence of Al, Si, and Fe that was attributed to solid particulates deposited from atmospheric pollution plus lesser amounts of Na and K derived from the marine aerosol that is pervasive across the urban area where the monument is located.	revelation of the deterioration of a cultural monument
2022	Richiero S. et al.	characterize the elemental composition of three lime mortar samples from three different geographical locations: Angers (France),	-sample 1: was retrieved from the Saint-Maurice of Angers Cathedral, contain some aggregates of sand	neodymium-doped yttrium aluminum garnet (Nd:YAG) laser emitting at the fundamental wavelength (1064 nm) with a pulse duration of 8 ns	The elemental composition of the samples is highly heterogeneous. They also have very different textures due to the properties and shapes of the	<p>- Characterization of archaeological samples</p> <p>- the micro-LIBS capability to discriminate neoformed lime carbonates from geological carbonates opens up promising new opportunities for</p>

		Dardilly (France), and Pompeii (Italy),	<p>- Sample 2: collected from Pompeii in the Hercules house (Italy). The sample analyzed here is obtained from the covering of hypogeous rooms under the house peristyle</p> <p>- sample3: collected from the Brevennes aqueduct ' (Dardilly, France). For its hydraulic function, the lime mortar is composed mainly of tile piece aggregates</p>	and a 100 Hz repetition	aggregates they contain.	improving the methods of dating buildings
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Table S4: IR

YEAR	AUTHORS	AIMS	MATERIALS and RESEARCH PROBLEMS	METHODS AND INSTRUMENTS	RESULTS and/or CRITICISMS	APPLICATION FIELDS and NEW PERSPECTIVES
2020	Carter E. A. et al.	Identification of cellulose nitrate and cellulose acetate film in historic photograph collections	<p>- 1890s to the early 2000s photographs by many notable maritime photographer s, from the Australian National Maritime Museum</p> <p>- preservation of cellulose nitrate and cellulose acetate film that pose a risk to humans and to other material that is stored with it.</p>	<p>- Principal component analysis was applied followed by the factor rotation method of Parsimax rotation leading to simple structure that produce components with enhanced chemical interpretability</p> <p>- Bruker ALPHA portable FTIR spectrometer (Bruker Optiks, Ettlingen, Germany) equipped with a QuickSnap™ ERM and integrated video camera to assist in the location of the</p>	- It was created a methodology based on infrared total reflection spectroscopy, for rapid identification of cellulose nitrate and cellulose acetate	<p>- determination of deterioration's state of cellulose nitrate and cellulose acetate film</p> <p>- All samples analysed were either sheet or still photographic film. Other formats, such as motion picture film, magnetic soundtrack, aerial, microfilm or x-rays were not analysed in this study and are necessary for future research and testing the validity of this method.</p>

				region of interest to be sampled		
2020	De Sa et al.	FTIR surface analysis for conservation	<ul style="list-style-type: none"> - historical plastic objects that were gathered in the Museu de Leiria from the 1930s to the present; they were type of polymer for variety of uses (everyday, kitchen, toys, etc.) - identify plastic types 	<ul style="list-style-type: none"> - the use of a neutral pH detergent with microfibre cloth was applied, followed by a rinse with distilled water. For the transparent and/or pristine and shiny objects sxy soil, was chosen instead of the detergent solution in order to minimize the number of rubs (imposed in the rinse) and to reduce the risk of surface abrasion - Handheld Agilent 4300 spectrophotometer, equipped with a ZnSe beam splitter, a Michelson interferometer and a thermoelectrically cooled DTGS detector 	- The carried-out analysis shows how conservation contributes to the preservation of such heritage but also to their knowledge and understanding in the contemporary world.	- study and characterization of plastic material
2020	Comite V. et al	characterization of black crusts on the facade of an historical cathedral	<ul style="list-style-type: none"> - BCs taken from the historical cathedral of Monza (dating to 14th century), placed in a polluted urban centre in the North of Italy - get information about the composition and texture of the BCs making it possible to identify the pollution sources causing the stone decay. 	<ul style="list-style-type: none"> - sampled from the cathedral façade studied in the present work, have developed on the different marbles used for the monument construction - FT-IR spectroscopy (Thermo Nicolet 6700) in Attenuated Total Reflectance (ATR) mode 	all BCs are mainly composed of gypsum, with some traces of oxalate and quartz. weddellite was mainly found in BCs belonging to older crusts	study physical–chemical decay of stone surfaces

2020	Conejo-Barboza G. et al.	combination of non-invasive and in-situ techniques to carry out a qualitative assessment of the pigments of painting and determination of actual state of conservation	- paintings from the nineteenth century made by the Italian painter Vespasiano Bignami. The paintings are known as La Poesía, La Música and La Danza and is located on the ceiling of the Foyer at the National Theatre of Costa Rica	- Technical photography to obtain high resolution images in the Vis and IR regions of the electromagnetic spectrum. - Photographs were acquired with a Nikon D7200 camera. Images were captured in the visible spectral range (Vis) and for the infrared range (IR)	new understanding of the pictorial palette and the state of conservation of three paintings at the National Theatre of Costa Rica .	Determination about the composition of painting and determination of state conservation - some insight into the few scenarios in which cultural heritage could be investigated in Central America along with Italy
2020	Rovella N. et al.	define the state of conservation of the stone materials used in the Cairo historical heritage	- eighteen stone samples, including their degradation products, were taken from the main facades and walls of seven monumental sites	Perkin Elmer Spectrum 100 spectrophotometer equipped with an ATR (attenuated total reflectance)	The main components detected in all the crusts are gypsum, oxalate and calcite, typical black crust compounds, oxalate (restoration works carried out in the past or to the presence of biological activity) and silicates (namely from the substrate where they are naturally present or from the deposit of soil dust)	characterization of stone materials and degradation products of monuments
2021	Beltran V. et al.	Identification of the Organic Particles in L'Arlès-sienne (Portrait of Madame Ginoux) by Van Gogh	- fragment from Van Gogh's painting L'Arlès-sienne (portrait of Madame Ginoux) - understand the composition, physical properties and historical background of the object and/or to	- thermal expansion of the sample induced by the irradiation with an IR laser, which is then measured using a visible probe laser - an atomic force microscope (AFM) coupled to infrared spectroscopy providing a spatial resolution up to 20 nm	identification micro- and nano-heterogeneities in the samples, with decrease the size of the samples needed for the analysis	Characterization of painting

			decipher possible degradation reactions			
2021	Vahur S. et al.	Quantitative mineralogical analysis of clay-containing materials	<ul style="list-style-type: none"> - altogether 222 samples covering natural clay sources and various archaeological / cultural heritage artefacts were used as calibration and validation standards - Classification and quantitative analysis of clay components 	<ul style="list-style-type: none"> - all the reference standards were ground using ball mill (standards of geological origin) or agate mortar and pestle (standards of archaeological and cultural heritage origin). - the ATR -FT-IR spectra were recorded using Thermo Scientific Nicolet 6700 FT-IR spectrometer with Smart Orbit diamond micro-ATR accessory. The FT-IR spectrometer has DLaTGS detector, CsI beamsplitter and Vectra Aluminium interferometer 	ATR-FT-IR-PLS method quantified quite well the higher contents of minerals like silica varieties (e.g. quartz), feldspars, for some samples also clay minerals (illite, illite-smectite, micas) and surprisingly well also iron-oxyhydroxides.	Quantitative mineralogical of clay materials
2021	Angelin E. et al.	characterization of plastic artifacts' composition to outline proper conservation strategies	<ul style="list-style-type: none"> - Polymer reference sample - samples of commercial and composite formulations from everyday plastic objects - Naturally aged historical objects from a Portuguese private collection 	<ul style="list-style-type: none"> - portable Alpha FT-IR spectrophotometer (Bruker Optics), equipped with a silicon carbide (SiC) globar source and temperature stabilized deuterated triglycine sulfate (DTGS) detector. - Agilent Handheld 4300 FT-IR spectrophotometer, equipped with wire wound IR source and a thermoelectrically cooled DTGS detector, coupled to a diffuse reflectance sampling module with a measuring spot of 10 mm diameter 	molecular characterization was possible without compromising the physical integrity of the historical plastic objects and with no limitations correlated to micro-sampling or pressure.	plastics' molecular characterization and degradation assessment

2022	Vouvoudi E. et al.	Study of commercial polycyanoacrylate adhesive of medium viscosity regarding its suitability for the restoration of glass objects of cultural heritage	<ul style="list-style-type: none"> - Leocite super Attak Glass, a commercial cyanoacrylate adhesive with ethyl cyanoacrylate as the main monomer - investigate the appropriateness of commercially available cyanoacrylate adhesive for the restoration of glass material 	<ul style="list-style-type: none"> - preparation of polycyanoacrylate films, valuated visually and manually in terms of equal thickness, smooth surface, lack of entrapped air bubbles, and colour uniformity 	<ul style="list-style-type: none"> - the data indicate that Loctite Super Attak Glass appears to be a promising alternative to traditional adhesives used for the conservation of glass objects, given the advantage of instant curing. - the extensive use will undermine the restoration process over long periods of time under intense conditions 	study of a polymer to evaluate its suitability for glass restoration
2022	Macchia A. et al.	multi-analytical approach implemented for the study of the oil painting "Il Venditore di Cerini" made by Antonio Mancini in 1878. for characterize both the original stratigraphy and the alleged non-original varnish on the surface.	<ul style="list-style-type: none"> - Three samples were taken from the upper, right, and bottom border of the painting Sample 1: includes the ground layer, the primer, and the paint layers without the varnish; sample 2 consists of the original canvas, the ground layer, the primer, the paint layers, and the varnish, while sample 3 includes the ground layer, the primer, the paint layers, and the varnish. 	<ul style="list-style-type: none"> - Nicolet Summit FTIR spectrometer equipped with the Everest™ Diamond ATR accessory, which allows analysis in attenuated total reflectance (ATR) 	The multi-analytical process enabled the characterization of the entire stratigraphy and the constituent materials of the oil painting on canvas. The multi-analytical process succeeded in guiding the cleaning treatment on the painting (Polar Varnish Rescue GEL)	evaluation of cleaning methods for paintings
2022	Longoni L et al.	Study of Binders and Multi-Layered Structures in Ancient Paintings	<ul style="list-style-type: none"> - "Madonna and Child" by Giovanni Antonio Boltraffio - "Nursing Madonna" by an anonymous 	<ul style="list-style-type: none"> - Were compared the results obtained by analysis on #pure binders (siccative oils, egg (white and yolk) and animal glue 	non-invasive detection of binders and information about the presence or absence of a preparatory layer, in particular a	determination of paintings' composition

			<p>Lombard school painter - "Madonna with Child" by Francesco Galli</p> <p>- "Ecce Homo" by Andrea Solario</p> <p>- "St. John the Baptist" by Bernardo Zenale</p> <p>- "St. Augustine and St. Jerome" by Ambrogio da Fossano</p> <p>- recognize specific binders, such as drying oils, egg yolk or even their mixtures, in complex multi-layered systems</p>	<p>#mock-up painting samples (two different preparatory layers were used, commonly adopted by artists, and respectively based on calcite and gypsum.</p> <p>#real samples</p> <p>- FTIR spectrophotometer with a reflection module for contactless measurements and a deuterated triglycine sulfate (DTGS) detector, operating at room temperature and ensuring a linear response in the spectral range between 7500 and 375 cm⁻¹</p>	<p>gypsum-based one, or of a priming layer.</p> <p>- this non-invasive approach cannot provide as much specific information on binders as destructive chromatographic analyses</p>	
2022	Sebestyen Z. et al.	<p>obtain information about the thermal stability, composition and molecular structure of four historical leather bookbindings dated between the 17th and 19th century and to identify correlations between their thermal, structural and chemical properties and deterioration mechanisms</p>	<p>- historical leather bookbindings manufactured and dated between the 17th and 19th centuries. Reference samples were tanned by chestnut and quebracho vegetable tanning agents, respectively</p>	<p>portable Alpha spectrometer (Bruker Optics) equipped with a Platinum ATR module. Spectra were recorded in the 4000 – 650 cm⁻¹ spectral range with a 4 cm⁻¹ resolution, using 32 scans.</p>	<p>- it was possible to observe the small differences in the thermal stability, chemical composition and molecular structure of historical leather bookbindings dated from 17th to 19th century, with different origins and conservation histories.</p> <p>- the difficulty to discriminate the single variations of collagen and tannins typical bands due to their overlapping, and to the presence of a number of bands originated by various chemical compounds used in the fabrication process and/or</p>	<p>Characterization of historical leather bookbindings</p>

					formed during aging and deterioration	
2022	Vigorelli L. et al.	Characterization of wooden objects and statuettes.	<ul style="list-style-type: none"> - painted wooden statuette, representing an offering bearer, found during the 1908 excavation season in the necropolis of Asyut (Egypt) - definition of a measuring protocol to study the most significant aspects of the artistic technique about wooden objects and statuettes. 	<ul style="list-style-type: none"> - non-invasive and imaging analyses. the taking of some micro-samples from the artefact is the last step of the diagnostic campaign necessary to answer specific questions that arise during the early stages of the investigation - Bruker Vertex 70 FT-IR spectrophotometer coupled with a Bruker Hyperion 3000 infrared microscope working in transmission with the aid of a diamond cell. 	FT-IR analysis results show the possibility to distinguish modern interventions, probably dated from the second half of the twentieth century and more ancient interventions, such as the insertion of wooden elements to complete the figure	<ul style="list-style-type: none"> - characterization of wooden objects - it will be possible to apply the same investigation strategy to other wooden artefacts and statuettes belonging to the same framework, in order to make comparisons among the objects.

Table S5: LASER ABLATION

YEAR	AUTHORS	AIMS	MATERIALS and RESEARCH PROBLEMS	METHODS AND INSTRUMENTS	RESULTS and/or CRITICISMS	APPLICATION FIELDS and NEW PERSPECTIVES
2020	Rivas et S. al.	Laser ablation on granitic rock	<ul style="list-style-type: none"> - Variscan granite of northwestern of Spain, from two adjacent but different coloured specimens - determine if the response to laser irradiation (in terms of physical damage, mineral melting, colour modifications, etc.) is different depending on whether the laser radiates 	- Applied to both the WS and YS specimens was a nanosecond (ns) Nd:YVO4 Coherent AVIA Ultra 355–2000 laser, operating at 355 nm, with pulse duration 25 ns, maximum pulse energy 0.1 mJ	<ul style="list-style-type: none"> - subtle mineralogical differences of two samples led to qualitatively and quantitatively very different laser responses in terms of: (a) colour modifications; (b) the minimum fluence at which the main minerals melted; and (c) the resistance of minerals to laser radiation, especially that of feldspars. It is concluded that the presence of these two mineral 	Laser ablation as a cleaning technique of granitic rock

			an area rich in flow textures or not.		phases enhanced the susceptibility of this type of granite to the laser.	
2020	Barreiro P. et al.	- evaluate influence of the Laser Wavelength on Harmful Effects on Granite Due to Biofilm Removal	<p>- A natural exposed granite slab with an intense biological colonization taken from a stone workshop in the NW Iberian Peninsula</p> <p>- removal of initial biocolonization from monuments to avoid greater damage from hyphae penetration and mineralogical transformations</p>	<p>- S Nd:YAG laser (Quanta Ray, INDI) with a 6 ns pulse duration that can deliver the fundamental 1064 nm beam (IR radiation), the second harmonic (532 nm—green Vis radiation) and the third harmonic (355 nm—UV radiation)</p>	<p>- 532 nm (second harmonic) induced the highest color modifications and also induced a slight melting and fracturing of the muscovite exfoliation planes.</p> <p>-(355 nm), at both fluences, did not cause visible changes to the surface</p> <p>-1064 nm-treated surfaces did not show coloration modifications in the granite</p>	Laser ablation for removal biocolonization on granite monuments
2020	Papanikolaou A. et al	Development of a hybrid photoacoustic and optical monitoring system for the study of laser ablation processes upon the removal of encrustation from stonework	<p>- commercial marble variety (Thassos White), commonly encountered in Greece. The mineralogical composition is 12% Calcite (CaCO_3), 86% Dolomite ($\text{CaMg}(\text{CO}_3)$) and 2% Quartz (SiO_2)</p> <p>- allowed for the precise determination of the critical number of laser pulses required for the elimination of the encrustation layer, while highlighting the dominant ablation mechanisms according to</p>	<p>- The crust simulation was a mixture of gypsum with 5% w/w carbon in the form of charcoal particles. The gypsum was in the form of pure hemihydrate. The mixture was hydrated using distilled water while the mock-ups were left to dry for at least 48 hours prior to any experiment.</p> <p>- BMI Q-switched Nd:YAG system (5022 DNS10 series, B.M. Industries, France) modified by IESL-FORTH to operate at the fundamental (1064 nm) and the third harmonic (355 nm)</p>	<p>- It was developed a hybrid photoacoustic and optical system for the in-situ and real-time monitoring of laser cleaning and the investigation of the laser ablation mechanisms that dominate the cleaning with IR and UV laser wavelengths. We also introduced a successful and novel photoacoustic data processing protocol which can be used to indicate the incident pulse that eliminates the crust layer</p>	- study of laser ablation to remove encrustation from stonework

			the irradiation wavelength	wavelengths individually and simultaneously		
2020	Ricci C. et al.	evaluation the combined cleaning treatment based on laser ablation followed by the application of chemical products for removing alkyl graffiti paint from two different types of stone	<p>- two Italian ornamental stones with different mineralogy and texture, commonly found in the historic centre of the city of Turin: a gneiss and a travertine</p> <p>- research the effects of laser ablation plus chemical cleaning with a low-toxic solvent mixture in relation to graffiti removal from porous stone surfaces</p>	<p>- each type of stone were covered by a graffiti paint commonly used on gneiss and travertine surfaces in Turin: violet spray paint from MONTANA Colors. The paint was applied in two stages separated by an interval of 24 h, The paint was sprayed on the stone at an angle of 45° and from a distance of 30 cm, for 3 s. The painted samples were left to air-dry in the laboratory for seven days.</p> <p>- Quanta System Smart Clean II laser operated at 1064 nm in Short Free Running (SFR) mode</p> <p>- EOS 1000 laser operated at 1064 nm in Long Q-switched (LQS) mode.</p> <p>- Thunder Art laser operated at 1064 nm in Q-switched (QS) mode</p>	<p>- For both types of stone, the reduction in graffiti remains (mainly in the travertine) and the less intense changes in roughness relative to the surfaces cleaned with laser treatment alone, indicate that the combined methods are more efficient and gentler on the underlying stone. The combined procedure enabled moderate use of laser thus preventing the associated damage to the stone surface.</p>	- paint removal from heritage stone
2021	Pozo-Antonio J.S. et al	Research effectiveness and durability of chemical- and laser-based cleanings of lichen	<p>- Lichen mosaics on different-textured schists located in the Coa Valley (Portugal) and Siega Verde (Spain) archaeological sites</p> <p>- research was focused on: 1) the effectiveness of cleaning</p>	- two Nd:YAG wavelengths (1064 nm and 266 nm)	<p>- Regarding laser cleaned surfaces, unsatisfactory cleaning was recorded at both sites, and they also showed intense recolonization during these 4 years. The most effective and durable effects were obtained with the biocidal treatments with Biotin T and</p>	recovery of sites contaminated by lichen patinas

			with ethanol at 50% (v/v), two biocides (Benzalkonium chloride and Biotin T) and two Nd:YAG wavelengths (1064 nm and 266 nm) applied to devitalize lichens 2) the durability of the cleaning after 4 years		benzalkonium chloride	
2021	Zou W. et al.	This study provides a new basis for audible acoustic monitoring method in the process of laser cleaning of paint on metal surfaces.	- paint from a metal surface - research the evidence for monitoring the effect of laser paint removal through acoustic signals	- were adopted analytical methods of the time domain, frequency domain and time-frequency domain - A Q-switched Nd: YAG laser (Beamtech Nimma-600), which a wavelength of 1064 nm, a pulse duration of 7 ns and a repetition rate of 1 Hz	(1) Time domain characteristics: In general, Audible acoustic signals have less time domain characteristics. (2) Frequency domain characteristics: It can be obtained from the FA spectra that when the amplitude of frequency of 0.04 kHz reach maximum, the paint can be removed completely. (3) Time-frequency domain characteristics: It can be obtained from the TF spectra that the amplitudes of power spectral density increase with the increase in laser fluence.	Laser ablation for removal paint on metal surface
2021	Di Francia E. et al.	Research novel procedure for laser ablation cleaning processes on Cu-based alloys	- Artificially-corroded Cu reference samples with a tailored chemical composition, microstructure, morphology, texture and colour of the corrosion products layers	- The reference Cu specimens were polished with 500 to 4000-grid SiC paper, rinsed in ethanol in ultrasonic bath for 5 min and well dried. Then, the reference samples were totally immersed in 0.5 M NaCl solution for two months at	The main results reveal that the laser treatment apparently does not change the elemental or micro-structural composition of the corrosion layers, but the amount of incorporated isotope is higher as the irradiance values increase.	Laser ablation for removal corrosion products on Cu samples

			<p>- developed involving ^{18}O isotopes evaluation by ToF-SIMS spectroscopy to assess the driving mechanisms of laser-surface interactions</p>	<p>room temperature. The solution was neither stirred nor aerated by bubbling. Immediately after submitting the samples to the laser-cleaning tests, they were embedded in epoxy Specifix-20-Struers resin in order to avoid any air-contamination before characterization</p> <p>-NIR Q-switched Yb:YAG fibre laser operating in the nanosecond pulsed regime</p>	<p>Thermal effects represent the main contribution to the incorporation of the oxygen isotope and the consequent re-oxidation processes happening, with all probability, through the grain borders</p>	
2022	Lopez A. J. et al.	The influence of lithology and texture to increase the hydrophobicity of ornamental stone.	<p>- Samples of slate (ardesia), a quartzite, a granite, and a marble</p> <p>- Investigation on laser texturing as a solution against colonization of surfaces by organisms, eliminating exposure to chemicals products with varying degrees of toxicity</p>	<p>- 3 slabs of each stone measuring approximately 10 cm \times 5 cm \times 2 cm were polished and their surfaces were cut: two slabs were used for laser texturing and the third one was used as an untreated reference stone.</p> <p>- Spirit system by Spectra-Physics, with an emission wavelength of 1040 nm and pulse width of less than 400 fs, as previously used for texturing purposes</p>	<p>- The results show a correlation statistically significant between the change in the contact angle θ, which characterizes the wettability of the stone, and the generated surface roughness; so that, in the group composed of slate, quartzite, and granite laser texturing caused a decrease in the contact angle and, therefore, made the surface even more receptive to water compared to the polished one; on the contrary, laser texturing was able to increase the contact angle of marble up to values $\theta_{\text{marble}} \approx 125^\circ$ thus giving a clear hydrophobic behavior to the stone surface</p>	- Stone conservation

2022	Ciofini D. et al.	validation study about laser ablation treatment of soiled featherworks	<p>- 17th Brazil Tupinambà feathered cape</p> <p>- research laser treatments application to the removal of soiling from fragile artefacts made of organic fibrous materials</p>	- fiber-coupled QS and LQS Nd:YAG (1064 nm) lasers	- high effectiveness and spatial accuracy of both pulse widths in the cleaning of red and yellow feathers from scarlet ibis. The treatment also included a few blue feathers, that were cleaned at about the same fluences as those of red and yellow feathers	- treatment of organic fibrous materials
2022	Di Francia E. et al.	assess possible laser-cleaning induced surface effects on different archaeological bronzes corrosion products structures through a systematic and multi-technique compositional study	<p>- Two archaeological coins:</p> <p>#Coin 1: Dupondio Marco Aurelio, a Roman Empire bronze coin (2nd Century dated)</p> <p>#Coin 2: Follis Massenzio, a Roman Empire bronze coin (4th century dated)</p> <p>- investigate laser results as cleaning technique</p>	<p>- Chemical-physical characterizations were performed on laser-cleaned and non-cleaned types of Cu-Sn archaeological corrosion products structures. The reference samples are artificially corroded</p> <p>- An Yb:YAG fibre laser (Jeanologia laser, model EasyMark-20), operating in the near-IR region at a wavelength of 1064 nm. The system operates in a QS regime, from 4 ns to 200 ns of pulse duration; the pulses are delivered by means of two galvanic mirrors and are focused with a f-Theta lens with 160 mm of focal distance</p>	- the laser-ablation does not seem to affect the composition of the ablated layers and, if the laser parameters are correctly set, the ablation process leave a Cu (I) layer. Being the archaeological corrosion layers thicker and denser than the artificially corroded ones, a three-times higher in fluence and irradiance values condition was more efficient in the removal of the unwanted corrosion layers on these real artefacts	-cleaning of bronze archaeological corrosion products
2022	Brand J. et al.	Investigate the ultrashort pulsed laser ablation of a high heritage value Australian granite.	- Australian granite from the Moruya area of New South Wales in south-eastern Australia,	- Carbide 40 W femtosecond laser (CB3-40W from Light Conversion, Lithuania), using its fundamental	- Optical and scanning electron microscopies showed no morphological changes on the minerals for	- cleaning of granite contaminations and pollutants

			<p>dominated by quartz, plagioclase, hornblende, biotite, and lesser potassium feldspar.</p> <p>- evaluate the use of lasers to remove contamination and pollutants from cultural heritage, both to increase stability and longevity, and to improve the aesthetic appearance</p>	<p>wavelength of 1029 nm. The pulse duration was set to 275 fs at up to 1 MHz maximum repetition rate and up to 0.4 mJ in energy</p>	<p>fluences below $1.1 \pm 0.1 \text{ J}\cdot\text{cm}^{-2}$. Consequently, a maximum fluence of $1.0 \text{ J}\cdot\text{cm}^{-2}$ should be used to clean granitic surfaces to avoid any laser induced damage to the granite surface.</p>	
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Table S6: THZ SPECTROSCOPY

YEAR	AUTHORS	AIMS	MATERIALS and RESEARCH PROBLEMS	METHODS AND INSTRUMENTS	RESULTS and/or CRITICISMS	APPLICATION FIELDS and NEW PERSPECTIVES
2020	Mikarov M. et al.	THz techniques to study samples of ancient pottery	- Roman and Punic era ceramic potsherds excavated from an archaeological site in Sardinia, Italy	<p>- This method combines highly accurate photogrammetric reconstruction and tomographic THz imaging methods to estimate the refractive index of arbitrary shaped samples in each pixel of an image.</p> <p>- (ABB IRB 120) with emitter and detector photoconductive antennas mounted in a monolithic package at the end of it.</p>	coarse wear sherds has a larger average index in the terahertz range, and also a greater degree of inhomogeneity. The degree of homogeneity is likely to provide a quantitative measure of the texture and density of the ceramic fabric	- Thz spectroscopy for study of ceramic samples
2020	Feng J. et al.	new nondestructive testing (NDT) method based on terahertz time-domain spectroscopy (THz-TDS) technology to measure the hollowing deterioration of stone relics	- Yungang Grottes	- Hollowing deterioration samples were strictly prepared, and a series of experiments were conducted to ensure the representativeness of the experimental results. A hollowing	- analysis suggests that THz technology can be applied to efficiently detect hollowing deterioration, as it reflects the thickness of hollowing deterioration. This analysis can be extended to	-measurement of relics stones' deterioration

				<p>thickness model was established by the relationship between the thickness of the hollowing deterioration sample and the time difference of the front flaked stone surface and the stone wall surface of the hollowing deterioration samples</p> <p>- THz-TDS1008 test system. The central wavelength of the laser is 800 nm, the pulse duration is 100 fs, the THz pulse width is 0.05~3.5 THz</p>	other cultural relics.	
2020	Sirro S. et al.	detect and inspect the paint layers below the surface independently of any surface features, using the for THz-TDS imaging system	- Image of the reverse side of the canvas with signatures applied under brown and green layers of paint (a) and the front side of the canvas with the image of a human head (19h century)	<p>- TeraPulse Lx system to produce ultrafast (~100s fs) terahertz (THz=1012Hz) pulse incident through the front side of painting and to detect structures on the back side of painting (on canvas) whilst the THz beam was scanned across the painting</p> <p>- TeraPulse system had a peak spectral range 0.06 THz – 6.00 THz, peak dynamic range > 95 dB, and was operated in reflection mode using a scanning gantry with a maximum speed of 16 sec per cm², and user-adjustable spatial resolution in the range 0.25 – 0.50 mm,</p>	- Features of the painting, which were located on the back side, were detected by scanning with THz incident through front surface of painting. THz images detected in this manner match the visible image done on the back side of object	Detection of paint layer
2021	Eun Lee J. et al.	Terahertz spectroscopy as an effective	- two types of vermilion samples	- Teraview TPS3000 (Teraview Ltd.,	- It was determined the refractive index and extinction	Identification of artist's pigments

		nondestructive identification tool for the study of artist's pigments.	<p>1) vermilion oil paint in free-standing form used for room temperature measurements</p> <p>2) The second type is a vermilion pigment mixed with polyethylene powder and pressed into tablet form. The PE matrix was there to stabilize vermilion in the low-temperature vacuum environment without disrupting the absorption features of vermilion in the terahertz range</p>	UK) in the frequency range of 0.1–3 THz. A femtosecond laser delivered 70 fs pulses centered at a wavelength of 800 nm at a repetition rate of 80 MHz	coefficient of vermilion at room temperature by performing terahertz time-domain spectroscopy (THz-TDS) on free-standing samples and a series of low temperature measurements to reliably examine the temperature dependence of the positions and linewidths of the three major absorption peaks of vermilion in the terahertz range	
2022	Wang T. et al.	Research a virtual unrolling technique that can extract content from structures similar to folded paper and scroll, exploiting the three-dimensional imaging capability provided by terahertz computed tomography (THz CT)	<p>- flat paintings, folded documents, parchment scrolls and some other curled objects</p> <p>- provide a capability to inspect samples with curled or folded structure, which are particularly prevalent in the field of heritage conservation or security (for example, letters, documents and painting art works)</p>	<p>- we treat the slice image as a “topographic map” and reasonably assume that with the limited resolution of the THz CT image, most of the information in the folded or rolled structure is attached to the ridgelines of the slice image and it is a feasible virtual unrolling scheme to find cross-sectional profile(ridgeline) of the object slice by slice, and then stitch these profiles(ridgeline) together to form the final image by some method</p> <p>- modification of the THz continuous wave transmission</p>	- conceived non-invasive inspection of cultural relic with special-shaped structures	- analysis of paper and scroll

				imaging system. A rotating motor is added to the transmission imaging system in confocal geometry to achieve multi angle measurement of the sample. A continuous wave at a frequency of 0.3 THz with an output power of 0.3 mW were delivered by the transmitter, which is a Gunn diode		
2022	Hu et al.	Research non-destructive imaging of marquetries based on a new infrared-terahertz fusion technique. To demonstrate the efficacy of the suggested technique, an experiment has been conducted on an ancient marquetry.	<ul style="list-style-type: none"> - The ancient marquetry consists of three layers. The support is made of fir wood, the middle is the animal glue, and the top is the ornamental layer, which is a composite of several materials, including but not limited to pearl (white tesserae) and bovine horn - design a fusion process to merge the information obtained by both active thermography and terahertz imaging 	<ul style="list-style-type: none"> -thermography analysis: dynamic line-scan technique. The setup is composed of a line heat source and a longwave infrared camera (FLIR Phoenix, NETD = 50 mK). - terahertz time-domain spectroscopy (THz-TDS): Menlo Systems GmbH, Munich, Germany. The system has a frequency resolution of 1.2 GHz, and a repetition rate of 100 MHz. The experiment is carried out in transmission mode, with the scanning step set to 0.5 mm. 	<ul style="list-style-type: none"> - The fusion method successfully reveals defects of various kinds, such as missing tesserae or splitting located at different depths. The experiment has demonstrated that the proposed fusion imaging has the potential to provide high-SNR defect information and high-thermal contrast results for the cultural heritage inspection. This complementarity must be commended 	<ul style="list-style-type: none"> - Thz for analysis of ancient marquetry.
2022	Ullmann I et al.	Investigate contactless Inspection of Handwritten Documents with Terahertz Imaging	<ul style="list-style-type: none"> - handwritten (non-historical) documents 	<ul style="list-style-type: none"> -In order to investigate the potential for scanning letters, three measurements were performed, which are illustrated in Fig. 6. First, the handwriting as such was imaged as a reference. Then, the writing was covered in 	<ul style="list-style-type: none"> -Letters with one-sided handwriting, covered in an envelope were imaged clearly. Regarding two-sided letters, the recognition of single characters or words becomes more difficult. The kind of ink as well as its 	<ul style="list-style-type: none"> - contactless inspection of ancient documents

				<p>two sheets of paper to simulate an envelope. In a third measurement two papers with writings on them were stacked in the envelope to evaluate the potential of reconstructing folded letters</p> <p>-vector network analyser (VNA, Rohde & Schwarz ZVA 24) combined with frequency extenders (Rohde & Schwarz ZVA-Z325) for the range of 220 GHz – 325 GHz</p>	concentration are essential for the feasibility of the proposed technique.	
2022	Lei Q. et al.	Comparative Study on an Old Hand-Bound Book of the XIXth Century using Infrared, Terahertz and Air-Coupled Ultrasonic Non-invasive Inspection for Artworks	<p>- children's ancient book, published in Paris, France</p> <p>- detection of possible damages and defects, as well as the evaluation of sub-surface features by trying to understand the execution phase of the time</p>	<p>- the pump wavelength was centered at 1550 nm, while the repetition rate was set at 100 MHz. The system had a 15 GHz frequency resolution</p>	<p>- THz techniques were able to retrieve information concerning materials composing the book cover and its thickness. THz technique can be used to analyze absorption coefficients related to materials as well as refractive indexes linked to thickness</p>	- evaluation of damages and defects of ancient book
2022	Niijima S. et al.	Estimation of Firing Temperatures of Ancient Ceramics	<p>- ancient Arita porcelain and Banko pottery shards</p> <p>- research a new method to accurately estimate the firing temperatures of ancient ceramic shards excavated from archaeological sites</p>	<p>- The estimation method is divided into two paths that depend upon the availability of raw materials used at the time that the ancient ceramics were produced: 1) If those raw materials were available, standard specimens were prepared from them. 2) If the raw materials used at the time of manufacture</p>	<p>- The firing temperature of the ancient Arita porcelain shard was estimated as $1241^{\circ}\text{C} \pm 3^{\circ}\text{C}$ using the refractive index in the THz region. The firing temperature of the ancient Banko pottery shard was estimated as $1141^{\circ}\text{C} \pm 1^{\circ}\text{C}$</p>	- study of ancient ceramics

				were unavailable, based on the chemical composition of the ancient ceramic shards, standard specimens were prepared by reproducing the ancient ceramics using currently available raw material		
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