



SuPerStAr



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Unit objectives

- Coordination of the project (**WP1**)
- Set-up and application of innovative micro-invasive analytical methods (**WP3**)
- Integration of the analytical methods in a protocol targeted to the characterization of paint and coating materials, to the control of conservation treatments, and to the long-term monitoring of the state of conservation (**WP3**)
- Responsibility for the transfer of knowledge, dissemination and communication activities (**WP6**)



Facilities

- Gas chromatograph - mass spectrometry (GC-MS)
- Analytical pyrolysis – gas chromatography - mass spectrometry (Py-GC-MS) with micro UV-irradiator system
- HPLC equipped with diode-array detector (DAD)
- High-performance liquid chromatography (HPLC) coupled through an electrospray source with a tandem quadrupole-time-of-flight (ESI-Q-ToF)
- Matrix assisted laser desorption ionization - mass spectrometry (MALDI-MS)
- Evolved gas analysis coupled with mass spectrometry (EGA-MS)
- Thermogravimetric analyser (TG) combined with FT-IR
- Differential Scanning Calorimeter (DSC)

Implementation of tools to obtain information on degradation phenomena of modern paint formulations using a minimum amount of sample, evaluating thermal properties and structural changes, highlighting oxidation, cross-linking or chain scission phenomena, or the formation of low molecular weight products

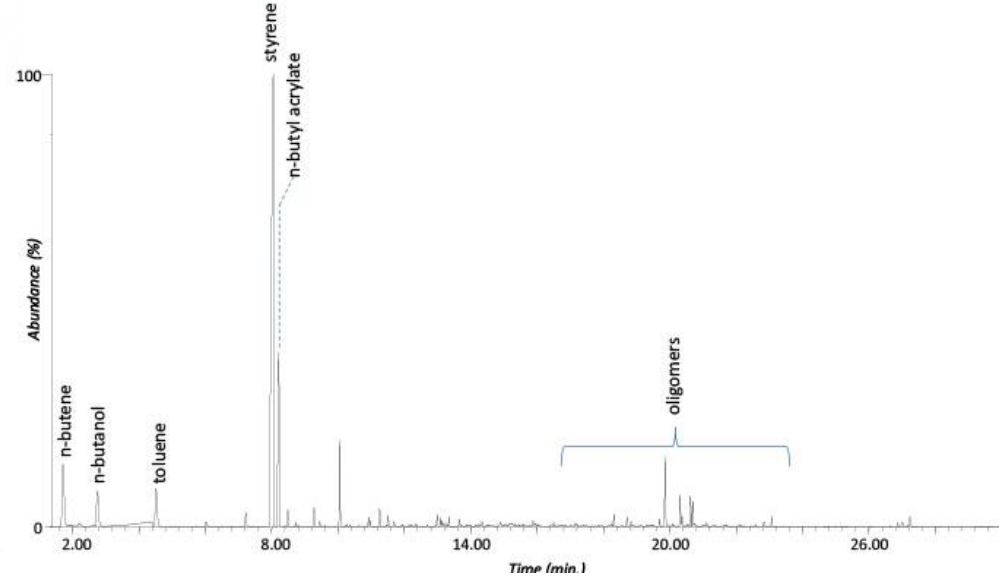
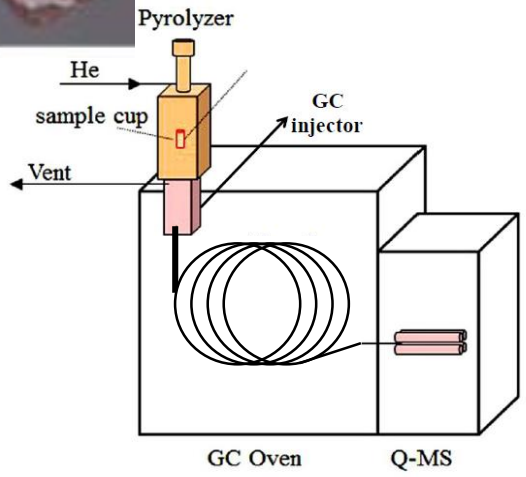
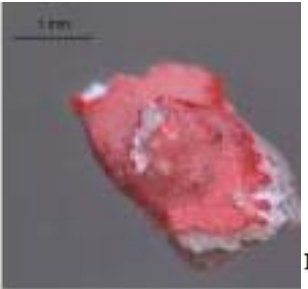


Analytical pyrolysis – gas chromatography - mass spectrometry (Py-GC-MS) with micro UV-irradiator system

<https://cisup.unipi.it/labs/multi-shot-pyrolyzer-gc-ms/>



K. Haring, Tuttomondo (Pisa), 1989



✓ Paint binder identification

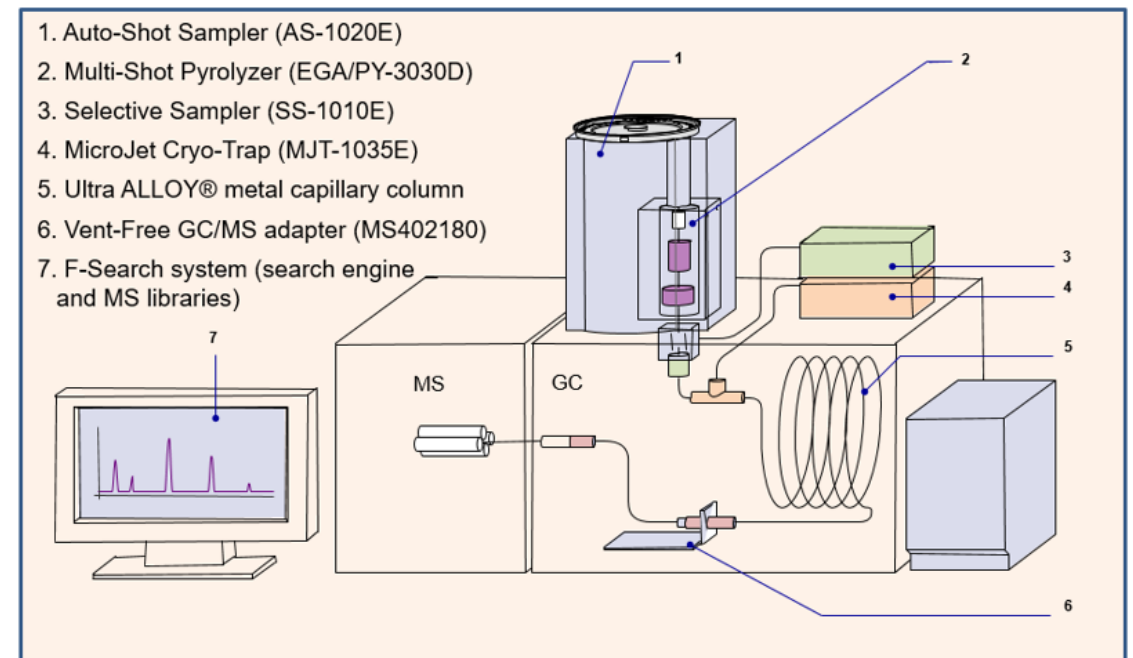
Analytical pyrolysis – gas chromatography - mass spectrometry (Py-GC-MS) with micro UV-irradiator system

(<https://cisup.unipi.it/labs/multi-shot-pyrolyzer-gc-ms/>)

- + Cryo trap
- + Online UV irradiator
- + Quick gas flow switcher



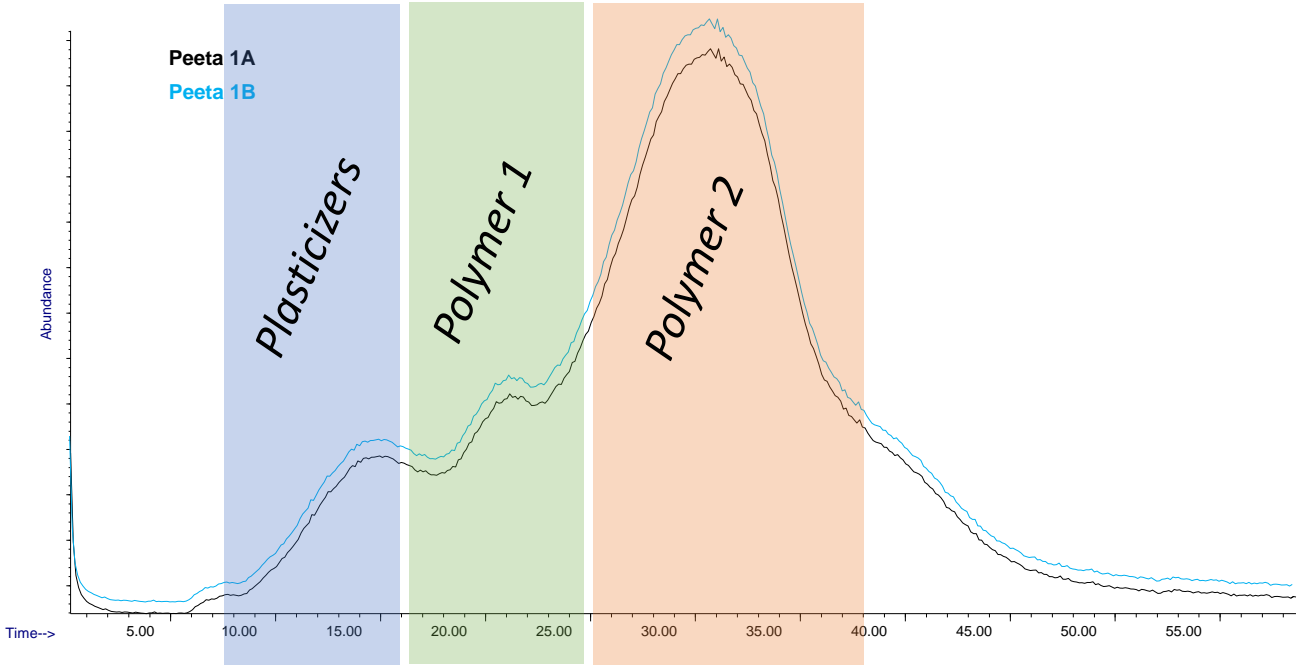
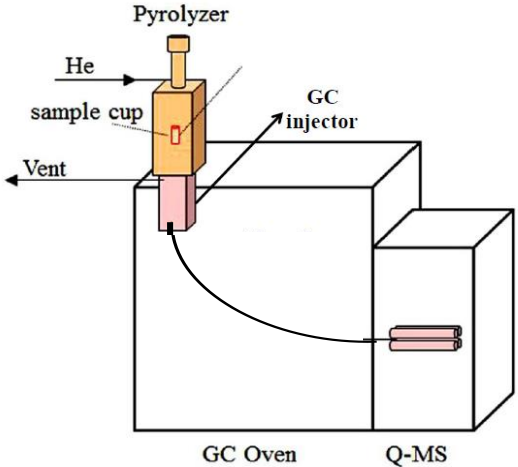
- ✓ **Chemical information on components with different molecular weights in the same micro-sample.**
- ✓ **Real-time identification of the degradation products that are released during photo-oxidation.**



Evolved gas analysis – mass spectrometry (EGA-MS)



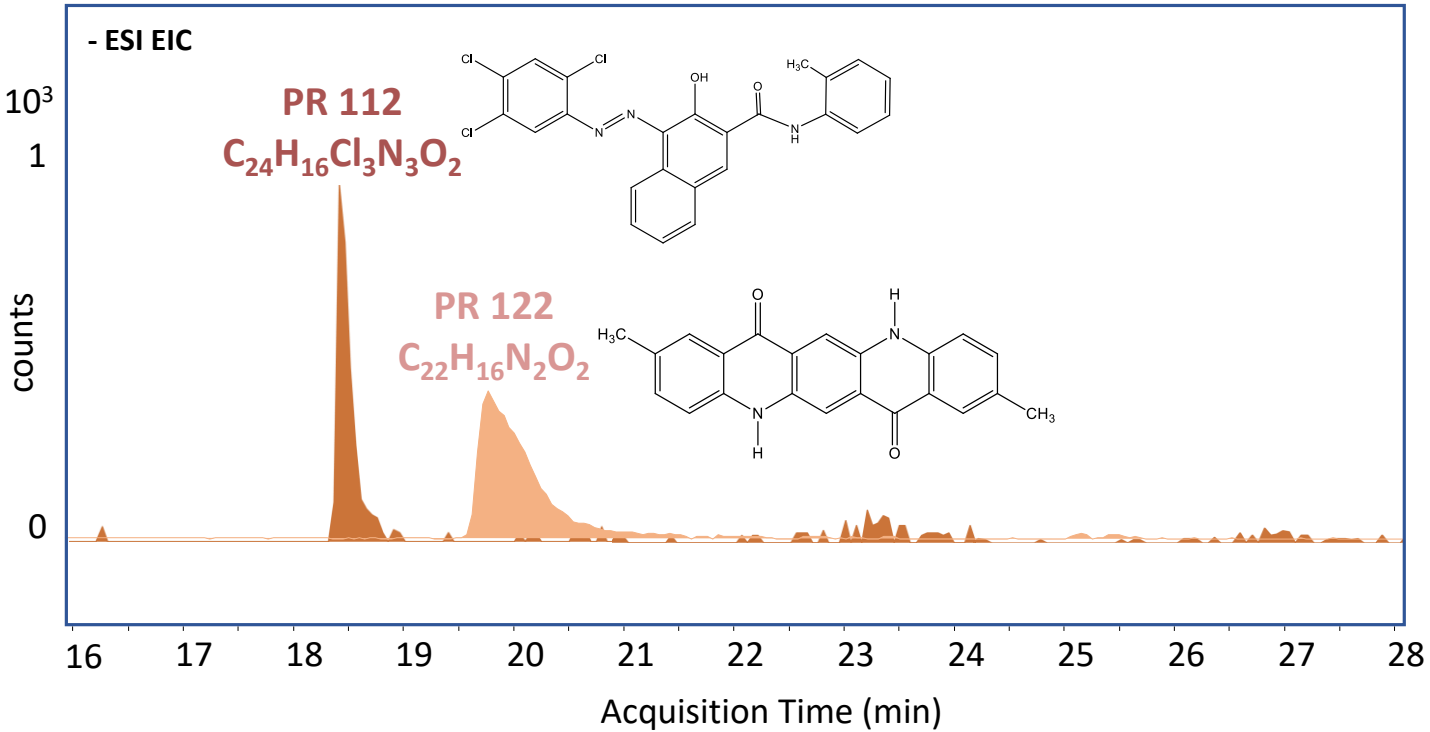
✓ Investigation of components with different molecular weight, volatility and thermal proprieties



High-performance liquid chromatography with quadrupole-time-of-flight detector (HPLC-ESI-Q-ToF)



Blu, Unk. (Rome), 2014



✓ Dyes identification



Matrix assisted laser desorption ionization - mass spectrometry (MALDI-MS)

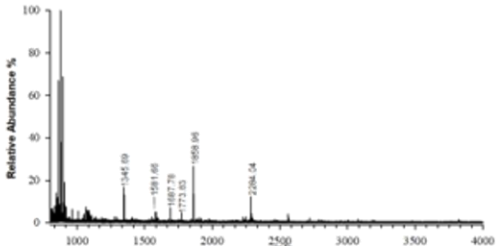


Mass Spectrometry

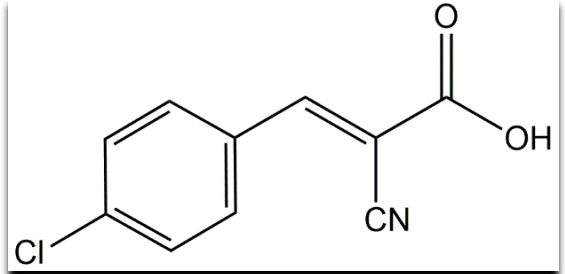
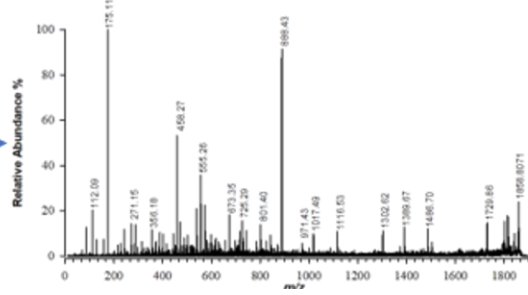


MALDI TOF-TOF

MALDI MS



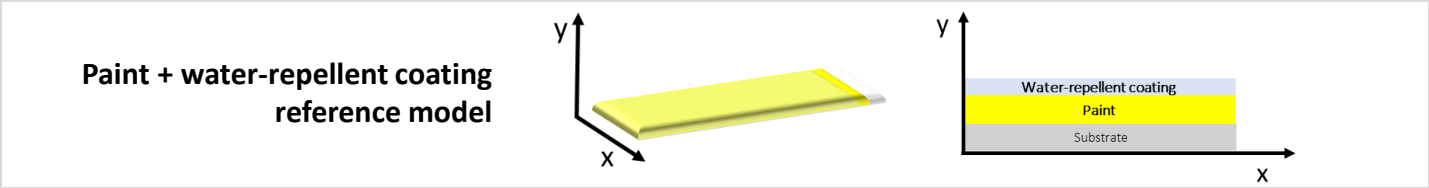
MALDI MS/MS



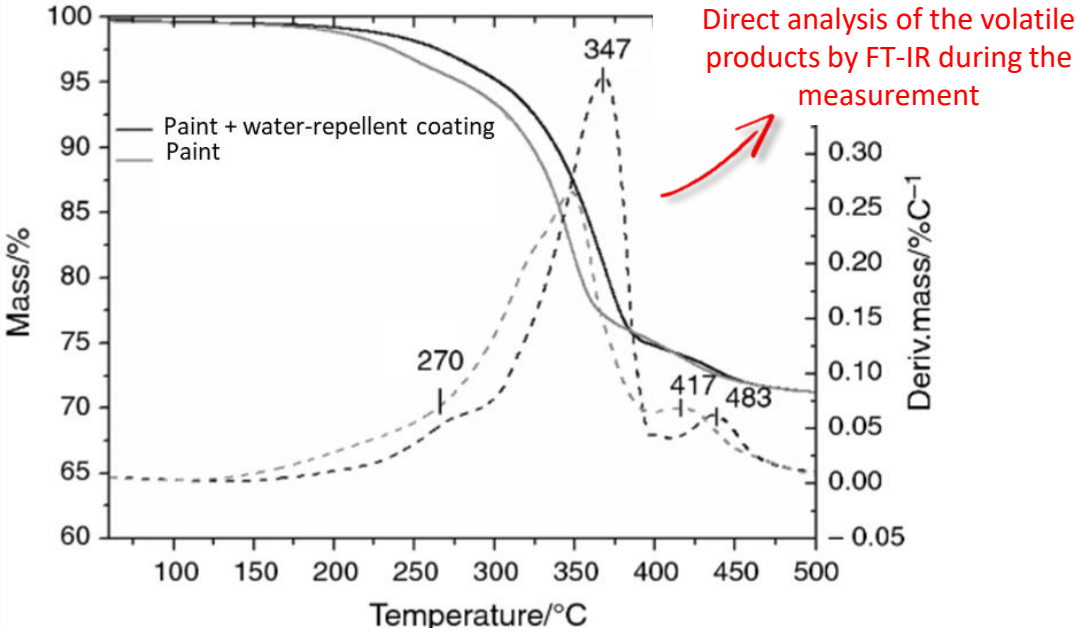
α-cyano-4-hydroxycinnamic acid

✓ Binder identification

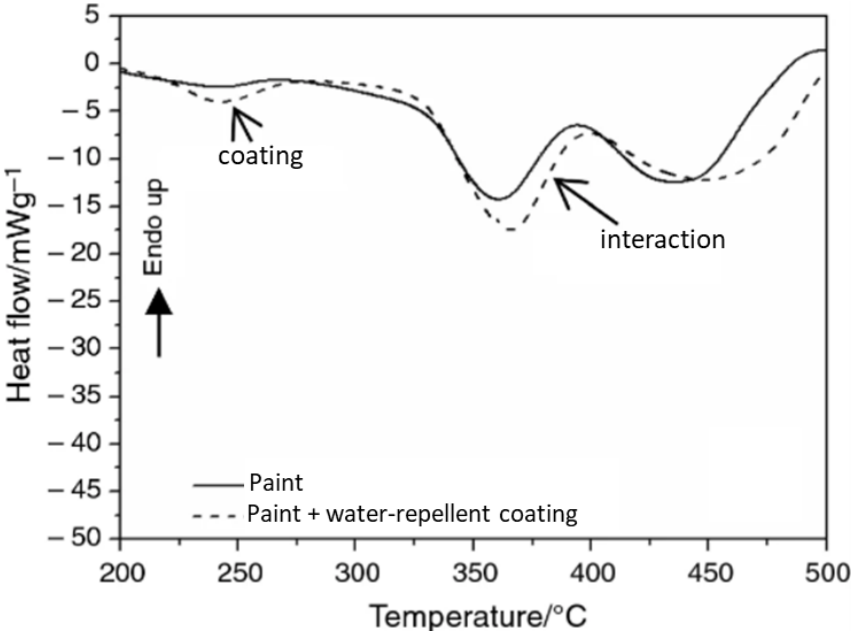
Thermoanalytical techniques



Thermogravimetry coupled with FTIR (TG-IR)



Differential scanning calorimetry (DSC)



✓ **Characterisation of the thermal behaviour and investigation of the interaction between paint and coating**

Spepi et al, *Chemico-physical characterization and evaluation of coating properties of two commercial organosilicons*, *J Therm Anal* 138 (2019) 3277



Publications

- La Nasa J, Orsini S, Degano I, Rava A, Modugno F, Colombini MP, A chemical study of organic materials in three murals by Keith Haring: A comparison of painting techniques, *Microchem J* 124 (2016) 940. <https://doi.org/10.1016/j.microc.2015.06.003>
- La Nasa J, Campanella B, Sabatini F, Rava A, Shank W, Lucero-Gomez P, De Luca D, Legaioli S, Palleschi V, Colombini MP, Degano I, Modugno F, 60 years of street art: a comparative study of the artists' materials through spectroscopic and mass spectrometric approaches, *J Cult Herit* 48 (2021) 129. <https://doi.org/10.1016/j.culher.2020.11.016>
- Degano I., Modugno F., Bonaucce I., Ribechini E., Colombini M P, Bonaduce I. Recent Advances in Analytical Pyrolysis to Investigate Organic Materials in Heritage Science. *Angewandte Chemie. International Edition*, 57 (2018) 7313. <https://doi.org/10.1002/anie.201713404>
- La Nasa J., Degano I., Modugno F., Colombini M.P. Alkyd paints in art: Characterization using integrated mass spectrometry. *Analytica Chimica Acta*, 797 (2013) 64. <https://doi.org/10.1016/j.aca.2013.08.021>
- Calvano, C.D., Rigante, E.C.L., Cataldi, T.R.I., Sabbatini, L. In Situ Hydrogel Extraction with Dual-Enzyme Digestion of Proteinaceous Binders: The Key for Reliable Mass Spectrometry Investigations of Artworks. *Analytical Chemistry* 92 (2020), 15, 10257 <https://doi.org/10.1021/acs.analchem.0c01898>
- Calvano, C.D., Rigante, E., Picca, R.A., Cataldi, T.R.I., Sabbatini, L. An easily transferable protocol for in-situ quasi-non-invasive analysis of protein binders in works of art. (202) *Talanta*, 215, 120882 <https://doi.org/10.1016/j.talanta.2020.120882>
- Spepi, A., Pizzimenti, S., Duce, C. Vozzi G., De Maria C., Tinè M.R. Chemo-physical characterization and evaluation of coating properties of two commercial organosilicons. *J Therm Anal Calorim* 138, 3277–3285 (2019) <https://doi.org/10.1007/s10973-019-08830-4>



Previous Projects

- **2020-2022: StAr project: Development of Storage and assessment methods suited for organic Archaeological artefacts.** Joint Programming Initiative on Cultural Heritage and Global Change (<http://jpi-ch.eu/>)
- **2013 - in progress: IPERIONCH project.** Work Programme 2014-2015 for European research infrastructures. Funded by the Italian Ministry of Education and Research (MIUR) in the context of call Horizon 2020
- **2018-2020: MS-MOMus regional project: Spettrometria di Massa SIFT portatile e identificazione di Materiali Organici in ambiente Museale** founded by Regione Toscana in the context of POR FSE 2014-2020 Asse A
- **2018-2020: “Advanced analytical pyrolysis to study polymers in renewable energy, environment, cultural heritage”** founded by the University of Pisa in the context of PRA 2018 (project's code PRA_2018_26).
- **2015-2018: Cleaning of modern oil paint (CMOP)** [Web](#) - Heritage Plus Joint Call [Web](#)
- **2017-2019: Saving Oseberg Phase II - From Lab to Pilot,** funded by the Norwegian State and the University of Oslo ([WebSite](#)).
- **2016: “Analytical chemistry applications for deepening the knowledge of materials and techniques in modern and contemporary art”** founded by the University of Pisa in the context of PRA 2016 (project's code PRA_2016_13).

