Università di Pisa

Dipartimento di Chimica e Chimica Industriale

Coordinatrice di unità

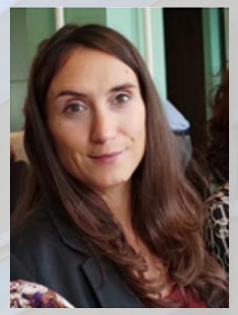
Prof. Ilaria Degano

ilaria.degano@unipi.it

UniPi Research Unit

Università di Pisa
Dipartimento di Chimica e Chimica Industriale

Prof. Francesca Modugno
francesca.modugno@unipi.it



Prof. Ilaria Degano
ilaria.degano@unipi.it

Dr. Jacopo La Nasa
jacopo.lanasa@for.unipi.it

CHEMICAL SCIENCE FOR THE SAFEGUARD OF CULTURAL HERITAGE GROUP

https://scibec.dcci.unipi.it/

COORDINATION OF WP3

wp3 will focus on obtaining the highest level of qualitative and quantitative information on the reference materials (also subjected to artificial ageing) by conventional and robust methods. In WP3 bulk microanalytical analysis techniques will be optimized to provide quantitative data of the reference plastic composition for the validation and the calibration of the NI approach developed in WP4. Furthermore, a workflow will be implemented to widen the range of information on composition obtainable using a minimum amount of material in case of micro-sample availability.

WP3
CHEMICAL (MICRO)-DESTRUCTIVE METHODS

optimization of bulk analysis techniques

↓

quantitative data on the reference plastic composition

↓

validation and calibration of the NI approach (WP4)

TASK 3.1 Characterization of polymers and additives by thermal analytical techniques and chromatography-mass spectrometry (Py-GC-MS, EGA-MS, TGA, DSC, TGA-GC-MS)

TASK 3.2 Characterization of polymers and pigments by micro-destructive spectroscopic methods, Solid and liquid state NMR, vibrational spectroscopies (Raman and FT-IR)

TASK 3.1 Characterization of polymers and additives by thermal analytical techniques and chromatography-mass spectrometry

FACILITIES

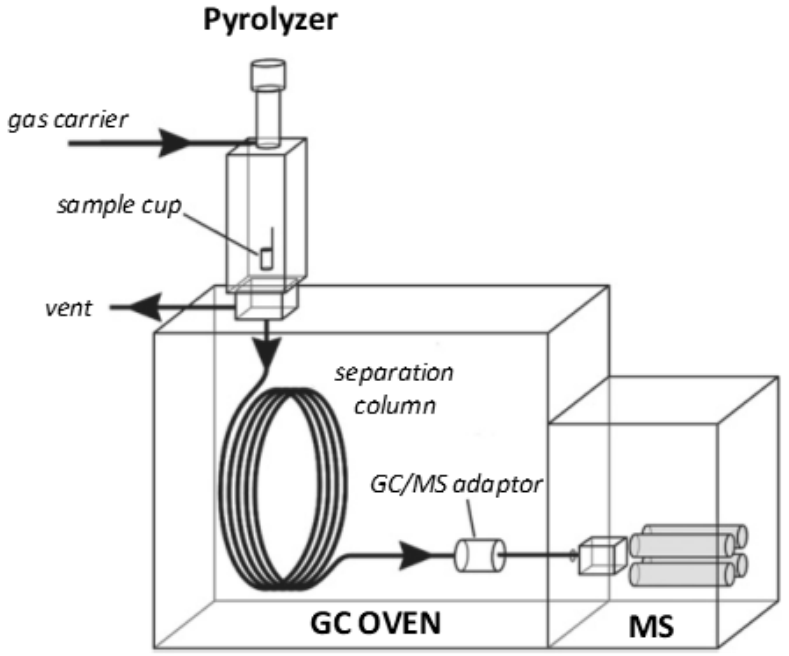
- Gas chromatograph - mass spectrometry (GC-MS)
- Analytical pyrolysis – gas chromatography - mass spectrometry (Py-GC-MS) with micro UV-irradiator system
- Evolved gas analysis coupled with mass spectrometry (EGA-MS)
- HPLC equipped with diode-array detector (DAD) or coupled through an electrospray source with a tandem quadrupole-time-of-flight (ESI-Q-ToF)
- Thermogravimetric analysis (TG) combined with FT-IR
- Differential Scanning Calorimetry (DSC)

Implementation of tools to obtain information on degradation phenomena of 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, loss of additives, such as phthalate plasticizers, as well as to define the degree of crosslinking or depolymerization of reference materials subjected to artificial ageing

MSPy-GC-MS: Multi Shot Pyrolysis – Gas Chromatography – Mass Spectrometry

Combination of thermal separation of different fractions and separation of the products from different components

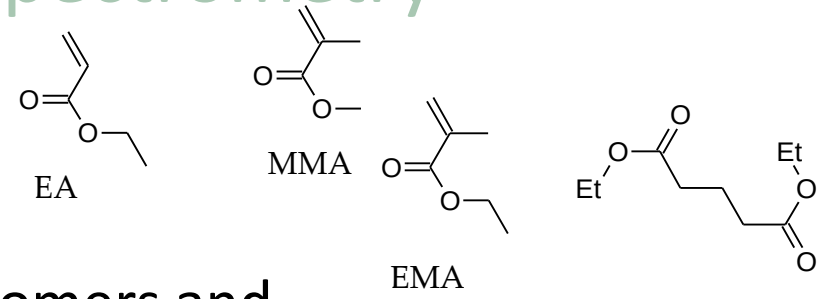
- Mutliple pyrolysis shots at different temperatures
- Chromatographic separation of the pyrolysis products produced at each pyrolysis shot
- Separate GC/MS investigation of different fractions of the sample



Multi-Shot Pyrolyzer® EGA/PY-3030D - Frontier Laboratories

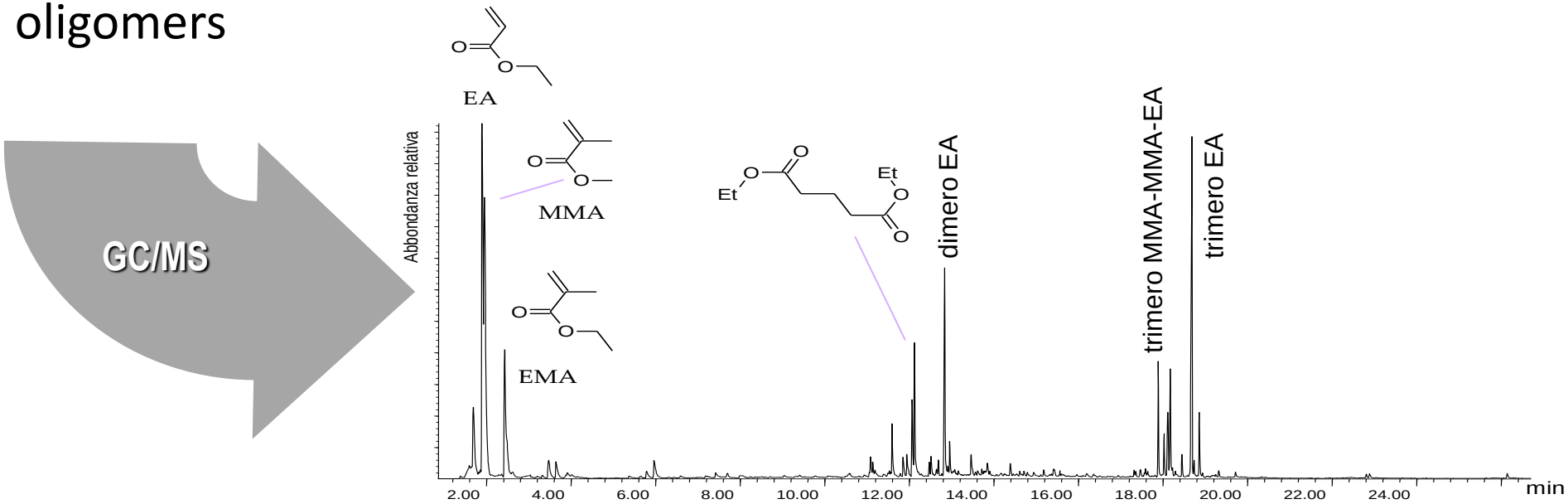
I. Degano, F. Modugno, I. Bonaduce, E. Ribechini, M.P. Colombini, Recent advances in analytical pyrolysis to investigate organic materials in heritage science, Angewandte Chemie -International Edition 57 (2018) 7313-7323

MSPy-GC-MS: Multi Shot Pyrolysis – Gas Chromatography – Mass Spectrometry



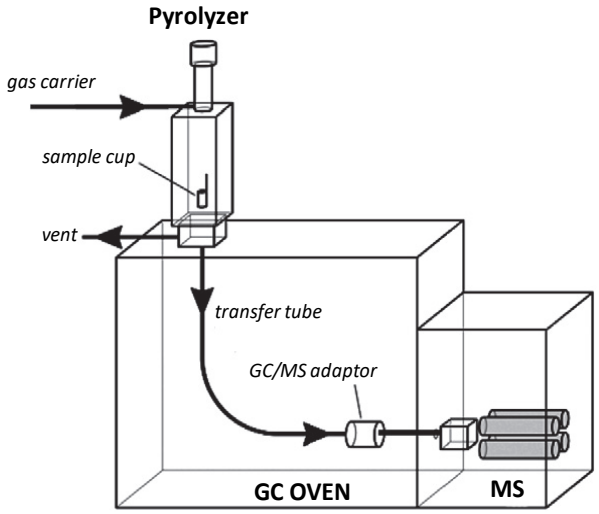
GC/MS separation and identification of specific monomers ➡ information on formulation

Monomers and oligomers

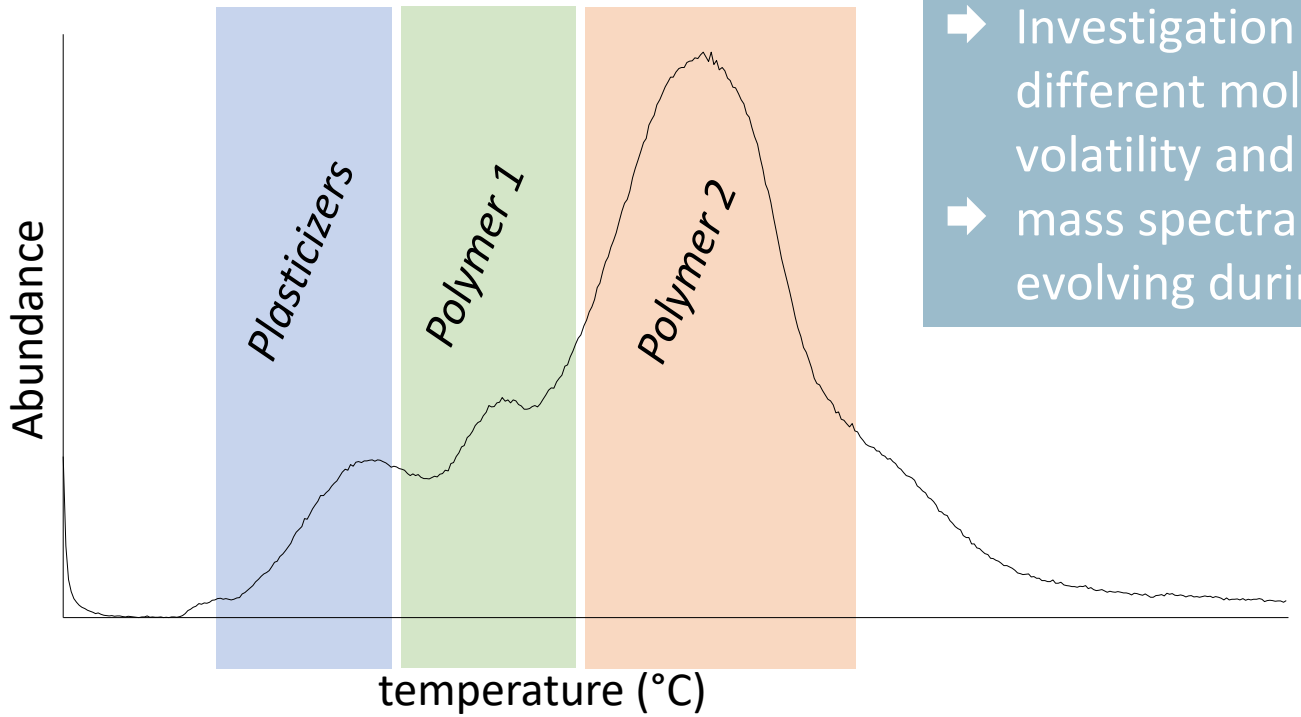


EGA-MS: Evolved gas analysis – mass spectrometry

EGA-MS: thermal separation of different fractions



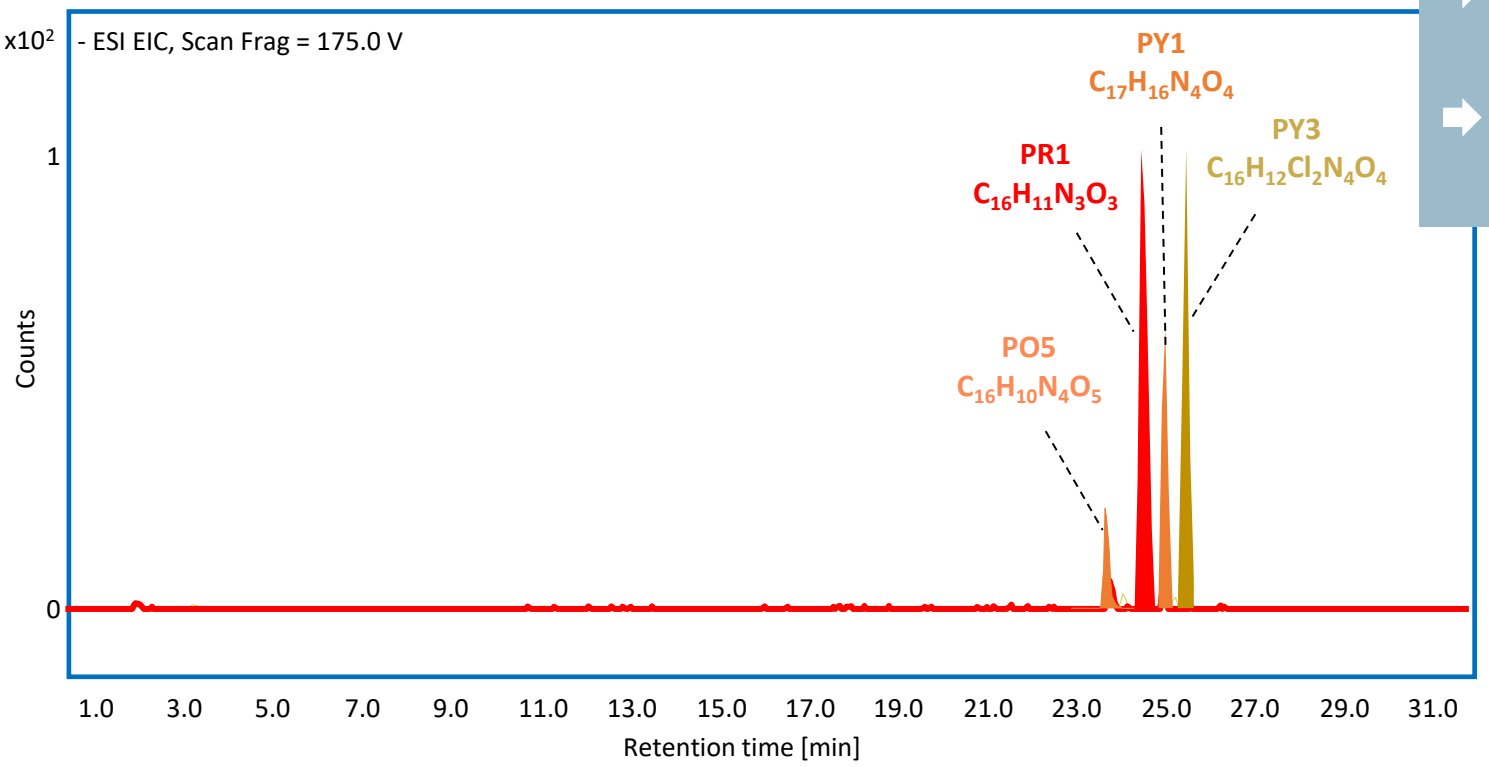
- No chromatographic separation
- MS monitoring during heating 50-800 °C (10 °C/min)



- thermal profile of the sample
- Investigation of components with different molecular weight, volatility and thermal proprieties
- mass spectra of the components evolving during heating

Liquid chromatography for the analysis of organic pigments and dyes

<100 µg sample

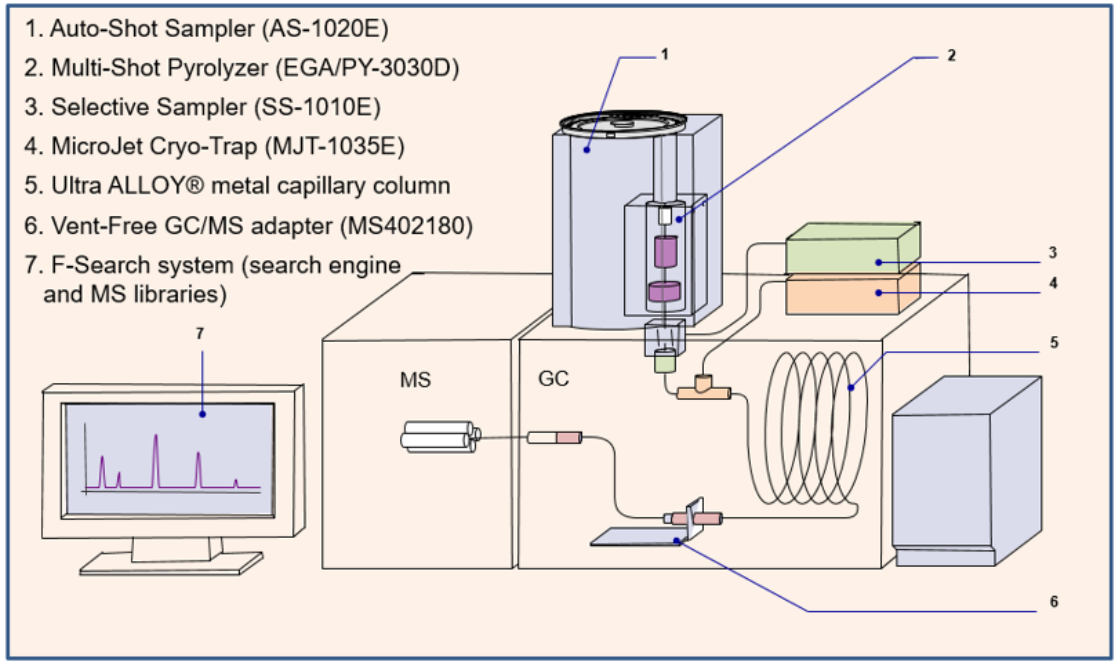


- Profile of dye components
- Identification of degradation products

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

Innovative approach

- ✓ Real-time identification of the degradation products released during photo-oxidation



Degano et al, Recent Advances in Analytical Pyrolysis to Investigate Organic Materials in Heritage Science, Angew.Chem., 2018,57, 7313

PUBLICATIONS

- Degano I., Modugno F., Bonauce I., Ribechini E., Colombini M P, Bonaduce I. (2018) Recent Advances in Analytical Pyrolysis to Investigate Organic Materials in Heritage Science. *Angewandte Chemie. International Edition*, 57, 7313.
- Sabatini F., La Nasa J., Guerrini C., Modugno F., Bonadio S., Ursino F., Tosini I., Colombini M. P., Degano I. (2021) On the set of Fellini's movies: Investigating and preserving multi-material stage costumes exploiting spectroscopic and mass spectrometric techniques. *Applied Sciences*, 11, 2954.
- La Nasa J., Biale G., Sabatini F., Degano I., Colombini M. P., Modugno F. (2019) Synthetic materials in art: a new comprehensive approach for the characterization of multi-material artworks by analytical pyrolysis. *Heritage Science*, 7, 8.
- La Nasa J., Biale G., Ferriani B., Colombini M.P., Modugno F. (2018). A pyrolysis approach for characterizing and assessing degradation of polyurethane foam in cultural heritage objects. *Journal of Analytical and Applied Pyrolysis*, 134, 562.
- Zuena, M., Legnaioli, S., Campanella, B., Modugno F., La Nasa, J., Nodari, L. (2020) Landing on the moon 50 years later: A multi-analytical investigation on Superficie Lunare (1969) by Giulio Turcato. *Microchemical Journal*, 157, 105045.
- La Nasa J., Biale G., Ferriani B., Trevisan, R., Colombini M.P., Modugno F. (2020) Plastics in heritage science: Analytical pyrolysis techniques applied to objects of design. *Molecules*, 25(7), 25071705.
- Sabatini F., Pizzimenti S., Bargagli I., Degano I., Duce C., Cartechini L., Modugno F., Rosi F., A Thermal Analytical Study of LEGO® Bricks for Investigating Light-Stability of ABS. *Polymers*, 15 (2023).
- Costantini R., Nodari L., La Nasa J., Modugno F., Bonasera L., Rago S., Zoleo A., Legnaioli S., and Tomasin P. (2023) Preserving the Ephemeral: A Micro-Invasive Study on a Set of Polyurethane Scenic Objects from the 1960s and 1970s. *Polymers*, 15, 2111.

PROJECTS

- **2021-2024: PRIN-2020 SUPERSTAR**, Sustainable Preservation Strategies for Street Art (https://prin2020superstar.dcci.unipi.it/)
- **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/)
- **2013-2019**: **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).