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

2023 activity report

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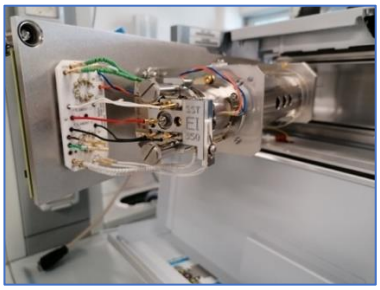
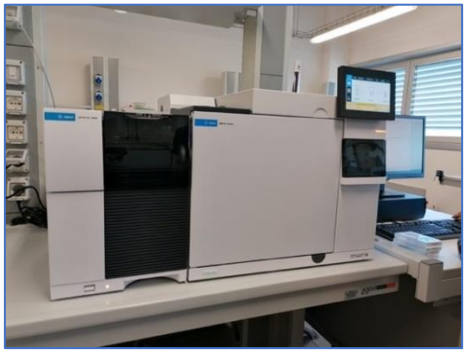
Laboratory web page: https://cisup.unipi.it/labs/multi-shot-pyrolyzer-gc-ms/






1. Price list

The price list is published on the CISUP website with the instructions for quote requests (Table 1) and has not changed since 2021.

Table 1: Price list 2023, VAT excluded.

Type of experiment	UNIPI	Research institutes	Privates
Price for routine analyses (including both the analysis time and the time needed for instrument setup)	45 €/h	60 €/h	100 €/h
Sample preparation (milling, high precision weight of the sample, derivatization, observation under the microscope and photographic documentation of sampling)	20 €/h	25 €/h	40 €/h
Interpretation of chromatograms and spectra, data analyses and data treatment, writing of scientific report	60 €/h	60 €/h	60 €/h
Teaching packages for master students (supervised by experts)	25 €/h		

All fares refer to standard/routine applications and include the presence and support of authorized experts. For standard applications to a relevant number of samples or hours, special fares can be applied upon discussion with the Scientific Committee and request of a quote.
The pricing for nonstandard applications (e.g. development of novel analytical procedures, application on non-routine samples) will be discussed for each individual case, including research projects, collaborations, agreements with research institutes. Interested users are invited to contact the Scientific Committee to discuss the specific case study and to request a quote.

2. Hours worked

Table 2 shows a breakdown of the hours worked by the Py-GC/MS instrument during 2023. In 2023, the laboratory worked for 1219.5 hours (maintenance hours excluded). The income is ~28.5 k€.

Table 2: Py-GC/MS usage in 2023

User type	Hours	%
UNIPI (projects)	355.5	29
UNIPI (single users)	119.5	10
UNIPI education	574.0	47
External/private	170.5	14
Total	1219.5	100

4. User statistics

The users of the instrument over 2023 include research groups from departments of the Università di Pisa, considering activities carried out for single analyses, more complex projects or PhD students' research (Dipartimento di Chimica e Chimica Industriale; Dipartimento di Scienze Agrarie, Alimentari e Agro-ambientali), in some cases in the framework of collaborations with Italian (Università di Bologna, Università di Torino, Università di Bari, Politecnico di Milano, CNR-SCITEC Perugia, Università Cattolica del Sacro Cuore , DISTAS - Department for Sustainable Food Process) and foreign universities and Research Institutions (University of Plymouth, UK; Univerity of York; University of Aalborg, Denmark; Marine Geosciences Unit IFREMER, Centre de Brest, France; Catalan Institute for Water Research ICRA, Girona) accounting for more than 85% of the total workload. The remaining 15% includes services for privates (in some cases in the framework of collaborations). The statistics show that for most of the workload was related to projects led by researchers of the Dipartimento di Chimica e Chimica Industriale.

Funded projects and collaborations:

- NanoFun, Nanocellulose-based membranes for for water purification with enhanced efficiency by chemical functionalization. Bilateral project (2023-2025) involving the Department of Chemistry and Industrial Chemistry of the University of Pisa (Italy) and the Council of Scientific and Industrial Research of Pretoria (South Africa). CISUP: Characterization of functionalized nanocellulose membranes by analytical pyrolysis;
- StAr project - *Development of Storage and assessment methods suited for organic Archaeological artefacts* - within the framework of Joint Programming Initiative on Cultural Heritage and Global Change (JPI-CH, http://jpi-ch.eu/) Conservation, Protection and Use (2020-2022);
- NAMC *North Atlantic Microplastic Centre, Pillar 1 – Sensitive Analytical Methods*, Research task: "Systematic assessment of matrix interference on the quali-quantitation of microplastics in environmental samples by Py-GC-MS" (2021-2022);
- JPI-Oceans HOTMIC project *Horizontal and vertical oceanic distribution, transport, and impact of microplastics* (2020-2023);
- PRIN2020 project SUPERSTAR *Sustainable Preservation Strategies For Street Art* (2022-2024);
- MOXY: G*reen Atmospheric Plasma Generated Monoatomic OXYgen Technology for Restoration of the Works of Art* Coordinated by Ghent University with a Horizon Europe grant in the call Green Technologies and Materials for Cultural Heritage: HORIZON-CL2-2021-HERITAGE-01-01 (grant agreement ID: 101061336) (2022-2026);
- ARIAH: *Chemical speciation of a Revolution in art history*, HORIZON TMA MSCA 2021-PF-01-01- Postdoctoral Fellowships (2022-2025);
- Collaboration with INAIL Italian Workers' Compensation Authority (INAIL), Rome, Italy;
- Università di Pisa Research project PRA 2020 "Microwave assisted approaches for heritage science, environment, and energy" (2022-2024).

- PNRR Project “NEST - Network 4 Energy Sustainable Transition” (2022-2025) funded in the framework of the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 funded from the European Union - NextGenerationEU.
- PRIN2022 Project Perspective *PolymEr Research Studies for PreventivE Conservation Through non invasIVe analytical strategiEs* (2023-2025)
- PRIN2022 PNRR Project DIORAMA “A deep dive into the study of microplastics in aqueous matrices (2023-2025)
- PNRR-PRIN2022 project “ArtDECOW – Natural Materials Development from Collagen-Based Wastes” funded in the framework of the National Recovery and Resilience Plan (NRRP)

PhD students:

- Tommaso Nacci (DCCI – DSCM, 36th cycle), thesis title “Investigating the potential of analytical pyrolysis coupled to mass spectrometry in the study of particles derived from textile fibers and tire wear in the environment”;
- Adele Ferretti (DCCI – DSCM, 37th cycle), thesis title “Multi-analytical approach for the identification and characterization of historical and modern inks”;
- Giulia Caroti, (DCCI – DSCM, 37th cycle), thesis title “The chemistry of oil/protein mixtures as paint binders”;
- Greta Biale (DCCI – DSCM, 37th cycle), thesis title “Study of the fate and interactions of microplastics and nanoplastics in the environment”;
- Irene Bertelli (Dottorato Nazionale in Heritage Science, 38th cycle), thesis title “Multi-component archaeological adhesives: an innovative analytical approach to study chemical interactions and natural ageing degradation”;
- Leonardo Barlucchi (DCCI – DSCM, 39th cycle), thesis title “Study of airborne microplastics and environmental pollutants”
- Cecilia Campi (DCCI – DSCM, 39th cycle), thesis title “Development of analytical tools for assessing the impact of conservation treatments on textiles”;
- Kirill Shumikhin (Dottorato Nazionale in Heritage Science, 39th cycle) PhD project focused on the evaluation of the effect of atomic oxygen cleaning on oil painting
- Vanessa Matteucci, (DCCI-DSCM, 38th cycle) “Controlled thermolysis of recycled polymeric materials for innovative and sustainable bituminous compounds for application in resilient low-noise asphalts and "warm asphalt" with high content of reclaimed asphalt pavement”
- Deborah Roversi (University of York, MSCA-ITN PhD student), thesis on “Examining charcoal and wooden artefacts in prehistoric archaeological assemblages”

Visiting scholars interested in the Py-GC/MS system:

- Hawa Diarra, National School of Engineering Abderhamane Baba TOURE (ENI-ABT), Bamako, Mali, CRETUS, EcoPast (GI-1553), Characterization study through analytical pyrolysis for the valorization of end-of-life tires.

- Mohamed Traore, Facultade de Bioloxía, Universidade de Santiago de Compostela, Spain, Chemometric approaches in wood chemistry and archaeometric applications in archaeological wood.
- Lúcia Helena Santos, Institut Català de Recerca de l'Aigua ICRA / Catalan Institute for Water Research ICRA, PyGCMS analysis of microplastics in water samples

5. Research products

The CISUP Py-GC/MS was used in several national and international research projects, theses and PhD research projects. The activities were mainly related to the field of environmental science, marine science, innovative materials for biomedical use, lignocellulosic materials and biomasses, and cultural heritage objects. This led to several publication in international journals as:

List of publications

1. Braccini S, Chen C-B, Łucejko JJ, Barsotti F, Ferrario C, Chen G-Q, et al. Additive manufacturing of wet-spun chitosan/hyaluronic acid scaffolds for biomedical applications. Carbohydr Polym. 2024;329:121788.
2. Della Latta, E., Sabatini, F., Micheletti, C., Carlotti, M., Martini, F., Nardelli, F., Battisti, A., Degano, I., Geppi, M., Pucci*, A., Pohl, S., Kickelbick, G., Performant flexible luminescent solar concentrators of phenylpolysiloxanes crosslinked with perylene bisimide fluorophores. Polymer Chemistry, 2023, 14, 1602-1612.
3. De Falco, F., Nacci, T., Durndell, L., Thompson, R.C., Degano, I., Modugno, F., A thermoanalytical insight into the composition of biodegradable polymers and commercial products by EGA-MS and Py-GC-MS. Journal of Analytical and Applied Pyrolysis, 2023, 171, 105937.
4. Sabatini F, La Nasa J, Degano I, Campanella B, Legnaioli S, Saccani I, Modugno F. Fluorescent Paints in Contemporary Murals: A Case Study. Heritage 2023, 6, 5689-5699.
5. 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 2023, 15.
6. Ferretti, A., Degano, I., Legnaioli, S., Campanella, B., Sainati, A., Colombini, M.P., Shedding light on the composition and degradation mechanism of dyes in historical ink's collection (19th-20th century). Dyes and Pigments, 2023, 220, 111672.
7. La Nasa J, Ceccarini A, Ducoli R, Manariti A, Lucejko JJ, Degano I, et al. The role of early synthetic materials degradation in the downfall of the Ansaldo A.1, an Italian World War I biplane fighter. Scientific Reports 2023, 13, 12170.
8. Corti A, La Nasa J, Biale G, Ceccarini A, Manariti A, Petri F, Modugno F, Castelvetro V, Microplastic pollution in the sediments of interconnected lakebed, seabed, and seashore aquatic environments: polymer-specific total mass through the multianalytical "PISA" procedure", Analytical and Bioanalytical Chemistry, 2023, 415, 2921
9. La Nasa J, Biale G, Fiorentini L, Ceccarini A, Carnaroglio D, Mattonai M, Modugno F, Characterization and quantification of microplastics and organic pollutants in mussels by

microwave-assisted sample preparation and analytical pyrolysis, Environmental Science: Advances, 2024, 3, 76
10. Mattonai M, Andrei L, Vîrgolici M, Ribechini E, Low-and high-molecular weight fractions of geological ambers detected by evolved gas analysis-mass spectrometry, Journal of Analytical and Applied Pyrolysis 2023, 172, 105994.
11. Bertelli I, Mattonai M, La Nasa J, Ribechini E, Study of thermal behavior and molecular composition of mixtures of resinous materials and beeswax found as adhesives in archaeological finds, Journal of Analytical and Applied Pyrolysis 2023, 171, 105936.
12. Costantini, R., Nodari, L., La Nasa, J., Modugno F.,Bonasera L-, Rago S., Zoleo A., Legnaioli, S., Tomasin, P., Preserving the Ephemeral: A Micro-Invasive Study on a Set of Polyurethane Scenic Objects from the 1960s and 1970s, Polymers, 2023, 15(9), 2111

Theses

Bachelor theses (Corso di laurea triennale in Chimica)

- Stefano Mazzoncini, "Studio dell'invecchiamento di salviette umidificate monouso tramite tecniche di pirolisi analitica, cromatografia e spettrometria di massa"
- Irene Porciani "Molecular characterization of condensed tannins of *Xanthorrhoea* resins"
- Marta Domenici "Energia delle biomasse: il potenziale delle foglie autunnali come fonte di energia rinnovabile. Lo studio tramite Py-GC/MS e ICP-OES."
- Elisa Maria Poggetti "Caratterizzazione di materiali pittorici utilizzati in opere di neomuralismo urbano nell'ambito del progetto Superstar"
- Marco Salvatori "Tecniche di pirolisi analitica applicate allo studio di materiali pittorici e di restauro nell'arte urbana".

Master theses (Corso di laurea magistrale in Chimica)

- Sara Bonifazi "Recupero e Valorizzazione degli Scarti di Cuoio attraverso Trattamenti di Idrolisi Chimica"
- Julia Gambetta Vianna "Indagine dei processi di degrado e lisciviazione di fibre e microfibre nell'ambiente"
- Marta Filomena "Metodi sostenibili di estrazione e frazionamento di molecole e sostanze organiche da biomasse di scarto dal settore agricolo, forestale e alimentare"
- Leonardo Barlucchi "Studio del degrado di microplastiche derivanti da biopolimeri"
- Lorenzo Fiorentini "Sviluppo e validazione di metodologie basate su microonde per l'analisi di microplastiche e contaminanti ambientali"
- Alessio Vaselli "Sviluppo e validazione di metodologie basate su microonde per l'analisi di materiali proteici"
- Niccolò Medica "Caratterizzazione multi-analitica di materiali pittorici provenienti da opere di street art"
- Federico Paolino "Metodi analitici strumentali per studiare e caratterizzare il legno fresco e archeologico a fini conservativi"

- Aurora Sainati “Guarnizioni per applicazioni industriali: Messa a punto del metodo e determinazione del contenuto di zolfo”
- Cecilia Campi “Chemical Investigation of Asian Lacquers”
- Riccardo Ducoli “The microstructure and chemistry of paints based on oil and proteins”

6. External services

Analyses were undertaken for private companies and research institutes, such as:

- Avantama AG (Switzerland): characterisation of polymeric thin layers by EGA-MS and Py-GC/MS;
- Dolomia (Italy) for the characterisation of plastic caps and labels on mineral water bottles;
- Institute of Environmental Biotechnology, Boku University, Austria, Study of the polymerization of lignosulfonates by Py-GC/MS and EGA-MS
- A. R. T. & CO. SRL (Italy) for the characterisation of the organic binders in wall paintings
- Enyax (Milano, Italy) for the characterisation of biopolymers
- Esaote (Italy) for the characterisation of materials in probes for medical imaging
- Gucci for the characterisation of raw materials and synthetic polymers used in their production of garments
- Pop2pack (Italy): monitoring of volatiles and solid residues during biodegradation of popcorn-based packaging
- Trinity College of Dublin (Ireland): EGA-MS analysis of polymers for 3D printing applications
- Novamont (Italy): EGA-MS analysis of biodegradable plastic bags
- SRA (Italy): characterisation of polymeric materials

In addition, the system was used as one of the several tools employed for diagnostic campaigns of works of art, in collaboration with renown conservation institutions as the Opificio delle Pietre Dure (Florence, Italy) and Venaria Reale CCR (Venaria, Torino, Italy), or private companies devoted to the analysis of painting materials (as RCArt, Adarte, etc).

7. Teaching activities

The instrumental set-up was employed in the Laboratory course of Analytical Chemistry III (Cod. 193CC), for the hands-on laboratory experience on analytical pyrolysis for the Master Students of the Master Course in Chemistry (Analytical Chemistry Curriculum).