

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

2024 activity report

Alessia Andreotti, Ilaria Bonaduce, Ilaria Degano, Jacopo La Nasa, Jeannette Lucejko, Marco Mattonai, Francesca Modugno, Erika Ribechini

- Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, I-56124 Pisa
- CISUP Centro per la Integrazione della Strumentazione Università di Pisa, Lungarno Pacinotti 42/43, I-56126 Pisa

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

















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 2024. In 2024, the laboratory worked for 832 hours (maintenance hours excluded). The income is \sim 20 k \in .

User type	Hours	%
UNIPI (projects)	246	30
UNIPI (single users)	67	8
UNIPI education	464.5	56
External/private	54.5	7
Total	832	100

Table 2: Py-GC/MS usage in 2024



4. User statistics

The users of the instrument over 2024 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 - Dipartimento di Chimica Ciamician; Università di Torino -Dipartimento di Chimica; Università di Bari - Dipartimento di Chimica; Politecnico di Milano -Dipartimento di Ingegneria dei Materiali,; Università di Venezia Ca' Foscari - Dipartimento di Chimica; CNRSCITEC Perugia; Università Cattolica del Sacro Cuore - DISTAS Department for Sustainable Food Process; Opificio delle Pietre Dure di Firenze; Accademia delle Belle Arti dell'Aquila; Centro di Conservazione e Restauro della Venaria Reale) and foreign Universities and Research Institutions (University of Plymouth, UK; University of York; University of Aalborg, Denmark; Marine Geosciences Unit IFREMER, Centre de Brest, France; Catalan Institute for Water Research ICRA, Girona; Lappeenranta University of Technology, Finland; NILU, Norway; NORCE, Norway; University of Southern Denmark, Department of Biology; Scualo Universitaria dellla Svizzera Italiana, Lugano) accounting for more than 85% of the total workload. The remaining 15% includes services for privates and companies (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 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;
- 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" (2021-2025);
- PRIN2020 project SUPERSTAR Sustainable Preservation Strategies For Street Art (2022-2025);
- MOXY: Green 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);
- LASERING-PH research project on the laser painting interaction: *Sustainable cleaning of Pictorial Heritage: optimization of laser ablation processes,* reference PID2021-123395OA-I00 and funded by the Spanish Government (Ministry of Science and Innovation) through the call Knowledge Generation Projects 2021-TypeA (2022-2025);
- 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_2022_58 "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)
- PRIN2022 PNRR project ArtDECOW Natural Materials Development from Collagen-Based Wastes) (2023-2025)

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 "Multicomponent 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
- Marta Filomena (DCCI DSCM, 40th cycle) PhD project focused on the study of the degradation of compostable bioplastics using advanced analytical techniques
- Federico Paolino (DCCI DSCM, 40th cycle) PhD project focused on the electronic devices printed on functionalized nanopaper

Grants supported by CISUP:

- One grant aimed at the "Study of the molecular composition of paints made of oil binders and proteins, through analytical chemistry" (6 months)



- One grant aimed at the "Application of analytical pyrolysis to the characterisation and study of materials based on collagen in samples of leather subjected to different tanning protocols" (4+4 months)
- One grant aimed at the "Sviluppo e applicazione di metodi analitici basati di pirolisi per la caratterizzazione di microplastiche e inquinanti organici in campioni di interesse ambientale" (12 months, Greta Biale)

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

- Vasiliki Sorsou, visiting PhD student University of Valencia
- Laura Andres Herguedas (University of Vigo, Spain)
- Pablo Barreiro (University of Vigo, Spain)
- Ezgin Yetiş 'Investigations of Painting Techniques and Organic Materials on Wall Paintings Found in Some Ottoman Mosques in Edirne-Turkey' funded by ARIT-American Research Institute in Turkey.

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 and laser cleaning. This led to several publications in international journals as:

List of publications

- 1. Sabatini F, Mattonai M, Doherty B, Degano I. Unveiling the composition of native Asian dye plants by EGA/MS and Py-GC/MS. Journal of Analytical and Applied Pyrolysis 2025, 186, 106979.
- 2. Cantini V, Becagli M, Mattonai M, Degano I, Cardelli R. Wood Distillate Interactions with Urea in Soil: A First Step to Developing a Slow-Release Next-Generation Fertilizer. Journal of Agricultural and Food Chemistry 2024, 72, 17455–64.
- Ferretti A, Degano I, Filomena M, La Nasa J, Campanella B, Legnaioli S, et al. Wall Drawing #736: Revealing Sol LeWitt's Ink Mural Technique Using a Multi-Analytical Approach. Heritage 2024, 7, 4265–81.
- 4. Zhang, L., Hoagland, L., Yang, Y., La Nasa J., Biale G., Modugno, F., Lucini, L., The combination of hyperspectral imaging, untargeted metabolomics and lipidomics highlights a coordinated stress-related biochemical reprogramming triggered by polyethylene nanoparticles in lettuce, Science of the Total Environment, 2025, 964, 178604
- 5. Barlucchi, L., Biale, G., La Nasa, J., Mattonai M., Pezzini S., Castelvetro, V., Modugno, F., Abiotic degradation and accelerated ageing of microplastics from biodegradable and recycled materials in artificial seawater, Science of the Total Environment, 2024, 954, 176832



- 6. Lykkemark, J., Mattonai, M., Vianello, A., ... Modugno, F., Vollertsen, J., Py–GC–MS analysis for microplastics: Unlocking matrix challenges and sample recovery when analyzing wastewater for polypropylene and polystyrene, Water Research, 2024, 261, 122055
- 7. Ferretti, A., Degano, I., Filomena, M., Todaro, C., Modugno, F., Wall Drawing #736: Revealing Sol LeWitt's Ink Mural Technique Using a Multi-Analytical Approach, Heritage, 2024, 7(8), pp. 4265–4281
- 8. Pomata, D., La Nasa, J., Biale, G., Barlucchi L., Modugno, F., Simonetti, G., Plastic breath: Quantification of microplastics and polymer additives in airborne particles, Science of the Total Environment, 2024, 932, 173031
- Marchelli, F., Mattonai, M., Ferrentino, R., La Nasa J., Pecorelli N., Modugno F., Ribechini E., Fiori, L., Fostering Bioplastics Circularity through Hydrothermal Treatments: Degradation Behavior and Products, ACS Sustainable Chemistry and Engineering, 2024, 12(24), pp. 9257–9267
- Maisto, M., Ranauda, M.A., Zuzolo, D., Tartaglia M., Postiglione A., Prigioniero A., Falzarano A., Scarano P., Castelvetro V., Corti A., Modugno F., La Nasa J, Biale G., Sciarrillo, R., Guarino, C., Effects of microplastics on microbial community dynamics in sediments from the Volturno River ecosystem, Italy, Chemosphere, 2024, 349, 140872
- 11. Vlata M., Rapti S., Boyatzis S., Bardet M., Lucejko J. J. and Pournou A., Melamineformaldehyde in the conservation of waterlogged archaeological wood: investigating the effect of the treatment on wood residual chemistry with FTIR, 13C NMR, Py(HMDS)-GC/MS and EGA-MS, Wood Science and Technology 2025 Vol. 59 Issue 1, DOI: 10.1007/s00226-024-01610-w
- Szwajca A., Lucejko J. J., Berdychowska N. and Zborowska M. Understanding changes in holocellulose and lignin compounds in wooden structure of veneers: Molecular insights post hydrothermal treatment and aging, International Journal of Biological Macromolecules 2024 Vol. 266 Pages 130920, https://doi.org/10.1016/j.ijbiomac.2024.130920
- M.L. Amadori, V. Mengacci, P. Callieri, A. A. Chaverdi, M. Bartolucci, N. Eftekhari, A.Andreotti, P. Holakooei, "Integrated Investigations of Painting Materials in the Sasanian City of Ardaxšīr Khwarrah, near Firuzabad (Southern Iran)", Heritage 7(3), March 2024, 1202–1220, https://dx.doi.org/ doi.org/ 10.3390/heritage7030058. 5973 nella parte sperimentale, anche se fatti un po' con cisup
- A. Sutter, C. Di Marco, Spada M., A. Trinchetti, M. Spampinato, A. Manariti, A. Andreotti, M.P. Colombini, "Combined use of Er:YAG and Nd:YAG lasers for cleaning the stone surfaces of the Monumental Cemetery of Pisa", Lasers in the Conservation of Artworks XIII - Proceedings of the International Conference on Lasers in the Conservation of Artworks XII, LACONA 2022, 2024, 207 – 218, DOI: 10.1201/9781003386872-22.
- 15. A. Andreotti, M.P. Colombini, E. Cantisani, D. Magrini, A. De Cruz, K. Nakahara, "Gradual cleaning of a seventeenth-century polychrome wood sculpture by Er:YAG laser", Lasers in the Conservation of Artworks XIII Proceedings of the International Conference on Lasers



in the Conservation of Artworks XII, LACONA 2022, 2024, 123 – 131, DOI: 10.1201/9781003386872-13.

16. Ranalli G, Andreotti A, Colombini MP, Corti C, Paris D, Rampazzi L, Saviano G, Vecchio R, Caprari C., "Investigation on Tattoo Ink (Hexadecachlorinate Copper Phthalocyanine) Removal: Novel Chemical and Biological Approach", Molecules. 2024; 29(23):5543. https://doi.org/10.3390/molecules29235543

Theses

Bachelor theses (Corso di laurea triennale in Chimica)

- Federica Tatarelli "Caratterizzazione multianalitica di pastelli Lefranc dei primi del Novecento"
- Marco Salvatori "Tecniche di pirolisi analitica applicate allo studio di materiali pittorici e di restauro nell'arte urbana".
- Alice Nesi "Determinazione della composizione della pianta di papiro tramite tecniche cromatografiche e di pirolisi analitica: un'analisi per la selezione del materiale scrittorio"
- Maria Teresa Zocchi "Studio delle frazioni molecolare e macromolecolare di ambre archeologiche tramite metodi basati su pirolisi analitica"

Master theses (Corso di laurea magistrale in Chimica)

- Niccolò Medica "Caratterizzazione multi-analitica di materiali pittorici provenienti da opere di street art"
- Marta Filomena "Metodi sostenibili di estrazione e frazionamento di molecole e sostanze organiche da biomasse di scarto dal settore agricolo, forestale e alimentare"
- Riccardo Ducoli "The microstructure and chemistry of paints based on oil and proteins"
- Gabriele Messina "Metodi sostenibili di estrazione e frazionamento di molecole e sostanze organiche da biomasse di scarto dal settore agricolo, forestale e alimentare"
- Stefano Mazzoncini "Metodi innovativi per quantificare il polietilene in buste di bioplastiche compostabili"

6. External services

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

- Adarte, Florence, for the characterisation of organic binders and patina in samples from paintings and historical artifacts
- ArtTest, Torino, for the characterisation of organic binders and in samples from contemporary and ancient artworks
- RCArt, Verona, for the characterisation of organic materials in samples from paintings
- SRA, Milano, for the characterisation of syntetice polymeric and composite polymers



- Georadar (Italy) for the quantification of phthalates in transistors used for soil monitoring
- Gucci (Italy) for the characterisation of raw materials and synthetic polymers used in their production of garments
- LHZ analytics GmbH (Germany) for the analysis of microplastics
- Institute for Chemical Research of Nakamura Lab, Kyoto University for the analysis of urushi samples
- Biorepack (Italy) for the quantification of polyethylene in bioplastics
- Superintendence of historical and artistic heritage of Cagliari for the characterization of the pictorial materials of the Domus de Janas, officially nominated to become a UNESCO heritage site
- Department of Pure and Applied Sciences, University of Urbino, Maria Letizia Amadori, for a) the Investigations of Painting Materials in the Sasanian City of Ardaxš⁻ir Khwarrah, near Firuzabad (Southern Iran); b) the characterization of samples of Andean and Egyptian mummies
- Cannizzaro, freelance restorer, for the investigation of the original and conservation material of the 'Volto Santo' from Lucca cathedral
- ICR (ROMA), prof.ssa Simona Pannuzi, for the characterisation of the organic binder in the Ghandara sculptures
- I S M E O. Associazione Internazionale di Studi sul Mediterraneo e l'Oriente, prof.ssa Anna Filigenzi, for the characterisation of the organic binder in the Ghandara sculptures
- Sophia Barton, freelance restorer, for the analysis of two samples of Medieval glaze or coating layer.

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), Istituto Centrale per il Restauro (Rome, Italy) and Venaria Reale CCR (Venaria, Torino, Italy).

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).

The instrumental set-up was also employed for the laboratory training of the CISUP Winter School "Advanced Techniques for the Analysis of Novel Materials Strategic for Sustainability Transitions: I. Bioplastics" (29th January – 2nd February 2024).