PROGRAMME INTITUTS ET INITIATIVES

Appel à projet – campagne 2021

Proposition de projet de recherche doctoral (PRD)

IMat - Institut des Matériaux

Intitulé du projet de recherche doctoral (PRD): Comprehensive Study of Polymeric Materials in Ancient Paintings by a Multimodal Analysis

Directeur.rice de thèse porteur.euse du projet (titulaire d'une HDR) :

NOM : **BRUNELLE** Prénom : **ALAIN**
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Adresse professionnelle : Sorbonne Université, Boîte Courrier 225, Tour 23, 3ème étage, bureau 310, 4 place Jussieu, 75005 Paris
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Unité de Recherche :
Intitulé : Laboratoire d'Archéologie Moléculaire et Structurale (LAMS)
Code *(ex. UMR xxxx)* : UMR8220

École Doctorale de rattachement de l'équipe (future école doctorale du.de la doctorant.e) : **ED397-Physique Chimie des Matériaux**

Doctorant.e.s actuellement encadré.e.s par la.e directeur.rice de thèse (préciser le nombre de doctorant.e.s, leur année de 1e inscription et la quotité d'encadrement) : 1 (C. Bouvier), 1ère année d'inscription 2018, 100%

Co-encadrant.e :

NOM : **SABLIER** Prénom : **MICHEL**
Titre : Directeur de Recherche ou HDR ☒
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Unité de Recherche :
Intitulé : Centre de Recherche sur la Conservation
Code *(ex. UMR xxxx)* : USR3224

École Doctorale de rattachement : **ED227-Sciences vie homme : évolution écologie**
Ou si ED non Alliance SU :

Doctorant.e.s actuellement encadré.e.s par la.e co-directeur.rice de thèse (préciser le nombre de doctorant.e.s, leur année de 1e inscription et la quotité d'encadrement) : 1 doctorant (Baptiste Zuber), 1ère année d'inscription 2019, 50%

SORBONNE UNIVERSITÉ

Co-encadrant.e :

NOM : Prénom :
Titre : Choisissez un élément : ou HDR ☐
e-mail :

Unité de Recherche :
Intitulé :
Code *(ex. UMR xxxx)* :

École Doctorale de rattachement : **Choisissez un élément :**
Ou si ED non Alliance SU :

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Cotutelle internationale : ☐ Non ☐ Oui, précisez Pays et Université :

Selon vous, ce projet est-il susceptible d'intéresser une autre Initiative ou un autre Institut ?
☒ Non ☐ Oui, précisez Choisissez l'institut ou l'initiative :

Avis favorable

École Doctorale Physique et Chimie des Matériaux
Directrice
Nadine WITKOWSKI
ED 397

Description du projet de recherche doctoral *(en français ou en anglais) :*

Ce texte sera diffusé en ligne : il ne doit pas excéder 3 pages et est écrit en interligne simple.

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut.

Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Indiquer les publications/productions des encadrants en lien avec le projet.
Préciser le profil d'étudiant(e) recherché.

Comprehensive Study of Polymeric Materials in Ancient Paintings by a Multimodal Analysis

Materials from cultural heritage contain organic substances which have polymerized, which may have suffered from degradation over time, and which are difficult to analyze and understand. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) imaging and pyrolysis comprehensive two-dimensional gas chromatography / mass spectrometry (Py-GCxGC/MS) are two methods which provide, the one a surface analysis at the sub-micrometric scale, but with some identification issues, and the other a complete analysis, but without location. Here we propose to develop a new multimodal analysis associating them. This approach has never been carried out, and their complementarity will allow a better knowledge at the micrometric scale of these fascinating materials.

State of the art:

Cross-sections of paintings are very complex materials, whose the chemical study of organic and mineral pigments and binders gives access to a large number of useful information: their identification provides fundamental information on the painter's pictorial technique, on their origin, on the aging and degradation of paintings (for example phenomena of saponification, oxidation, blackening, discolorations). This chemical information can then help:

(i) a conservator to adapt his/her method to the artwork on which he/she is protecting or restoring,

(ii) an expert on the possible identification of a copy or a forgery, or

(iii) the curator on the history of the work analyzed.

Many chemical analysis methods can be used to characterize pigments and binders directly on the paintings or on the surface of cross-sections of minute samples. X-ray diffraction, X-ray fluorescence, infrared imaging, electron microscopy, micro-Raman, etc. are methods already established and currently used for the analysis of paintings. However, with these techniques, information on the exact composition of the several components likely to interact in the medium revealed to be difficult.

Mass spectrometry imaging of cross-sections of samples is a surface analysis method and is the only one that provides access to the distribution and chemical composition of a large number of compounds mixed on a surface. TOF-SIMS mass spectrometry imaging is particularly well suited for locating with an accuracy of a few hundred nanometers organic or mineral materials composing the surface of a cross-section. We have shown the feasibility of this micro-destructive method on cross-sections of old paintings, initiated a few years earlier by other authors.1,2 However, at this scale, and despite the great increase in sensitivity made over the past twenty years, the principle of desorption-ionization itself under ion impact has reached a certain limit of sensitivity, and the large fragmentations of the molecules analyzed have the consequence that certain identifications may remain problematic. While oils are well characterized, egg and protein binders are less well characterized, as are resins and waxes. Consequently, to fully complete the knowledge of painting materials, mass spectrometry imaging may require the help of complementary separation techniques which can overcome the above quoted drawbacks.

Py-GCxGC/MS allows the separation of complex mixtures of hundreds of components (unresolved under usual monodimensional GC/MS analysis), a qualitative and semi-quantitative analysis of trace level constituents, and the determination of targeted and non-targeted substances. This technique uses two capillary columns connected via a cryogenic modulation system to optimize the complementary separation capabilities of columns of different polarities. Addition of a mass spectrometer as a detector adds another dimension in its separation capability with the identification of compounds through mass spectra analysis. A comprehensive two-dimensional gas chromatography/mass spectrometry (GC×GC/MS) system offers much higher resolution, peak separation capacity, selectivity and lower detection limit for the analysis of organic samples, making it one of the most powerful analytical systems. The coupling of pyrolysis to GCxGC/MS, in a micro-destructive approach, allows the characterization of polymer samples (resins, waxes) in an unsurpassed analytical way when the analysis of tiny quantities is the rule.3,4

Each of these methods has its own advantages and drawbacks, each of them has already been the subject of feasibility studies, and even of applications, in the fields of the analysis of heritage materials, independently of one of them.1–4

Thesis project:

The object of this thesis project will initially be to use the capabilities of Py-GCxGC/MS to “shed light” on TOF-SIMS analyses of heritage materials, which have now reached a point where questions would otherwise remain unanswered without the help of a powerful separation method. The proposed strategy will lie firstly by the analysis of simulations (mock-up) of paint materials or artificially aged ones. These model samples will be analyzed in part by Py-GCxGC/MS and by TOF-SIMS, and this approach based on a material multimodal analysis, with no doubt, will make it possible to better understand the complexity of the mass spectra obtained in TOF-SIMS imaging. Especially, a particular effort will be made to identify resins and waxes, which are more difficult to characterize in TOF-SIMS until now, as well as to mixtures between pigments and binders or between very thin layers of different binders themselves.

The second phase of the research project will focus on samples from paintings and painted objects of relatively low heritage value on which we will take large samples to combine the two techniques, before focusing at the end of the thesis project on the analysis of old paintings, only in TOF-SIMS because this technique can preserve the samples, but with an understanding of the composition of materials which will have been greatly improved by Py-GCxGC/MS. Thanks to a long term collaboration with LAMS, the samples of paintings will be provided by the National Museum of Capodimonte, Naples, and we will consider the practices of painters like Giovani Bellini, Raphael and

Titian.

The originality of the proposed thesis project therefore lies in the combination of these two powerful and original techniques which are each already used for the analysis of heritage materials, the first at LAMS with Alain Brunelle, and the second at CRC with Michel Sablier. This combination of two methods will make it possible to overcome a major bottleneck in TOF-SIMS imaging, by the precise knowledge of material composition provided by Py-GCxGC/MS. Beyond the context of cultural heritage, the development of this new method of material multimodal analysis will also be a valuable tool for the analysis of materials in a larger sense, in particular complex materials like mixtures between pigments and binders, between mineral and organic materials, and / or with a structure requiring localized analysis at a micron scale or less.

This thesis project is proposed in partnership between the Laboratoire d'Archéologie Moléculaire et Structurale (LAMS, UMR 8220 Sorbonne Université CNRS) and the Centre de Recherche sur la Conservation (CRC, USR 3224, Muséum National d'Histoire Naturelle, CNRS, Ministère de la Culture), under the co-supervision of Alain Brunelle and Michel Sablier.

It answers to the Theme 4 of the 2021 call for projects "Méthodes, Techniques, Innovation".

Applicants should hold a Master, or be in second year, preferentially in Materials Chemistry or Analytical Chemistry.

(1) Keune, K.; Boon, J. J. Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van Der Weyden. Anal. Chem. 2004, 76 (5), 1374–1385. https://doi.org/10.1021/ac035201a.

(2) Noun, M.; Van Elslande, E.; Touboul, D.; Glanville, H.; Bucklow, S.; Walter, P.; Brunelle, A. High Mass and Spatial Resolution Mass Spectrometry Imaging of Nicolas Poussin Painting Cross Section by Cluster TOF-SIMS. J. Mass Spectrom. 2016, 51 (12), 1196–1210. https://doi.org/10.1002/jms.3885.

(3) Han, B.; Daheur, G.; Sablier, M. Py-GCxGC/MS in Cultural Heritage Studies: An Illustration through Analytical Characterization of Traditional East Asian Handmade Papers. J. Anal. Appl. Pyrolysis 2016, 122, 458–467. https://doi.org/10.1016/j.jaap.2016.10.018.

(4) Okamoto, S.; Honda, T.; Miyakoshi, T.; Han, B.; Sablier, M. Application of Pyrolysis-Comprehensive Gas Chromatography/Mass Spectrometry for Identification of Asian Lacquers. Talanta 2018, 189 (June), 315–323. https://doi.org/10.1016/j.talanta.2018.06.079.

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Fichier envoyer simultanément par e-mail à l'ED de rattachement et au programme :
cd_instituts_et_initiatives@listes.upmc.fr avant le 20 février.