UNIVERSITÉ DE TOULON

Contrat doctoral Etablissement 2024/2027
Formulaire de candidature

Titre de la thèse	**Raman spectroscopy analysis of micro and nanoplastics**

Ecole Doctorale	ED548
Laboratoire	MAPIEM
Discipline	Physique et chimie des matériaux
Directeur(s) de Thèse & Encadrant(s)	Directeur : Alexandre Merlen (UTLN) 50% Encadrant : Andreas Ruediger (INRS, Canada) 15% Lénaïk Belec (UTLN) 20% Olivia Gerigny (Ifremer) 15%

Description du sujet de recherche

(3 pages maximum - contexte scientifique, objectifs, mots clé, références)

Contexte, originalité et pertinence par rapport à l'état de l'art :

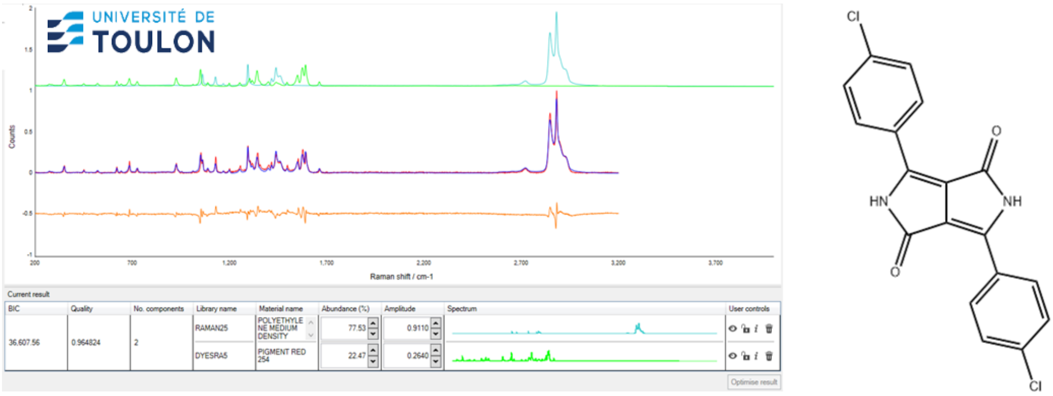
Microplastics present in the Western Mediterranean are directly linked to strong anthropogenic pressure on its coasts. Land-based plastic waste generated by human activity can be transported by precipitations to rivers which then flow into the sea. Maritime activities such as navigation, transport and fishing also generate a lot of waste from lost or abandoned equipment which contribute to that pollution. Plastic fragments can also be transported over very long distances by marine aerosols.

The identification of the main polymers present in Mediterranean sea has already given rise to a large number of studies [3,4] with harmonization of sampling and analysis methods. However, few studies focus on the release of plastics additives during aging, which environmental impact could be even greater than that of the polymer himself. Their identification and quantification remain a technical challenge given their size and proportion in plastics. In addition, the presence and identification of nanoplastics, already demonstrated in bottled water [1,2] remains an open question for seawater.

Objectifs :

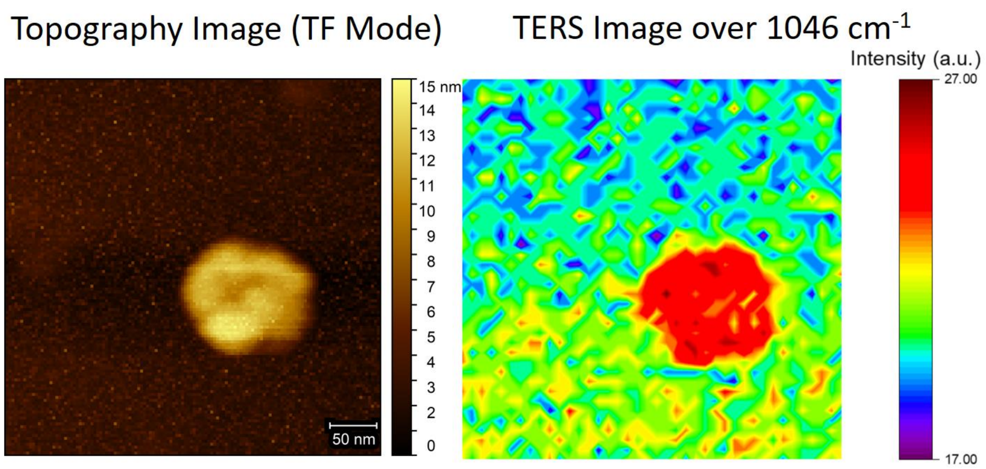
The first objective of the study is to identify the additives present in microplastics scattered in the Mediterranean Sea and to evaluate their rate of release into the environment over time. This implies having concrete data on these potential pollutants which will be decision aids for sustainable management of maritime spaces.

Raman spectroscopy, makes it possible to identify a part, notably pigments, and is considered the most effective tool suitable for the analysis of microplastics in marine environments, in particular for the study of their aging [5].



An example of an additive identification in a plastic sample (bottle cap) through Raman spectroscopy: the red dye pigment 254

The identification of the polymer itself can be easily done, but this is not the case for the additives, in particular those who have a small signature in the recorded spectrum. The contribution of Artificial Intelligence would be decisive for this task as the multi-compounds identification in complex and noisy spectra remains a challenge. AI has already proves its decisive contribution for the identification of the polymer [6] itself but to our knowledge it is has not been applied to the additives. In addition, an AI software is already in development at IFREMER for the automatic identification of microplastics in pure optical images, Raman spectroscopy would be useful to the estimate its efficiency and confirms the rightness of the process. The second objective is to use optical near field Raman spectroscopy for the identification of nanosplastics as a proof of concept. Our approach will use Tip Enhanced Raman Spectroscopy (TERS) a technique based on the optical coupling between a Raman spectrometer and a near field microscope. Professor's Ruediger team (INRS, Canada) has a 15 years' experience using this kind of complex device and the collaboration with the University of Toulon has already lead to several publications in the field. An example of TERS mapping is shown in the figure below:



Left: a near field image of a ceramic nanoparticle, with a typical size less than 100 nm. Right: the corresponding Raman signature at 1046 cm^{-1} mapping using TERS configuration. The optical resolution is estimated at around 10 nm, far beyond the Rayleigh criterion of standard optical microscopy. Those images have been obtained at the INRS in 2024.

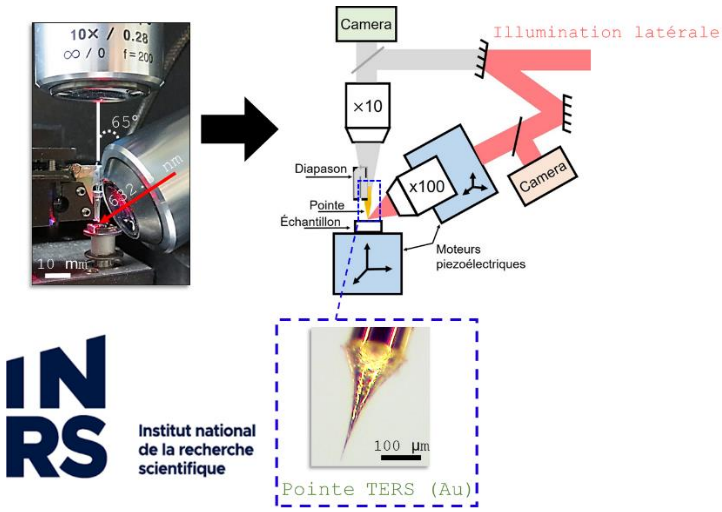
The optical resolution associated to this technique is typically a few nanometers and is perfectly adapted for the detection and identification of nanoplastics.

Méthodes :

We propose 2 different approaches to push forward the study of plastics In seawater with Raman spectroscopy:

-The identification of additives through resonant Raman spectroscopy, an approach using a specific laser excitation related to the optical absorption of the additives. We have already obtained first results with dye molecules. We also would like to test the contribution of artificial intelligence in this task.

-The identification of nano-plastics, impossible with standard Raman spectroscopy, but possible with Tip Enhanced Raman spectroscopy (TERS), a near field technique with a nanometer spatial resolution.



The basic principle of the TERS device at INRS. Almost 10 years of development have been required before getting reproducible and high resolution Raman images. It is now fully efficient.

The combination of those two techniques is unique in the study of plastics pollution.

Those two approaches are only based on Raman spectroscopy but of course this technique is not enough to get a full comprehensive understating of the mechanism of aging and degradation of plastics. We also plan to use IR measurements, a technique more sensitive to the aging of the polymer itself even if its spatial resolution is not enough for the detection of nanoplastics. The latest generation of FTIR equipment recently acquired by the laboratory, including a micro-ATR (Attenuated Total Reflectance) module, could be used to map the gradients of the properties of microplastics during ageing. We also plan to study the crystallinity of the polymer through Differential Scanning Calorimetry (DSC) measurements, as its evolution is a key parameter for polymer degradation which may impact the release of additives. Regarding their identification, the contribution of Pyrolysis–gas chromatography–mass spectrometry (PyGCMS) will also be decisive thanks to the techniques's ability to detect trace elements

Retombées attendues :

We expect two proofs of concept, related to the two main techniques that will be used during this thesis:

-Some additive molecules in plastics can be identified through Raman spectroscopy. This approach will pave the way for a better understanding of additives aging and release in seawater.

-The chemical identification of nanoplastics through TERS. We expect a spatial resolution down to a few ten nanometers, far lower than can be reached with standard analytical methods.

In the field of microplastics, which has seen an explosion in publications over the last ten years, the use of specialized and complementary methods and skills should make it possible to broaden publication opportunities.

Mots clés : **Raman Spectroscopy, micro and nanoplastics, marine pollution, nano-analysis**

Références :

[1] L'eau en bouteille polluée par des nanoparticules de plastique, article du Monde du 11 janvier 2024

[2] Naixin Qian et al. « Rapid single-particle chemical imaging of nanoplastics by SRS microscopy" PNAS, 2024, 121 (3) e2300582121 (https://doi.org/10.1073/pnas.2300582121)

[3] Simon-Sanchez et al. "Are research methods shaping our understanding of microplastic pollution? HAS literature review on the seawater and sediment bodies of the Mediterranean Sea", Environmental Pollution, 292, Part B, 2022, 118275

[4] Kedzierski et al. "Chemical composition of microplastics floating on the surface of the Mediterranean Sea" Marine Pollution Bulletin,174 , 2022, 113284

[5] S. Phan, J. L. Padilla-Gamino, C. K. Luscombe, The effect of weathering environments on microplastic chemical identification with Raman and IR spectroscopy: Part I. polyethylene and polypropylene, Polymer Testing, 116, 2022 107752

[6] Yazhou Qin, Jiaxin Qiu, Nan Tang, Yingsheng He, Li Fan, Deep learning analysis for rapid detection and classification of household plastics based on Raman spectroscopy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 309 (2024) 123854

Encadrement et conditions matérielles pour le doctorant

→ The PhD candidate will be associated to two universities (co-tutelle) : University of Toulon in France and Institut National de la Recherche Scienfique (INRS) in Montréal, Canada (see the letter of support from professor Ruediger attached to this demand). IFREMER is also associated to the supervision of this thesis.

The PhD candidate will work on the Raman spectrometer of the MAPIEM laboratory, with its specific modulus dedicated to micro and nanoplastics analysis (Particle analysis). This system has been installed last year and is now ready to use.

In Canada, the candidate will work on the Tip Enhanced Raman System (TERS) from professor Ruediger's team. Alexandre Merlen and Andreas Ruediger have a strong collaboration using this device since years.

Compétences attendues et personnes à contacter

Compétences attendues :

→ We except a physico-chemist scientist, with an expertise in optical spectroscopy. The candidate should have a strong affinity for experimental studies and international collaborations.

Personne(s) à contacter :

→ Alexandre Merlen (merlen@univ-tln.fr, 04 94 14 24 77)