

## LASER BASED DETECTION OF MICROPLASTICS IN WATER

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### Abstract

Finding fast and accurate ways for detection of microplastics in water with a limited number of measurements, easy processing and sampling is a challenging task. In this respect, this work aims to bring new knowledge about the detection of very small particles of plastics in a host fluid droplet, using laser radiation as light source for Raman scattering measurements. The combination of the enhanced sensitivity of Raman spectroscopy obtained using very small samples (microdroplets) with the latest developments in the topics of optofluidics may constitute an advance in the field of real time monitoring of environmental pollutants.

### 1 Introduction

One major side effect of the abundance of plastic products in modern society is microplastic (MP) pollution, where small size polymer particles of diverse origins and types enter the environment. These particles are only partially removed by the wastewater treatment plants [1].

Plastics are organic polymers, synthesized from the polymerization of monomers extracted from oil or gas, whose global production rose continuously. Approximately 10% end up in marine environment and only a very small fraction is recycled annually [2]. Although initially considered a revolutionary material, it has slowly become a global threat to the environment, with ubiquitous distribution in marine and freshwater ecosystems. The natural environmental conditions of these ecosystems, especially the dynamics of water currents, solar radiation, abrasion and interactions with vessels and organisms, cause plastic products to degrade slowly and to fragment into smaller particles than usual, known as microplastics [3,4].

Regardless of the current disagreements over the definition of MP particles, fragments less than 5 mm in diameter with no lower restriction are considered [5]. The diversity in properties and wide particle size range means that as a group of analytes, they are challenging to efficiently detect and identify in complex environmental matrices, especially when very small (micro-/nanometric) range dimensions are involved [6].

On the other hand, concerns are raising regarding the potential for MP to represent new spreading substrates for microorganisms, especially harmful and pathogenic ones

[7]. Also, various organic pollutants, such as polycyclic aromatic hydrocarbons [8], polychlorinated biphenyls [9], and antibiotics [10], can be adsorbed onto MP. This is a research area where many uncertainties exist, with respect to both detection, analysis and identification.

In this connection, we performed Raman spectroscopy measurements on water droplets containing polymethyl methacrylate (PMMA) microparticles. The sampling, control, and acquisition parameters of the experimental set-up have been optimized to better record the Raman scattering spectra. Additional analysis of PMMA microplastic dispersion in water samples were carried out by molecular modelling, as well as UV-Vis absorption and FTIR spectroscopy.

PMMA is also known as acrylic, acrylic glass, or Plexiglas. It is a versatile transparent thermoplastic often used as an alternative to glass, being lighter and resistant to breakage. The recent developments in the applications of PMMA in different areas such as biomedical, optical, solar, sensors, battery electrolytes, nanotechnology can be a potential source of polymer microparticles occurrence in the environment.

### 2 Experimental Setup

The block scheme of the laboratory-built experimental setup for Raman spectroscopy is shown in Figure 1. Individual droplets with volumes ranging from 1 to 4  $\mu\text{L}$  were optically pumped using a pulsed laser radiation source. We used the 2<sup>nd</sup> harmonic generation of the Nd:YAG laser (Surelite II, Continuum, Excel Technology, USA) emitted at 532 nm, with frequency of 10 Hz, 9 ns pulse duration (FTWHM), and pulse energies ranging from 2.5 to 24 mJ. For bulk sampling experiments laser beam energies up to 100 mJ were used. The laser beam of 6 mm waist was focused by a lens of 150 mm focal length. The droplet was placed at 122 mm from the lens, so that the collimated beam is equal to or less than the drop diameter.

The droplets were generated by a computer controlled programmable pump (Dual Syringe Dispenser, Mircolab ML560C, Hamilton, USA). The samples were loaded on a capillary circuit from a stock-volume. Droplets were automatically generated, controllable drop by drop, with a resolution of 0.05% of the employed syringe capacity (50 $\mu\text{L}$ ).

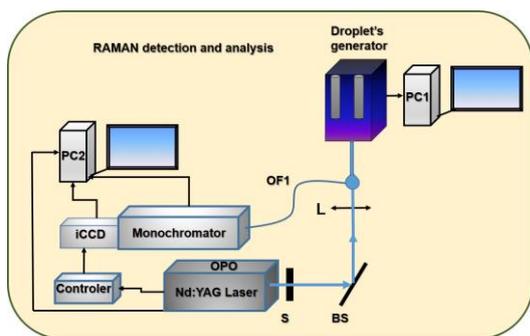


Figure 1 The Raman spectroscopy set-up

The capillary tips used had external diameters of 0.51 mm (for volume generation ranging from 1 to 3  $\mu\text{L}$ ) and 0.91 mm (for volume greater than 2  $\mu\text{L}$ ). The generated droplets had diameters ranging from 1.24 mm to 2 mm, depending on the ratio between the diameter of the drop and the diameter of the capillary tip.

The droplet's Raman scattering radiation was collected at  $90^\circ$  with respect to the pumping laser beam using an optical fiber positioned in the droplet's plane.

For pulse-to-pulse and 5-pulse-series data acquisition, a pulse delay generator (SRS DG535) was used. It generates TTL signals for synchronizing the laser pulse with the data acquisition system (Acton Research/Princeton Instruments) through a mechanical shutter. A spectrograph (SpectraPro SP2750, in Czerny-Turner configuration, with focal length of 750 mm, and 0.8 nm resolution) is coupled with an iCCD-PIMAX Camera detector (Intensifier 25 mm, resolution of 64 lp/mm, 2ns minimum gate opening). The spectrum was acquired using a grating of 2400 grooves with an optical resolution of 0.016 nm for a 10  $\mu\text{m}$  input slot of the spectrograph. The shutter (Digital Shutter Controller 845 HP, Newport) provides a controllable optical pump time window ranging from ms to s.

PMMA was purchased from Sigma Aldrich and MicroParticles (Germany) as microparticle suspensions in water with various standard sizes ranging from 100 nm to 100  $\mu\text{m}$ .

### 3 Results and Discussions

We performed Raman spectroscopy measurements on water droplets containing PMMA microparticles. Supplementary analysis of PMMA microplastic dispersion in water were carried out by molecular modelling, as well as UV-Vis absorption and FTIR spectroscopy.

#### 3.1 Vibrational Spectroscopy

The Raman spectra of different concentration of MP-contaminated water droplets were recorded, and the parameters of the experimental configuration were optimized to ensure the best Raman signal. The compared Raman spectra of PMMA microplastic (100 $\mu\text{m}$ ) dispersed

in water in bulk of 1  $\text{cm}^3$  volume, and in droplets of 2  $\mu\text{L}$  volume are plotted in Figure 2.

Among the registered Raman bands, the most prominent one was observed at 2960  $\text{cm}^{-1}$ , which corresponds to the stretching vibration of the C–H bonds.

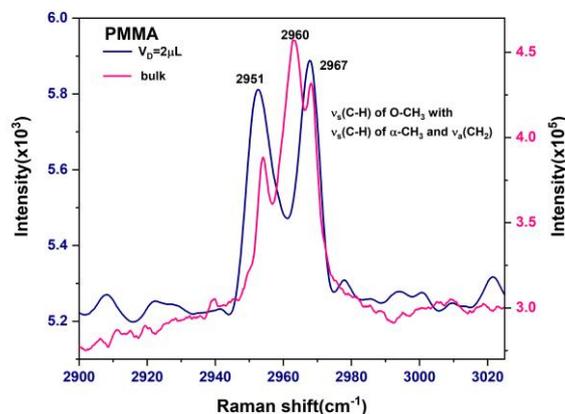


Figure 2 The Raman spectra of PMMA in bulk vs. droplet

According to the literature [11], the band centered at 2960  $\text{cm}^{-1}$  is due to an overlap of the  $\nu_{\text{CH}}$  modes in the  $\text{CH}_2$  groups of the skeleton, the  $\alpha\text{-CH}_3$  groups and the  $\text{CH}_3$  ester groups.

An intensity decrease of the scattering is seen in droplets Raman spectra when compared to PMMA bulk samples probable because the used laser beam energy was limited to a few mJ for droplets sampling.

The FTIR spectra (not shown) were recorded using the Nicolet™ iSTM50 spectrometer, in the range 4000-500  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  and a mediation on 32 spectra was made. The samples (20  $\mu\text{L}$ ) of MP dispersed in water were dried on a KRS-5 support.

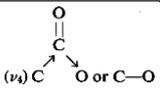
The results are consistent with both the data published in the literature and the calculated spectra, presented below as additional investigations.

#### 3.2 Molecular Modelling

PMMA ( $\text{C}_5\text{O}_2\text{H}_8$ ) $_n$ , molecular structures were drawn, 3D protonated, and energy-optimized (using MMFF94X force field at 0.05 gradient with Gasteiger (PEOE) partial charges) using MOE software. After the optimisation protocol we have predicted the 2D and the i3D molecular descriptors. Compounds with a hydrophobic surface area are more likely to be colonized by bacteria [7]. The high predicted number of hydrophobic atoms (21) and the total hydrophobic surface area (730.97) may indicate that PMMA is a hydrophobic compound.

Molecular modelling was performed for PMMA using Gaussian 09 [12] and GaussView 5.0 [13]. Density Functional Theory (DFT) with B3LYP and the 6-311G augmented base set were used for both structural optimization and calculation of the molecules' chemical bonds frequencies. The influence of the dispersive

environment (water) on the process of structural optimization and calculation of FTIR and Raman spectra was implemented in the calculation scheme by selecting the IEFPCM module.

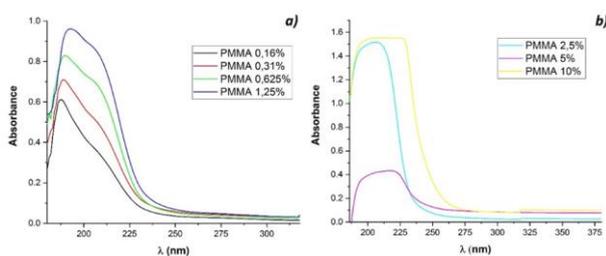
FTIR [cm <sup>-1</sup> ]	RAMAN [cm <sup>-1</sup> ]	Assignment
759	745	$\nu(\text{C-C})$ skeleton
894	879	$\omega(\text{CH}_2)$
944	921	$\omega(\text{CH}_3)$
994	976	$\omega(\text{O-CH}_3)$
1096	1058	$\nu(\text{C-C})$ skeleton
1189	1176	$\nu(\text{C-O-C-})$
1271	1271	
1347	1353	$\delta(\text{C-H})$ a $\text{CH}_3$
1488	1482	$\delta(\text{CH}_2)$
3100	3045	$\nu(\text{C-H})$ a $\text{O-CH}_3$

**Table 1** Calculated vibrational modes of the PMMA molecule

### 3.3 UV-Vis Absorption Spectroscopy

The absorption spectra of different percent MP dispersion in water were registered by a UV-Vis-NIR Lambda 950 (Perkin-Elmer, USA) spectrophotometer between 175 - 3300 nm. The spectral resolution of device is  $\geq 0.05$  nm in UV-Vis spectral range, and  $\geq 0.20$  nm in NIR. The intrinsic error of the apparatus is 0.004%.

The absorption spectra of MP in water solutions are represented in Figure 3(a) for samples having percentage concentration from 0.16% to 1.25% and in Figure 3(b) for those with percentage concentration between 2.5% - 10%.



**Figure 3** The UV-Vis absorption spectra of PMMA in water, at concentrations between: a) 0.16% - 1.25% and b) 2.5% - 10%.

The appearance of the absorption bands in Figure 3(b) and the fact that their absorbance does not increase progressively with increasing concentration of samples may be due to the fact that MP particles do not have the same roughness, so some samples have a higher scattering coefficient, thus influencing the light intensity passing through the sample.

## 4 Acknowledgement

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## 5 References

- [1] Sun, J., Dai, X., Wang, Q., van Loosdrecht, M. C. M., Ni, B.-J. Microplastics in wastewater treatment plants: Detection, occurrence and removal. *Water Research* 152, 21–37 (2019).
- [2] Coyle, R., Hardiman, G., Driscoll, K. O. Microplastics in the marine environment: A review of their sources, distribution processes, uptake and exchange in ecosystems. *Case Studies in Chemical and Environmental Engineering* 2, 100010 (2020).
- [3] Zeng, E. Y. *Microplastic Contamination in Aquatic Environments: An Emerging Matter of Environmental Urgency*. (Elsevier, 2018).
- [4] Thompson, R. C. Microplastics in the Marine Environment: Sources, Consequences and Solutions. in *Marine Anthropogenic Litter* (eds. Bergmann, M., Gutow, L., Klages, M.) pp. 185–200 (Springer International Publishing, 2015).
- [5] Kershaw, P. J. Ed. Sources, fate and effects of microplastics in the marine environment: a global assessment Rep. Stud. GESAMP No. 90. GESAMP <http://www.gesamp.org/publications/reports-and-studies-no-90> (2019).
- [6] Wirnkor, V. A., Ebere, E. C., Ngozi, V. E. Microplastics, an Emerging Concern: A Review of Analytical Techniques for Detecting and Quantifying Microplastics. *Analytical Methods in Environmental Chemistry Journal* 2, 13–30 (2019).
- [7] Miao, L., Wang, P., Hou, J., Yao, Y., Liu, Z., Liu, S., et al. Distinct community structure and microbial functions of biofilms colonizing microplastics. *Science of The Total Environment* 650, 2395–2402 (2019).
- [8] Rochman, C. M., Manzano, C., Hentschel, B. T., Simonich, S. L. M., Hoh, E. Polystyrene Plastic: A Source and Sink for Polycyclic Aromatic Hydrocarbons in the Marine Environment. *Environ. Sci. Technol.* 47, 13976–13984 (2013).
- [9] Velzeboer, I., Kwadijk, C. J. A. F., Koelmans, A. A. Strong Sorption of PCBs to Nanoplastics, Microplastics, Carbon Nanotubes, and Fullerenes. *Environ. Sci. Technol.* 48, 4869–4876 (2014).
- [10] Li, J., Zhang, K., Zhang, H. Adsorption of antibiotics on microplastics. *Environmental Pollution* 237, 460–467 (2018).
- [11] Thomas, K. J., Sheeba, M., Nampoore, V. P. N., Vallabhan, C. P. G., Radhakrishnan, P. Raman spectra of polymethyl methacrylate optical fibres excited by a 532 nm diode pumped solid state laser. *J. Opt. A: Pure Appl. Opt.* 10, 055303 (2008).
- [12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. *Gaussian 09, Revision E.01*. (Gaussian, Inc., 2009).
- [13] Roy Dennington, Todd Keith, and John Millam. *GaussView*. (2009).