

### **Summary Stage Report III**

Within the III<sup>rd</sup> Stage of the project, the concept of the microfluidic subsystem of the experimental device for the detection of microplastics in liquids was first updated with the latest results published in the literature. Colloidal particles can adsorb spontaneously or under the influence of external factors (such as laser radiation) that change their properties at the interface between two fluids, becoming active on the surface. In this sense, the profile analysis tensiometry (PAT) of the bubble and the drop is one of the most versatile tools for characterizing the properties at the interface and is one of the pillars that supports the new laser-based subsystem for the detection of microplastics in water by microfluidics.

The microfluidic subsystem of the laser-assisted experimental device was developed for the detection of microplastic particles in water, which was tested in several conditions. Thus, the recording of the dynamic values of the tension at the interface was realized both for the non-irradiated samples and in different conditions of their irradiation: (i) during the irradiation and (ii) after the end of the irradiation session. Also, measurements were made in two configurations of the experimental system: in suspended drop, respectively in the emergent bubble configuration.

Efforts were made to optimize the working parameters (optical, detection, microfluidic, optofluidic). Promising results were obtained for an air bubble volume of 12  $\mu\text{L}$ , the use of a capillary with an outer diameter of 1.65 mm and small concentrations of microplastics - 0.02 - 0.1% w/v. Activity at the interface of nanoplastics (10 nm) is difficult to measure due to strong light diffusion.

For the irradiation process, laser beams emitted at two wavelengths  $\lambda = 532$  nm, respectively 266 nm, at a frequency of 10 Hz and with a FWHM pulse duration of  $\sim 9$  ns were tested. The energies per pulse were between 6.5 mJ and 45 mJ, with satisfactory results for values of 6.5 mJ and 8 mJ in the case of emerging bubble configuration and 12 mJ for the suspended drop configuration. The alignment of the irradiation system allowed the laser radiation to be focused with a size of 6 mm through a lens with a focal distance of  $f = 500$  mm. The 20x10x2.5 mm cell was positioned at a distance  $d = 370$  mm from the lens. The irradiation time varied depending on the energy used. Thus, irradiation times starting from 30 s at 45 mJ up to 5 min at 6.5 mJ were used.

Next, the microfluidic properties of water samples containing microplastics were evaluated. In this step, microparticles of polymethyl methacrylate (PMMA) and polystyrene (PS) with a standard diameter of 10  $\mu\text{m}$  were chosen. The direct measurement of polymer adsorption at liquid interfaces proved to be a rather complicated technical problem. As a general observation, the dynamic values of the surface tension decrease substantially in the initial phases of the measurements, followed by a smooth and gradual decrease. This is a typical behavior of polymer compounds and can be interpreted as a diffusion phenomenon that governs the initial stages of the adsorption process, followed by a reorganization of the adsorbed polymer at the air/water interface.

The most appropriate conclusions can be formulated in the conditions where, in addition to the dynamic and equilibrium surface tensions (at the interface), complementary data obtained through other experimental techniques are available, such as optical methods - FTIR and Raman spectroscopy, as well as microscopy techniques, among others. In this sense, experimental sessions dedicated to the evaluation of the influence of laser beams on water samples with microplastic content, in bulk, were carried out using techniques of: optical microscopy, scanning electron microscopy (SEM), UV-VIS and FTIR spectroscopy and, additionally, dynamic light scattering (Dynamic Light Scattering, DLS).

In the natural environment, microplastics are subject to aging and/or fragmentation processes under the action of natural factors, such as physical abrasion, chemical oxidation, weathering or exposure to

UV radiation. Thus, the dynamic variation of the surface tension of the polymers exposed to laser radiation is related to the photodegradation process, which usually starts from the outer surface of the microplastic and gradually penetrates most of the material. During the exposure of microplastics to UV radiation, the C–H bonds can break and form free radicals, which can react with oxygen to form peroxy radicals. This mechanism results in the formation of alcohols, acids, aldehydes, ketones and unsaturated groups. The studies carried out during this stage using UV-Vis and FTIR spectroscopy techniques highlighted this aspect. The degradation process induced by exposure to UV laser radiation emitted at 266 nm is suggested by changes in the FTIR spectrum of the vibrations corresponding to the aromatic ring, both in terms of the deformation of the C-H bonds and the stretching of the C=C bonds. Also, maxima can be observed in the characteristic area of stretching vibrations of O-H bonds.

During the aging process, the surface of the microparticles undergoes changes, which influence their adsorption properties. Thus, a series of pollutants from the environment in which the microplastics are located can be adsorbed on them, with an impact on the properties at the interface of the complex. In this context, we studied the impact on the properties at the air-water interface of PS and PMMA following the adsorption of the methylene blue dye (MB). The dynamic variation of the tension at the interface indicates constant values (approx. 72.8 mN/m) of the surface tension for the virgin samples, while the samples exposed to laser radiation emitted in the Vis spectrum (532 nm) show a decrease in the values of the surface tension that varies depending on the irradiation time, but also on the type of microplastic. The dynamic variation of the surface tension for the microplastic samples complexed with MB dye measured after different irradiation time intervals highlights the changes in the adsorption behavior at the air-water interface, opening perspectives for more in-depth studies regarding the possibility of detecting microplastics using optofluidic methods.

Preliminary molecular modelling studies predict the hydrophobic character of PMMA and PS based on the high number of hydrophobic atoms (21.00 for PMMA and 31.00 for PS) and the high total hydrophobic surface (730.97 for PMMA and 745.47 for PS). According to the surface map that was generated, PS has a large hydrophobic surface, but the moderate polar surface is greater than that of PMMA. Similar to PMMA, PS does not have hydrophilic surfaces. Almost the entire PS surface is lipophilic.

The analysis of the images taken by optical microscopy and SEM techniques suggests that after exposure to laser radiation, micro/nanoparticles are generated that are randomly distributed in the volume of water. The particles of nanometer size are oriented towards the micrometric surfaces and in the case of microplastics complexed with methylene blue, chains of micro/nanoparticles are formed which for the most part are grouped around the microparticles of larger sizes.

The validation of the two subsystems, the improved Raman spectroscopy and, respectively, the microfluidic subsystem of the new laser-based device was carried out using natural water samples collected from the Black Sea, Vacaresti Lake (Bucharest), Snagov Lake, Batca Doamnei Lake (Piatra Neamt), Dambovită river (Joita), Danube (Galati), s.a. Raman spectra on a narrow range, specific to the C-H bond stretching vibration characteristic of CH/CH<sub>2</sub>/CH<sub>3</sub> groups, were recorded using the Raman subsystem with drop detection, taking into account that the spectral range 2780–2980 cm<sup>-1</sup> is one of the three suitable ranges for the detection of the most common polymers. Although the signal is not very intense, it seems that all three analyzed samples (from Batca Doamnei Lake, Argeș - Vidraru river and Black Sea-Constanța) could contain traces of contaminants of the type of microplastics, namely: polyethylene (PE), polypropylene (PP), polyacrylic (PA), polyvinyl chloride (PVC), ethylene vinyl acetate (EVA), polymethyl methacrylate (PMMA) and polyurethane (PU).

Additional analyzes of spectroscopy (FTIR, UV-Vis), microscopy (SEM) and dynamic light scattering (DLS) were carried out to confirm the result obtained by Raman spectroscopy in the drop using the experimental system developed within the project. Thus, the analysis by FTIR spectroscopy confirms the presence of microplastics in the natural water samples taken from the Danube (in Galati), the Vacaresti Lake (Bucharest), the Batca Doamnei Lake (Piatra Neamt), and from the Black Sea by highlighting the peaks in the spectral domains specific to polymers. The spectral range between 1400–1480  $\text{cm}^{-1}$  characteristic of the deformation vibrations of the C-H bonds of  $\text{CH}_2/\text{CH}_3$  and the stretching vibrations of the benzene ring allows the detection again of PE, PP, PS, PET, PA and especially PVC. PTFE can be identified using the spectral range between 1087-1174  $\text{cm}^{-1}$ . The spectral bands present in this field are characteristic of stretching vibrations of C=C, C-O,  $\text{CF}_2$  bonds, deformation of C-H bonds in the aromatic ring and methyl radicals.

Natural water samples were also analyzed using the microfluidic subsystem for the detection of microplastic in water using the drop configuration. The dynamic variation of the interface tension (DIT) was measured for a time interval of 4 h. All samples show surface activity. The DIT values decrease slightly in the initial phases of the measurements (the first 14 min), followed by a substantial decrease, because later, after approx. 45 min the descent should be smooth and gradual. The surface tension of natural water samples starts from a value of  $\sim 72$  mN/m and, depending on the composition of each sample, reaches an equilibrium between  $\sim 65$  and 69 mN/m. This behavior of the surface tension curves suggests the presence of hydrophobic compounds that are adsorbed at the water/air interface and shows a similarity with the measurements of standard polymers measured. These results need to be correlated with complementary results obtained through other analytical techniques.

Thus, the project objectives for this stage were fulfilled and the estimated results were obtained.