BABEȘ-BOLYAI UNIVERSITY

Faculty of Physics

Doctoral School of Physics

Summary of the doctoral thesis

Plasmonic nanostructured substrates for SERS and SERRS detection of nanoplastics: from molecular optimization to particle-substrate matching

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Cluj-Napoca

2026

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Introduction

Plastic pollution has become a major environmental concern, with increasing attention now focused on nanoplastics, whose small size, heterogeneous morphology and composition, and high mobility not only increase their potential ecological and human health impacts but also make their detection and characterization particularly challenging [1]. Despite growing awareness of these risks, reliable methods for the detection and quantification of nanoplastics remain limited. Raman spectroscopy is one of the most widely used techniques for plastic identification due to its high chemical specificity and minimal sample preparation requirements. However, its application to nanoplastics is hindered by the inherently weak Raman signal of nanoscale particles. Surface-Enhanced Raman Scattering (SERS) spectroscopy has emerged as a promising strategy to overcome this limitation by amplifying Raman signals through plasmonic enhancement [2]. Nevertheless, most plasmonic substrates reported in the literature have been designed and optimized for molecular analytes, whereas nanoplastics interact with localized electromagnetic fields in a fundamentally different manner because of their larger dimensions and complex particle-substrate interactions. Consequently, the design principles established for molecular SERS cannot be directly transferred to nanoplastic detection, highlighting the need for plasmonic substrates specifically tailored to nanoscale plastic particles.

The present thesis addresses this challenge by developing plasmonic nanostructured substrates and Raman-based analytical methodologies dedicated to nanoplastic detection. To achieve this goal, the work focused on three complementary research directions. First, plasmonic nanostructured substrates were designed and optimized to improve the SERS detection of nanoplastics. Second, the relationship between nanoplastic particle size and morphology and the geometry of the plasmonic substrate was systematically investigated in order to establish the factors governing SERS enhancement for nanoplastic analytes. Finally, the developed plasmonic platforms were combined with resonance Raman spectroscopy to enable the detection and quantitative analysis of environmentally relevant blue nanoplastics using the SERRS effect. The thesis is organized into four chapters, one chapter addresses the state of the art in nanoplastic pollution and analysis, and three experimental chapters that progressively address the objectives proposed.

Chapter 1 presents the current state of the art in nanoplastic analysis, introducing the sources and environmental impact of nanoplastic pollution, reviewing the analytical techniques currently available for nanoplastic detection, and discussing the principles of Raman spectroscopy, surface-enhanced Raman scattering (SERS), and plasmonic nanostructured substrates. Particular emphasis is placed on the current challenges associated with nanoplastic detection and quantification, as well as on the limitations of existing analytical methodologies in the context of emerging regulatory requirements, thereby establishing the scientific motivation for the present work.

Chapter 2 investigates the influence of plasmonic substrate morphology on the SERS detection of nanoplastics using colloidal lithography-derived gold film-over-nanosphere (AuFoN) substrates. By comparing the SERS response of molecular and nanoplastic analytes, this chapter demonstrates that substrate designs optimized for molecules cannot be directly translated to nanoplastic detection and introduces the concept of particle-substrate matching as a key design criterion.

Chapter 3 presents the fabrication, optimization, and analytical evaluation of nanobowl-based plasmonic substrates with tunable geometries. Their performance is assessed for the detection of reference polystyrene nanoplastics and environmentally relevant PET nanoplastics, while a dedicated measurement protocol demonstrates their capability for the quantitative analysis of reference nanoplastics.

Chapter 4 extends the developed analytical strategies to environmentally relevant blue micro- and nanoplastics by exploiting the resonance Raman response of the copper phthalocyanine pigment present in weathered blue polypropylene fishing nets. The chapter first demonstrates the detection of individual blue nanoplastics down to 500 nm using resonance Raman spectroscopy and subsequently combines this approach with optimized nanobowl-based plasmonic substrates to establish a surface-enhanced resonance Raman scattering (SERRS) platform. The analytical performance and quantitative potential of the developed methodology are evaluated using realistic plastic samples, highlighting both the advantages of combining resonance and plasmonic enhancement and the challenges associated with heterogeneous environmental materials.

The original contributions of this thesis consist in demonstrating that the design principles of the plasmonic nanostructured substrates established for molecular SERS cannot be directly translated to nanoplastic detection and that efficient plasmonic substrates must instead be designed by considering the physical characteristics of environmental nanopalstic particles. This concept of particle-substrate matching, developed and investigated throughout the thesis, represents the central scientific contribution of the work. In addition, the thesis presents the development of tunable nanobowl-based plasmonic substrates capable of detecting both reference and environmentally relevant nanoplastics, establishes a quantitative SERS methodology for model nanoplastics, demonstrates the use of resonance Raman spectroscopy for the detection of naturally weathered blue nanoplastics down to 500 nm, and introduces a SERRS platform for environmentally relevant blue micro- and nanoplastics.

CHAPTER 1

Current detection techniques and their versatility towards nanoplastic detection

1.1 The source and impact of nanoplastic pollution

Plastic pollution has become a major environmental challenge due to increasing plastic production, widespread consumption, and inadequate waste management [3], [4], [5]. Through weathering processes, larger plastic debris progressively fragments into small microplastics (MPs, 1 μm - 1 mm) and nanoplastics (NPs, smaller than 1 μm) [6], [7]. These particles are widely distributed across marine and freshwater ecosystems, soils, sediments, and the atmosphere, including remote regions, demonstrating their environmental persistence and long-range transport [8], [9], [10], [11]. Their detection in drinking water, seafood, agricultural products, and human tissues raises concerns about their potential ecological and health impacts [12], [13], [14], [15].

MPs can cause physical damage, impaired feeding, reduced growth, and reproductive dysfunction in organisms, while also facilitating the transfer of hazardous chemicals and pathogens through food webs [16], [17], [18]. However, increasing attention has focused on NPs because their smaller size, larger specific surface area, and enhanced physicochemical reactivity may increase their environmental mobility and biological effects [1], [19]. These properties enable NPs to remain suspended in water, interact with environmental contaminants, and potentially transport toxic substances [20]. Furthermore, their nanoscale dimensions may facilitate their passage across biological barriers, promoting cellular uptake and intracellular accumulation [21], [22]. Their widespread occurrence, potential toxicity, and limited detectability therefore make NPs an emerging environmental concern, highlighting the need for further research into their environmental behaviour and long-term ecological and human health impacts.

1.2 The gold standards in nanoplastics analysis

The analysis of nanoplastics remains challenging due to the lack of standardized analytical methodologies, their extremely small size, low mass, weak analytical signals, and the limitations of conventional detection techniques. Consequently, their environmental abundance may be substantially underestimated [23]. Various complementary techniques have been developed to characterize particle size, morphology, chemical composition, and concentration [24]. Electron microscopy (SEM and TEM) and atomic force microscopy (AFM) provide high-resolution morphological information, while dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), and field-flow fractionation (FFF) support particle sizing, concentration measurements, and sample separation [25], [26], [27], [28], [29], [30], [31].

For chemical identification, Fourier-transform infrared (FTIR) and Raman spectroscopy are widely used reference methods, while mass spectrometry-based techniques, such as pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), enable polymer identification and mass quantification [32], [33], [34]. However, these methods have limitations in spatial resolution or their ability to provide information on particle morphology and number, complicating the reliable characterization of

nanoplastics [35]. To overcome these limitations, advanced techniques such as surface-enhanced Raman scattering (SERS), tip-enhanced Raman spectroscopy (TERS), AFM-IR, and optical photothermal infrared spectroscopy (O-PTIR) have emerged, offering improved sensitivity and spatial resolution [36], [37], [38], [39]. Among these approaches, SERS is particularly promising because plasmonic enhancement significantly amplifies Raman signals, enabling sensitive chemical identification of nanoplastics at very low concentrations [2], [40], [41].

The performance of SERS largely depends on the active substrate, which should provide high enhancement, uniformity, reproducibility, stability, low background interference, and cost-effective fabrication [42], [43]. SERS substrates are generally classified as colloidal or solid-state systems. While colloidal gold and silver nanoparticles offer simple preparation and strong enhancement, solid substrates provide improved signal uniformity, stability, reproducibility, and compatibility with quantitative analysis and routine environmental monitoring [37], [42]. Their fabrication relies on top-down approaches, such as lithography, which enable precise control over nanostructure geometry but often involve high costs and complex procedures, or bottom-up approaches, including self-assembly, colloidal lithography, and electrochemical deposition, which offer more cost-effective and scalable alternatives. Hybrid strategies combine the advantages of both approaches [44], [45]. Developing reproducible, stable, and scalable solid-state substrates is particularly important for improving analytical reliability and enabling the broader application of SERS in environmental monitoring.

However, most of the current reported approaches for nanoplastic detection using SERS remain proof-of-concept demonstrations, with limited validation using heterogeneous nanoplastics and environmentally relevant samples. Future development should prioritize substrate sensitivity, reproducibility, stability, and scalable fabrication. Ultimately, combining rational substrate design with advanced computational methods is essential for establishing SERS as a standardized analytical platform for routine nanoplastic monitoring.

1.3 Challenges and current trend for nanoplastic detection relative to the current regulations

The widespread occurrence of micro- and nanoplastics in environmental, food, and biological samples has increased regulatory attention and highlighted the need for reliable analytical methods. In the European Union, Commission Regulation (EU) 2023/2055 introduced restrictions on intentionally added synthetic polymer microparticles under the REACH framework, while the Drinking Water Directive (EU) 2020/2184 led to the adoption of a harmonized Raman- and infrared-based methodology for monitoring microplastics in drinking water [46], [47], [48]. However, current regulatory measures primarily address microplastics, with nanoplastics still excluded from routine monitoring due to the lack of validated analytical methods. The WHO and EFSA have identified the

development of reliable analytical methodologies for nano and microplastics as a research priority for assessing exposure and potential health risks [49], [50].

Among the emerging analytical techniques, SERS has attracted considerable attention due to its high sensitivity, chemical specificity, and potential for single-particle analysis. Nevertheless, its application to realistic environmental samples remains challenging due to the complex characteristics of environmental nanoplastic samples. Furthermore, the limitations in reproducibility and comparability between studies, and the absence of certified reference materials, standardized validation procedures, and interlaboratory comparisons also hinders regulatory implementation.

Current research therefore focuses on developing substrates with optimized morphology, accessible electromagnetic hot spots, and improved particle-substrate interactions, alongside machine learning-based spectral analysis. Combining optimized SERS platforms with standardized analytical workflows and automated data processing is essential to improve reliability and support future regulatory frameworks for nanoplastic monitoring.

CHAPTER 2

Translating molecular SERS optimization to nanoplastic detection: limitations and design considerations

2.1 Introduction

In this chapter is investigated whether the optimization strategies developed for molecular SERS detection can be directly translated to the identification of individual nanoplastic particles. To address this question, nanostructured plasmonic SERS substrates with distinct surface morphologies and tunable plasmonic responses were fabricated using colloidal self-assembly combined with air-plasma etching and metal deposition. In the first part of this chapter, their performance was evaluated through wavelength-scanned SERS measurements in the near-infrared region using benzenethiol as a molecular Raman reporter. Based on these results, the substrates were further tested for the detection of individual polystyrene spherical nanoplastic particles with diameters of 300 and 500 nm, and the experimental observations were supported by finite-difference time-domain (FDTD) simulations.

2.2 Experimental methodology

Three gold-based SERS substrates were fabricated using colloidal lithography. First, 460 nm polystyrene (PS) nanospheres were self-assembled at an air-water interface and transferred onto cleaned PS plates. The arrays were subsequently etched using air plasma for 150 or 270 s to obtain different morphologies, followed by deposition of a 150 nm gold film through electron-beam evaporation, producing AuFoN, AuFoEN-150, and AuFoEN-270 substrates. Their morphology was characterized by scanning electron microscopy (SEM) and *ImageJ* analysis, while their optical response was evaluated through specular reflection spectroscopy.

The enhancement performance of the substrates was investigated using wavelength-scanned SERS measurements with benzenethiol as a Raman reporter, allowing the enhancement factors to be determined. The AuFoEN-270 substrate was additionally evaluated for the detection of thiabendazole using a confocal Raman spectrometer. Nanoplastic detection experiments employed monodisperse PS particles with diameters of 300 and 500 nm. After centrifugation and washing, the particles were dispersed in ethanol and deposited onto UV-ozone-treated AuFoN and AuFoEN-270 substrates, with cleaned glass serving as a reference. Raman spectra of individual particles were recorded using 785 nm excitation and processed by baseline subtraction.

Finally, finite-difference time-domain (FDTD) simulations were performed using Ansys Lumerical to investigate electromagnetic near-field distributions around AuFoN and AuFoEN-270 structures, both with and without PS nanoplastic particles of 100, 300, and 500 nm. The simulations used 785 nm illumination, a refined 4.6 nm mesh near the structures, and calculations of the electric field averaged over the substrate surface and particle volume. These combined experimental and computational approaches enabled the assessment of substrate morphology, plasmonic enhancement, and particle-substrate interactions in SERS-based nanoplastic detection.

2.3 Results and Discussion

2.3.1 Characterization of the SERS substrates

Three gold film-over-nanosphere substrates (AuFoN, AuFoEN-150, and AuFoEN-270) were fabricated to investigate the influence of surface morphology on surface-enhanced Raman scattering (SERS) performance. Scanning electron microscopy (SEM) revealed that increasing the plasma etching time reduced the nanosphere diameter and increased the interparticle spacing and surface roughness, resulting in a quasi-three-dimensional structure. Among the investigated substrates, AuFoEN-270 exhibited the greatest surface roughness, which could facilitate the formation of electromagnetic hot spots and improve the local enhancement of the Raman signal. Optical reflectance measurements further showed that plasma etching modified the plasmonic response of the substrates, with their optical properties supporting SERS excitation across the visible-near-infrared region.

SERS performance was evaluated using benzenethiol (BT) as a Raman reporter and wavelength-scanned measurements. All substrates displayed characteristic BT vibrational bands, while the calculated enhancement factors increased with excitation wavelength across the investigated range. AuFoEN-270 achieved the strongest enhancement, attributed to its greater surface roughness and quasi-three-dimensional morphology, although reproducibility decreased with increasing etching time. Subsequent testing with thiabendazole (TBZ) revealed characteristic Raman fingerprints and good spot-to-spot reproducibility. Quantitative analysis yielded a calibration curve with a linear correlation coefficient of R^2=0.97 and a limit of detection (LOD) of approximately $2 \cdot 10^{-7}$ M. These findings demonstrate the potential of AuFoEN-270 for sensitive molecular detection and emphasize the importance of substrate morphology in optimizing SERS performance.

2.3.2 SERS performance of the optimized substrates for nanoplastic detection

Following the optimization of SERS substrates for molecular analytes, the applicability of AuFoN and AuFoEN-270 was investigated for detecting polystyrene (PS) nanoplastic particles with diameters of 300 and 500 nm. The results (Fig. 2.1. a and b) showed that AuFoN provided clear characteristic Raman signals of polystyrene, including prominent bands near 1003 and 1033 cm^{-1}, associated with ring-breathing and C-H deformation modes [51], [52].

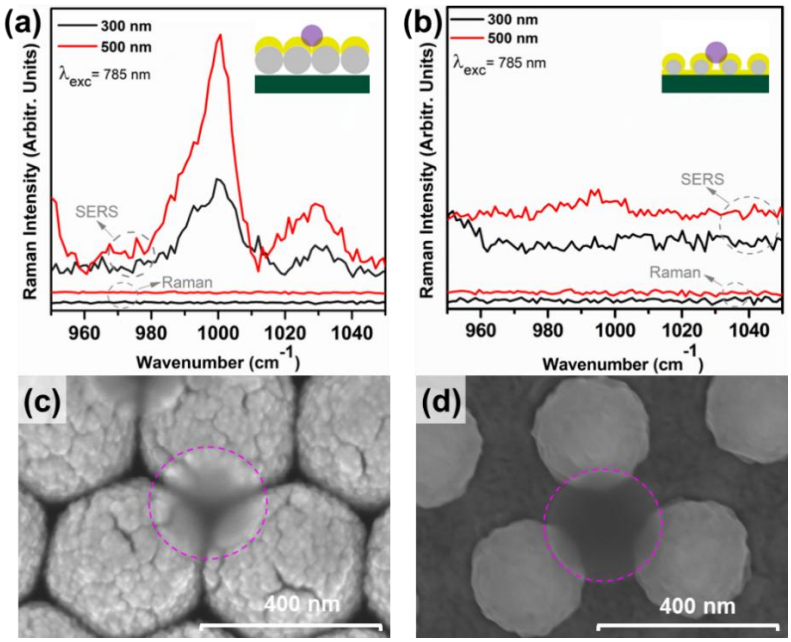


Figure 2.1. Average SERS spectra of individual SNPs of 300 nm and 500 nm spread on **(a)** AuFoN, and on **(b)** AuFoEN substrates, respectively (785 nm excitation), together with Raman spectra of 300 nm and 500 nm SNPs on cover glass; SEM images of 300 nm PS SNPs dispersed on **(c)** AuFoN and **(d)** AuFoEN-270 substrates, respectively. Adapted from I. Cârdan, V. Zani, A. Maria, M. Gherman, R. Signorini, R. Pilot and C. Farcău. From molecular to nanoplastic SERS detection: insights into the role of analytes in plasmonic substrate design. Nanoscale, 2025, 17 (44), 25680-25690 [53].

Signal intensity was generally higher for the larger, 500 nm particles. In contrast, AuFoEN-270 produced considerably weaker signals despite its superior performance in molecular SERS detection. As shown in Fig. 2.1. c and d, SEM imaging revealed that the nanoparticles preferentially accumulated in the interstitial regions between three neighbouring nanospheres on both substrates. These findings indicate that SERS performance for nanoplastics depends not only on electromagnetic enhancement but also on particle size, substrate morphology, and the spatial interaction between particles and metallic nanostructures. Therefore, substrates optimized for molecular detection may not necessarily provide optimal performance for nanoplastic analysis, highlighting the importance of application-specific substrate design.

2.3.3 Interpretation of molecular and nanoplastic SERS performance by FDTD simulations

Unlike small molecules, which can adsorb directly onto metallic surfaces and access regions of strong electromagnetic enhancement, nanoplastic particles interact with the substrate only through a limited contact area. Consequently, effective SERS detection depends on the spatial distribution of the enhanced electric field within the particle itself. Three-dimensional finite-difference time-domain (FDTD) simulations were performed to

investigate these effects for 300 and 500 nm polystyrene particles placed on glass, AuFoN, and AuFoEN-270 substrates. The AuFoN generated a stronger and more uniformly distributed electric field throughout the particle volume than AuFoEN-270, despite comparable surface field enhancement for the bare substrates. Volume-averaged electric field calculations and estimated enhancement factors, based on the fourth power of the electric field ratio relative to glass, confirmed the superior performance of AuFoN, particularly for smaller particles.

Further simulations examined the influence of particle diameter (100, 300, and 500 nm), substrate etching, and gold film thickness (50 and 150 nm). The results demonstrated that optimal SERS enhancement depends on the geometric compatibility between the particle and substrate. Although smaller particles sometimes exhibited higher calculated enhancement factors, the integrated electric field indicated that larger particles could still generate stronger measurable signals because of their greater volume.

Overall, the simulations demonstrate that substrate optimization must be tailored to the analyte. AuFoEN-270 is more effective for small molecular analytes, owing to its strong surface-localized electromagnetic hotspots, whereas AuFoN provides greater enhancement for nanoplastic particles by generating stronger fields within their volume. These findings highlight the importance of particle size, substrate morphology, and gold film thickness in developing SERS platforms for nanoplastic detection.

CHAPTER 3

Tunable nanobowl-based plasmonic substrates for SERS detection of nanoplastics

3.1 Introduction

The previous chapter demonstrated that optimizing AuFoN substrates using molecular SERS probes does not necessarily translate to nanoplastic detection, as particle size, morphology, substrate contact and interaction with localized electromagnetic fields also influence enhancement. To address these factors, this chapter investigates metal-coated nanobowl substrates fabricated through colloidal self-assembly and template-assisted soft lithography. Their morphology promotes particle confinement and enrichment, while the absence of underlying polystyrene spheres avoids potential interference from the polymer template. Furthermore, nanobowl dimensions can be adjusted to accommodate different particle sizes and tune the plasmonic response.

The substrates are evaluated using progressively more complex samples, beginning with monodisperse polystyrene nanoplastics, followed by irregular PET nanoplastics and, finally, quantitative measurements. By varying nanobowl geometry and metallic coating, the localized surface plasmon resonance can also be matched to the excitation wavelength. This approach enables systematic investigation of the factors governing SERS enhancement and supports the development of application-specific substrates for nanoplastic detection.

3.2 Experimental methodology

The experimental methodology involved the fabrication and characterization of nanobowl-based plasmonic SERS substrates, the preparation of reference and environmentally relevant nanoplastic samples, and the evaluation of their performance for particle detection and quantification. The SERS substrates were fabricated using a hybrid colloidal template-assisted soft lithography method. Polystyrene (PS) spheres with diameters of 600 and 750 nm were assembled into ordered, close-packed arrays using convective self-assembly. These templates were replicated in polydimethylsiloxane (PDMS) by casting and curing the elastomer at 80 °C for 2 h, producing negative replicas with hexagonal nanobowl structures. The replicas were subsequently coated by electron-beam evaporation with a 3 nm titanium adhesion layer and either 100 nm of gold or 120 nm of silver, yielding four substrates: Au-NBL^{600}, Ag-NBL^{600}, Au-NBL^{750}, and Ag-NBL^{750}.

Reference PS nanoplastics with diameters of 100, 300, and 500 nm were cleaned through repeated centrifugation and washing with ethanol, followed by ultrasonication to ensure adequate dispersion. Environmentally relevant polyethylene terephthalate (PET) nanoplastics were produced from used PET bottles through cryogenic grinding, milling, filtration, and solvent evaporation, following a previously published protocol [54].

Raman and SERS measurements were performed using a Renishaw inVia Reflex confocal Raman spectrometer. Individual PS nanoparticles were analysed on glass and on the Au-NBL^{600} and Au-NBL^{750} substrates using 632.8 nm excitation, a 100x objective, a 40 s acquisition time, and 1.7 mW laser power. SERS mapping was additionally

performed for 300 and 500 nm PS particles. PET nanoplastics were investigated using gold and silver substrates at 532 nm excitation, with a 10 s acquisition time and 20 mW laser power. Analytical enhancement factors were calculated using the conventional definition [43], and a per-particle analytical enhancement factor AEF^P was introduced to evaluate the enhancement obtained from individual nanoplastic particles

Finally, quantitative analysis was conducted using 500 nm PS particles at concentrations of 200, 100, 20, and 2 μg/mL. Samples were deposited onto the Ag-NBL^{600} substrate and analysed by Raman mapping under 532 nm excitation.

3.3 Results and Discussion

3.3.1 Structural and plasmonic characterization of the nanobowl substrates

The structural and optical properties of the fabricated nanobowl-based SERS substrates were investigated to assess their suitability for nanoplastic detection. Optical microscopy and scanning electron microscopy confirmed successful transfer of the template morphology to the PDMS replicas.

SEM confirmed that the metal-coated substrates exhibited highly ordered nanobowl structures. The average nanobowl diameters were 445 $\pm$ 2 nm for substrates fabricated using 600 nm PS spheres and 552 $\pm$ 5 nm for those prepared from 750 nm spheres. Reflectance measurements revealed two main spectral features associated with the plasmonic responses of the substrates.

Overall, the results demonstrate that the fabrication method enables the production of ordered nanobowl-based SERS substrates with tunable structural and optical properties. Their distinctive morphology is expected to promote the retention and confinement of nanoplastic particles within the nanobowls and adjacent surface features, thereby improving particle accessibility for subsequent SERS detection.

3.3.2 Influence of particle size and substrate geometry on the SERS detection of reference PS nanoplastics

The influence of nanoplastic particle size and substrate morphology on SERS performance was investigated using commercial PS nanoparticles with diameters of 100, 300, and 500 nm deposited on Au-NBL^{600} and Au-NBL^{750} substrates. Identical measurement conditions were applied to compare their responses. Both substrates produced detectable SERS signals, confirming their applicability for nanoplastic detection.

It was observed that the absolute SERS intensity generally increased with particle diameter, particularly for Au-NBL^{750} substrate (Fig. 3.1). However, the per-particle analytical enhancement factor AEF^P generally followed the opposite trend, with smaller particles exhibiting higher enhancement efficiency.

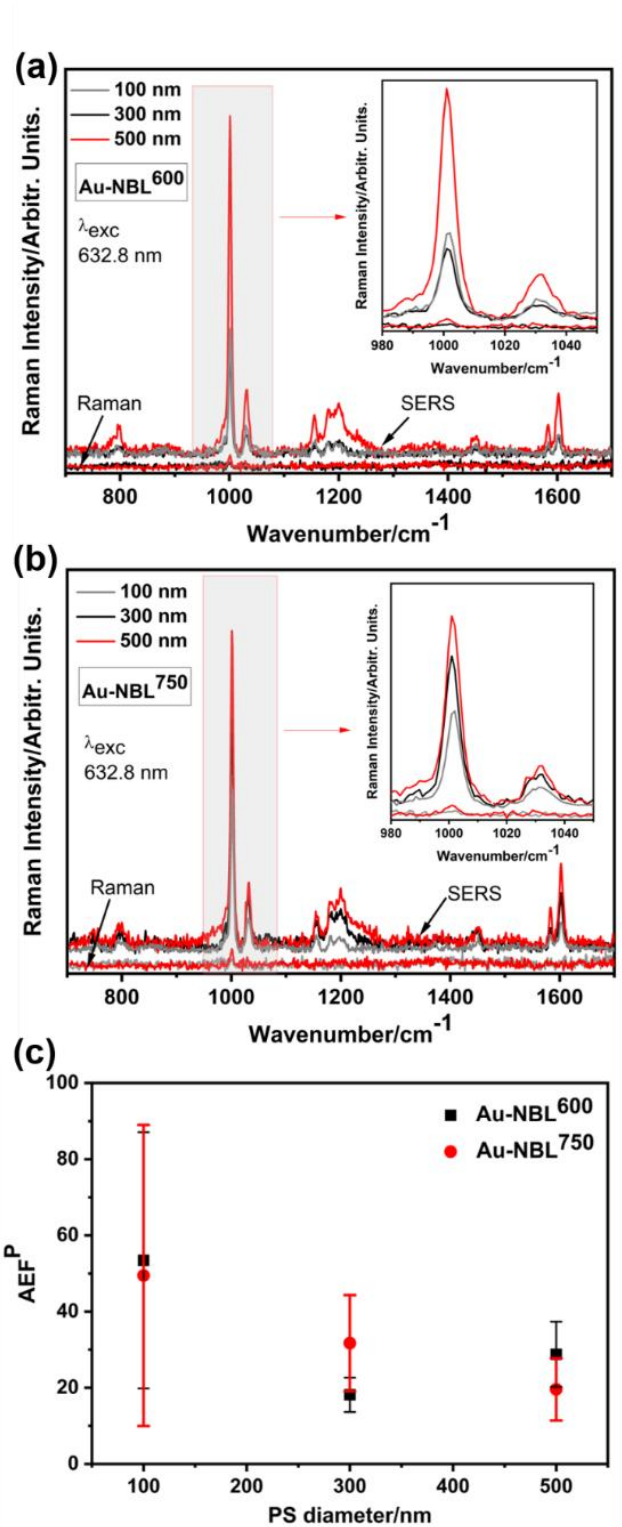


Figure 3.1. SERS spectra of 100 nm, 300 nm and 500 nm reference PS nanoplastics obtained using two nanobowls substrates: **(a)** Au-NBL^{600} and **(b)** Au-NBL^{750}; Raman spectra of 300 nm and 500 nm PS nanoplastics are also included. **(c)** AEF^{P} variation of PS diameter in case of the two substrates.

This behaviour is attributed to the highly localized electromagnetic near-field, which is concentrated close to the metallic surface and within the nanobowl structures [55]. As larger particles extend beyond these enhanced regions, only a limited portion of their volume experiences strong enhancement, whereas smaller particles can interact more effectively with the SERS-active regions. SERS mapping and SEM-EDX analysis further demonstrated that particle positioning within the nanobowls influences signal intensity and reproducibility. Smaller particles may occupy the nanobowl cavities more effectively, while larger particles can extend beyond the enhanced field region.

As shown in Fig. 3.1, these results highlight the relationship between particle diameter, substrate geometry, SERS intensity, and AEF^P. These findings demonstrate that reliable nanoplastic detection depends on both particle dimensions and their spatial interaction with the nanostructured substrate. Further electromagnetic simulations are needed to clarify the influence of particle positioning and confinement within the nanobowl cavities.

3.3.3 Detection of environmentally relevant PET nanoplastics

The applicability of nanobowl-based SERS substrates was further evaluated using environmentally relevant PET nanoplastics produced by mechanical fragmentation of PET bottles. Unlike spherical, monodisperse polystyrene (PS) nanoparticles, PET particles exhibited irregular shapes and a broad size distribution, as confirmed by SEM imaging. To investigate the influence of the plasmonic material, PET nanoplastics were analysed using Au-NBL^{600} and Ag-NBL^{600} substrates, which share the same nanobowl morphology but differ in their metal coating. Both substrates produced characteristic PET Raman bands at approximately 1613 and 1725 cm^{-1}, assigned to the aromatic ring vibration and ester carbonyl stretching, respectively [56], [57]. The calculated per-particle analytical enhancement factors AEF^P were 4.0 ± 2.3 for Au-NBL^{600} and 8.5 ± 5.9 for Ag-NBL^{600}.

Despite its higher enhancement efficiency, Ag-NBL^{600} exhibited considerable measurement variability. This was attributed to the irregular morphology of PET particles, which produces differences in contact area, particle orientation, and distance from the substrate's electromagnetic hotspots. Compared with spherical PS nanoparticles, PET particles therefore experience less uniform enhancement, resulting in lower and more variable AEF^P values. Overall, the results demonstrate that silver-coated nanobowl substrates offer improved SERS performance for PET nanoplastics under 532 nm excitation, while also highlighting the importance of particle morphology and substrate-particle interactions. These findings emphasize the need to validate SERS-based detection methods using environmentally relevant nanoplastics, since idealized spherical reference particles may not fully represent the analytical challenges posed by real-world samples.

3.3.4 Quantitative SERS analysis of reference PS nanoplastics

The quantitative performance of the nanobowl-based SERS platform was evaluated using 500 nm PS nanoplastics and the Ag-NBL^{600} substrate, selected for its plasmonic response in the green spectral region, matching the 532 nm excitation wavelength. A measurement protocol combining a small deposition volume (0.5 µL), the hydrophobic properties of the substrate, and large-area SERS mapping was developed to maximize particle sampling while maintaining a practical acquisition time. The average SERS intensity increased with PS concentration, and integration of the characteristic Raman band at 1000 cm^{-1} demonstrated a linear response across the investigated concentration range, with successful detection down to 2 µg/mL (Fig. 3.2). This confirms the potential of the Ag-NBL^{600} substrate for quantitative nanoplastic analysis and highlights the importance of optimizing both substrate properties and measurement conditions. Overall, these findings establish nanobowl-based substrates as a versatile platform for quantitative SERS detection, with potential for adaptation to a broad range of analytical applications.

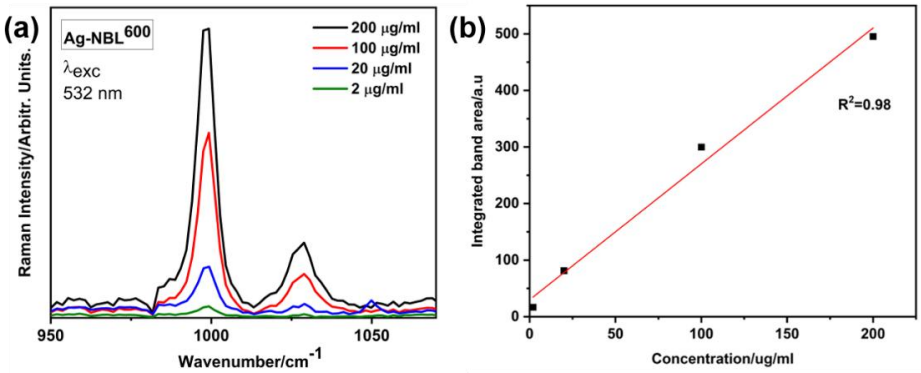


Figure 3.2. (a) Average SERS spectra of 500 nm PS suspension at various concentrations and **(b)** integrated area under 1000 cm^{-1} band as a function of PS concentration.

CHAPTER 4

Blue plastic abundance from macro to nano and its detection and quantification

4.1 Introduction

This chapter investigated Raman-based approaches for identifying and quantifying CuPc-containing plastics across different size ranges. First, resonance Raman spectroscopy was used to identify naturally weathered blue nanoplastics as small as 500 nm in approximately 20-year-old fishing-net fragments, demonstrating the potential of the PB15 signal as a marker for environmental plastic detection. Subsequently, CuPc resonance Raman scattering was combined with gold- and silver-coated nanobowl SERS substrates to improve detection sensitivity. Their performance was evaluated on individual naturally weathered particles, followed by the development of a quantitative protocol using ball-milled blue micro- and nanoplastics. Overall, the study establishes complementary Raman-based strategies for blue nanoplastic detection while identifying challenges associated with the quantitative analysis of heterogeneous environmental samples.

4.2 Resonance Raman detection of environmentally relevant blue nanoplastics

4.2.1 Experimental methodology

Copper phthalocyanine (CuPc) pigment, chemically synthesised at Babeș-Bolyai University, was investigated alongside blue plastic samples ranging from macro- to microscale. The macroplastic collection comprised 26 naturally degraded blue and green items representing LDPE, HDPE, PP, and PS, while 81 blue microplastic particles were collected from spring and river waters in Romania [58], [59], [60]. Additionally, blue fishing-net filaments recovered from the Bay of Bistrina in June 2019 were analysed. Estimated to have undergone approximately 20 years of marine ageing, these plastics exhibited pronounced brittleness and fragmented into fine blue powder, likely due to prolonged environmental degradation.

CuPc pigment and blue plastic samples were characterized using a Renishaw InVia Reflex confocal Raman spectrometer. Measurements employed excitation wavelengths of 785, 632.8, and 532 nm, with laser power and acquisition parameters adjusted according to the specific experiment. For the naturally fragmented blue powder, micro-Raman analysis was performed using 632.8 nm excitation and a 100x objective (NA 0.9), enabling the identification of extremely small blue fragments visible as microscopic dots under confocal microscopy.

4.2.2 Results and Discussion

4.2.2.1 Spectroscopic characterization of the CuPc pigment

The UV-Vis absorption spectrum of copper phthalocyanine (CuPc), also known as Pigment Blue 15 (PB15), contains a B-band in the near-UV region and a Q-band in the visible region, with absorption features around 611, 645, and 718 nm arising from $\pi \rightarrow \pi^*$ electronic transitions [61], [62]. To investigate the resonance Raman (RR) effect, CuPc was analysed using 532, 632.8, and 785 nm excitation.

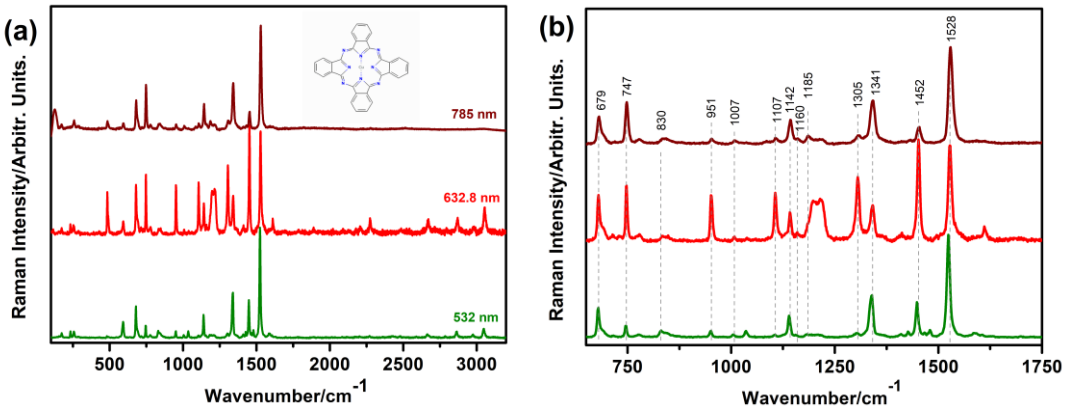


Figure 4.1. Raman spectra of the CuPc pigment at three excitation wavelengths, 532 nm, 632.8 nm, and 785 nm in the range of **(a)** 100–3200 cm^{-1} and **(b)** 600–1750 cm^{-1}; the inset image is representing the molecular structure of CuPc. Adapted from I. Cârdan, I. Nesterovschi, L. Barbu-Tudoran & S. C. Pînzaru. Blue micro-/nanoplastics abundance in the environment: a double threat as a Trojan horse for a plastic-Cu-phthalocyanine pigment and an opportunity for nanoplastic detection via micro-Raman spectroscopy. Environ Sci Nano. 2025; 12 (4), 2357–2370 [65].

As shown in Fig. 4.1, the 632.8 nm laser produced strong enhancement of characteristic pigment bands at 951, 1107, 1305, and 1452 cm^{-1}, assigned to vibrations of the CuPc chromophore [63], [64]. The most intense band across all excitation wavelengths occurred at 1528 cm^{-1}, corresponding to C-N-C stretching. These findings confirm that red excitation provides selective enhancement of the PB15 Raman signature.

The influence of excitation wavelength on pigment identification in blue plastics was subsequently investigated using blue macroplastic samples. Three spectral behaviours were observed, depending on the relative contributions of pigment and polymer signals. Under 632.8 nm excitation, pigment bands generally dominated, whereas 785 nm excitation often revealed additional polymer-specific features. Measurements at 532 nm were frequently affected by fluorescence, hindering spectral interpretation. Variations between measurement locations also indicated a heterogeneous pigment distribution within some polymer matrices, suggesting that fragmented plastics may contain predominantly pigment, polymer, or both.

Overall, 632.8 nm excitation provided the most reliable detection of PB15 through resonance enhancement, although the strong pigment signal could obscure polymer-specific bands and complicate polymer identification. Complementary measurements at 785 nm can help reveal polymer characteristics, while the fluorescence background associated with 532 nm excitation limits its applicability.

4.2.2.2 Characterization of blue macro- and microplastics

A total of 107 blue and green plastic samples, including 26 macroplastics and 81 microplastics collected from environmental sources, were analysed using micro-Raman spectroscopy with 785 nm excitation to investigate the presence of PB15 and its influence on

polymer identification. Among the macroplastics, 21 exhibited characteristic PB15 Raman bands alongside polymer signals, indicating that the pigment was incorporated into the plastic matrix. PB15 was detected in all analysed polypropylene (PP) samples and all green and turquoise items, while five blue samples showed no detectable pigment signature. Its spectral features varied between polymer types and individual samples, partly due to overlapping Raman bands. The most consistently identifiable PB15 bands occurred at 748 and 1528 cm^{-1}, providing useful markers for pigment detection.

Among the 81 microplastics, 41 (51%) displayed PB15 signals. In many cases, pigment bands dominated the spectra, while polymer-specific signals were weak or absent, preventing reliable polymer identification. Microplastics from spring and river waters exhibited different PB15 spectral patterns, including variations in band intensity and slight shifts that may indicate changes in pigment characteristics. Potential interference from biofilms was also investigated, as carotenoid Raman signals can overlap with the main PB15 band.

Overall, these results demonstrate that PB15 can serve as a useful Raman marker for detecting blue and green microplastics, even when their polymer composition cannot be determined. Its characteristic spectral signature offers potential for monitoring plastic contamination and degradation in environmental systems, particularly when combined with complementary excitation wavelengths and advanced Raman techniques.

4.2.2.3 Resonance Raman detection of blue nanoplastics

The feasibility of detecting environmentally relevant blue nanoplastics through the RR signature of PB15 was investigated using the naturally aged polypropylene sample PP-BL-003. After approximately 20 years of marine ageing and storage, the material became highly susceptible to fragmentation into micro- and nanoscale particles. Individual particles were subsequently analysed by micro-Raman spectroscopy, with their minimum Feret diameter estimated using *ImageJ*.

Plastic particles with average diameters of approximately 500 and 800 nm were successfully detected using Resonance Raman spectroscopy, and the signals exhibited characteristic PB15 Raman bands, while polypropylene signal was undetectable. This demonstrates that resonance enhancement enables the detection of sub-micrometre blue plastics based on their pigment signature. However, other particles in the micrometre range exhibited only polypropylene signals, confirming heterogeneous pigment distribution within the plastic matrix. SEM-EDX further supported this variability through differences in carbon-to-copper content between particles.

Measurements at different excitation wavelengths showed that 785 nm excitation was ineffective for detecting particles around 1 μm or lower, whereas 632.8 nm provided strong pigment signal for sub-micrometer plastic particles and 532 nm enabled more balanced detection of pigment and polymer signals. Despite potential fluorescence interference at 532 nm, red excitation offered a practical approach for identifying PB15-containing nanoplastics. Overall, these findings establish PB15 as a useful tracer for detecting and monitoring environmentally derived blue micro- and nanoplastics, including investigations of their uptake

and fate in living systems. They also highlight the potential significance of pigment-containing plastics as carriers of chemical additives, whose environmental and biological effects warrant further investigation.

4.3 SERRS detection and quantification of environmentally relevant blue micro- and nanoplastics using nanobowl-based plasmonic substrates

4.3.1 Experimental methodology

Nanobowl-based plasmonic SERS substrates were fabricated using the nanosphere lithography and soft lithography approach described in Chapter 3. Two batches of blue micro- and nanoplastics were investigated: naturally weathered particles obtained from degraded blue fishing nets and particles produced by mechanical fragmentation. Working suspensions at 200, 100, and 20 μg/mL were prepared for quantitative analysis.

Particle size distributions were characterized by dynamic light scattering (DLS) and particle morphology and elemental composition were investigated using scanning SEM-EDX.

Raman and surface-enhanced resonance Raman scattering (SERRS) measurements were performed using a Renishaw InVia Reflex confocal Raman spectrometer. Single-particle measurements of naturally weathered nanoplastics were conducted under 632.8 nm excitation on Au-NBL^{600}, Au-NBL^{750}, and Ag-NBL^{750} substrates, using a 100x objective, a 10 s acquisition time, and 8.5 mW laser power. For quantitative analysis, mechanically fragmented nanoplastics were deposited onto Ag-NBL^{600} substrates at the three concentrations and mapped over an area of 10,600 μm² using 532 nm excitation, a 20x objective, and a 0.8 μm step size.

4.3.2 Results and Discussion

4.3.2.1 Characterization of blue micro-and nanoplastic suspensions

The morphology and size distribution of two blue micro- and nanoplastic samples were investigated. The first sample consisted of naturally weathered plastics that had undergone approximately 15 years of aquatic ageing followed by five years of indoor degradation. SEM analysis revealed irregular particle shapes and a broad size distribution, reflecting the effects of environmental degradation processes [66], [67]. DLS measurements identified two main particle populations with median hydrodynamic diameters of approximately 163 nm and 1370 nm, and a polydispersity index (PDI) of 0.39, indicating a heterogeneous distribution and particle agglomeration.

The second sample was produced by ball-milling blue fishing-net material. SEM analysis showed irregularly shaped particles resembling those of the naturally weathered sample. DLS revealed populations with median hydrodynamic diameters of 245-376 nm and 1.5-1.7 μm, with PDI values of 0.21-0.36. A third population around 10 μm was also observed,

although its size could not be accurately determined due to instrument limitations. Overall, both samples exhibited morphological heterogeneity and broad size distributions, making them suitable models for evaluating SERS performance under conditions representative of environmentally relevant micro- and nanoplastics.

4.3.2.2 SERRS detection of environmentally relevant blue micro- and nanoplastics

The detection of environmentally relevant blue nanoplastics was investigated using surface-enhanced resonance Raman scattering (SERRS), combining the resonance Raman response of the embedded CuPc pigment under red laser excitation with the electromagnetic enhancement provided by plasmonic nanobowl substrates. Two gold-coated substrates (Au-NBL^{600} and Au-NBL^{750}) and one silver-coated substrate (Ag-NBL^{750}) were selected based on their plasmonic response in the red spectral region. Individual particles were analysed to assess substrate performance and particle-substrate interactions. The SERRS spectra were dominated by the characteristic PB15 pigment bands at 747, 1452 and 1528 cm^{-1}, with no significant band shifts or changes in relative intensities compared with the resonance Raman spectrum, indicating no evident chemisorption effects.

The calculated average enhancement factors (AEF^{P}) were 7.2 $\pm$ 3.2, 7.0 $\pm$ 3.2 and 3.7 $\pm$ 2.7 for Au-NBL^{600}, Au-NBL^{750} and Ag-NBL^{750}, respectively. These relatively low values reflect the practical nature of AEF^{P}, which accounts for the entire analyte population, although only the particle regions in direct contact with plasmonic hot spots experience substantial enhancement. The similar performance of the two gold substrates may result from the micrometre-sized particles covering multiple nanobowls, thereby reducing the influence of individual nanobowl dimensions. Despite their similar far-field plasmonic responses, Au-NBL^{750} outperformed Ag-NBL^{750}, suggesting that local electromagnetic-field distributions, surface morphology and metal stability also influence SERRS efficiency.

Particle size was found to be a key factor governing enhancement. Smaller particles produced more intense signals and higher signal-to-noise ratios because they could be better accommodated within individual nanobowls, increasing their interaction with localized electromagnetic fields. In contrast, larger particles extended across multiple nanobowls, limiting the fraction of analyte exposed to the strongest enhancement regions. Overall, these findings demonstrate that efficient SERRS detection depends not only on the substrate's plasmonic properties but also on the geometric relationship between the analyte and the nanostructure.

4.3.2.3 Quantitative SERRS analysis of environmentally relevant blue micro- and nanoplastics

Following the successful quantitative detection of monodisperse 500 nm polystyrene nanoplastics using Ag-NBL^{600} substrates, the quantitative approach was extended to heterogeneous blue micro- and nanoplastics produced by ball milling, at concentrations of 200,

100 and 20 µg/mL. The aim was to evaluate the detection method under more environmentally relevant conditions, where particles exhibit broad size and morphological distributions.

The average SERRS spectra showed an apparent increase in the PB15 characteristic band at 1528 cm^{-1} with increasing concentration (Fig. 4.2. a). However, integration of this band did not reveal a clear linear relationship between signal intensity and concentration (Fig. 4.2. b), unlike the results obtained for monodisperse PS nanoplastics. This limitation was mainly attributed to sample heterogeneity which resulted in variable proportions of micro- and nanoparticles within each mapped area. Since particle size, morphology, orientation, aggregation and proximity to SERS-active regions influence signal intensity, local variations in particle distribution generated substantial measurement fluctuations.

Overall, these findings demonstrate that quantitative SERS analysis of environmentally relevant plastic samples is considerably more challenging than the detection of monodisperse model particles. Factors such as dispersion stability, drying behaviour and heterogeneous particle populations introduce additional sources of variability that prevent the direct transfer of established calibration protocols. Addressing these limitations is essential for developing reliable quantitative SERS methodologies for complex environmental samples.

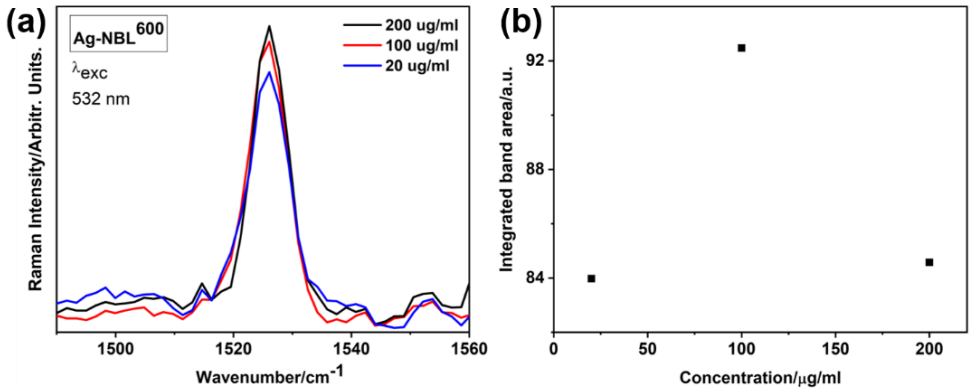


Figure 4.2. (a) Average SERRS spectra of blue micro- nanoplastic suspension at various concentrations and **(b)** integrated area under 1528 cm^{-1} band as a function of blue micro-nanoplastic suspension concentration.

Conclusions, impact and perspectives

The results presented throughout this thesis establish a comprehensive framework for the design of plasmonic nanostructured substrates dedicated to the Raman-based detection of nanoplastics, bridging the gap between conventional molecular SERS optimization and analyte-specific substrate engineering. Starting from the comparison of colloidal lithography-derived AuFoN and AuFoEN substrates, it was demonstrated that plasmonic architectures optimized for molecular analytes do not necessarily provide optimal enhancement for nanoplastics, revealing that particle size, morphology, and accessibility to electromagnetic hot spots are decisive factors governing the SERS response. This concept was subsequently translated into the development of nanobowl-based plasmonic substrates, whose tunable geometry enabled efficient confinement of nanoparticles within SERS-active regions, providing sensitive detection and quantitative analysis of model nanoplastics while also demonstrating applicability to environmentally relevant PET particles. The work further expanded the analytical capabilities of Raman spectroscopy by exploiting the resonance Raman response of the copper phthalocyanine pigment present in blue plastics, enabling reliable single-particle detection of environmentally relevant blue nanoplastics down to 500 nm without plasmonic enhancement. Finally, combining this resonance effect with optimized nanobowl substrates established a SERRS platform capable of enhancing the detection of realistic blue micro- and nanoplastics, while simultaneously revealing the challenges associated with quantitative analysis of heterogeneous environmental samples.

Collectively, these findings demonstrate that successful plasmonic substrate design for nanoplastic detection requires not only optimization of electromagnetic enhancement but, more importantly, careful matching of substrate morphology to the physical characteristics of the target particles. By advancing from molecular optimization to particle-substrate matching and validating the developed strategies using increasingly realistic plastic systems, this thesis provides both fundamental insights into SERS/SERRS enhancement mechanisms for particulate analytes and practical guidelines for the future development of robust Raman-based methodologies for environmental nanoplastic analysis.

Bibliography

[1] T. Yang, J. Liu, J. Nicell, A. Praetorius, M. Fang, and Z. Wang, "Diverse origins and chemical complexity of nanoplastics," *Nature Nanotechnology 2026 21:5*, vol. 21, no. 5, pp. 628–634, May 2026, doi: 10.1038/s41565-026-02168-3.

[2] M. Moskovits, "Surface-Enhanced Raman Spectroscopy: a Brief Perspective," in *Surface-Enhanced Raman Scattering: Physics and Applications*, Topics in Applied P…., vol. 103, K. Kneipp, M. Moskovits, and H. Kneipp, Eds., Springer, Berlin & Heidelberg , 2006, pp. 1–17. doi: 10.1007/3-540-33567-6_1.

[3] R. C. Thompson, C. J. Moore, F. S. V. Saal, and S. H. Swan, "Plastics, the environment and human health: current consensus and future trends," *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 364, no. 1526, pp. 2153–2166, Jul. 2009, doi: 10.1098/RSTB.2009.0053.

[4] A. L. Andrady and M. A. Neal, "Applications and societal benefits of plastics," *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 364, no. 1526, pp. 1977–1984, Jul. 2009, doi: 10.1098/RSTB.2008.0304.

[5] P. G. C. Nayanathara Thathsarani Pilapitiya and A. S. Ratnayake, "The world of plastic waste: A review," *Cleaner Materials*, vol. 11, p. 100220, Mar. 2024, doi: 10.1016/J.CLEMA.2024.100220.

[6] S. S. Ali *et al.*, "Degradation of conventional plastic wastes in the environment: A review on current status of knowledge and future perspectives of disposal," *Science of The Total Environment*, vol. 771, p. 144719, Jun. 2021, doi: 10.1016/J.SCITOTENV.2020.144719.

[7] "ISO/TR 21960:2020 - Plastics — Environmental aspects — State of knowledge and methodologies." Accessed: May 23, 2025. [Online]. Available: https://www.iso.org/standard/72300.html

[8] C. Shi *et al.*, "Emergence of nanoplastics in the aquatic environment and possible impacts on aquatic organisms," *Science of the Total Environment*, vol. 906, Jan. 2024, doi: 10.1016/j.scitotenv.2023.167404.

[9] Y. Arif, A. R. Mir, P. Zieliński, S. Hayat, and A. Bajguz, "Microplastics and nanoplastics: Source, behavior, remediation, and multi-level environmental impact," *J. Environ. Manage.*, vol. 356, p. 120618, Apr. 2024, doi: 10.1016/J.JENVMAN.2024.120618.

[10] I. Goßmann *et al.*, "Occurrence and backtracking of microplastic mass loads including tire wear particles in northern Atlantic air," *Nat. Commun.*, vol. 14, no. 1, pp. 1–9, Jun. 2023, doi: 10.1038/s41467-023-39340-5.

[11] D. K. Gupta, D. Choudhary, A. Vishwakarma, M. Mudgal, A. K. Srivastava, and A. Singh, "Microplastics in freshwater environment: occurrence, analysis, impact, control measures and challenges," *International Journal of Environmental Science and Technology*, vol. 20, no. 6, pp. 6865–6896, Apr. 2022, doi: 10.1007/S13762-022-04139-2.

[12] I. V. Kirstein, A. Gomiero, and J. Vollertsen, "Microplastic pollution in drinking water," *Curr. Opin. Toxicol.*, vol. 28, pp. 70–75, Dec. 2021, doi: 10.1016/J.COTOX.2021.09.003.

[13] J. Zhang *et al.*, "Identification of Poly(ethylene terephthalate) Nanoplastics in Commercially Bottled Drinking Water Using Surface-Enhanced Raman Spectroscopy," *Environ. Sci. Technol.*, vol. 57, no. 22, pp. 8365–8372, Jun. 2023, doi: 10.1021/ACS.EST.3C00842.

[14] N. Qian *et al.*, “Rapid single-particle chemical imaging of nanoplastics by SRS microscopy,” *Proc. Natl. Acad. Sci. U. S. A.*, vol. 121, no. 3, 2024, doi: 10.1073/PNAS.2300582121.

[15] E. P. on C. in the F. C. (CONTAM), “Presence of microplastics and nanoplastics in food, with particular focus on seafood,” *EFSA Journal*, vol. 14, no. 6, p. e04501, Jun. 2016, doi: 10.2903/J.EFSA.2016.4501.

[16] T. S. Galloway, M. Cole, and C. Lewis, “Interactions of microplastic debris throughout the marine ecosystem,” *Nature Ecology & Evolution 2017 1:5*, vol. 1, no. 5, pp. 0116-, Apr. 2017, doi: 10.1038/s41559-017-0116.

[17] C. J. Foley, Z. S. Feiner, T. D. Malinich, and T. O. Höök, “A meta-analysis of the effects of exposure to microplastics on fish and aquatic invertebrates,” *Science of the Total Environment*, vol. 631–632, pp. 550–559, Aug. 2018, doi: 10.1016/j.scitotenv.2018.03.046.

[18] M. Marelja, C. Ma, B. W. Ibelings, and V. I. Slaveykova, “Species-specific impacts of fibrous microplastics on behavior, survival and oxidative stress in freshwater zooplankton,” *J. Hazard. Mater.*, vol. 501, p. 140718, Jan. 2026, doi: 10.1016/J.JHAZMAT.2025.140718.

[19] N. Joksimovic *et al.*, “Nanoplastics as an Invisible Threat to Humans and the Environment,” *J. Nanomater.*, vol. 2022, no. 1, p. 6707819, Jan. 2022, doi: 10.1155/2022/6707819.

[20] V. K. Sharma, X. Ma, E. Lichtfouse, and D. Robert, “Nanoplastics are potentially more dangerous than microplastics,” *Environ. Chem. Lett.*, vol. 21, no. 4, pp. 1933–1936, Aug. 2023, doi: 10.1007/S10311-022-01539-1.

[21] A. Khan and Z. Jia, “Recent insights into uptake, toxicity, and molecular targets of microplastics and nanoplastics relevant to human health impacts,” *iScience*, vol. 26, no. 2, p. 106061, Feb. 2023, doi: 10.1016/J.ISCI.2023.106061.

[22] Y. Lee *et al.*, “Potential lifetime effects caused by cellular uptake of nanoplastics: A review,” *Environmental Pollution*, vol. 329, p. 121668, Jul. 2023, doi: 10.1016/J.ENVPOL.2023.121668.

[23] B. E. Cunningham, E. E. Sharpe, S. M. Brander, W. G. Landis, and S. L. Harper, “Critical gaps in nanoplastics research and their connection to risk assessment,” *Frontiers in Toxicology*, vol. 5, p. 1154538, Apr. 2023, doi: 10.3389/FTOX.2023.1154538/BIBTEX.

[24] R. Zhang *et al.*, “A review of advancements and challenges in nanoplastics detection,” *Cell Rep. Phys. Sci.*, vol. 7, no. 1, p. 103042, Jan. 2026, doi: 10.1016/J.XCRP.2025.103042.

[25] Akira. Otsuki, “Non-destructive material characterization methods,” p. 842, 2024, Accessed: Jul. 14, 2026. [Online]. Available: https://books.google.com/books/about/Non_Destructive_Material_Characterizatio.html?id=CIysEAAAQBAJ

[26] I. Ali *et al.*, “Micro- and nanoplastics in the environment: Occurrence, detection, characterization and toxicity – A critical review,” *J. Clean. Prod.*, vol. 313, p. 127863, Sep. 2021, doi: 10.1016/J.JCLEPRO.2021.127863.

[27] C. M. Maguire, M. Rösslein, P. Wick, and A. Prina-Mello, “Characterisation of particles in solution – a perspective on light scattering and comparative technologies,” *Sci. Technol. Adv. Mater.*, vol. 19, no. 1, pp. 732–745, Dec. 2018, doi: 10.1080/14686996.2018.1517587.

[28] V. Filipe, A. Hawe, and W. Jiskoot, “Critical Evaluation of Nanoparticle Tracking Analysis (NTA) by NanoSight for the Measurement of Nanoparticles and Protein Aggregates,” *Pharmaceutical Research 2010 27:5*, vol. 27, no. 5, pp. 796–810, Mar. 2010, doi: 10.1007/S11095-010-0073-2.

[29] K. Altmann *et al.*, “Characterizing nanoplastic suspensions of increasing complexity: inter-laboratory comparison of size measurements using dynamic light scattering,” *Environ. Sci. Nano*, vol. 12, no. 12, pp. 5242–5256, Dec. 2025, doi: 10.1039/D5EN00645G.

[30] M. Baalousha, B. Stolpe, and J. R. Lead, “Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: A critical review,” *J. Chromatogr. A*, vol. 1218, no. 27, pp. 4078–4103, Jul. 2011, doi: 10.1016/J.CHROMA.2011.04.063.

[31] C. Schwaferts, R. Niessner, M. Elsner, and N. P. Ivleva, “Methods for the analysis of submicrometer- and nanoplastic particles in the environment,” *TrAC Trends in Analytical Chemistry*, vol. 112, pp. 52–65, Mar. 2019, doi: 10.1016/J.TRAC.2018.12.014.

[32] M. Kaur, C. T. Gibson, S. J. Fraser-Miller, S. C. Leterme, and M. Macgregor, “A physical chemistry lens on environmental nanoplastics analysis challenges. Part II: detection techniques – principles, limitations and future directions,” *Environ. Sci. Nano*, vol. 13, no. 6, pp. 2585–2603, Jun. 2026, doi: 10.1039/D5EN00630A.

[33] A. Käppler *et al.*, “Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman or both?,” *Anal. Bioanal. Chem.*, vol. 408, no. 29, pp. 8377–8391, Nov. 2016, doi: 10.1007/S00216-016-9956-3/TABLES/3.

[34] J. Zhang *et al.*, “Mass spectrometry detection of environmental microplastics: Advances and challenges,” *TrAC Trends in Analytical Chemistry*, vol. 170, p. 117472, Jan. 2024, doi: 10.1016/J.TRAC.2023.117472.

[35] H. Cai, E. G. Xu, F. Du, R. Li, J. Liu, and H. Shi, “Analysis of environmental nanoplastics: Progress and challenges,” *Chemical Engineering Journal*, vol. 410, p. 128208, Apr. 2021, doi: 10.1016/J.CEJ.2020.128208.

[36] R. S. Das and Y. K. Agrawal, “Raman spectroscopy: Recent advancements, techniques and applications,” *Vib. Spectrosc.*, vol. 57, no. 2, pp. 163–176, Nov. 2011, doi: 10.1016/J.VIBSPEC.2011.08.003.

[37] N. K. Mogha and D. Shin, “Nanoplastic detection with surface enhanced Raman spectroscopy: Present and future,” *TrAC Trends in Analytical Chemistry*, vol. 158, p. 116885, Jan. 2023, doi: 10.1016/J.TRAC.2022.116885.

[38] S. L. Belontz, J. Brahney, C. E. Caplan, E. Dillon, T. Yan, and G. Dominguez, “Combining Submicron Spectroscopy Techniques (AFM-IR and O-PTIR) To Detect and Quantify Microplastics and Nanoplastics in Snow from a Utah Ski Resort,” *Environ. Sci. Technol.*, vol. 59, no. 26, p. 13362, Jul. 2025, doi: 10.1021/ACS.EST.4C12170.

[39] J. R. Macairan, A. Saherwala, F. Li, F. Monteil-Rivera, and N. Tufenkji, “Label-Free Identification and Imaging of Microplastic and Nanoplastic Biouptake Using Optical Photothermal Infrared Microspectroscopy,” *Environ. Sci. Technol.*, vol. 59, no. 30, pp. 15612–15622, Aug. 2025, doi: 10.1021/ACS.EST.4C14367.

[40] R. Pilot, R. Signorini, C. Durante, L. Orian, M. Bhamidipati, and L. Fabris, “A Review on Surface-Enhanced Raman Scattering,” *Biosensors (Basel).*, vol. 9, no. 2, p. 57, Apr. 2019, doi: 10.3390/BIOS9020057.

[41] X. X. Han, R. S. Rodriguez, C. L. Haynes, Y. Ozaki, and B. Zhao, “Surface-enhanced Raman spectroscopy,” *Nature Reviews Methods Primers*, vol. 1, no. 1, pp. 1–17, Jan. 2022, doi: 10.1038/S43586-021-00083-6.

[42] M. J. Natan, “Concluding Remarks: Surface enhanced Raman scattering,” *Faraday Discuss.*, vol. 132, no. 0, pp. 321–328, Apr. 2006, doi: 10.1039/B601494C.

[43] E. C. Le Ru, E. Blackie, M. Meyer, and P. G. Etchegoint, “Surface enhanced raman scattering enhancement factors: A comprehensive study,” *Journal of Physical Chemistry C*, vol. 111, no. 37, pp. 13794–13803, Sep. 2007, doi: https://doi.org/10.1021/jp0687908.

[44] M. E. Stewart *et al.*, “Nanostructured Plasmonic Sensors,” *Chem. Rev.*, vol. 108, no. 2, pp. 494–521, Feb. 2008, doi: 10.1021/CR068126N.

[45] K. Srivastava, H. Le-The, J. J. A. Lozeman, A. van den Berg, W. van der Stam, and M. Odijk, “Prospects of nano-lithographic tools for the fabrication of surface-enhanced Raman spectroscopy (SERS) substrates,” *Micro and Nano Engineering*, vol. 23, p. 100267, Jun. 2024, doi: 10.1016/J.MNE.2024.100267.

[46] “Regulation - 2023/2055 - EN - EUR-Lex.” Accessed: Jul. 16, 2026. [Online]. Available: https://eur-lex.europa.eu/eli/reg/2023/2055/oj

[47] “Delegated decision - EU - 2024/1441 - EN - EUR-Lex.” Accessed: Jul. 16, 2026. [Online]. Available: https://eur-lex.europa.eu/eli/dec_del/2024/1441/oj/eng

[48] D. MĖHN, C. CELLA, G. BUCHER, F. S. FUMAGALLI, H. H. EL, and D. GILLILAND, “Analysing microplastics in drinking water,” vol. JRC143205, 2025, doi: 10.2760/1240697.

[49] World Health Organization, *Microplastics in drinking-water*. World Health Organization, 2019.

[50] E. Food *et al.*, “Literature review on micro- and nanoplastic release from food contact materials during their use,” *EFSA Supporting Publications*, vol. 22, no. 10, p. 9733E, Oct. 2025, doi: 10.2903/SP.EFSA.2025.EN-9733.

[51] A. Palm, “Raman spectrum of polystyrene,” *Journal of Physical and Colloid Chemistry*, vol. 55, no. 8, pp. 1320–1324, 1951, doi: 10.1021/J150491A005.

[52] J. R. Anema, A. G. Brolo, A. Felten, and C. Bittencourt, “Surface-enhanced Raman scattering from polystyrene on gold clusters,” *Journal of Raman Spectroscopy*, vol. 41, no. 7, pp. 745–751, Jul. 2010, doi: 10.1002/JRS.2504.

[53] I. Cârdan *et al.*, “From molecular to nanoplastic SERS detection: insights into the role of analytes in plasmonic substrate design,” *Nanoscale*, 2025, doi: 10.1039/D5NR02181B.

[54] S. Ducoli *et al.*, “Characterization of polyethylene terephthalate (PET) and polyamide (PA) true-to-life nanoplastics and their biological interactions,” *Environmental Pollution*, vol. 343, p. 123150, Feb. 2024, doi: 10.1016/J.ENVPOL.2023.123150.

[55] F. Xing *et al.*, “Superhydrophobic Surface-Enhanced Raman Spectroscopy (SERS) Substrates for Sensitive Detection of Trace Nanoplastics in Water,” *Anal. Chem.*, vol. 97, no. 4, pp. 2293–2299, Feb. 2025, doi: 10.1021/ACS.ANALCHEM.4C05554.

[56] D. O. Sigle, E. Perkins, J. J. Baumberg, and S. Mahajan, “Reproducible Deep-UV SERRS on Aluminum Nanovoids,” *J. Phys. Chem. Lett.*, vol. 4, no. 9, pp. 1449–1452, May 2013, doi: 10.1021/JZ4004813.

[57] F. J. Boerio, S. K. Bahl, and G. E. McGraw, “VIBRATIONAL ANALYSIS OF POLYETHYLENE TEREPHTHALATE AND ITS DEUTERATED DERIVATIVES.,” *J Polym Sci Part A-2 Polym Phys*, vol. 14, no. 6, pp. 1029–1046, Jun. 1976, doi: 10.1002/POL.1976.180140607;PAGE:STRING:ARTICLE/CHAPTER.

[58] C. Zhu, N. Tong, L. Song, and G. Zhang, “Investigation of Raman spectra of polyethylene terephthalate,” *https://doi.org/10.1117/12.2205157*, vol. 9656, p. 72, Aug. 2015, doi: 10.1117/12.2205157.

[59] I. Nesterovschi *et al.*, “Subterranean transport of microplastics as evidenced in karst springs and their characterization using Raman spectroscopy,” *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 298, p. 122811, Oct. 2023, doi: 10.1016/J.SAA.2023.122811.

[60] I. Nesterovschi *et al.*, “Have You Ever Seen a Microplastic? A Collaborative High School–Academia Approach for Identification, Quantification and Raising Awareness of Microplastics in a River Crossing Urban Area,” *J. Chem. Educ.*, Jul. 2025, doi: 10.1021/ACS.JCHEMED.4C01484.

[61] “ROMÂNIA, TE IUBESC! - ROMÂNIA LA PET,” PROTV documentary. Accessed: May 27, 2024. [Online]. Available: https://www.youtube.com/watch?v=DYb3MtMRwMk&t=423s&ab_channel=ROMANIA%2CTEIUBESC%21

[62] B. W. Caplins, T. K. Mullenbach, R. J. Holmes, and D. A. Blank, “Femtosecond to nanosecond excited state dynamics of vapor deposited copper phthalocyanine thin films,” *Physical Chemistry Chemical Physics*, vol. 18, no. 16, pp. 11454–11459, Apr. 2016, doi: 10.1039/C6CP00958A.

[63] N. Touka, H. Benelmadjat, B. Boudine, O. Halimi, and M. Sebais, “Copper phthalocyanine nanocrystals embedded into polymer host: Preparation and structural characterization,” *Journal of the Association of Arab Universities for Basic and Applied Sciences*, vol. 13, no. 1, pp. 52–56, 2013, doi: 10.1016/J.JAUBAS.2012.03.002.

[64] W. Fremout and S. Saverwyns, “Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library,” *Journal of Raman Spectroscopy*, vol. 43, no. 11, pp. 1536–1544, Nov. 2012, doi: 10.1002/JRS.4054.

[65] C. Li, L. Zhang, M. Yang, H. Wang, and Y. Wang, “Dynamic and steady-state behaviors of reverse saturable absorption in metallophthalocyanine,” *Phys. Rev. A (Coll. Park).*, vol. 49, no. 2, p. 1149, Feb. 1994, doi: 10.1103/PhysRevA.49.1149.

[66] I. Cârdan, I. Nesterovschi, L. Barbu-Tudoran, and S. C. Pînzaru, “Blue micro-/nanoplastics abundance in the environment: a double threat as a Trojan horse for a plastic-Cu-phthalocyanine pigment and an opportunity for nanoplastic detection via micro-Raman spectroscopy,” *Environ. Sci. Nano*, vol. 12, pp. 2357–2370, 2025, doi: 10.1039/D4EN00820K.

[67] A. L. Andrady, “Microplastics in the marine environment,” *Mar. Pollut. Bull.*, vol. 62, no. 8, pp. 1596–1605, Aug. 2011, doi: 10.1016/J.MARPOLBUL.2011.05.030.

[68] S. N. Dimassi, J. N. Hahladakis, M. N. D. Yahia, M. I. Ahmad, S. Sayadi, and M. A. Al-Ghouti, “Degradation-fragmentation of marine plastic waste and their environmental implications: A critical review,” *Arabian Journal of Chemistry*, vol. 15, no. 11, p. 104262, Nov. 2022, doi: 10.1016/J.ARABJC.2022.104262.

List of publications on the subject of the thesis

Web of Science: https://www.webofscience.com/wos/author/record/KCJ-8441-2024
H-index: 8
Citations: 204; 180 without self-citations
No. of publications: 19

Google Scholar:
https://scholar.google.com/citations?user=gLl9F8IAAAAJ&hl=en&authuser=1
H-index: 8
Citations: 262
No. of publications: 19

- **Scientific Publications**

No.	ISI Ranking zone[a]	Title	Authors, bibliographic information	Year	Impact factor[b]	AIS InCites JCR[c]
1	Q1	Quasi-3D sculpted gold film over nanospheres (AuFoN) for enhanced SERS detection of emerging pollutants	**I. Cârdan**, A. Fălămaș, D. Cuibus, V. Zani, R. Signorini, R. Pilot and C. Farcău *Microchemical Journal*. 228, 118905. DOI10.1016/j.microc.2026.118905	2026	5.2	0.538
2	Q1	SERS of Bottled Water: Automated PET Nanoplastic Detection and Quantification	I. Nesterovschi**, I. Cârdan**, K. Maskaric, A. Couți, L. Barbu-Tudoran, S. Cîntă Pînzaru *Analytical Chemistry*. DOI10.1021/acs.analchem.6c04234.	2026	7.3	1.054
3	Q2	From molecular to nanoplastic SERS detection: insights into the role of analytes in plasmonic substrate design	**I. Cârdan**, V. Zani, A. Maria, M. Gherman, R. Signorini, R. Pilot and C. Farcău *Nanoscale*, 17 (44), 25680-25690 DOI10.1039/d5nr02181b	2025	5.2	0.851
4	Q2	Have You Ever Seen a Microplastic? A Collaborative High School–Academia Approach for Identification, Quantification and Raising Awareness of Microplastics in a River Crossing Urban Area	I. Nesterovschi, **I. Cârdan**, D. Condor, A. Couţi, E. Levei, V. Pop and S. C. Pînzaru, *J Chem Educ*. 102 (8), 3277-3287 DOI10.1021/acs.jchemed.4c01484	2025	3	0.272
5	Q2	Blue micro-/nanoplastics abundance in the environment: a double threat as a Trojan horse for a plastic-Cu-phthalocyanine pigment and an opportunity for nanoplastic detection via micro-Raman spectroscopy	**I. Cârdan**, I. Nesterovschi, L. Barbu-Tudoran & S. C. Pînzaru *Environ Sci Nano*. 12 (4), 2357–2370 DOI10.1039/d4en00820k	2025	5.6	0.850
6	Q1	Interaction of Low-Density Polyethylene Nanofragments with Autotrophic and Chemotrophic Bacteria	A. Ciorîţă, M. Suciu, A. M. Rostas, A. Tarţa., G. Popovici, M. Bocăneală, F. Nekvapil, S. G. Macavei, M. Potara, **I. Marica**, I. Kacso, C. S. Moldovan, R. I. Ştiufiuc, C. S. Tuta, S.C. Pînzaru, & L. Barbu-Tudoran *ACS Sustainable Chemistry and Engineering*. 12 (29): 10831–10840 DOI10.1021/acssuschemeng.4c02440	2024	7.3	1.289
7	Q2	A Raman spectral database of naturally aged plastics: A proof-of-concept study for waste plastic sorting	**I. Marica**, S.C. Pînzaru, J. Raman Spectrosc. 54 (3), 305–313 DOI10.1002/jrs.6484	2023	2.4	0.534
8	Q1	Subterranean transport of microplastics as evidenced in	I. Nesterovschi, **I. Marica**, E. Andrea Levei, S. Bogdan Angyus, M. Kenesz, O.	2023	4.3	0.522

		karst springs and their characterization using Raman spectroscopy	Teodora Moldovan, S. C. Pînzaru Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 298, 122811 DOI10.1016/j.saa.2023.122811			
9	non-ISI (BDI)	Detection of blue nanoplastics using resonance Raman spectroscopy coupled with plasmonic nanostructured substrates	**I. Cârdan**, S. Cîntă-Pînzaru, L. Barbu-Tudoran and C. Farcău, https://doi.org/10.1117/12.3062631, 13570, 20–26	2025	-	-
				Total	**40.3**	**5.91**

[a]ISI ranking zone as of date of publication (or most recent available data)
[b]Impact factor according to Clarivate Journals Citation Report (publication year or most recent available data)
[c]AIS InCites JCR – Article influence score according to InCites Journal Citation Reports (publication year or most recent available data)

- **Conferences**

Oral contributions

1. **I. Cârdan,** S. Cîntă Pînzaru and C. Farcău, "Addressing Nanoplastic Detection and Quantification with Customized Nanostructured SERS Substrates". *International Conference MICRO 2026: Plastic Pollution from Macro to Nano*. [12/10/2026 – 16/10/2026] Cadiz, Spain
2. **I. Cardan**, S. Cîntă Pînzaru, L. Barbu-Tudoran and C. Farcău, "Detection of blue nanoplastics using resonance Raman spectroscopy coupled with plasmonic nanostructured substrates". *SPIE Optical Metrology - Multimodal Sensing and Artificial Intelligence for Sustainable Future*. [23/06/2025 – 27/06/2025] Munich, Germany
3. **I. Marica**, I. Nesterovschi, C. Farcău, S. Cîntă Pînzaru. "Blue, naturally degraded nanoplastics abundance and their detection via two Raman-based approaches". *28th International Conference on Raman Spectroscopy – ICORS 2024* [27/07/2024 – 02/08/2024] Rome, Italy

Poster contributions

1. **I. Cârdan**, D. Cuibus, A. Fălămaș, S. Cîntă Pînzaru and C. Farcău, "Nanostructured SERS platforms fabricated by colloidal lithography for trace detection of emerging pollutants" *21st European Conference on the Spectroscopy of Biological Molecules (ECSBM 2026)* [30/08/2026 – 03/09/2026] Cluj-Napoca, Romania
2. **I. Cârdan**, A. M. M. Gherman, L. Barbu-Tudoran, S. Tripon, D. Cuibus, S. Ducoli, S. Federici, S. Cîntă Pînzaru, C. Farcău, "Nanostructured SERS Substrates Engineered via Colloidal Lithography for Environmental Nanoplastics Detection". *International Conference on Raman Spectroscopy (ICORS)* [23/08/2026 – 27/08/2026] Istanbul, Turkiye
3. **I. Cardan**, I. Nesterovschi, A. Couți, S. Ducoli, S. Federici, S. Cîntă Pînzaru, and C. Farcău, " SERS detection of environmental nanoplastics by using customized plasmonic nanostructured substrates". *Microplastic Days 2026 Conference* [03/02/2026 – 05/02/2026] Ljubljana, Slovenia
4. **I. Cârdan**, S. Cîntă Pînzaru, V. Zani, A. M. M. Gherman, R. Signorini, R. Pilot, L. Barbu-Tudoran and C. Farcău, "Blue nanoplastics detection by SERRS: insights from molecules

to single-nanoplastic particle detection". *15th International Conference on Processes in Isotopes and Molecules - PIM 2025* [16/09/2026 – 19/09/2026] Cluj-Napoca, Romania

5. **I. Cardan**, S. Cîntă Pînzaru, L. Barbu-Tudoran and C. Farcău, "Resonance Raman-assisted SERS detection of blue nanoplastics: blue pigment as an analytical marker". *Final Conference of the Cost Action PRIORITY* [02/09/2025 – 05/09/2025] Leoben, Austria
6. **I. Marica**, A M M Gherman, A Colnita, V Zani, R Signorini, R Pilot, and C Farcau, "Plasmonic nanostructured substrates fabricated by colloidal lithography for nanoplastics SERS detection". *International Conference on Processes in Isotopes and Molecules (PIM 2023)* [19/09/2023 – 22/09/2023] Cluj-Napoca, Romania.
7. **I. Marica**, V. Zani, R. Signorini, R. Pilot, S. Cîntă Pinzaru, C. Farcău, "Optical properties and SERS analysis of quasi-3D plasmonic nanostructures fabricated by colloidal lithography". *International Conference on Advanced Vibrational Spectroscopy (ICAVS12)* [27/08/2023 – 01/09/2023] Krakow, Poland.
8. **I. Marica**, I Nesterovschi and S Cîntă Pînzaru "A sustainable plastic waste initiative from macro- to microplastics based on Raman spectroscopy technique" *International Conference on Physics of Advanced Materials (ICPAM-14)* [08/09/2022 – 15/09/2022] Dubrovnik, Croatia

- **Patent Application**

I. Cârdan, C-A. Farcău. A method based on colloidal lithography for obtaining SERS substrate consisting of quasi-three-dimensional plasmonic nanostructures. Patent Application no. A/00291. 09.07.2025.

List of other publications

- **Scientific Publications**

No.	ISI Ranking zone[a]	Title	Authors, bibliographic information	Year	Impact factor[b]	AIS InCites JCR[c]
1	Q1	Nanomolar concentration tracking of the carotenoid astaxanthin by surface-enhanced Raman spectroscopy	F. Nekvapil, **I. Cârdan**, D. Cuibus, and C. Farcău, Microchemical Journal. 226, 118424 DOI10.1016/j.microc.2026.118424	2026	5.2	0.538
2	Q1	Camera-based colorimetric refractive index sensing using silver film over nanospheres (AgFoN) plasmonic substrates	F. Toadere, D. Cuibus, **I. Cârdan**, and C. Farcău, Sensors and Actuators A: Physical. 412 DOI10.1016/j.sna.2026.118564	2026	5.1	0.752
3	Q2	Self-Assembly Route Controls Nanoscale Structural Order and SERS Sensing Performance in Ag Film-over-Nanosphere Plasmonic Substrates	D. Cuibus, **I. Cârdan**, N. Toșa, A. M. M. Gherman, and C. Farcău, *ACS Appl. Nano Mater*. 9, 14177–14187 DOI10.1021/acsanm.6c01583	2026	5.8	0.764
4	Q2	Dye-Dependent Fluorescence Enhancement in ZnO Nanorod–Polymer Films: Excitation and Emission	A. Falamas, **I. Cardan**, D. Cuibus, M. Stefan, and C. Farcau *Appl. Spectrosc.* https://doi.org/10.1177/00037028261470429	2026	2.2	0.530

		Contributions Probed by Time-Resolved Fluorescence				
5	Q1	A simple approach for coffee-ring suppression yielding homogeneous drying patterns of ZnO and TiO2 nanoparticles	**I. Marica**, M. Stefan, S. Boca, A. Falamaş, C. Farcău J. Colloid Interface Sci. 2023; 635, 117–127 DOI10.1016/j.jcis.2022.12.113	2023	9.4	1.235
6	Q2	Surface enhanced fluorescence potential of ZnO nanoparticles and gold decorated ZnO nanostructures embedded in a polyvinyl alcohol matrix	A. Falamas, **I. Marica**, F. Nekvapil, M. Stefan, G.S. Macavei, L. Barbu-Tudoran, C. Farcau J. Photochem. Photobiol. A Chem. 438, 114516 DOI10.1016/j.jphotochem.2022.114516	2023	4.1	0.485
7	Q1	Raman technology application for plastic waste management aligned with FAIR principle to support the forthcoming plastic and environment initiatives	**I. Marica**, M. Aluaș, S. Cîntă Pînzaru Waste Manag. 144, 479–489 DOI10.1016/j.wasman.2022.04.021	2022	8.1	1.248
8	Q3	Zinc oxide nanostructures for fluorescence and Raman signal enhancement: a review.	**I. Marica**, F. Nekvapil, M. Ștefan, C. Farcău, A. Falamaș Beilstein J. Nanotechnol. 1340 13, 472–490 DOI10.3762/bjnano.13.40	2022	3.1	0.477
9	Q2	Size-dependent spectroscopic insight into the steady-state and time-resolved optical properties of ZnO photocatalysts	A. Falamas, **I. Marica**, A. Popa, D. Toloman, S. Pruneanu, F. Pogacean, F. Nekvapil, T. D. Silipas, M. Stefan. Mater. Sci. Semicond. Process. 145, 106644 DOI10.1016/j.mssp.2022.106644	2022	4.1	0.511
10	Q2	A novel observation upon the near-resonant Raman excitation of zinc oxide nanoparticles: Widening of the E2(high) band	F. Nekvapil, M. Stefan, **I. Marica**, A. Falamaș J. Raman Spectrosc. 53, 872–879 DOI10.1002/jrs.6323	2022	2.5	0.491
11	non-ISI (BDI)	The management and stewardship of medical plastic waste using raman spectroscopy to sustain circular economy	**I. Marica**, M. Aluas, S.C. Pinzaru 7th E-Health Bioeng. Conf. EHB 2019. 2019. ISSN 2575-5137 DOI10.1109/ehb47216.2019.8970076	2019	-	-
				Total	**49.6**	**7.031**

[a]ISI ranking zone as of date of publication (or most recent available data)
[b]Impact factor according to Clarivate Journals Citation Report (publication year or most recent available data)
[c]AIS InCites JCR – Article influence score according to InCites Journal Citation Reports (publication year or most recent available data)

- **Conferences**

Poster contribution

1. **I. Marica**, M. Stefan, S. Boca, A. Falamaș, C. Fracau, "Evaporation induced self-assembly of ZnO and TiO2 colloidal nanoparticles into highly uniform films for spectroscopic applications". *14th International Conference on Surfaces, Coatings and Nanostructured Materials (NANOSMAT)* [10/07/2023 – 14/07/2023] Athens, Greece
2. **I**. **Marica**, I. Nesterovschi, M. Aluaș, S. Cîntă Pînzaru, "Environmental degradation and pigments influence on plastics waste determined by Raman Spectroscopy: sorting algorithm and plastic Raman database". International Conference "Processes in Isotopes and Molecules (PIM 2021) [22/09/2021 – 24/09/2022] Cluj-Napoca, Romania
3. **I. Marica**, M. Aluaș and S. Cîntă Pînzaru, "Sorting of mixed plastic waste using the Raman spectroscopy technique as a sustainable solution". International Conference "Life sciences for sustainable development [23/09/2021 – 24/09/2021] Cluj-Napoca, Romania