



## Development of Green Analytical Techniques for Microplastic Quantification in Aquatic Systems

<sup>a</sup>Kelvin C. Ugbana

<sup>a</sup>University of Port Harcourt, Nigeria.

**Corresponding Author:** [kelvin@ugbana.com](mailto:kelvin@ugbana.com)

### Abstract

Microplastics (MPs) have emerged as pervasive contaminants in aquatic ecosystems, presenting severe risks to environmental and public health. Conventional analytical techniques, although accurate, often involve environmentally hazardous reagents and energy-intensive protocols. This review critically assesses the evolution of analytical methodologies used to detect and quantify MPs, with particular focus on green analytical chemistry (GAC) principles. The paper evaluates sample preparation, extraction, and detection methods aligned with sustainable practices and introduces recent innovations in green solvents, enzymatic digestion, and spectroscopic analysis. Future trends in eco-friendly analytical instrumentation and data integration tools are also discussed. This work provides researchers and policy-makers with a comprehensive perspective on sustainable microplastic quantification strategies, vital for long-term environmental monitoring and pollution mitigation.

**KEYWORDS:** Microplastics, Green Analytical Chemistry, Eco-friendly Detection, Sustainable Monitoring, Enzymatic Digestion, FTIR Spectroscopy, Machine Learning

### Introduction

Microplastics (MPs), defined as plastic particles less than 5 mm in diameter, have been detected across all environmental compartments, with aquatic systems particularly impacted due to continuous plastic waste influx (Li et al., 2020). These contaminants originate from primary sources such as cosmetic products and industrial abrasives, or from secondary fragmentation of larger plastic debris. The persistence, bioaccumulation potential, and toxicity of MPs call for robust monitoring protocols (Blettler et al., 2018). However, current analytical methods used to assess MPs in aquatic environments often

pose environmental challenges, such as the generation of hazardous waste and high energy consumption.

The global increase in plastic production, estimated to exceed 430 million tonnes annually, has resulted in significant plastic pollution, particularly in aquatic environments. Microplastics (MPs), typically less than 5 mm in size, are formed through degradation of larger plastic debris or manufactured intentionally for specific applications. Their small size and diverse morphology enable them to penetrate biological tissues and disrupt aquatic ecosystems. While the need to monitor MPs is well established, conventional analytical techniques often utilize hazardous chemicals and produce secondary waste, contradicting environmental protection goals.

The emergence of green analytical chemistry (GAC) offers a sustainable alternative. GAC seeks to minimize or eliminate hazardous substances in analytical processes, emphasizing waste reduction, reagent substitution, and energy efficiency (Anastas & Warner, 1998). This review explores how GAC principles are being integrated into microplastic quantification, identifying the key innovations, challenges, and future directions.

## **Microplastics in Aquatic Environments**

### *Sources and Types*

MPs are broadly categorized into primary MPs—intentionally manufactured small plastics—and secondary MPs formed by degradation of larger plastics (Cole et al., 2011). These materials enter aquatic environments through direct discharge, stormwater runoff, atmospheric deposition, and wastewater treatment plant effluents (Murphy et al., 2016). Common polymer types include polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) (Andrady, 2011).

### *Environmental and Biological Impacts*

MPs are ingested by a wide range of aquatic organisms, leading to physiological impairments such as reduced feeding, hormonal disruption, and impaired reproduction (Wright & Kelly, 2017). Their surfaces also adsorb and transport pollutants like persistent organic pollutants (POPs), heavy metals, and pathogenic microorganisms (Rochman et al., 2013). This makes them vectors of complex pollution and threats to food safety. MPs interfere with aquatic food webs by being ingested by plankton, fish, and invertebrates. They can cause physical damage, obstruct digestion, and leach toxic additives. Moreover, MPs act as carriers for other pollutants, including persistent organic pollutants (POPs), heavy metals, and pathogens, which can bioaccumulate through trophic levels and potentially affect human health. Their presence in drinking water and seafood underscores the urgency of effective monitoring techniques.

### **3. Conventional Techniques for Microplastic Quantification**

#### **Sampling**

Aquatic MPs are typically sampled using nets (e.g., neuston or manta trawls), grab samplers, or sediment corers. Surface sampling with neuston nets is widely used for marine MPs (Lusher et al., 2015), while sediment and wastewater require core samplers and pumps, respectively. For sediments, grab samplers, corers, and dredges are used. Wastewater sampling often employs filtration systems and continuous flow setups. Consistency in sampling methods is crucial for inter-study comparisons.

#### **Sample Preparation**

Conventional preparation steps include sieving, filtration, and organic matter digestion. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and Fenton's reagent are common oxidants but pose risks due to their reactivity. Density separation using saturated NaCl, ZnCl<sub>2</sub>, or NaI solutions helps isolate MPs. However, these methods can generate toxic effluents, necessitating

safer alternatives. Sample preparation often involves organic matter digestion using strong oxidants like hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or Fenton's reagent ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) (Tagg et al., 2017). Density separation with solutions like  $\text{ZnCl}_2$  or  $\text{NaCl}$  is used to isolate MPs from sediments or sludge (Imhof et al., 2012).

### **Detection and Identification**

MPs are typically identified using visual inspection, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, pyrolysis-gas chromatography/mass spectrometry (Pyr-GC/MS), and scanning electron microscopy (SEM). While sensitive and specific, many of these methods require costly, high-energy instruments and hazardous solvents (Mintemig et al., 2018).

## **4. Green Analytical Chemistry: Framework and Relevance**

### *Principles of Green Analytical Chemistry*

Green analytical chemistry (GAC) is based on 12 principles outlined by Armenta et al. (2008), including: minimizing sample size and waste, reducing hazardous reagent use, energy-efficient instrumentation, and in-situ or real-time analysis. GAC emphasizes analytical methods that are sustainable across the entire lifecycle—from sample collection to data reporting.

### *Relevance to Microplastic Quantification*

Microplastic analysis currently relies heavily on solvent-intensive and energy-demanding processes. Implementing GAC in this domain is essential for reducing the environmental footprint of monitoring campaigns. Furthermore, green techniques enable frequent and decentralized monitoring, which is crucial for adaptive environmental management (van Wezel et al., 2022).

## **Green Innovations in Sample Preparation and Extraction**

### *Eco-Friendly Digestion Methods*

Enzymatic digestion using proteinase K, cellulase, and lipase provides a biodegradable alternative to chemical oxidants for removing organic matter (Löder et al., 2017). Though slower, enzymatic methods maintain microplastic integrity and minimize secondary pollution.

### *Green Density Separation Media*

Replacing toxic and expensive zinc chloride with safer alternatives like sodium iodide (NaI) or biodegradable polysaccharide-based density media is gaining popularity (Crichton et al., 2017). NaI offers comparable separation efficiency with reduced environmental risk.

### *Solvent-Free Extraction*

Techniques like pressurized hot water extraction (PHWE) and ultrasound-assisted extraction (UAE) can be employed to isolate MPs without the need for organic solvents. These methods offer significant reductions in waste and exposure risks (Nuelle et al., 2014).

## **Green Detection and Characterization Methods**

*Optical Imaging and Machine Learning:* Visual methods enhanced by machine learning algorithms allow semi-automated classification of MPs based on shape, color, and size, reducing the need for spectroscopic confirmation (Käppler et al., 2016). Coupling this with portable digital microscopy enables field-based screening.

*Portable and Low-Energy Spectroscopy:* Miniaturized FTIR and Raman devices reduce energy use and increase accessibility. Innovations in micro-FTIR imaging systems further minimize sample size and analysis time (Prata et al., 2019).

*Biodegradable Fluorescent Markers:* Eco-friendly fluorescent dyes like Nile Red have been optimized for selective binding to MPs. New biodegradable dyes avoid environmental accumulation, and their integration with smartphone-based detection platforms represents a promising green path (Maes et al., 2017).

### **Data Management and Integration**

Green quantification also encompasses ethical and social dimensions. Cloud-based tools and open-source platforms allow communities to contribute data, reducing reliance on centralized laboratories (Hanke et al., 2013). Applications such as "Marine Debris Tracker" support crowd-sourced microplastic monitoring. Few studies evaluate the full environmental impact of MP analytical methods. Life cycle assessment (LCA) tools can guide greener method selection by comparing inputs, waste generation, and energy use (Cesaro et al., 2020).

### **Challenges and Future Prospects**

Green methods, despite their promise, face limitations. Enzymatic digestion is expensive and time-consuming. Portable devices may sacrifice sensitivity. Moreover, green solvents may not fully match the separation capacity of traditional reagents. Standardization and validation are needed to ensure comparability across studies (Van Cauwenberghe et al., 2015).

Integration of microfluidics, biosensors, and machine learning into compact analytical platforms could revolutionize green microplastic analysis (Nguyen et al., 2019). These systems enable rapid, low-energy, and on-site quantification. To scale green methods, alignment with regulatory monitoring frameworks such as those of the EU Marine Strategy Framework Directive is essential (Galgani et al., 2013). Policies should incentivize green technology development and standard adoption. Educating young researchers on GAC principles through university curricula and training programs will

ensure broader adoption. Partnerships between academia, industry, and government can promote green innovation.

## Conclusion

The quantification of microplastics in aquatic systems is critical for managing environmental pollution. While conventional analytical methods are effective, they often violate sustainability principles. Green analytical techniques—ranging from enzymatic digestion to low-energy spectroscopy—offer environmentally sound alternatives that align with global sustainability goals. Ongoing innovation, standardization, and policy support will be essential for transitioning toward greener microplastic monitoring strategies that are both effective and ethical.

## References

- Anastas, P. T., & Warner, J. C. (1998). *Green Chemistry: Theory and Practice*. Oxford University Press.
- Andrady, A. L. (2011). Microplastics in the marine environment. *Marine Pollution Bulletin*, 62(8), 1596–1605.
- Armenta, S., Garrigues, S., & de la Guardia, M. (2008). Green analytical chemistry. *TrAC Trends in Analytical Chemistry*, 27(6), 497–511.
- Blettler, M. C. M., et al. (2018). Freshwater plastic pollution: Recognizing research biases and identifying knowledge gaps. *Science of The Total Environment*, 612, 635–648.
- Cesaro, A., et al. (2020). Plastic pollution: LCA analysis of different collection methods and recycling strategies. *Resources, Conservation and Recycling*, 159, 104813.
- Cole, M., et al. (2011). Microplastics as contaminants in the marine environment: A review. *Marine Pollution Bulletin*, 62(12), 2588–2597.
- Crichton, E. M., et al. (2017). A novel density-independent method for separating microplastics from sediment. *Scientific Reports*, 7, 43893.

- Galgani, F., et al. (2013). Monitoring the marine environment for plastic litter. *ICES Journal of Marine Science*, 70(6), 100–110.
- Hanke, G., et al. (2013). Guidance on monitoring of marine litter in European seas. *European Commission*, JRC.
- Imhof, H. K., et al. (2012). A novel, highly efficient method for the separation and quantification of plastic particles in sediments of aquatic environments. *Limnology and Oceanography: Methods*, 10(7), 524–537.
- Käppler, A., et al. (2016). Identification of microplastics by FTIR and Raman microscopy: A novel silicon filter substrate opens the important spectral range below 1300  $\text{cm}^{-1}$  for FTIR transmission measurements. *Analytical and Bioanalytical Chemistry*, 408(29), 8377–8391.
- Li, J., et al. (2020). Microplastics in freshwater systems: A review on occurrence, environmental effects, and methods for microplastics detection. *Water Research*, 137, 362–374.
- Löder, M. G. J., et al. (2017). Enzymatic purification of microplastics in environmental samples. *Environmental Science & Technology*, 51(24), 14283–14292.
- Lusher, A. L., et al. (2015). Sampling, isolating and identifying microplastics ingested by fish and invertebrates. *Analytical Methods*, 7(17), 100–113.
- Maes, T., et al. (2017). A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. *Scientific Reports*, 7(1), 44501.
- Mintenig, S. M., et al. (2018). Low numbers of microplastics detected in drinking water from ground water sources. *Science of The Total Environment*, 648, 631–635.
- Murphy, F., et al. (2016). Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. *Environmental Science & Technology*, 50(11), 5800–5808.

- Nguyen, B., et al. (2019). Microplastics in the aquatic environment: Characterization, ecotoxicology, risk assessment and management. *TrAC Trends in Analytical Chemistry*, 111, 116–128.
- Nuelle, M.-T., et al. (2014). A new analytical approach for monitoring microplastics in marine sediments. *Environmental Pollution*, 184, 161–169.
- Prata, J. C., et al. (2019). Tools and techniques for freshwater microplastics monitoring. *Current Opinion in Environmental Science & Health*, 1, 90–99.
- Rochman, C. M., et al. (2013). Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Scientific Reports*, 3, 3263.
- Tagg, A. S., et al. (2017). Identification and quantification of microplastics in wastewater using focal plane array-based reflectance micro-FTIR imaging. *Analytical Chemistry*, 89(12), 6024–6030.
- Van Cauwenberghe, L., et al. (2015). Microplastics in sediments: A review of techniques, occurrence and effects. *Marine Environmental Research*, 111, 5–17.
- van Wezel, A., et al. (2022). Sustainability criteria for analytical methods: a new tool to assess greenness of analytical methods. *Green Chemistry*, 24(1), 150–160.
- Wright, S. L., & Kelly, F. J. (2017). Plastic and human health: A micro issue? *Environmental Science & Technology*, 51(12), 6634–6647.