Electronic supplementary information

When microplastics meet electroanalysis: future analytical trends for an emerging threat

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Table 1. Recent studies reporting the use of spectrophotometric methods for the identification and quantification of MPs.

Type of analysis	Sample	Size (μm)	MPs analyzed	Observations	Complications	Ref
μ-FTIR(T)	Soil	> 33	PE, PP, PS, PA, PVC and PET	3 h for sample preparation and 20 min for identification	Sample pretreatment is crucial	1
μ-FTIR(T)	Soil	10 - 400	PE, PA, PET and PVC	Oxidative enzymatic methods for sample preparation	MPs require pretreatment, purification and clean-up	2
μ-FTIR(ATR)	Sand	≥ 20	PE, PP, PS, PA and PVC	Peroxidation via H_2O_2 and density separation with NaCl	60% spectral matching by diffuse reflexion	3
μ-FTIR(ATR)	Fresh water	200	PE, PP, PS and PA	Digestion with H_2O_2 + KOH. 70% error in determinations	7 days of pretreatment and clean-up	4
μ-FTIR(ATR)	Oysters	> 5	PP, PA and ABS	Extraction and purification increase the quality of the analysis.	Sample digestion, purification, and clean-up	5
μ-FTIR(ATR)	Seawater, freshwater and wastewater	10 - 500	PE, PP, PA, PS, PET, PVC	Digestion organic matter using H_2O_2 / Fenton and KOH.	14 days to complete digestion ad analysis process	6
μ-FTIR(T) and μ-RAMAN	Sea water	> 1	PE, PP, PA, ABS, PVA, PU and PET	Purification by basic enzymatic protocol	13 days to complete MPs analysis	7
μ-RAMAN	Commercial drinking water	≥ 10	PP, PET and PA	Main fraction of MPs detected less than 20 μm	Sample purification and clean-up	8
μ-RAMAN	MPs generated when opening plastic packaging	2 - 100	PE, PP, PS and PET	Simple sampling method to detect MPs simultaneously. Mass changes of small particles of MPs (10-30 ng) were detected.	Complementary techniques to determine mass and composition of MPs	9
μ-RAMAN	Marine atmosphere	1 - 100	PE, PP and PS	Filters facilitates the analysis. No need to clean-up the sample.	1 μm MPs were not detected	10
μ-RAMAN	Human placenta	5 - 10	PE, PP and PET	Identification was possible with a data base	Sample purification and clean-up	11
μ-RAMAN	River water and sediments	≥ 2	PE, PP, PS, PET and PVC	Nile Red was used in MPs tinction to facilitate micro-Raman identification.	Sample preparation and clean-up procedures are required to use Nile Red. False positive results were registered for fluorescence effect.	12

ABS: acrylonitrile butadiene styrene, PA: Polyamide, PE: polyethylene, PET: polyethylene therephtalate, PP: polypropilene, PS: polystyrene, PU: polyurethane, PVA: polyvinyl alcohol, PVC: polyvinyl chloride.

Table 2. Thermal analytical methods applied to the characterization of environmental samples containing MPs.

Type of analysis	Sample	Size (μm)	MPs analyzed	Observations	Complications	Ref
DSC	Sea water	> 20	PEVA, PP, ABS, PS, PTFE, PET, PE-LD, and PE-HD	11 different sites were sampled.	Sample washing and separation	13
DSC	Simulated water	-	PE-HD, PE-LD, PA and PET	Preheating/ cooling reduce interferences signals. LOQ from 0.05 to 0.19 mg (depending on the polymer)	Peak overlapping. PVC, PUR and PS are not detectable.	14, 15
DSC	Water solutions	23-256, 256-645 , 645-1000	PE-LD, PE-HD, PP and PET of different sizes.	Melting point temperature and peak area are affected by particle size	Need of sample treatment	16, 17
Py-GC/MS	Sediments	≤ 500	PE, PP, PS, PET and PVC	Sediment into the matrix interfere with measurements	The residual organic matter has a negative effect	18
Py-GC/MS[2]	Air	≤ 2.5	PE	High recovery (97-110%) and sensitivity (LOD = 1 pg) without sample pre-treatment	-	19
Py-GC/MS	River, sea, effluent water	PS (25, 60, 1000 nm) PMMA (25, 75 nm)	PS and PMMA	The nanoplastics keep in their original shape and size after the cloud-point extraction step employing Triton X-45	LOD ≥ 10 $\mu g\ L^{-1}$ MPs	20
Py-GC/MS	Sediment, soil and seawage sludge	10 – 50 200-400	PE, PP and PS	Pressurized liquid extraction allow analysis in less than 7 h. LOQ of 7 $\mu g\ g^{-1}$	Large particles (200-400 μm) aggregate resulting in high deviation.	21
Py-GC/MS	Soil	250 - 500	PE, PS and PP.	1,2,4-trichlorobenzene was used to dissolve PE, PP and PS. LOD from 1 – 86 $\mu g\ g^{-1}$. Analysis time: 2-3 h	Changes in particle crystallinity and surface properties could affect the polymer solubility	22

Py-MS (portable)	Pelagic and demersal fish	20 - 125	PE, PP, PS, PET, PVC, PMMA, PC, PA and methylene-diphenyldiisocyanate-PUR	Thermochemolysis increase the reliability of mass related data. Improved sensitivity for PET and PC.	Sample pre-concentration	23
Py-MS (portable)	Beach sediments	< 5000	PE, PP, PS and PMMA	MPs affected by environmental conditions (aging and UV) were successfully identified in less than 5 min	Sample extraction and purification	24
TED-GC/MS	Water sedimetns	145 - 198	PE, PP and PS (LOQ of 10, 1 and 0.2 µg)	A thermogravimetric furnace (TGA) is coupled to solid-phase absorbers and transferred to GC/MS. Large sample input (up to 100 mg)	Manual operation affect the reproducibility	25

ABS: acrylonitrile butadiene styrene, PA: polyamide, PE: polyethylene, PE-HD: high-density polyethylene, PE-LD: low-density polyethylene, PET: polyethylene therephtalate, PEVA: polyethylene co-vinyl acetate, PMMA: polymethyl methacrylate, PC: polycarbonate, PP: polypropilene, PS: polystyrene, PTFE: polytetrafluoroethylene, PVC: polyvinyl chloride.

Table 3. Electrochemical methods or proof-of-concept applied to the characterization of solutions prepared with MPs.

Type of analysis	Sample	Size	Observations	Highlights	Complications	Ref
Collision electrochemistry (Amperometry)	Carboxylated latex	50 nm	Au planar UME and FcMeOH	Detection of insulating nanoplastic, proof-of-concept.	Enhanced radial diffusion Limited to low sized particles	26
Collision electrochemistry (Amperometry)	PS	530 nm	Au planar UME, FcMeOH and KCl	Enhanced electromigration	Enhanced radial diffusion Limited to low sized particles	27
Collision electrochemistry (Amperometry)	PS	1-2 µm, 400 nm	Hemispherical Hg UME	No radial diffusion	Limited to low sized particles	28
Collision electrochemistry (Cathodic coulometry)	PS	1-4 µm	Carbon fiber UME and NaCl	Size distribution, counts. Proof-of concept.	Limited to low sized particles	29
Collision electrochemistry (FFT- EIS)	PS	1 µm	UME, FcMeOH and KCl	Size distribution, counts. Proof-of-concept.	Limited to low sized particles	30
Tunnable resistive pulse sensor	PS	40 nm – 10 µm	Ability to analyze particles with different size in one step	Particle size and counts. Portable.	Need of calibration. Membrane pores can be obstructed.	31, 32
Impedance flow cytometry	PE	300 – 1000 µm	Ability to solve samples containing MPs and biological particles/organisms	Particle size (range) and counts. No pretreatment for simulated seawater samples. Portable.	Limited to solve small MPs. Sensitive to bubbles.	33
Electrochemical impedance spectroscopy	PS	0.08, 0.1, 1, 7.5, 10 and 20 µm	Ability to analyze particles with different size and concentrations	Chemometric analysis is needed Real tap water samples were used	Best results were obtained for concentrations of 1 mg mL^{-1}	34

PE: polyethylene, PS: polystyrene

References

1 M. Liu, Y. Song, S. Lu, R. Qiu, J. Hu, X. Li, M. Bigalke, H. Shi and D. He, A method for extracting soil microplastics through circulation of sodium bromide solutions, *Sci. Total Environ.,* 2019, **691**, 341–347.

2 J. N. Möller, I. Heisel, A. Satzger, E. C. Vizsolyi, S. D. J. Oster, S. Agarwal, C. Laforsch and M. G. J., C. Löder, Tackling the Challenge of Extracting Microplastics from Soils: A Protocol to Purify Soil Samples for Spectroscopic Analysis, *Environ. Toxicol. Chem*., 2021, **41**, 844-857

3 C. Rathore, M. Saha, P. Gupta, M. Kumar, A. Naik and J. de Boer, Standardization of micro-FTIR methods and applicability for the detection and identification of microplastics in environmental matrices, *Sci. Total Environ*., 2023, **888**, 164157.

4 E. O. Akindele, S. M. Ehlers and J. H. E. Koop, First empirical study of freshwater microplastics in West Africa using gastropods from Nigeria as bioindicators, *Limnologica.*, 2019, **78**, 125708.

5 F. Corami, B. Rosso, M. Roman, M. Picone, A. Gambaro and C. Barbante, Evidence of small microplastics (<100μm) ingestion by Pacific oysters (Crassostrea gigas): A novel method of extraction, purification, and analysis using μ-FTIR, *Mar. Pollut. Bull*., 2020, **160**, 111606.

6 J. Yang, M. Monnot, Y. Sun, L. Asia, P. Wong-Wah-Chung, P. Doumenq and P.Moulin, Microplastics in different water samples (seawater, freshwater, and wastewater): Methodology approach for characterization using micro-FTIR spectroscopy, *Water Res.,* 2023, **232**, 119711.

7 M. G. J. Löder, H. K. Imhof, M. Ladehoff, L. A Löschel, C. Lorenz, S. Mintenig, S. Piehl, S. Primpke, I. Schrank, C. Laforsch and G. Gerdts, Enzymatic Purification of Microplastics in Environmental Samples, *Environ. Sci. Technol.*, 2017, ***51*****,** 14283–14292.

8 D. Schymanski, C. Goldbeck, H. U. Humpf and, P. Fürst, Analysis of microplastics in water by μ-Raman spectroscopy: Release of plastic particles from different packaging into mineral water, *Water Res*., 2018, **129**, 154–162.

9 Z. Sobhani, Y. Lei, Y. Tang, L. Wu, X. Zhang, R. Naidu, M. Megharaj and C. Fang, Microplastics generated when opening plastic packaging, *Sci Rep.*, 2020, **10**, 4841.

10 M. Trainic, J. M. Flores, I. Pinkas, M. L. Pedrotti, F. Lombard, G. Bourdin, G. Gorsky, E. Boss, Y. Rudich, A. Vardi and I. Koren, Airborne microplastic particles detected in the remote marine atmosphere, *Commun. Earth Environ*., 2020, **1**, 1–9.

11 A. Ragusa, A. Svelato, C. Santacroce, P. Catalano, V. Notarstefano, O. Carnevali, F. Papa, M. C. A. Rongioletti, F. Baiocco, S. Draghi, E. D'Amore, D. Rinaldo, M. Matta and E. Giorgini Plasticenta: First evidence of microplastics in human placenta. *Environ. Int*., 2021, **146**, 106274.

12 J. C. Prata, J. P. da Costa, A. J. S. Fernandes, F. M. da Costa, A. C. Duarte and T. Rocha-Santos, Selection of microplastics by Nile Red staining increases environmental sample throughput by μ-Raman spectroscopy, *Sci. Total Environ*., 2021, **783**, 146979.

13 S. H. Shabaka, M. Ghobashy, R. S. Marey, Identification of marine microplastics in Eastern Harbor, Mediterranean Coast of Egypt, using differential scanning calorimetry, *Mar. Pollut. Bull*., 2019, **142**, 494-503.

14 H. Bitter and S. Lackner, Fast and easy quantification of semi-crystalline microplastics in exemplary environmental matrices by differential scanning calorimetry (DSC), *J. Chem. Eng*., 2021, **423**, 129941.

15 M. R. Chialanza, M. F. Samarra, S. F. Samarra and P. A. Parada, Modeling microplastic with polyethylene (PE) spherical particles: a differential scanning calorimetry approach for quantification, *Environ Sci Pollut Res*., 2022, **29**, 2311–2324.

16 M. R. Chialanza, I. Sierra, A. P. Parada and L. Fornaro, Identification and quantitation of semi-crystalline microplastics using image analysis and differential scanning calorimetry, *Environ Sci Pollut Res.*, 2018, **25**, 16767–16775.

17 D. Sorolla-Rosario, J. Llorca-Porcel, M. Pérez-Martínez, D. Lozano-Castelló and A. Bueno-López, Study of microplastics with semicrystalline and amorphous structure identification by TGA and DSC, *J. Environ. Chem. Eng.*, 2022, **10**, 106886.

18 N. Bouzid, C. Anquetil, R. Dris, J. Gasperi, B. Tassin and S. Derenne. Quantification of microplastics by pyrolysis coupled with gas chromatography and mass spectrometry in sediments: Challenges and implications, *Microplastics.*, 2022, **1**, 229-239.

19 P. Luo, M. Bai, Q. He, Z. Peng, L. Wang, C. Dong, Z. Qi, W. Zhang, Y. Zhang and Z. Cai, A Novel Strategy to Directly Quantify Polyethylene Microplastics in PM2. 5 Based on Pyrolysis-Gas Chromatography–Tandem Mass Spectrometry, *Anal. Chem.,* 2023, **95**, 3556-3562.

20 X. X. Zhou, L. T. Hao, H. Y. Wang, Y. J. Li and J. F. Liu, Cloud-Point Extraction Combined with Thermal Degradation for Nanoplastic Analysis Using Pyrolysis Gas Chromatography-Mass Spectrometry, *Anal. Chem*., 2019, **91**, 1785–1790.

21 G. Dierkes, T. Lauschke, S. Becher, H. Schumacher, C. Földi and T. Ternes, Quantification of microplastics in environmental samples via pressurized liquid extraction and pyrolysis-gas chromatography, *Anal. Bioanal. Chem*., 2019, **411**, 6959–6968.

22 Z. Steinmetz, A. Kintzi, K. Muñoz and G. E. Schaumann, A simple method for the selective quantification of polyethylene, polypropylene, and polystyrene plastic debris in soil by pyrolysis-gas chromatography/mass spectrometry, *J. Anal. Appl. Pyrolysis.,* 2020, **147**, 104803.

23 M. Fischer and B. M. Scholz-Böttcher, Simultaneous Trace Identification and Quantification of Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography-Mass Spectrometry, *Environ. Sci. Technol.*, 2017, **51**, 5052–5060.

24 X. Zhang, H. Zhang, K. Yu, N. Li, Y. Liu, X. Liu and J. Jiang. Rapid monitoring approach for microplastics using portable pyrolysis-mass spectrometry, *Anal. Chem*., 2020, **92**, 4656-4662.

25 R. Becker, K. Altmann, T. Sommerfeld and U. Braun, Quantification of microplastics in a freshwater suspended organic matter using different thermoanalytical methods – outcome of an interlaboratory comparison, *J. Anal. Appl. Pyrolysis.,* 2020, **148**, 104829.

26 B. M. Quinn, P. G. Van't Hof and S. G., Lemay, Time-resolved electrochemical detection of discrete adsorption events, *J. Am. Chem. Soc.*, 2004, **126**, 8360-8361.

27 A. Boika, S. N. Thorgaard and A. J. Bard, Monitoring the electrophoretic migration and adsorption of single insulating nanoparticles at ultramicroelectrodes, *J. Phys. Chem. B.,* 2013, **117**, 4371-4380.

28 Z. Deng, R. Elattar, F. Maroun and C. Renault, In situ measurement of the size distribution and concentration of insulating particles by electrochemical collision on hemispherical ultramicroelectrodes, *Anal. Chem.,* 2018, **90**, 12923-12929.

29 K. Shimizu, S. V. Sokolov, E. Kätelhön, J. Holter, N. P. Young and R. G. Compton, In situ Detection of Microplastics: Single Microparticle- electrode Impacts, *Electroanalysis.*, 2017, **29**, 2200-2207.

30 B. Roehrich, E. Z. Liu, R. Silverstein and L. Sepunaru, Detection and Characterization of Single Particles by Electrochemical Impedance Spectroscopy, *J. Phys. Chem. Lett*., 2021, **12**, 9748-9753.

31 F. Caputo, R. Vogel, J. Savage, G. Vella, A. Law, G. Della Camera and L. Calzolai. Measuring particle size distribution and mass concentration of nanoplastics and microplastics: addressing some analytical challenges in the sub-micron size range, *J. Colloid Interface Sci.*, 2021, **588**, 401-417.

32 W. Anderson, D, Kozak, V. A. Coleman, A. K. Jämting and M. Trau, A comparative study of submicron particle sizing platforms: accuracy, precision and resolution analysis of polydisperse particle size distributions, *J. Colloid Interface Sci*., 2013, **405**, 322–330.

33 B. C. Colson and A. P. M. Michel, Flow-Through Quantification of Microplastics Using Impedance Spectroscopy, *ACS Sensors.*, 2021, **6**, 238–244.

34 H. Du, G. Chen and J. Wang, Highly selective electrochemical impedance spectroscopy-based graphene electrode for rapid detection of microplastics, *Sci. Total Environ*., 2023, **862**, 160873.