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Mass spectrometry as a powerful analytical tool for the characterization of indoor airborne microplastics and nanoplastics

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Development of analytical methods for the characterization (particle size determination, chemical identification, and quantification) of the low μm-range microplastics (MPs; 1–10 μm) and nanoplastics (NPs; 1 nm to 1 μm) in air – coarse (PM_{10}; <10 μm), fine ($PM_{2.5}$; <2.5 μm) and ultrafine (PM_1; <1 μm) particulate matter – is a quickly emerging scientific field as inhalation has been identified as one of the main routes of human exposure. The respiratory tract may serve as both target tissue and port of entry to the systemic circulation for the inhaled MPs and NPs with their small particle size. As an outcome, the interest of the scientific community, policy makers, and the general public in indoor airborne MPs and NPs increased tremendously. However, there is a lack of detailed knowledge on the indoor and outdoor sources of MPs and NPs, their levels, and their health impact. This is mainly related to a lack of standardized sampling and analytical methods for size determination, chemical identification, and quantification. In this review, recent developments in mass spectrometry-based analytical methods for size determination, chemical identification, and quantification of the MPs and NPs in indoor air and dust, are discussed.

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1. Introduction to airborne microplastics and nanoplastics

Particulate plastics include a group of plastic polymers from 5 mm down to the nanometer range.[1] They are ubiquitously present and scientists have pointed out their persistent nature[2] and their possible impacts on humans who can be exposed to particulate plastics *via* ingestion, inhalation, and dermal contact.[3] In environmental sciences, the term microplastics (MPs) is used for plastic particles with a size range between 1 μm and 5 mm (<5 mm) in diameter. The term nanoplastics (NPs) refers to plastic particles with a size <1 μm.[1] Inhalation has been identified as one of the main routes of human exposure to coarse (PM_{10}; <10 μm) and especially fine ($PM_{2.5}$; <2.5 μm) and ultrafine (PM_1; <1 μm) particulate matter, and many studies report on the impact of air pollution on human health.[4–6] So far, however, few studies on the presence of indoor and outdoor airborne coarse plastic (2.5–10 μm) and fine plastic (1–2.5 μm) particles (further referred as low μm-range MPs; 1–10 μm) have been conducted to date.[3,6–9] Only limited number of studies exist on the actual occurrence of indoor and outdoor airborne ultrafine plastics (further referred to as NPs; 1 nm to 1 μm).[10–12] This is mainly due to the lack of standardized sample collection and preparation strategies, as well as of analytical methods for their detection, quantification and characterization. The complex composition of MPs and NPs including different types of polymer material (*e.g.*, polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyurethane (PU), nylon, acrylic), their different sizes and shapes (*e.g.*, fibers, fragments), surface morphologies and charges makes method development even more difficult and novel approaches are required. In addition, there is a limited knowledge on exposure sources and levels, kinetics, and toxicity (including mechanisms of action and dose–response relations) for the different types of MPs and NPs.[5,12,13] Low μm-range MPs and NPs in outdoor air may originate from tire wear, road paintings, agricultural plastic foil, reuse of sewage treatment plant sludge, waste incineration, industrial discharge, and aerosolization of sea water.[7,14,15] It is not yet known to what extent wear and tear of, for instance, synthetic carpets, furniture, painting, 3D printed items and synthetic fabrics contribute to MPs and NPs occurring in indoor

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air.[7,12,15,16] As people spend approximately 70–90% of their lifetime indoors (whether at home or at work),[17] it has been hypothesized that indoor MPs, including microfibers, and NPs can have a significant impact on human exposure and health.[18] However, due to the lack of sufficiently powerful and versatile analytical approaches and thus, of correct data on the presence and distribution of MPs and especially NPs in air, it is very difficult to assess the exposure risk of inhaled MPs and NPs and its impact on human health,[5] as a result there is an urgent need for method development.

2. Deposition of inhaled particles in the human respiratory tract

Several studies have revealed that indoor airborne MPs concentrations may be very low (1.7 and 16.2 particles per m^3).[3,19] However, various parameters *e.g.*, ventilation rate, air flow, room partitioning and climatic conditions affect their dispersion and presence in indoor air.[16,19] In a very first study on human exposure to MPs and microfibers breathing thermal manikin was used to simulate human respiration.[3] From this experiment it was estimated that a male person with light activity inhales 272 MPs per day.[3] In another study, inhalation of airborne MPs including microfibers (length > 5 μm, with diameter < 3 μm) *via* indoor air has been estimated at 26–130 airborne MPs per day.[19] Considering that fibers of size 250 μm have been found in the deep human lung,[12] the presence of indoor airborne low μm-range MPs and NPs and reliable exposure assessment should be investigated very carefully.

Regional deposition of inhaled MPs and NPs in the human respiratory tract is mainly dependent on the particle size (Fig. 1). The interplay between the properties of the MPs and NPs (size, shape, and density), human physiology and lung anatomy are essential factors influencing human exposure and has been extensively studied in recent years.[20–24] Lower density polymers (*e.g.*, PE), fibers and plastic particles with a size below 5 μm have a higher potential to be deposited in the lower airways.[25] After deposition, clearance relies on mucus progression towards the pharynx by beating epithelial cell cilia, alveolar macrophage phagocytosis, or translocation to the circulation or lymphatic system. The large surface area of small particles in the respiratory system may induce chronic inflammatory responses.[26] It has been shown that PS nanospheres (64 nm) lead to the influx of neutrophils into and inflammation of rat lungs, as well as proinflammatory gene expression in epithelial cells, due to the confirmed high oxidant activity caused by the large surface area of these nanospheres.[27] *In vitro*, PVC particles induced significant cytotoxicity in rat and human pulmonary cells and gave rise to hemolysis.[28] Occupational exposure to airborne MPs in workers active in the synthetic textile, flocking or the vinyl chloride or PVC industries has been associated with respiratory symptoms and the development of airway and interstitial lung disease due to absence of proper protection in the work area.[29–33] The reported correlation is interesting because the same inflammatory responses can be expected to occur in susceptible individuals with a compromised respiratory system who are exposed to lower indoor airborne MPs and NPs, as well as children due to the deposition of the plastic particles on the floor.[15,16,34] Consequently, powerful analytical tools are required in order to fill the knowledge gap on the:

(1) sources and occurrence of low μm-range MPs and NPs among the atmospheric and settled particles in indoor

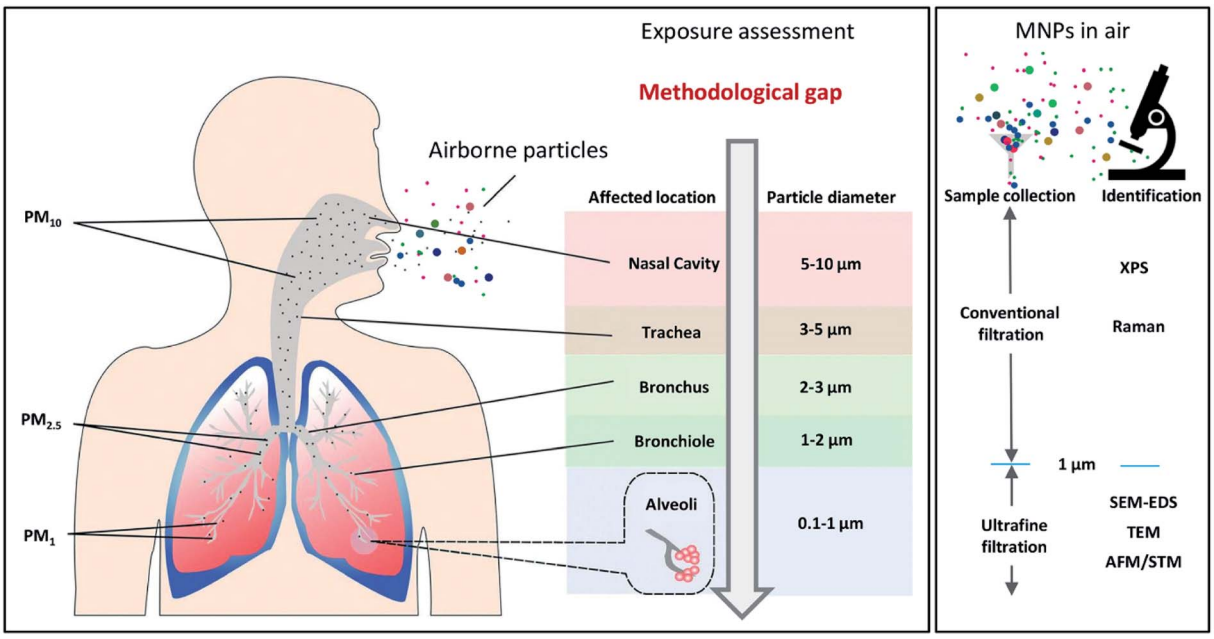

Fig. 1 Left: size-dependent regional deposition of inhaled particles with different size (PM_{10}, $PM_{2.5}$, and PM_1) in the specific regions of respiratory tract. Right: overview of conventional analytical techniques available to collect and potentially identify low μm-range MPs and NPs in indoor air. Partly expanded, adapted, and redrawn, with permission from Poh *et al.* 2018.[35]

environments where people spend most of their time including home, the workplace, schools and kindergartens;

(2) potential exposure and translocation of low μm-range MPs and NPs from the respiratory system to blood and other tissues;

(3) respiratory system toxicity and/or systemic health effects of low μm-range MPs and NPs after inhalation exposure.

3. Analytical challenges

There is a lack of standardized sampling and analytical methods for size determination, chemical identification, and quantification of low μm-range MPs including the fibers and NPs in air and dust, thus hampering a reliable exposure assessment.[36] So far, very few studies have focused on the detection and size distribution of airborne MPs in the indoor and outdoor environment.[16] As a result, airborne MPs, microfibers and NPs present a relevant analytical challenge. Optical methods such as Fourier-transform infrared spectroscopy (FTIR)[37] or Raman microspectroscopy (μRaman)[38] can be deployed for the analysis of MPs (Fig. 2), but due to existing limitations of these analytical methodologies (related to, *e.g.*, the wavelength of the light source and interferences coming from the contamination of samples with other particles from other sources), chemical identification of individual particles below 10 μm for FTIR and below 0.5 μm for μRaman is troublesome.[38] Several other analytical methods that can provide information on particle size (*e.g.*, transmission electron microscopy, dynamic light scattering, nanoparticle tracking analysis) are not capable of identification of the type of polymer. Finally, analytical techniques for the detection and characterization (*i.e.*, shape, size, polymer composition) of low μm-range MPs and especially NPs in indoor air require relatively high particle concentrations (number/mass) for analysis. Therefore, further research in this field is required to develop reliable analytical methods for characterization of individual plastic particles and fibers in the low micrometer and nanometer range.

The major challenges facing research in this area are (i) the complex composition of low μm-range MPs and NPs, their different sizes and irregular shapes; (ii) the absence of reference materials mimicking the intrinsic properties of such particles, except for the PS particle size standards intended for the validation and monitoring of particle counters and supporting sample preparation processes; (iii) the difficulty of obtaining/maintaining plastic-free test systems; (iv) the observation that analytical methods that can provide information on particle size are typically not capable of identification of the type of polymer, and *vice versa*. According to size distributions demonstrated in recent studies, an increase in the plastic particle number is observed with decreasing size, which raises concerns as to human exposure to smaller-sized plastic particles and their potential impact on human health. Methods for NP sampling, sample pre-treatment and determination are non-specific and still in a development phase.[4] Consequently, emerging promising techniques will have to be anticipated to contribute towards the characterization of airborne low μm-range MPs and NPs (Fig. 2).

This review will summarize novel developments in mass spectrometry (MS)-based analytical methods that could play an important role for size determination, chemical identification, and quantification of MPs and NPs in indoor air and dust, and discuss how these contribute to exposure assessment. Challenges in sample collection and pre-treatment will also discussed.

4. Sample collection and preparation strategies

Characterization of airborne and settled low μm-range MPs and NPs in indoor environments highly relies on the sample collection procedures and pre-treatment protocols that are in a development phase only.[40] Sample collection and preparation strategies preceding low μm-range MPs and NPs analysis are crucial steps and have to be successfully accomplished to enable adequate results to be obtained. Obliviously, the smaller the size of the plastic particles in indoor air, the more difficult it is to isolate them. It is evident that there is no standardized procedure for sampling and sample treatment of airborne low μm-range MPs and NPs yet.[4] However several methods have been described for other matrices, including: (i) sieving for aquatic systems,[41] (ii) density separation for sediments,[42] and chemical/enzymatic digestion for food and biota samples.[43] In general, conventional air sample collection includes (i) active air sampling that provides necessary information on particles concentration and is necessary for exposure assessments, and (ii) passive sampling of settled particles giving the possibility to provide mass balance calculations. For collection of airborne and settled low μm-range MPs and NPs different types of sampling devices, sample pumps, sampling filters, sampling volumes, sampling times, and sampling conditions can be used. Up to now, a stand-alone sampling pump was used for collection of airborne MPs.[16] To collect settled MPs, a vacuum pump or vacuum cleaner can be used.[4,34] However, these methods are still in a development phase and have not been tested for indoor air NPs yet. In addition, existing airborne dust samplers: (i) stationary cascade impactors for simultaneous collection of airborne particles of different size fractions; (ii) stationary cowled sampling heads (with an aluminum filter for sampling plastic fibers); (iii) particle sampling by filtration on a porous TEM grid (operational in the 5–150 nm size range);[44] and (iv) personal cascade impactors available with 6, 8, and 10 impaction stages, to obtain size-fractionated particle samples as small as 56 nm can be of use. For collecting settled dust, (i) wipe sampling methods for other types of particles (*e.g.*, particulate matter, floor dust, *etc.*),[45] (ii) tape lift sampling, and (ii) micro-vacuum sampling[46] might be used. All these sampling procedures are relevant for spectroscopic identification of low μm-range MPs (Fig. 2). As an illustration, low-pressure cascade impactors are extensively used to characterize the mass size distribution of airborne particles and as such necessary for the exposure studies/assesment.[47] Many cascade impactors capable

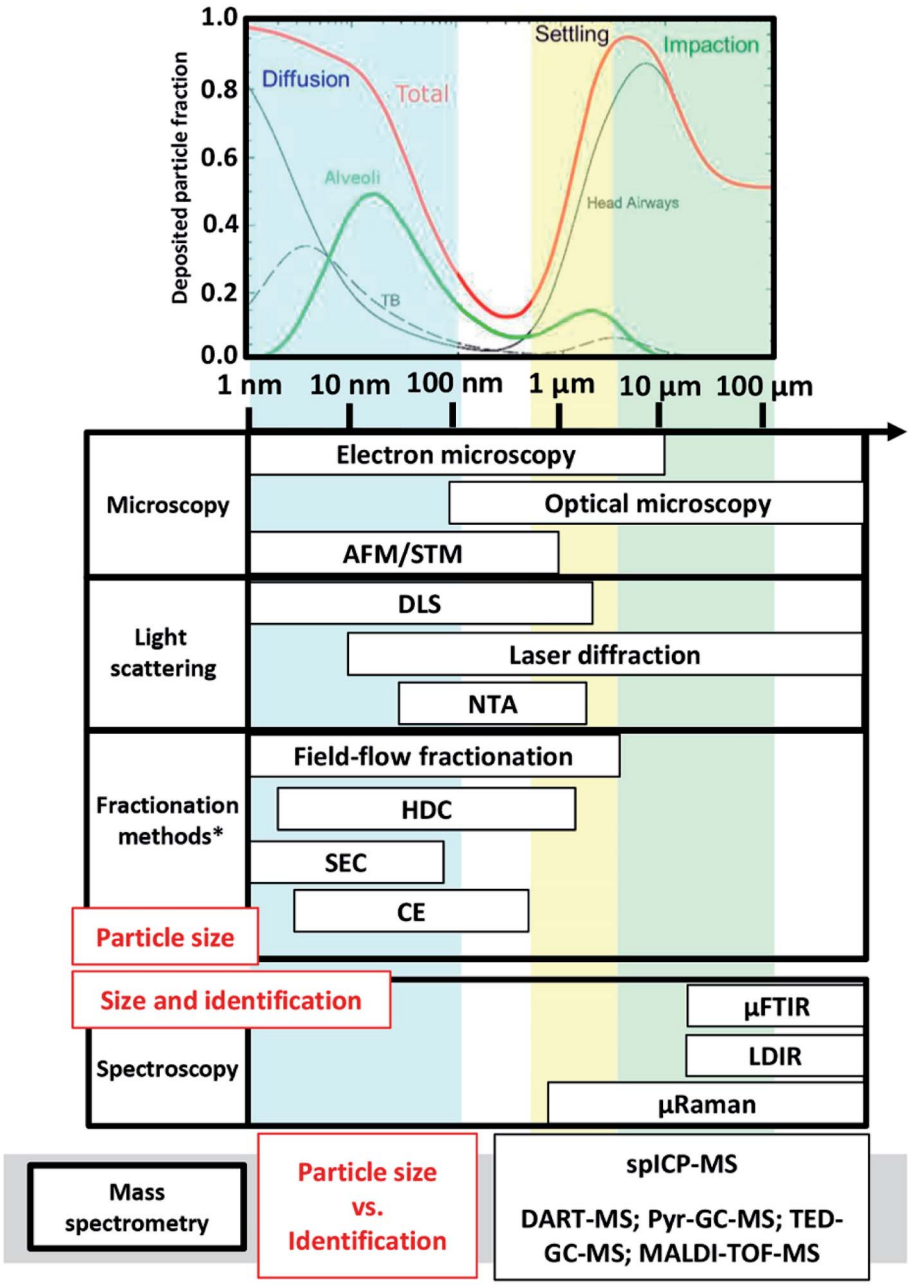

Fig. 2 Capabilities and limitations of different analytical techniques to characterize MPs and NPs in terms of particle size and/or composition in comparison to size dependent regional deposition of inhaled particles in the respiratory tract based on the International Commission on Radiological Protection model provided by Oberdörster *et al.*, 2005.[39] *In combination with light scattering, ultraviolet-visible (UV-vis) absorption spectrometry, and/or mass spectrometry (MS) for particle detection.

of classifying particles into different size fractions in the range of approximately 30 nm to 10 µm are already available.[48,49] The basic operating principle of a low-pressure cascade impactor is classification of particles based on their aerodynamic diameter: where the larger particles with more inertia are collected first in the uppermost impactor stages, the smaller particles with less inertia are collected downstream the gas flow of 10 or 30 L min^{-1} (Fig. 3). The size classified particles are collected on Ø25 mm collection substrates with aluminum foils that are convenient for spectroscopy measurements.

Dry sampling methods should be extended to wet sampling methods and extensive sample preparation procedures including matrix removal in order to show full potential of MS-based analytical methods for MPs and NPs characterization. The removal of organic material is crucial for the detection and characterization of MPs and NPs by spectroscopy-based methods and even more for MS-based analytical methods. Consequently, MPs and NPs collected using a cascade impactor should be further treated.[49] As an example, after MPs and NPs are collected and dispersed in water by ultrasonic-assisted

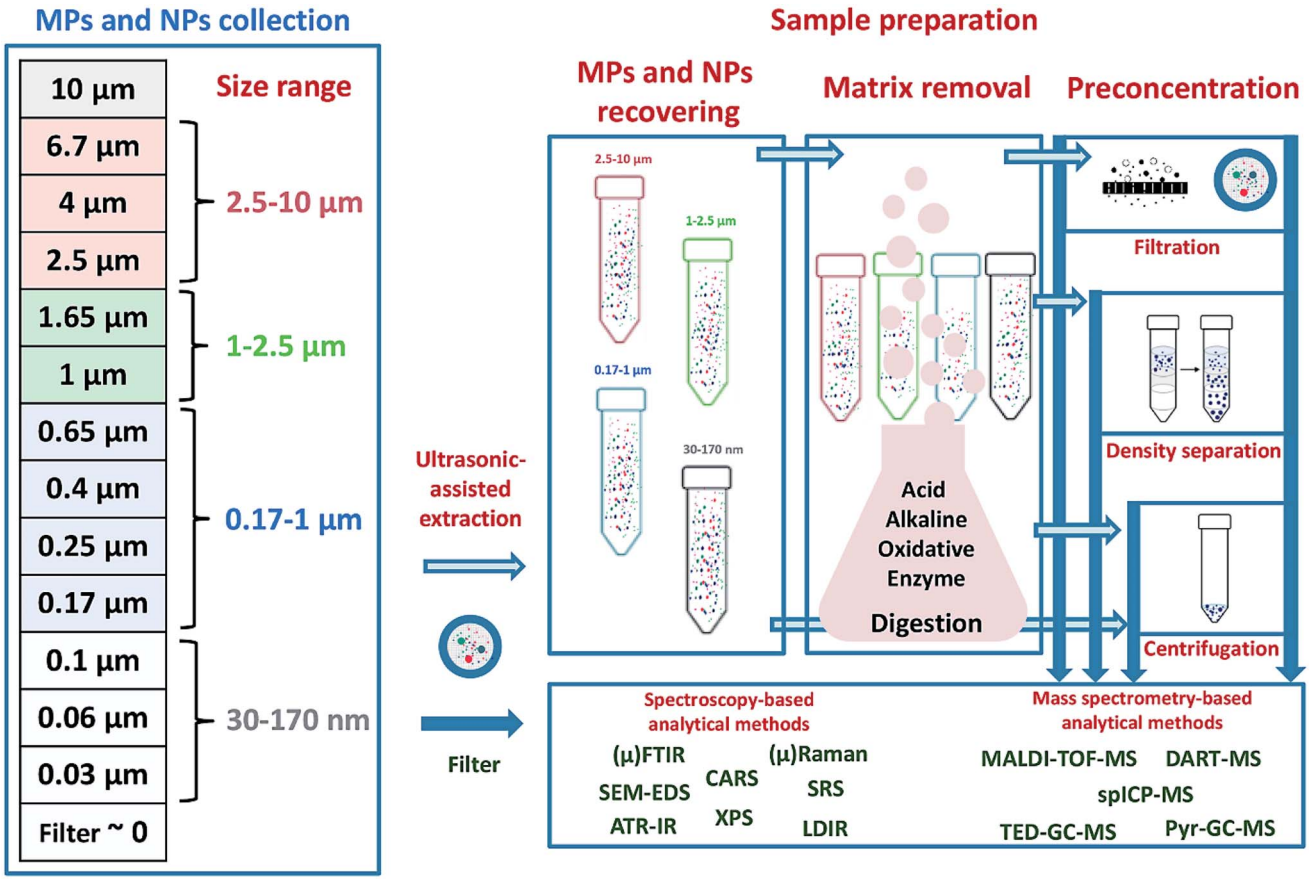

Fig. 3 Analytical process for sample collection (*e.g.*, size-partitioning using a cascade impactor) and preparation, as well as characterization of MPs and NPs in airborne dust and settled dust including spectroscopy and MS-based analytical methods as complementary analytical techniques.

extraction or pressurized liquid extraction, matrix removal, and MPs and NPs extraction protocols will play an important role for further analysis (Fig. 3) taking into account that insufficient matrix removal introduces matrix effects in the mass spectrometry analysis. Of course, it needs to be ensured that the plastic particles are not affected during the matrix removal and/or MPs and NPs extraction protocols used, which could include: (1) oxidizing procedures,[50] (2) wet acid treatment,[51] (3) alkaline digestion,[52] (4) enzymatic digestion,[43] and (5) density separation.[53] Preconcentration and filtration steps are also needed in order to meet the specific requirements of the MS-based techniques employed in this context. In general, validation of matrix removal/MPs and NPs extraction procedures is rarely mentioned in most of the recent publications dealing with MPs and NPs in environmental samples.[54] Therefore, there is a clear need to verify the impact of the current sample preparation approaches and evaluate possible risk of blank contamination, losing MPs and NPs, and finally degradation of low µm-range MPs and NPs by introducing standardized materials in recovery tests. Finally, pre-concentration techniques (filtration, density separation, centrifugation) for MPs and NPs analysis in relevant sample extracts should also be considered to allow sufficient concentration of low µm-range MPs and NPs for further analysis.

5. Mass spectrometry-based analytical methods for microplastics and nanoplastics characterization

Mass spectrometry (MS) and microspectroscopy are state-of-the-art techniques that are rapidly developing and increasingly tested for the characterization of MPs and possibly NPs. To characterize MPs down to 10 µm size, microspectrosopic techniques (*e.g.*, µRaman, µFTIR, LDIR) are being extensively used. However, for analyzing the low-µm-range MPs and NPs, it is evident that other techniques are better suited to provide a full characterization. In this context, recent developments in MS techniques could play an important role in size determination, chemical identification, and (semi)-quantification of low-µm-range MPs including microfibers and NPs in indoor air. By combining the unique advantages of different MS techniques (*e.g.*, spICP-MS for particle detection, size characterization and mass quantification, thermal decomposition followed by GC-MS for polymer identification and (semi)-quantification in bulk sample), researchers may be able to adequately address the challenges raised in the field of low-µm-range MPs and NPs research.

5.1 Single particle ICP-MS for MPs and NPs particle size determination and mass/number quantification

Since its introduction by Degueldre *et al.*,[55] the popularity of single-particle inductively coupled plasma-mass spectrometry (spICP-MS) has grown very rapidly. The fact that different international directives demand the characterization of engineered nanomaterials, definitely contributed to this success. Nowadays, spICP-MS is generally considered a well-established technique for analysis of samples containing low concentrations (mass/number) of (engineered) nanoparticles.[56,57] In contrast to traditional ICP-MS analysis characterized by the continuous introduction of a sample solution into the ICP ion source, spICP-MS relies on the introduction of a diluted suspension of (engineered) nanoparticles. Each nanoparticle reaching the ICP leads to a burst of ions, giving rise to a short transient signal, also called single event. Provided characterization of the transport efficiency, the number of events detected can be related with the number of particles in suspension, while the intensity of every individual signal can be related to the analyte mass provided adequate calibration. As such, spICP-MS provides a wide range of relevant nanoparticle information, such as elemental composition, size (spherical equivalent diameter – nm) and size distribution, particle number density (particles per mL) and mass concentration (mg L^{-1}). Furthermore, the continuous baseline can also be used to calculate the ionic content, and thus, spICP-MS provides information on elements present in both dissolved and nanoparticulate form.[56]

Recently, ICP-MS manufacturers have developed instruments, offering shorter detector dwell times, enhancing the ability to detect short temporally resolved signals, as the signal of each individual nanoparticle can now be described by a few data points instead of a single one.[58] The use of dwell times within the microsecond range has significantly improved the signal-to-background ration and thus, the size detection limits attainable *via* spICP-MS.

Very recently, Bolea-Fernandez *et al.*[57] reported for the first time ever on the use of spICP-MS based on carbon monitoring for the detection and size characterization of microplastics (1 and 2.5 μm polystyrene microspheres). This method relied on the monitoring of the ^{13}C isotope (relative abundance = 1.07%), the use of microsecond dwell times and the introduction of microplastic suspensions at very low liquid flow rates (10 μL min^{-1}). Potential issues related with poor transport efficiencies for relatively large particle sizes were circumvented by using a high-efficiency sample introduction setup originally designed for the introduction of intact cells. After this proof-of-concept study, a very similar approach has been applied to the analysis of microplastics in some consumer products, including the screening of microplastics in personal care products and those released from food packaging, thus demonstrating the potential of this technique for analyzing real-life samples.[59] Although polymer identification by this technique is not possible, and one must rely on other techniques for this purpose, it is evident that spICP-MS is highly promising for the

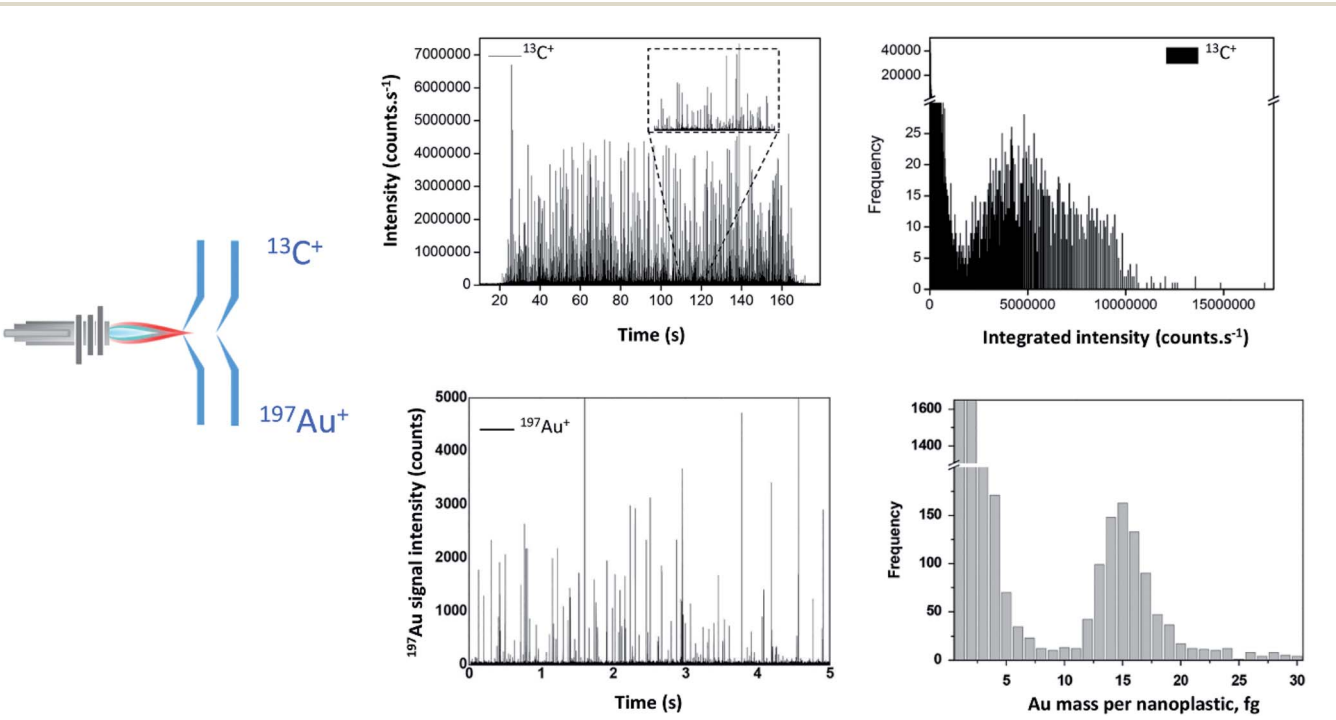

Fig. 4 Use of spICP-MS for MPs and NPs size determination and quantification. After the introduction of a diluted suspension of MPs and NPs into the ICP, a burst of ions is generated for each particle, giving rise to a short transient signal, also called single event. The number of events detected is related with the number of particles in suspension, while the intensity of every individual signal can be related to the analyte mass. Upper panels: spICP-MS based on C-monitoring. Lower panels: spICP-MS based on Au-monitoring (after labeling of the NPs). Adapted with permission from Bolea-Fernandez *et al.*[57] Copyright © 2020 The Royal Society of Chemistry and Javier Jiménez-Lamana *et al.*[60] Copyright © 2020 American Chemical Society.

detection and characterization of low μm-range MPs (Fig. 4). Furthermore, it needs to be noted that dissolved atmospheric CO_2 and other C-species present in the samples of interest, as well as C impurities originating from the Ar gas still give rise to a high background signal, limiting the practical size detection limit to sizes close to 1 μm and thus, hampering the detection of NPs.[57,59]

The spICP-MS technique can be used for the monitoring of NPs (lowest detectable size of 135 nm) upon metal labeling by using positively charged gelatin-coated gold nanoparticles (AuNPs@gel) as tags adsorbed to polystyrene NPs to make them more easily detectable by ICP-MS.[60] This approach can be seen as an "indirect" way (*i.e.* metal-labelling) of obtaining accurate particle number density results for NPs by relying on the monitoring of the ^{197}Au nuclide. Although this method was successfully applied to the detection and quantitative determination of the number concentration of NPs with sizes up to 1 μm in different water samples, it does not allow yet obtaining information on the size or mass concentration of NPs (Fig. 4).

It is clear that while the use of spICP-MS for MPs and NPs characterization is still in a very early stage. The works published so far point towards a great potential of this technique for becoming a standard tool for low μm-range MPs and NPs particle size determination and mass/number quantification in the not so distant future and become crucial for exposure and risk assessment studies.

5.2 Thermal decomposition coupled with MS-based techniques for MPs and NPs chemical identification and (semi)-quantification

Thermal decomposition coupled with mass spectrometry-based techniques have been increasingly applied for the bulk identification of low μm-range MPs and NPs in very complex environmental samples as a complementary method to spectroscopic approaches (μFTIR and μRaman).[38] The main principle of thermal decomposition coupled with MS-based techniques relies on chemical analysis of the polymer breakdown products formed during thermal degradation of polymer mixture and includes different analytical techniques being: (1) pyrolysis gas chromatography mass spectrometry (Pyr-GC-MS), (2) thermogravimetry (TGA), (3) TGA-mass spectrometry (TGA-MS), (4) thermal extraction desorption-gas chromatography-mass spectrometry (TED-GC-MS), (5) TGA-differential scanning calorimetry (TGA-DSC), (6) thermal desorption/pyrolysis direct analysis in real time (DART)-high resolution mass spectrometry.[61–64] Taking into account that only bulk information on the polymers present can be obtained without achieving an insight into the particle size distribution by applying destructive thermal analysis methods[65] followed by MS-based chemical analysis and extensive data processing, we will summarize most promising techniques for low μm-range MPs and NPs chemical identification and/or (semi)-quantification[66] *i.e.* Pyr-GC-MS, TED-GC-MS[67] and thermal desorption/pyrolysis DART-MS.[64]

Pyr-GC-MS. The main principle of Pyr-GC-MS relies on the thermal degradation of polymer materials in their monomers and additives at high temperatures (>500 °C) under an inert atmosphere and their sequential separation by GC.[68] Specific polymer break-down markers and their indicator ions can be further identified and (semi)-quantified by MS with high confidence.[64] Pyr-GC-MS is gaining a lot of attention for both qualitative and quantitative analysis of MPs and NPs present within bulk sample that are not able to be detected by micro-spectroscopic techniques.[62] The main advantages of Pyr-GC-MS are (1) no sample preparation procedures are required, (2) analysis is independent on the individual size and shape of the MPs and NPs, (3) the approach offers very low detection limits (down to ppt to ppm), and (4) a fully automated system can be used.[68–70] The main limitations of using Pyr-GC-MS for chemical identification and (semi)-quantification of low μm-range MPs and NPs, however, are (1) destruction of samples, (2) the method allows 0.5 mg of sample only and larger amounts will potentially lead to the system overload and/or contamination, (3) the data processing is extensive and complex, (4) inorganic additives cannot be detected, (5) individual MPs and NPs cannot be analyzed in terms of the particle size, (6) particle-by-particle analysis is not feasible, and (7) it is limited to a few restricted polymers (*e.g.*, PS, PVC).[63,71] The most recent studies show that in combination with sample deposition on PTFE filters as sample support, pyrolysis gas chromatography time of flight mass spectrometry (Pyr-GC-TOF-MS) allows chemical identification and (semi)-quantification of MPs and NPs present within complex aqueous sample at concentrations of 50 ppb and down to particle sizes >100 nm.[72] This improved performance and use of filters (used in existing air sampling procedures) as sample support suggest that chemical identification and (semi)-quantification of airborne MPs and NPs without further sample preparation steps is possible. Finally, recent studies showed that the use of filters as sample support is also beneficial to first determine the particle size distribution by μFTIR and successively use Pyr-GC-MS for reliable polymer-type determination in bulk sample.[73]

TED-GC-MS. The main advantage of TED-GC-MS over Pyr-GC-MS is the possibility to analyze the most frequently identified microplastic such is PE. The higher sensitivity and selectivity of TED-GC-MS comes from 2 separate steps in the process, *i.e.* (1) the thermal extraction/desorption and (2) GC-MS-based chemical analysis.[67] TED-GC-MS relies on the thermal extraction/pyrolysis of the sample on the TGA balance inside the TGA furnace combined with solid phase extraction of complex volatile hydrocarbons released at high temperatures. In the second step the solid-phase adsorber is transferred to the TD-GC/MS analysis system. In this, the polymer breakdown markers are thermally desorbed in the introduction system and analyzed by the GC/MS system for polymer identification and (semi)-quantification. Interestingly, using TED-GC-MS for analysis of air filtration fractions without additional sample preparation step would be possible as the major part of the environmental matrix will be eliminated at high temperatures. In addition, this enables analysis of significantly larger sample quantities (up to 100 mg) without risk of system overload or contamination, and thus allows analysis of more representative samples.[67,74] The main drawbacks of using TED-GC-MS are similar as these for Pyr-GC-MS, with emphasis on the complex

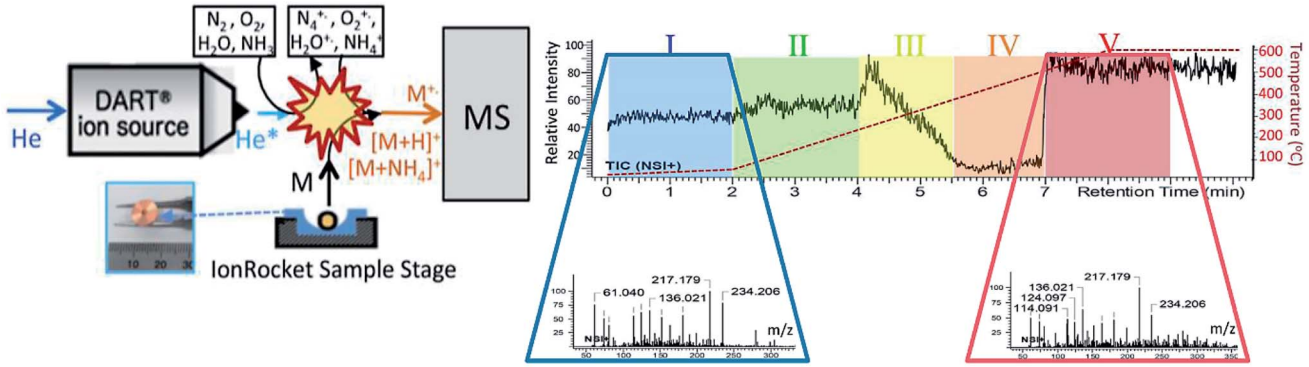

Fig. 5 Ionization mechanism of the IonRocket thermal desorption/pyrolysis unit coupled with DART-MS with an example of mass spectra generated as a sample is heated from ambient temperature to 600 °C, during which thermal desorption of volatile compounds in the polymers and pyrolysis (thermal decomposition) of the polymers occur (adapted with permission of Zhang *et al.*, 2020,[64] Copyright © 2020 Elsevier).

data interpretation, extensive and time-consuming method development and no possibility for particle-by-particle analysis.

Thermal desorption/pyrolysis DART-MS. While other techniques might require extensive sample preparation procedures, expensive equipment, and time-consuming analyses to acquire analytical results, DART-MS potentially leads to a rapid and straight forward identification of polymer additives in different plastic products without any previous sample pretreatment.[75] The combination of thermal desorption/pyrolysis and DART-MS (Fig. 5) has recently been put forward as a novel approach for rapid fingerprinting of environmental microplastics and the screening of additives.[64] As previously reported, thermal desorption and pyrolysis experiments produce chemical fingerprints inclusive those of additives for characterization and classification of MPs by polymer types.[64] The main principle of thermal desorption/pyrolysis DART-MS involves thermal degradation of the polymer additives present in MPs at high temperatures (>600 °C) from ~5 mg samples and ionization of the compounds thus formed by DART operated in the positive mode using He as the reagent gas, involving a ion–molecule reactions with the sample molecules and consequent production of analyte (indicator) ions.[76] Indicator ions for additives released *via* thermal desorption and polymer degradation products generated by pyrolysis are further identified and (semi)-quantified by collecting high-resolution mass spectra (*m*/*z* 50–750).[64] Although, thermal desorption/pyrolysis DART-MS presents a promising tool for MPs chemical identification and (semi)-quantification, the minimal particle size that can be addressed is not yet known. Further research should be devoted to the development of coupling strategies for NPs characterization where size separation techniques (*e.g.*, size exclusion chromatography, capillary electrophoresis) can be guided to the mass spectrometer through the DART ion source.[76]

5.3 MALDI-TOF-MS

A novel method for chemical identification and quantification of MPs and NPs is by using matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI-TOF-MS).[66,77] As is the case for DART-MS, MALDI-TOF-MS is being applied in many fields including (bio)polymers analysis.[78] The main principle of MALDI-TOF-MS includes a soft ionization of sample components, their separation in a time-of-flight analyzer and detection over a wide mass range.[66,77] Recent studies showed that coupling the thermal fragmentation with MALDI-TOF-MS significantly enhances the intensities of fingerprint peaks in low-mass regions making chemical identification and mass quantification of PS and PET MPs/NPs possible.[66] Matrix normalized MALDI-TOF-MS can be applied for environmentally relevant PS and PET MPs/NPs identification, by dissolving the samples, environmental matrix and cationization reagents in tetrahydrofuran.[77] It can be anticipated that after further development, this technique will be suited to the chemical identification of MPs and NPs in indoor air.

5.4 LC-HRMS

A simple method for the direct quantification of polycarbonate (PC) and PET MPs in environmentally relevant samples (sludge, marine sediments, indoor dust, digestive residues in mussel and clam, sea salt and rock salt) relying on alkali-assisted thermal hydrolysis and subsequent determination of the depolymerization products (*e.g.*, bisphenol A and *p*-phthalic acid) using liquid chromatography-tandem mass spectrometry (LC-MS/MS) was reported.[79] However, until very recently it was rarely used. In order to extend this analytical technique to quantitative analysis of NPs, liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS), equipped with an atmospheric pressure photo ionisation source (APPI), operated in negative conditions was applied successfully.[80] Finally, isocratic chromatographic separation of particles bellow 144 nm was achieved using an advanced polymer chromatographic column and toluene isocratic as the mobile phase. As a result, remarkable low method limits of detection and mass quantification of approximately 30 pg L^{-1} and 100 pg L^{-1}, respectively for particles bellow 144 nm were achieved.[79]

6. Perspectives and outlook

Due to their different nature, low μm-range MPs including microfibers and NPs existing in indoor air present new analytical challenges and no single method will provide all the

information required for a comprehensive characterization (size determination, chemical identification, and (semi)-quantification). As making the right decision of the methods used to attempt characterization of the low μm-range MPs and NPs is still challenging, there is limited knowledge on the indoor and outdoor low μm-range MPs and NPs sources, levels, extent, and human health impact after inhalation exposure. In order to close the present knowledge gaps allowing dedicated policy actions to improve air quality and accomplish health benefits, further research is urgently needed with special attention to:

- Careful optimization of sample collection and preparation strategies;

- Development and optimization of MS-based analytical methods to improve their capabilities and reduce the size detection limits;

- Further establishment of standardized analytical methods for chemical identification, and (semi)-quantification of MPs and NPs in indoor air and dust;

- Monitoring studies to obtain information on relevant sources, levels, and extent of airborne low μm-range MPs and NPs as well as chemical additives and the sorbed pollutants that have potential to leach of plastics in order to assess exposure to MPs and NPs in view of risk assessment.

This review shows that although further research in this area is definitely still needed, the existing expertise in air sampling procedures and the new developments in MS-based analytical methods hold great promise for adequate characterization of the sources of indoor as well as outdoor low μm-range MPs and NPs, their levels, characteristics and exposure assessment in view of health impact. Finally, the choice of the method/combination of methods depends on the research question asked and has to be evaluated carefully.

Abbreviations

(sp)ICP-MS	(Single-particle) inductively coupled plasma-mass spectrometry
μRaman	Raman microspectroscopy
AFM	Atomic force microscopy
CE	Capillary electrophoresis
DART-MS	Direct analysis in real time-mass spectrometry
DLS	Dynamic light scattering
FTIR	Fourier-transform infrared spectroscopy
HDC	Hydrodynamic chromatography
MALDI-TOF-MS	Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
MALS	Multi-angle light scattering
MPs	Microplastics
NPs	Nanoplastics
NTA	Nanoparticle tracking analysis
PE	Polyethylene
PET	Polyethylene terephthalate
PU	Polyurethane
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
Pyr-GC-MS	Pyrolysis-gas chromatography mass spectrometry
SEC	Size exclusion chromatography
STM	Scanning tunneling microscopy
TED-GC-MS	Thermal extraction/desorption-gas chromatography-mass spectrometry
TEM	Transmission electron microscopy

Conflicts of interest

There are no conflicts to declare.

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