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Micro(Nano)plastic analysis: a green and sustainable perspective

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ABSTRACT

Within the last years aspects such as green, eco-friendly and sustainable are making their way into analytical chemistry. The field has changed with the introduction of these concepts. Information on the consumption of toxic solvents and energy is now a part of everyday life. This green analytical chemistry could be playing a pioneering role in the analysis of micro(nano)plastics in the environment. We discuss the roles of green analytical and sustainability within micro(nano) plastics determination and its possible applications. We explain its many advantages, like their function to preserve the environment and operator health or their role in the so-called eco-friendly methodologies, but we also highlight points such as an efficiency in the determination that should be viewed critically. Finally, we describe how micro(nano)plastics analysis is implementing the green analytical chemistry and the challenges faced.

1. Introduction and problem overview

We are convinced that most readers of this article have heard of the term Anthropocene as the result of the exponential increase in human population over the last 200 years. This growing is the main cause of some of Earth's most serious environmental threats, such as global change and pollution. Among the different pollution types brought by the Anthropocene, plastic pollution has become a global concern, as our planet is drowning in plastic litter, microplastics and nanoplastics. This problem that has raised a great social concern is still affected by an outstanding dichotomy: while the most alarming predictions indicate that by 2050 the weight of plastics will exceed that of fish in the sea, we are still questioning whether plastic, microplastics and nanoplastics could be toxics to biota and humans. They simply should not be there because they degrade ecosystems and unnecessarily expose biota and humans not only to them but also to the thousands of chemical compounds they contain (Barceló and Picó, 2019; Picó and Barceló, 2019'; Prata et al., 2019b; Rahman et al., 2021). We are not going to include a detailed list, but scientific articles are full of alarming data about the large production of plastics and microplastics, the huge percentage of them that end up in the environment, the low recycling rate and the numerous transportation, transformation and distribution processes that worsen the situation and that should be enough on their own.

Researchers have already been concerned about the microplastics topic for almost 20 years with a growing trend towards research and monitoring of micro and most recently nanoplastic concentrations. To give a clear idea on the situation, Fig 1 shows the number of papers per year of a Web of Science (WOS) search (December 29, 2021) using the keyword "microplastics". In 10 years (2011 to 2021) we have gone from 21 to 2822 articles published yearly. Analysis of these studies shows that microplastics have been determined in all environmental compartments (water, soil, biota, air, and so on) and many analytical methods have been developed involving both, visual quantification and chemical identification (Adomat and Grischek, 2021; Barceló and Picó, 2019; Chen et al., 2020; Pico et al., 2019; Picó and Barceló, 2020; Prata et al., 2020a; Prata et al., 2019a; Prata et al., 2019b; Prata et al., 2021; Schirinzi et al., 2020; Shruti et al., 2021; Silva et al., 2018; Yang et al., 2021). In addition to developed methods, numerous research studies attest to its presence in almost all known ecosystems (Llorca et al., 2021; Pico et al., 2019; Picó et al., 2020; Picó and Barceló, 2019; Pinto da Costa et al., 2019; Rahman et al., 2021; Rocha-Santos and Duarte, 2015; Schirinzi et al., 2019; Yang et al., 2021). Instead, nanoplastics are yet to be successfully and reproducibly isolated from environmental matrices other than water (Li et al., 2022). Scientists are making a major effort to reverse this situation. These nanoplastics are directly emitted to the environment (e.g., through 3D printing). While there is no doubt that the determination of microplastics is a widely studied topic and nanoplastics will be in the future, there is little concern about the safety of the methods used, the amount of waste they produce and the energy consumption. However, these methods may affect the environment and degrade it.

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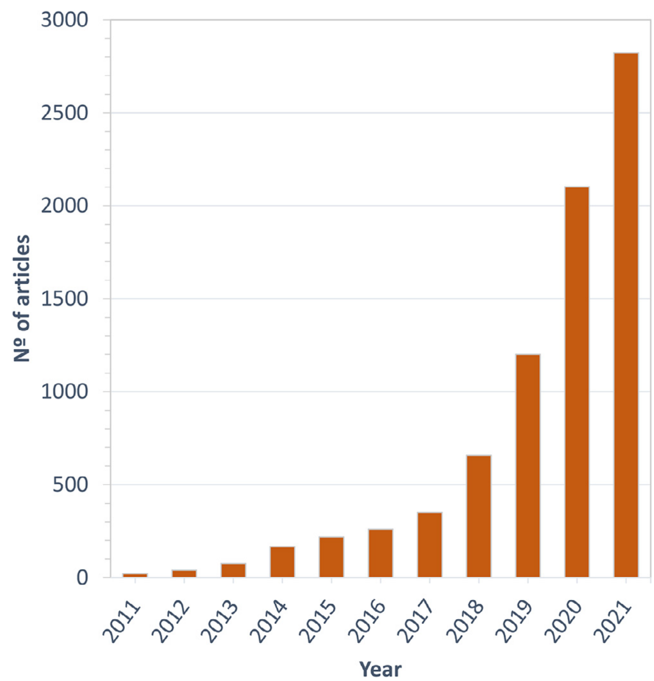


Fig. 1. Articles per year corresponding to a search in the Web of Science (WOS) using the keyword "microplastic".

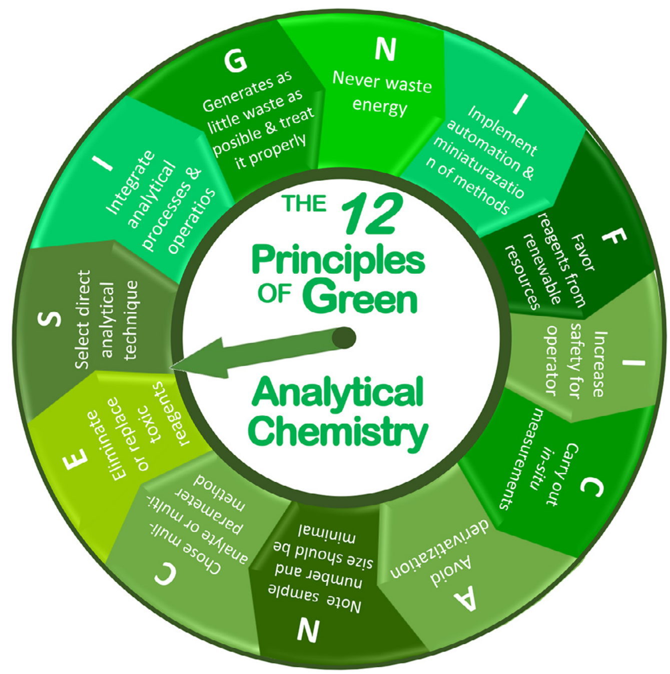


Fig. 2. Twelve principles of GAC

Reducing chemical pollution at its sources by reducing or even eliminating hazardous chemical feedstocks, reagents, solvents and chemicals is now an imperative. Several concepts have been proposed, such as sustainable chemistry, green chemistry, environmentally friendly chemistry, to coin this discipline that benefits environment although it seems that the one that has most caught on has been green chemistry (Tobiszewski et al., 2010). The IUPAC defined green chemistry, such as "The invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances" (Tundo et al., 2000). It is based on twelve principles, which involve designing and conducting chemical processes to reduce the use and formation of harmful substances (Kaya et al., 2022).

The principles of green chemistry have been percolating through analytical chemistry for at least 20 years but have not been fully implemented in the laboratory. Scale is one reason, as analytical laboratories generate less waste compared to industry. But analytical lab wastes add up and need to be considered an environmental threat. The aim of this opinion is to highlight the toxic reagents used and the waste generated in the analytical methods to determine microplastics and to show different approaches for grouping these methods according to their safety. A better understanding of the greenness and sustainability of the analytical methods to determine micro(nano)plastics could assist in the optimization of performance of new methods to fully meet principles of green analytical chemistry (GAC).

2. The characteristics of the analytical methods to determine microplastics

In this section, the different types of methods and the reagents used in each of the crucial steps, sampling, sample handling and determination, are summarized.

2.1. Sample processing

Sieving, isolation and/or removal of interfering materials and filtration are most important steps involved in sample processing. Isolation and removal of interferences are the most complex ones and could include (i) chemical oxidation, (ii) enzymatic digestion, (iii) density separation and (iv) extraction in a lipophilic media (Barceló and Picó, 2019; Lee and Chae, 2021; Shruti et al., 2021). These 4 techniques could be used alone or combined depending on the requirements.

In chemical oxidation, several acids (HCl, HNO_3, H_2SO_4), alkalis (KOH, NaOH), and oxidants (H_2O_2), their mixtures or their combination with catalyzers (Fe^{2+}) are used to mineralize organic matter trying to preserve intact micro(nano)plastics (Prata et al., 2019b). Enzymatic digestion requires incubation with enzymes (celluloses, proteases, lipases, amylases, among other) alone or in combination depending on the sample properties to eliminate organic tissues keeping also intact micro(nano)plastics. Reagents, such as ethylenediaminetetraacetic acid (EDTA) and surfactants (e.g., sodium dodecyl sulfate) are required to stabilize the enzymatic reaction. Density-based separation requires the immersion of the sample in a solution denser than water, such as NaCl (1.2 g/mL), $CaCl_2$ (1.3 g/mL), sodium polytungstate (1.4–1.5 g/mL), $ZnCl_2$ (1.64 and 1.8 g/mL), $KHCO_3$ (1.4 g/mL), $ZnBr_2$ (1.7 g/mL), NaI (1.8 g/mL), sodium polytungstate (~3.2 g/mL), and others, and the separation of the microplastics by gravity or elutriation. Selection of this dense solution is based on criteria such as cost, sample density, microplastics size and microplastic type, among others. Micro(nano)plastics are usually less dense (0.9 – 1.5 g/mL) than these solutions, then, they tend to float and separate of the denser materials that sediments. This separation is very used for sediments (specific density is ca. 2.6 g/mL). Microplastics whose density is higher than that of the saline solution applied will remain precipitated and will not be detected (Cutroneo et al., 2021)

Extraction in a lipophilic media is based on solubility of micro(nano)plastics in oil (canola, castor, olive and others) or non-polar organic solvents (hexane, dichloromethane, toluene) (He et al., 2021). Solvent extraction has been successfully used to characterize simultaneously microplastics and nanoplastics consisted of soluble polymers as well as additives and plasticizers. Conventional solvent extraction requires mechanical shaken to provide the needed energy to favor the extraction. Pressurized liquid extraction (PLE) in which extraction is helped by high pressures and temperatures (Llorca et al., 2021; Okoffo et al., 2020; Schirinzi et al., 2019) and microwave assisted extraction (MAE) in which extraction is supported by microwaves were

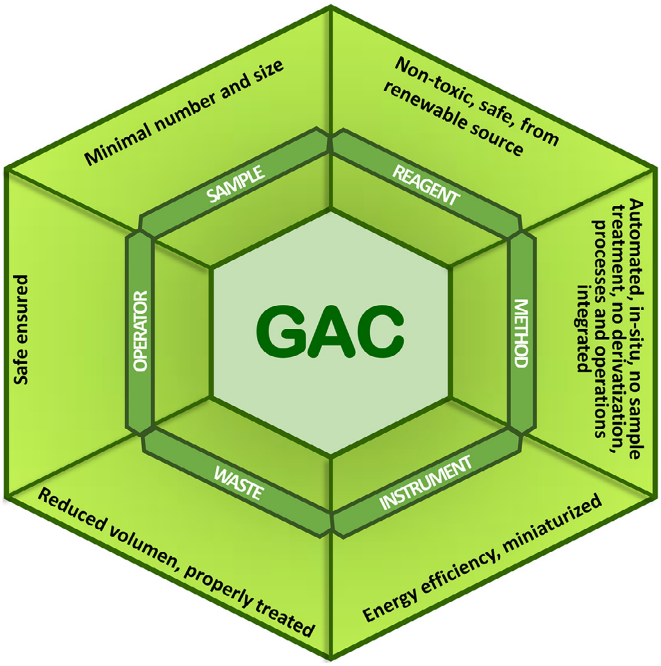


Fig. 3. GAC principles implemented in each step of the analytical methodology

recently reported (La Nasa et al., 2021). Both, PLE and MAE showed that the most promising solvent to enlarge the types of polymers determinable is dichloromethane.

2.2. Micro(nano)plastics determination

The detection of micro(nano)plastics is carried out by visualization or microscopy. Sizes > 0.1 mm can be visualized with a naked-eye, sizes < 0.1 mm and >10 μm with a stereo (magnification up to 160 x) or an optical (up to 1500x) microscope, and sizes < 10 μm with an electron microscope (up to 10,000,000x) (Silva et al., 2018). After detection, chemical confirmation is required to avoid misidentification of other particles (fly ash, silica, natural fibers, and so on) as microplastics. Specific staining (i.e., staining of natural and non-plastics particles) (Prata et al., 2020a) or the coupling of scanning electron microscopy (SEM) to energy-dispersive X-ray spectroscopy (EDS) could achieve altogether detection and identification of the polymer type.

Optical microscopy coupled to Fourier-transform infrared (FT-IR) or Raman spectroscopy (μFT-IR or μRaman) accomplish the visualization (up to 20 μm) and the chemical characterization of the microplastics of each spot) according to the energy or light absorption of the functional group characteristic of these MPs. These have become the most reported techniques for the chemical identification. Imaging version of these techniques as focal plane array (FPA)-FT-IR detectors are based on the simultaneous fast collection of thousands of IR spectra over considerable areas of a sample (each spectra will be a pixel in the image) (La Nasa et al., 2020; Picó and Barceló, 2019; Zantis et al., 2021). This method can image the entire membrane filters as well as detect small microplastic in it given more robust results with to minimal analytical bias without the need of visual preselection of the particles to be characterized (Tagg et al., 2015). However, these techniques are less used probably because their cost and complexity. All these techniques detect microplastics but not nanoplastics.

Thermal analysis involving pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS), thermal desorption (TD)-GC-MS or in a lesser extend thermogravimetry coupled to differential scanning calorimetry (TGA-DSC) are also good alternatives to determine micro(nano)plastics. Pyr-GC-MS is becoming a technique of choice to identify and quantify the total amount of any type plastics (micro and nanoplastics) in environmental samples due to the high identification power of mass spectrometry (Picó and Barceló, 2020). This is due to its capacity of simultaneously identify polymer types of MP particles and associated organic plastics additives to obtain a precise MP weight. Other studies that also characterize simultaneously micro and nanoplastics proposed advanced gel permeation chromatography column coupled to high-resolution mass spectrometry via atmospheric pressure photoionization source (LC(APC)-APPI-HRMS) to identify polymers and additives (Llorca et al., 2021; Schirinzi et al., 2019).

3.-What is GAC?

GAC means to develop safer methods for the human being and the environment, substituting toxic reagents and generating less solvent waste as well as less energy consumption as part of sustainability initiatives (Farré et al., 2010; Tobiszewski et al., 2009). Gałuszka et al. (2013), established twelve principles to ensure that an analytical method is green and the mnemonic SIGNIFICANCE to remember them, which are summarized in **Fig. 2**. The way to introduce GAC principles in the analytical methodology is shown in **Fig. 3**. All this without losing the efficiency, reproducibility and repeatability, as well as the ability to detect and identify of the analytical methods used. In some cases, it is extremely difficult to reconcile these two aspects.

4.-The different approaches to measure the greenness of an analytical method

One of the problems in GAC is the development of metrics to determine the relative ecology of methods. Recently, several metrics have emerged to create standard measures to gauge the greenness of a method Sajid and Płotka-Wasylka (2022) described and discussed all currently used GAC metrics, such as analytical method volume intensity (AMVI), chemical hazard evaluation for management strategies (CHEMS-1), green analytical procedure index (GAPI), high performance liquid chromatography - environmental assessment tools (HPLC-EAT), life cycle assessment (LCA), national environmental methods index (NEMI), analytical greenness calculator metric (AGREE), preference ranking organization method for enrichment evaluations (PROMETHEE), analytical eco-scale, green certificate-modified eco-scale, HEXAGON, technique for order of preference by similarity to ideal solution (TOPSIS) and Red-Green-Blue (RGB). To go into so much detail is beyond the scope of this paper, however, if the reader wants to deepen into the fundamentals and application of metrics, this mentioned study is highly recommended. Here, and to maintain the coherence of the topics included in this opinion, **Table 1** summarized the main advantages and disadvantages of the methods to be applied in the determination of micro(nano)plastics.

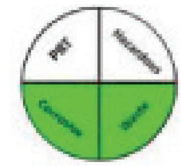
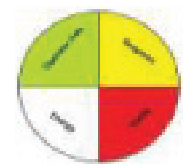
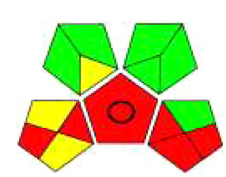
Within the GAC many metrics can be applied to the analytical methods for determining micro(nano)plastics and that compare the greenness of the methods.

5.-Pros and cons of the micro(nano)plastics analytical methods: the green and sustainable point of view

So, what are the GAC aspects that analytical methods to determine micro(nano)plastics already have into account in our opinion?

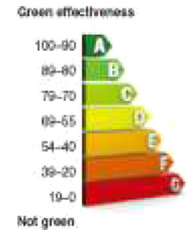
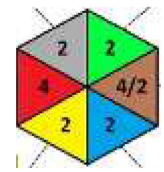
Considering GAC, reduced samples offer a clear advantage of micro(nano)plastics analysis because it reduces the volume of the sample that is transported to the laboratory. Many studies still take bulk samples (Bai et al., 2022; Picó and Barceló, 2019), some work has already been published on the minimum volume of water needed to reliably determine microplastics (Prata et al., 2020b). Such estimations are usually the first step in reducing the sample volume, which always facilitate the transport of the samples to the laboratory and reduce energy cost and gas generation. Other proposed solutions to make sampling more sustainable not applied yet in the micro(nano)plastics analysis are the use

Table 1
Advantages and disadvantages of the existing metrics for greenness assessment of micro(nano)plastics analytical procedures. Reported information has been summarized from Nowak et al., 2020; Pena-Pereira et al., 2020; Sajid and Płotka-Wasylka, 2022; Tobiszewski et al., 2015

Metric	Disadvantages	Advantages	Pictogram
NEMI	• Only consider solvent and reagents • Search in an official list with not all existing reagents • NO waste, instrument, energy or sampling • Qualitative	• Simple method • Clear pictogram • Covers all type of reagent including salts • Good idea of the environmental impact	
pictograms	• Not included sample • Qualitative • Not clearly define the information sources	• Considers reagent, energy, waste and operator's safety • Simple method	
Advanced AEco-Scale	• Only qualitative aspects regarding instruments and operator's safety • Not included sampling	• Includes reagent, instrument, wastes and operator's safety • Gives a value that could be used for comparison	No
AAGREE	• The values are in some cases assigned without a clear rational behind.	• Follow the 12 principles of GAC • Covers reagents, energy, waste, operator's safety including sampling. • Clear information • Free available software	
CHEM-1	• Number without information on the threat • Local guide on the solvent's toxicity	• Consider reagents, operators' toxicity and environmental toxicity	No
HPLC-EAT	• Restricted HPLC that is very little used in micro(nano)plastics analysis	• Simple and with free available software • Operator's risk, toxicity, hazards	No
AMVI	• Restricted HPLC that is very little used in micro(nano)plastics analysis • Not include reagent toxicity	• Only method that considers the diversity of micro(nano)plastics that exits	No
PROMETHEE	• Toxicity of the solvents is not considered • Complex procedure with a complex software • Complex software	• Quantitative procedures • Tailored method that allows the selection of criteria and their weights	No
LCA	• Complex methodology not fully developed • Needs new toxicity indicators to assess of the aspects coverable	• Considers all the steps of the process including synthesis and disposal of reagents	No
GAPI	• Complex method • Complex pictogram	• Evaluate the whole analytical procedure	

(*continued on next page*)

Table 1 (*continued*)

Metric	Disadvantages	Advantages	Pictogram
Green certificated (modified eco-Scale)	• No information on the nature of the threat • Not included sampling • No full information on the origin of the value assigned.	• Include hazard, reagents, waste and operator's safety • First sight idea on hazards	
HEXAGON	• Difficulty to assign the penalty points of the methods • Lack of clarity in the scaling of the hexagon	• Also considers the method's analytical features • Cover all GAC aspects • Multicriteria approach • Clear pictogram	
TOPSIS	• Complex method • How some method's parameters are ranking is unclear • Semi quantitative method	• Also considers the method's analytical features • Considers toxicity of solvent and wastes • Considers productivity and waste • Multicriteria approach	No
RGB	• Requires simplifications and assumptions • Complex model • High number of potential variables	• Also consider the method's analytical features • Flexibility to select different criteria • Quantitative assessment possible • Multicriteria approach	No but color scale

of chemometrics to reduce the amount of sample (Kalinowska et al., 2021)Sample treatments to determine micro(nano)plastics typically involve four basic types of reagents: (I) oxidants, (ii) organic solvents, (iii) salt solutions and (iv) enzymes. Throughout this discussion it must be kept "in mind" that no substance is totally safe, and all chemicals produce some toxic effects if living systems are exposed to a sufficiently large amount of the substance. **Table 2** details the toxic effects described for these methods in aquatic biota. Oxidants are highly corrosive, hazardous, wasteful and many of them increase or reduce the pH of the medium. Organic solvents are a wide class of organic chemicals of changeable lipophilicity and volatility. The toxicity of salts used to prepare solutions of different densities varies depending on the specific nature of the salt. Some salt solutions such as $ZnCl_2$, $ZnBr_2$ and NaI are toxic and/or corrosive. However, others such as NaCl are considered safe reagents. The toxicity of these methods to the environment also depends on whether the laboratory has implemented procedures to treat the waste generated during analytical operations and to achieve its final disposal. Those laboratories located in developed countries have systems for the proper disposal of solvents and toxic waste and therefore pollute less. However, laboratories that dispose of these solvents into the sewage system may become a source of pollution. Proper management and disposal of solvents, consumables and hazardous waste can have a significant impact on operating costs and return on investment. Reducing their use has always economic advantages. Trying to reduce the consumption of hazardous reagents should always be a priority, not only for micro(nano)plastics analysis, but for all analytical methods. As an interesting example, Malafaia et al. (2022) studied several solvents to detaching micro(nano)plastics from cellulose filters both, washing and digesting. Considering the simplest GAC metrics of NEMI, some of the solvents tested in the study, such as, chloroform, dichloromethane and xylene that are classified as hazardous should not even have been tested. This, which is very easy to say, in practice requires the existence of a few viable alternatives to its use. According to the principles of green chemistry, the ideal solution for the treatment of samples containing micro(nano)plastics would be to eliminate extraction and directly analyze the sample. However, the matrices are complex and the characterization difficult, and this step is currently necessary. Because of this solvent reduction and replacement have become one of the best alternatives. Reducing the volume of solvent, or the concentration of any other toxic reagent (to less than 50 g per extraction) is one way to reduce the environmental impact. In this sense PLE and MAE assisted extractions reduced substantially the volume of solvents (La Nasa et al., 2021; Okoffo et al., 2020). Techniques that reduce or eliminate the use of organic solvents, such as pressurized fluid extraction (PFE) (Fuller and Gautam, 2016), or electrostatic and magnetic separation (Gong and Xie, 2020) have been proposed as alternative to the use of solvent. However, gases as well as electric and magnetic fields replacing the organic solvents are not harmless to the operator either. Other alternative not fully developed yet, is the replacement of organic solvent by ionic liquids, which have already been proposed for the removal of nanoplastics (Elfgen et al., 2020). Other solutions that are applied in other fields of analytical chemistry and have not yet been applied to microplastics are miniaturization and automation to use less amount of toxic substances and generate less waste (Tobiszewski et al., 2015). These assumptions are far from being applied.

Table 2
Effects of different reagents on the environment

Reagents	Effects on the environment	Ref.
Acids	pH < 5.6 affects phytoplankton and macrophytes pH <5, fish has higher susceptibility to infections and reproductive problems pH< 4 fish mortality Decrease bioavailability of Ca_2CO_3 basic to form the shell of the mollusk Biodiversity reduction by colonization of acid-tolerant species (algae and mosses) Increase the solubility of metals in water (aluminum, lead, copper and cadmium) that become more bioavailable	(LacoulP. et al., 2011)
Bases	pH>9 + NH_4^+ pH>10 damage of gills and skin, death	
Oxidants (little stable)	H_2O_2, •OH, •O_2^- produce DNA damage	(Gomes et al., 2016)
Salts	$ZnCl_2$, $ZnBr_2$, NaI are embryotoxic $ZnCl_2$ is corrosive Increase of Zn in water and accumulation in sediments: • Affect zinc-dependent enzymes that regulate RNA and DNA. • Induction of metallothionein • Gills could be physically damaged	(He et al., 2021) (Hogstrand, 2011)
Organic solvents	Increased mortality Reduced reproductive capacity Effects on the progeny Genetic damages Alter immune function Neurological effects	(Dave et al., 1979)
Others	EDTA: irritant, corrosive and could decrease pH <5 Surfactants: Severe gill damage Destroy the fish outer mucus (protect of bacteria/ parasites) Destroy fish eggs (concentration > 5 mg L^{-1}) Massive dye (concentrations =15 mg L^{-1}) Decrease reproductive capacity of aquatic organisms. Decrease the water surface tension, favor uptake of organic pollutants	(Ucan-Marin and Dupuis, 2015)

Although it is challenging to evaluate the greenness of microplastic determination techniques, to compare different techniques may be increasingly difficult because they are so diverse. The instruments used are mainly microscopes (binocular, conventional, electron, confocal) alone or coupled to other techniques such as FTIR, Raman, EDX, chromatographic and thermal techniques (Py-GC-MS, LC-MS) (Bai et al., 2022; Picó and Barceló, 2019). These instruments are nowadays designed smaller, lighter, more energy efficient, use less material in construction and fewer hazardous chemicals to perform the measurements and generate less waste without loss of efficiency that is also important (Koel and Kaljurand, 2021). This makes instrumentation required to analyze microplastics greener than before. Microscopy and imaging techniques are considered green techniques even through few reagents are used to measure the samples (Bellasi et al., 2021). These techniques are the most highly used within the field and if combined with chemometrics to reduce the number of samples needed to optimize the methods and with software to automatically process the images are a good choice from the GAC point of view (Bai et al., 2022). Light microscopy, in any of its types, is now greener than before since mercury or metal halide arc-based lamps are now being substituted by through alternative, modern light sources such as solid-state light-emitting diodes (LED) that are more energy efficient and mercury free (Zeiss, 2022). Electron microscopy has become greener specially in sample preparation when the matrix is water and have passed from traditional steps involving dehydration, chemical or cryo-fixation and embedding in an epoxy resin with several toxic reagents to deposit few drops of water in a special grid (Assaiya et al., 2021).

FTIR and Raman spectroscopy are always coined as “green” techniques. However, reduction of the instrument size as well as toxicity and solvents used have improved even more these situation (Kelani et al., 2020).

Of all these techniques, Py-GC-MS and LC-MS are the most important and useful techniques for the specific analysis of the chemical characteristics of the polymer or of the monomers and other additives forming the micro(nano)plastics. Nevertheless, from the GAC point of view, chromatography methods have several drawbacks such as long operation and analysis time, large amounts of solvents or gases used as mobile phases, high amount of waste generated, operator risk, high energy consumption (more than 0.1 kW h per sample), several method optimization’s steps and high cost (Bai et al., 2022; Kalinowska et al., 2021). Although these techniques are not very green, a lot of work has been done to reduce solvent and gas consumption, operator exposure and waste generation. In fact, some of the green metrics have been developed specifically for chromatography (Kalinowska et al., 2021; Koel and Kaljurand, 2021). The change of LC to ultra-high performance liquid chromatography (UHPLC) has saved both, energy and solvent volume, using small columns and high pressures to decrease analysis times and increase separation power (Koel and Kaljurand, 2021; Thayer, 2015). In the same way, GC has incorporated modules that reduce the volume of helium needed for injections and as a carrier gas. In this sense, it must be said that the efficiency and identification capacity make it difficult to replace these techniques with less polluting ones (Thayer, 2015)

Here again, there is an important difference between developed and developing countries. For example, the European Union has regulated the disassembly and recycling of equipment through the Waste Electrical & Electronic Equipment Directive (Directive2012/19/EU, 2012) as well as restricted the use of heavy metals and other dangerous substances in electronic materials through the Restriction of Hazardous Substances Directive (Directive2011/65/EU, 2011). Companies must complain with it designing the instruments for environmentally friendly disposal at the end of their useful life. Instead, in other countries there are no regulations for the disposal of these instruments.

5.-Conclusions and recommendations

Clearly with the pros and cons described above, micro(nano)plastics analysis benefits from several general measures that are adopted in all laboratories in developed countries, and especially in the European Union, as they are subject to legislation. However, there is no clear discussion on which methods are the most appropriated. There are only two studies focused directly on this type of analysis Bellasi et al. (2021). qualitatively examined 49 studies carried out from 2004 to 2020 to evaluate the more promising protocols by considering precision, reproducibility, economic viability and greenness (in term of used reagents). The authors proposed lipophilic separation with oil and density separation based on sucrose density gradient achieve densities > 1.2 g/L (corresponding to NaCl). However, in this interesting analysis, the authors do not consider the adverse ecological effects that oil can have in the environment as well as the toxic substances that the non-edible ones can have.

Quantitative green analytical metrics have been little applied within the microplastics field. Only our previous study (Picó and Barceló, 2021), presented a critical overview of the characteristic analytical methodologies applied to determination of micro(nano)plastics assessing their greenness using the NEMI, Analytical Eco-Scale, and AGREE metrics. The results of the assessment pointed out that most of the methods reported to analyze micro(nano)plastics cannot be considered green, and they need certain improvements, such as replacing toxic reagents, decreasing the use of reagents and energy, and intensifying operator safety. Furthermore, considering the procedures most reported (selective sample and visual identification, oxidation or density separation followed by FTIR, and solvent extraction followed by Py-GC-MS, the most environmentally friendly method would be selective sampling and in-situ visual identification as it does not require any further steps. This is not reliable because it limits the size of MPs determinable. The next method would be to obtain reduced samples and separate them by density using harmless salts such as NaCl and determination by μFT-IR. However, these methods do not reach the efficiency of solvent extraction followed by Py-GC-MS that is becoming an almost irreplaceable technique because its ability to detect nanoplastics and its quantitative characters.

We would like to emphasize here the importance of implementing GAC for determination micro(nano)plastics to ensure that the intensive study of these contaminants carried out nowadays does not became a source of other pollutants that can be even worse. These aspects have hardly been considered in the methods developed so far and they should. It is important to know that in all steps of the method (i) sampling, (ii) sample preparation and (iii) identification and quantification measures can be taken to make the method more environmentally friendly and sustainable, safer for the operator. It is difficult to recommend a single method for determining microplastics, as the ideal method will depend on the study proposal, the size of microplastics to be determined and the focus on quantitative aspects. It is likely that the identification of all its characteristics will require the application of several methods. In this sense the GAC aspects have been little considered in the microplastics analysis but their but from now on its implementation will be increasingly mandatory. In this perspective, many methods will have to be revisited to make modifications to take these aspects into account. At the end, GAC must be considered as a more global aspect, in which laboratory safety, good practices, and the implementation of systems for the proper disposal of waste and equipment can play a more important role than the reagents used in a particular analysis. This, however, does not exclude the fact that even if they do not have equal weight, both factors deserve consideration. At present, the environment is so degraded that any grain of sand to improve this situation can contribute to ensure a better future for the planet. In the greenness of analytical methods for micro(nano)plastics several issues that can contribute to increase method's safety for the environment remain to be addressed such as in situ sampling, use of direct methods, miniaturization and automation of methods, replacement of hazardous reagents by less hazardous ones, and application of chemometrics to reduce the number of samples analyzed. It is to be hoped that future studies dedicated to the analysis of these compounds will address this problem and implement these solutions for a more sustainable future.

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