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Thermogravimetric analysis of microplastics: A mini review

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ABSTRACT

This mini review identifies several thermogravimetric analysis (TGA)-based methods for the identification and quantification of different microplastics in both proof-of-concept studies and environmental samples, and highlights method-specific limitations associated with their application. Well-separated and non-overlapping melting peaks are a conditional requirement for the identification and quantification of microplastics using thermogravimetric analysis-differential scanning calorimetry (TGA-DSC). Other TGA-based methods, such as coupled Fourier transform infrared spectroscopy (TGA-FTIR) or mass spectrometry (TGA-MS), as well as thermal extraction desorption-gas chromatography-mass spectrometry (TED-GC-MS), are dependent on the presence of at least one unique thermal degradation product for use as a marker in the identification and quantification process. Varying degrees of time expenditure and complexity of analysis are present within the reviewed methods, with one consistent factor underlying the evaluation: an underutilization of information extracted from the TGA signal itself. As such, in this mini-review, we advocate the development of methods in which stand-alone TGA can be applied towards the chemical identification of microplastics. Although the main hindrance to this is the presence of overlapping thermal transitions, stand-alone TGA has long been used as a routine and robust method for the analysis of polymers, and methods for optimizing the resolution of complex mixtures are available. Current results in literature emphasize the complementarity of analysis methods, and TGA has potential to play a role as a rapid and facile method that can guide the chemical identification of polymers and address needs of current methods.

Introduction

Originating from the debris of plastic products and their fragmentation into smaller pieces by various environmental and weathering factors, plastic pollution has made its way to the most isolated regions on earth (Allen et al., 2019; Ross et al., 2021), and sanctuaries (Bauer et al., 2008; Andrades et al., 2018; Guerrini et al., 2019), as well as rivers, oceans and soils (Peñalver et al., 2020; Woodward et al., 2021; Zabala, 2018). The ubiquitous fragments, which are known as microplastics (MPs) and nanoplastics, can adsorb and transport toxins, eventually contaminating our food and water (Alfaro-Núñez et al., 2021; Chapron et al., 2018; Lee et al., 2019; Lehmann et al., 2020), although the significance of the MP transportation role is debatable (Arienza et al., 2021). Research and standardized methods for the identification and quantification of micro/nanoplastic pollution in the environment are severely lacking, and the effects of MPs and nanoplastics on wildlife are essentially unknown (Müller et al., 2020). In recent years, the detection of MPs in sea, freshwater, land environment and organisms (He et al.,

2018; Liu et al., 2018), coupled with the increasing growth in demand and consumption of plastics (Ma et al., 2020; Silva et al., 2018) has catapulted MP pollution into a global issue (Browne et al., 2011; De Souza Machado et al., 2018; Eriksen et al., 2014; Li et al., 2018; Ng and Obbard, 2006; Wang et al., 2021). The propensity for uptake by biota poses emerging concerns for food safety and human health (Lee and Chae, 2021; Smith et al., 2018). MP particles are loosely defined as plastic pieces with fragments that are less than 5 mm (Koelmans et al., 2019; Thompson, 2015), while nanoplastics are typically defined as plastic pieces that are below 1 μm , but lack a formal definition for the lower size limit (Koelmans et al., 2015; Koelmans et al., 2019).

A range of analytical tools have been used for the chemical identification of MPs, each with their own advantages and drawbacks pertaining to such factors as the limit of detection, approximate costs, expenditure of time, and fieldwork capability (Primpke et al., 2020). Although spectroscopic methods are among the most commonly used methods (Hanvey et al., 2017; Xu et al., 2019), recently thermogravimetric analysis (TGA) methods, specifically those that involve coupling

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with other analytical instruments, herein referred to as TGA-based methods, have taken center-stage to the determination of MPs in environmental samples (Becker et al., 2020; Goedecke et al., 2020; La Nasa et al., 2020). TGA belongs to the methodology of thermal analysis, a class which also includes other variants such as differential scanning calorimetry (DSC) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), all of which individually have regular applications in polymer analysis. Fundamentally, TGA and TGA-based methods differ from the other variants as their capabilities include the measurement of the weight loss of a sample as it is heated at a controlled rate. In general, there are well-known advantages associated with TGA such as ease, speed and the ability to accommodate varying sample amounts. TGA has long been used to investigate the thermal properties of polymers, and coupling of TGA with analytical instruments, such as Fourier-transform infrared (FTIR) spectroscopy or GC-MS can be powerful for characterizing polymers based on their gaseous decomposition products (Liu et al., 2021). The objective of this mini-review is two-fold: to describe and examine TGA-based methods with respect to the capabilities and limitations associated with MP identification and quantification, and to provide a perspective regarding the potential of maximizing the information that can be derived from TGA in order to contribute to the body of work on MP identification and quantification.

TGA-based methods for the analysis of microplastics

In comparison to microscopic methods, destructive thermal analysis methods generally lack the ability to determine size distribution (Elert et al., 2017; Huppertsberg and Knepper, 2018). Spectroscopic methods (such as FTIR and Raman) on the other hand are capable of providing correlated information regarding the number and size in situations where a few particles bear a small contribution to the overall mass content (Eisentraut et al., 2018). Qualitative analysis of MPs by using micro-FTIR and micro-Raman spectroscopy were achieved with particle sizes of 20 μm (Li et al., 2019; Silva et al., 2018; Wang and Wang, 2018), and 1 μm , respectively (Araujo et al., 2018; Chen et al., 2020; Lenz et al., 2015; Silva et al., 2018). Drawbacks to spectroscopic methods, which include the expense of the equipment, a requirement for specialized

operators (Chen et al., 2020), and a typically long expenditure of time for analysis, in turn necessitates the development and use of automated methods (Lee and Chae, 2021; Primpke et al., 2020). Automated methods may potentially allow for identification of weathered polymers when specific absorptions such as oxidation peaks are implemented in the spectral libraries (Scopetani et al., 2020), but other factors, such as the presence of contaminated samples, could affect the ability to conduct automated identification by spectral library searches (Lenz et al., 2015). Additionally, other advances have been made to notably shorten the analysis time using spectroscopic methods via the implementation of FTIR mapping with focal plane array detectors (Tagg et al., 2015; Scopetani et al., 2019). Table 1. summarizes TGA-based instrumentation and evaluation methods for the identification and quantification of MPs. Long time expenditure is considered as greater than or equal to 2 hours. Short time expenditure is considered as less than 2 hours.

For the assessment of environmental plastic samples, typically there is a need for extensive sample pre-treatment to separate plastics from the environmental matrix. This is an important contributing factor to the long expenditure time associated with the typical spectroscopic analysis of MP-containing samples (Xu et al., 2019; Eisentraut et al., 2018; Hurley et al., 2018), although some studies have indicated the utilization of focal plane array detector-based FTIR spectroscopy for assessing MPs in their environmental matrix (Cincinelli et al., 2017; Scopetani et al., 2019). Meanwhile, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) is considered a promising technique for the identification and quantification of MPs (Fischer and Scholz-Böttcher, 2019) due to its ability to analyze samples without a need for pre-treatment (Picó and Barceló, 2020). Other demonstrated capabilities include the simultaneous identification of polymers polyethylene (PE), polypropylene (PP), polystyrene (PS), polyamide (PA), chlorinated PE, and chlorosulfonated PE along with associated organic plastic additives (Fries et al., 2013; Picó and Barceló, 2020; Silva et al., 2018). However, a notable disadvantage associated with Py-GC-MS as an analytical method involves the requirement for small sample amounts (5–200 μg) (Picó and Barceló, 2020); an inability to process larger sample aliquots can call into question the representativeness of the analysis (Silva et al., 2018).

TGA, on the other hand, can accommodate sample masses that are

Table 1
TGA-based methods for the identification and quantification of microplastics.

Method	Analysis Type	Highlights	Complications	Polymer type
TED-GC-MS	Quantification in spiked soil, suspended solids and mussel samples (Dümichen et al., 2015); Identification in river samples and ferment residue samples (Dümichen et al., 2017); Quantification in street runoff and sediment (Eisentraut et al., 2018); Quantification in water of urban sewage systems (Altmann et al., 2019); Quantification in spiked suspended matter (Becker et al., 2020; Goedecke et al., 2020).	Capable of a one-step analysis and most researched TGA-based method for MP identification/quantification to date.	Long expenditure time; Complex data analysis; Operational challenges. Fully automated system has been developed, but has not achieved mainstream adoption.	PE, PP, PS, PET, PA
TGA-FTIR	Quantification in mussels, sea water, and soil (Yu et al., 2019); Quantification in spiked suspended matter (Becker et al., 2020; Goedecke et al., 2020).	Widely available instrument, capable of analysis in a short time period.	Operational challenges. Plastics may be limited to those with unique absorption bands. Pre-concentration may be required.	PE, PP, PS, PET, PVC
TGA-DSC	Quantification in wastewater effluent extracts (Majewsky et al., 2016).	Widely available and robust instrument, capable of analysis in a short time period.	Plastics may be limited to those that are well-separated and do not overlap.	PE, PP
TGA-MS	Quantification in spiked soil; Quantification in spiked suspended matter (Becker et al., 2020; Goedecke et al., 2020).	Capable of a one-step analysis. An alternative to TED-GC-MS	Operational challenges. Possibility of interference from high organic matter content.	PE, PP, PS, PET, PVC
TGA-FTIR-GC/MS	Quantification in mussel tissue extracts (Liu et al., 2021).	Used to quantify the broadest scope of polymers in real (non-spiked) samples).	Operational challenges; Complex data analysis; Long expenditure time; Instrument not widely available.	PE, PP, PS, PVC

around 200 times greater than those used with Py-GC-MS (Dümichen et al., 2015). However, unlike vibrational spectroscopy, TGA cannot provide information about particle size as most of the MPs melt prior to their pyrolysis (Dümichen et al., 2015; Yu et al., 2019). Dümichen et al., developed the TGA-based thermal extraction-desorption gas chromatography mass spectrometry (TED-GC-MS) method for quantification of plastics in environmental samples (Dümichen et al., 2015). This method advantageously incorporates the ability to accommodate large sample masses and to avoid the extensive pre-treatment of environmental samples. Using this method, thermal extraction is first performed via TGA on solid phase absorbers, followed by desorption coupled with gas chromatography-mass spectrometry. Identification of PE was achieved in spiked soil, suspended solids and mussels (Dümichen et al., 2015). Subsequent to this proof-of-concept work, the TED-GC-MS approach was demonstrated as capable of the identification of MPs in aquatic samples from various rivers and ferment residue samples from a biogas plant. The method was expanded to theoretically handle the detection and quantification of PP, PS, PA, polyethylene terephthalate (PET) as well as PE, by determining characteristic decomposition products. In addition to profiling the thermal degradation patterns of the environmental matrices, TGA was performed in duplicate, serving to ensure that the samples were homogenous and lacked high deviations in mass losses between the duplicated measurements (Dümichen et al., 2017). Although still in its relatively nascent stages, subsequent analysis via TED-GC-MS has demonstrated this method as suitable for a quantification of MPs in water from urban sewage systems (Altmann et al., 2019), street runoff, and sediment (Eisentraut et al., 2018), as well as other spiked suspended matter matrices (Becker et al., 2020; Goedecke et al., 2020).

An alternative to the TED-GC-MS method is the TGA-MS method in which gaseous degradation products are transferred into a quadrupole MS without chromatographic separation via GC. In their proof-of-concept work, David et al., demonstrated the suitability of TGA-MS for quantification of PET spiked soil without prior separation of the PET from its environmental matrix. Soil samples containing 1.61 ± 0.15 wt % organic matter were spiked with PET and it was found that characteristic decomposition products of PET could be distinguished from those of soil and the organic contents due to the differing temperatures of decomposition (David et al., 2018). However, interference with the pyrolysis products of PET may occur in the case of samples with high soil organic matter (SOM), for example when SOM is present at a concentration greater than 10% (Yan et al., 2004) or in the presence of other MPs (David et al., 2018). The capability of TGA-MS in identifying other plastics including polyvinylchloride (PVC), PE, PP and PS in spiked suspended matter was additionally demonstrated (Becker et al., 2020; Goedecke et al., 2020). Differentiation between PE and PP was made possible through the use of a model calculation. Specifically, the use of TGA-MS allowed for the detection of PVC, advantageously to TED-GC-MS analysis, which did not identify PVC (Goedecke et al., 2020).

Similarly to both the TED-GC-MS method (Dümichen et al., 2015; Dümichen et al., 2017) and TGA-MS methods (David et al., 2018), the success of TGA-FTIR is mainly contingent upon the identification of unique degradation products pertaining to the polymers (Yu et al., 2019). The coupling of FTIR allows for an acquisition of evolving FTIR spectra which shows intensity changes in certain absorption bands as the sample is pyrolyzed and decomposition gases are released. The temperature of maximum weight loss, which corresponds to the maximum of the derivative thermogravimetric (DTG) curve, provides the optimal signal to noise ratio for analysis of the decomposition gases. Yu et al., examined the feasibility of using TGA-FTIR to both identify and quantify MPs extracted from mussels and seawater, and present in soil. The method was tested using PE, PP, PVC, PA, PET and PS. TGA-FTIR analysis indicated that the decomposition products of PVC and PS can be distinguished from other MPs through characteristic absorption bands and successfully quantified via the preparation of calibration

curves based on the peak area and mass (Yu et al., 2019). The quantification of PS, as well as PET, PP and PE in spiked suspended matter using TG-FTIR was also achieved (Becker et al., 2020; Goedecke et al., 2020). A model calculation was used to differentiate between PE and PP, similar to that used in the comparative analysis performed using TGA-MS, and thus involved an added analytical complexity to the respective methods. When the TGA-FTIR was additionally coupled to GC-MS, quantification of PE and PP, in addition to PVC and PS MPs was demonstrated in mussel tissue (Liu et al., 2021).

While TED-GC-MS and TGA-FTIR are pyrolysis-based methods in which decomposition products are used for identification and quantification, assessment of MPs via differential scanning calorimetry (DSC) employs the melting of crystalline domains and the resultant contribution to an endothermic signal for determination of the relative content of MPs in the sample (Table 1). The chemical identification of MPs by DSC had been demonstrated by Castañeda et al., in their detection of PE microbeads in river sediments (Castañeda et al., 2014). Pertinent to this mini-review on TGA-based methods is a TGA-DSC study performed by Majewsky et al., in which a quantitative analysis of PE and PP in extracts derived from wastewater effluent samples using the TGA-DSC method was demonstrated. The quantification and identification was performed via the DSC signal using the area of the melting peak and its relation to the sample mass, and the TGA signals were used to provide a profile of the thermal degradation patterns of the pure polymers and the wastewater extracts (Majewsky et al., 2016).

Efforts in the field have led to a demonstrated quantification of key polymers and highlighted several advantages associated with TGA. A “one-step” assessment, which refers to the identification and/or quantification of polymers that requires minimal or no sample pre-treatment to separate MPs from their environmental matrix, represents a significant advantage accomplished by TGA-based methods (Table 1). In addition to the aforementioned lengthy time expenditure involved, separation methods notably lack harmonization and are possibly destructive to polymers, thereby potentially inhibiting their proper characterization and quantification (Bläsing and Amelung, 2018; Dümichen et al., 2015; Huppertsberg and Knepper, 2018; Lv et al., 2021; Thomas et al., 2020). When considering time expenditure for the analysis alone, the measurement time per sample analyzed via TED-GC-MS is approximately 2–3 h, which is less than that of micro-spectroscopic methods (Dümichen et al., 2017; Huppertsberg and Knepper, 2018). Advances in reducing the time demand of spectroscopic analysis have been made, including for example, the implementation of focal plane array detectors in micro-FTIR analysis of wastewater samples which saw a reduction of the time demand from several days (when using a single-element detector) to approximately 9 h (Tagg et al., 2015). However, this is still considerably greater than that of the aforementioned TGA-based methods. TGA-FTIR analysis performed on the mussel and seawater derived MPs was less than 35 min (Yu et al., 2019), and thus notably shorter than the analysis time of TED-GC-MS. Comparatively, amongst the TGA-based methods, this renders a designation of TED-GC-MS, as one that requires a long time expenditure (Table 1). Moreover, both TGA-FTIR methods and TED-GC-MS methods stipulate the need for detecting characteristic degradation products in order for an unambiguous identification to be made (Dümichen et al., 2015; Dümichen et al., 2017; Yu et al., 2019), and these “markers” must be validated in all examined matrices to exclude interferences (Huppertsberg and Knepper, 2018). Dümichen et al., have developed calibration methods using the peaks of dialkenes in soil samples and applied it to measure PE in samples other than soil, which includes mussels and suspended solids (Dümichen et al., 2015). The authors indicated that there is a need to investigate the soil matrix calibration’s suitability to quantify PE in these other matrices. The required validation experiments, as well as calibration experiments and data interpretation must be taken into account when considering and comparing time expenditure and efficiency.

In addition to time expenditure, another method-specific limitation

is related to operational challenges of TGA-based methods that are devoid of the intermediary absorber unit present in TED-GC-MS. Coupling of analytical instruments (FTIR or MS) directly to a TG instrument presents inherent operational challenges (Table 1) generally related to blockage of the capillary/transfer line that is used to transfer pyrolysis products directly from the TGA to the FTIR or MS due to condensation of pyrolysis products (David et al., 2018; Dümichen et al., 2014; Dümichen et al., 2017; Dümichen et al., 2019; Schindler et al., 2013). David et al., addressed this challenge via a cleaning and checking procedure to ensure blockage did not occur or interfere with the assessment of PET in soil (David et al., 2018). Moreover, one reason for the absence of a mainstream adoption of TED-GC-MS may have been due to another operational challenge, hence the later development of a system which automates the formerly manual transfer of the thermal desorption tubes to the thermal desorption unit (Dümichen et al., 2019).

The variety of MPs identified and/or quantified using the TGA-based methods suffer from method-specific limitations. For example, PP, PA and PET could not be determined with certainty in any of the river environmental samples analyzed using TED-GC-MS method (Dümichen et al., 2017), while PE and PS could be identified. Although the plastic sampling techniques may have been a contributing factor, the lack of specificity of the degradation products identified using this method may also have played a role, according to the authors.

The quantification of PE in wastewater extracts by the TGA-DSC method was accomplished (Majewsky et al., 2016), based on its melting endotherm occurring in the lower temperature range (101 ± 2 °C) and being well-separated from those of other plastics of environmental interest. Although measurements were validated for PP (164 ± 1 °C), it remained undetected in the environmental sample. Other plastics of environmental concern, including PVC, PES (polyester), PET, and PU, all have melting peak temperatures between 250 °C and 291 °C and are largely overlapping each other, particularly the broad peaks of PVC and PU (Majewsky et al., 2016). This poses challenges with respect to their unambiguous identification using TGA-DSC, thereby possibly precluding the ability to form a quantitative analysis. Using TGA-FTIR, polymers such as PP, PE, and PET produced olefins without notable absorption peaks and therefore the authors were unable to identify them in their analysis of extracts from seawater, mussels, and soil. Another limitation related to the detection of the pyrolysis products by the TGA-FTIR method was noted in the analysis of the soil samples (Yu et al., 2019), in which characteristic absorption peaks of PVC and PS were unobserved, despite being observed in mussels (PVC) and sea water extracts (PS), and the authors indicated that a pre-concentration may be necessary to reach the detection limit.

Perspective

The assessment of MPs should be approached from the fit-for-purpose perspective. The aforementioned TGA-based methods have the potential to yield complex data and even require specialized personnel for operation and analysis. This in turn presents a need for an alternative method that is facile, robust, provides data that is simple to analyze and can leverage instruments and databases that are widely available. Analysis via stand-alone TGA meets such criteria.

As of the coverage date of May 2021 for this mini-review, stand-alone TGA has not been employed for the identification or quantification of MPs in environmental samples, indicating an underutilization of its detection capability in the framework of the assessment of MPs. There is a general consensus that the overlapping of the temperature range of decomposition of the various polymers with one another, as well as with the organic matter present in the environmental matrices precludes the possibility of identifying and quantifying polymers by using the thermal decomposition profile acquired from TGA (Dümichen et al., 2017). However, options for separating thermal decomposition signals in TG analysis do exist and may profoundly improve the state of qualitative identification of MPs within mixtures. Such options are mainly based on

modifications made to the heating rate, and are facile to implement. For example, in a study by Rizzarelli et al. which aimed to quantify PE in compostable carrier bags, the influence of different TGA heating rates was investigated on the change of PE signals in a mixture of biodegradable polymer blends. An optimized heating rate was determined such that PE could be detected with a suitable enough resolution among the other components, subsequently allowing for a quantification to be made in compostable carrier bags (Rizzarelli et al., 2016). Moreover, various TG analysis manufacturers include the ability to perform high-resolution and auto-stepwise TG techniques, which significantly improve the differentiation ability in the analysis of multicomponent samples by slowing or stopping the increase in temperature during the TG run (Prime et al., 2009). Using the high-resolution technique, the heating rate is dynamically adjusted with the rate of weight loss in order to acquire a very slow heating rate at the temperatures of maximum decomposition, consequently resulting in an increased sensitivity and greater resolution compared to a constant heating rate, while also achieving a reduction in experimental time (Fernández-Berridi et al., 2006; Prime et al., 2009; Ng et al., 2018). Via the use of the high-resolution technique, Rennecker et al. demonstrated the quantification of PE and PP components of thermoplastic wood composites and achieved a high enough level of differentiation such that three distinguishable degradation processes related to PE could be identified (Rennecker et al., 2004). In another study by Fernández-Berridi et al., high-resolution TGA was used to quantify the elastomer composition of styrene/butadiene rubber and natural rubber in tire formulations, and the quantification was made possible by achieving separation of the DTG curves for each elastomer component via the high-resolution technique (Fernández-Berridi et al., 2006).

Each peak of the DTG curve represents a separate event, visually allowing the user to distinguish between different mass loss events and provides the temperatures of the maximum rate of mass loss which are characteristic of the components presents in the sample (Ng et al., 2018; Prime et al., 2009). Due to the differing thermal stabilities of such polymers of environmental concern (Majewsky et al., 2016) and depending on the ability to resolve the DTG peaks of their decomposition, thermoanalytical data guiding the identification of such polymers in a mixture can be acquired. Comparison of this data with online databases can then be leveraged for such identification (Schindler et al., 2017).

As such, analysis via stand-alone TGA can provide (1) Routine and rapid general analyses regarding plastic detection and identification; (2) Guidance towards decision-making regarding appropriate complementary analyses methods that match the needs (plastic type), resources (instrument type) and other considerations (pre-treated samples or not).

In this mini review, thermogravimetric-based methods for the identification and quantification of MPs have been identified, along with their capabilities and short-comings. Overall, these methods have demonstrated the characterization and quantification of key polymers of environmental concern, and concurrently highlighted an **underutilization** of the analytical capabilities of TGA itself. At the same time, the pervasiveness of plastics pollution and far-reaching environmental impact showcases the contemporary need for analyses methods that bypass use of highly-specialized personnel and a lengthy expenditure of time. TGA is a reliable, robust and rapid method, one that has long been used for the characterization of polymers, and maximizing the information yielded by taking advantage of the available techniques for improving the separation of thermal decomposition events may establish a new route in which stand-alone TGA plays a more dominant role in the rapid chemical identification of plastics.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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