



Towards harmonization of metal(loid)s determination in conventional and compostable plastics: Comparison of acid digestion protocols in LDPE and PBAT/TPS blends

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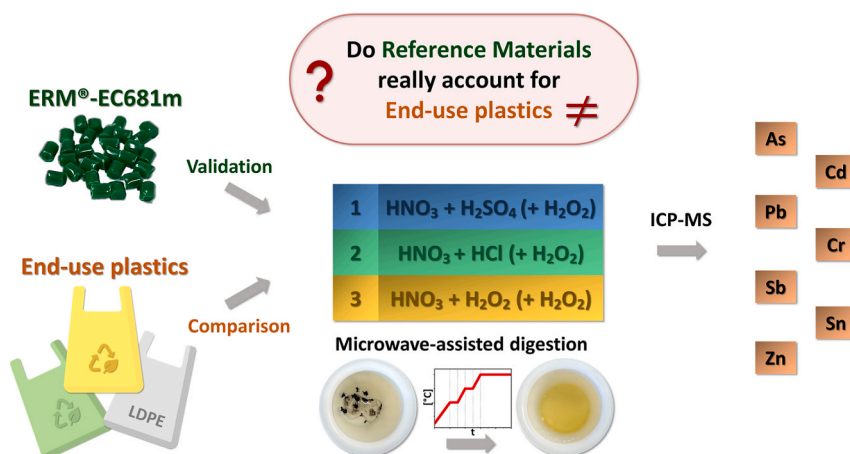
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HIGHLIGHTS

- Six acid digestion protocols for plastics were validated on a reference material.
- Validated protocols were applied to environmentally relevant end-use plastics.
- H₂SO₄ combined with HNO₃ and H₂O₂ showed the best digestion performance.
- End-use plastics showed a more complex array of additives than the reference material.
- Future steps towards harmonized metal (loids) determination protocols in plastics are suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

The determination of metal-containing additives in plastic materials via acid digestion protocols has attracted growing interest to address potential environmental implications. However, the lack of protocol harmonization hinders data comparability within the literature. Here, six acid digestion protocols were employed to determine the metal(loid) content in plastics: these included three different acid mixtures (HNO₃ combined with H₂SO₄,

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Metalloids
Acid digestion
Additives
Microplastics

HCl or H₂O₂) for microwave-assisted digestion, with or without an additional room-temperature digestion step with H₂O₂.

Each protocol was first validated for seven metal(loid)s (As, Cd, Cr, Pb, Sb, Sn and Zn) using a low-density polyethylene (LDPE) certified reference material (ERM®-EC681m). Then, validated protocols were applied on end-use materials, including conventional (i.e., LDPE) and compostable (i.e., PBAT/TPS) plastics.

The combination of H₂SO₄ and HNO₃ with a further digestion step with H₂O₂ was the most suitable protocol: it successfully passed validation thresholds for all metal(loid)s (recoveries in the range 98.6–101.0 %) and yielded the highest concentrations in end-use materials. All other protocols resulted in a less efficient digestion of the sample matrix, leading to lower recoveries and the formation of solid residues. Notably, end-use plastics showed a great variability in metal(loid) concentrations, likely due to their additive-rich composition, in contrast to the minimal content of acid-soluble additives of the reference material.

This study represents an initial step towards the harmonization of acid digestion protocols and highlights new challenges in accurately analyzing end-use plastic materials, due to their complex additive composition.

1. Introduction

Plastic materials are used in an extensive range of application fields. Polymer producers have designed several inorganic, organic and organometallic compounds as additives to tune specifically required properties of end-use plastic objects (Hahladakis et al., 2018; Wiesinger et al., 2021). These intentionally added compounds and processing aids include, for example, fillers, pigments, plasticizers, antioxidants, flame retardants, biocides, slip agents and catalysts (Hahladakis et al., 2018; Dufton, 1998). Other contaminants present in plastic products stem from residues or impurities after manufacturing or recycling processes, and are collectively known as non-intentionally added substances within the packaging field (Geueke, 2015; Pritchard, 2012; Wäger et al., 2012). Several of these compounds may pose adverse effects to biota, including humans, and their occurrence in plastics is consequently receiving increased attention from researchers, risk assessors and stakeholders: major concerns are raised in the context of food contact materials and for plastics dispersed in environmental compartments (Deubzer et al., 2016; Directive, 2009; Hänsch and Kinkel, 1995; Cunha Marques et al., 2015; Merkisz-Guranowska et al., 2018; European Parliament, 2005; European Parliament, 2011).

Although additives represent an essential component of plastics, their leaching from consumer products is an important issue (Li et al., 2024; Luo et al., 2022; Peng et al., 2023; Tan et al., 2023; Turner and Filella, 2021, 2023). Several studies have also attempted to uncover the role of plastic materials as potential sources or vectors of other organic and inorganic pollutants in the environment (Do et al., 2022; Maddela et al., 2023; Musa et al., 2024; Sridharan et al., 2022). In this context, organic compounds have received the majority of the attention, whereas the determination of inorganic compounds – namely metals and metalloids – remains scarcely explored: only a small number of studies have focused on the content of metals in plastic objects thus far (Li et al., 2024; Turner and Filella, 2021; Carnati et al., 2023; Gao et al., 2021). For example, some recent studies preliminarily assessed the total mass fractions of metals in plastic fragments (Ashton et al., 2010; Klöckner et al., 2021; Mohsen et al., 2022; Vedolin et al., 2018; Wijesekara et al., 2018), while a more limited number of studies has also tried to detect the bioavailable fractions and the speciation of metals associated with environmental plastics (Carnati et al., 2023; Binda et al., 2023; Chen et al., 2022; Gao et al., 2019; Munier and Bendell, 2018; Xie et al., 2022). The determination of the total metal content in plastic is, either way, an essential process for both approaches (Catrouillet et al., 2021; Hildebrandt et al., 2020).

Several methods and related techniques have been deployed to analyze metal(loid)s in plastic polymers (Binda et al., 2021; Dimitrakakis et al., 2009; Kutralam-Muniasamy et al., 2021; Pořízka et al., 2023). Microwave-assisted acid digestion followed by the analysis of the solution obtained remains the most commonly applied procedure to determine the total content of metal(loid)s in plastic, owing to the higher sensibility and cost efficiency (Catrouillet et al., 2021; Hildebrandt et al., 2020; Prunier et al., 2019; Rodrigues et al., 2023).

However, this approach covers a variety of methods with significantly differing reagents and conditions. Although Certified Reference Materials (CRMs) are ideal tools for verifying the effectiveness of digestion procedures, there are only a few polymeric CRMs which provide certified values for inorganic additives, making exact matrix-matched quantification notably difficult to perform (Hildebrandt et al., 2020; Amaral et al., 2016). Additionally, end-use plastic materials exhibit a heterogeneous composition of inorganic additives, with different speciation of metals in the polymer matrix (i.e. inorganic salts, oxides or organometallic compounds). This complexity can hinder the complete digestion of the matrix, prompting the application of non-traditional digestion techniques (Cho and MyungSeung-Woon, 2011; European Commission, 2015; Lehtimäki and Väisänen, 2017). These constraints collectively impede accurate measurements of metal(loid)s in plastics and limit data comparability. Harmonization of the adequate acid mixtures to be employed is still lacking and comparisons of digestion performances among different protocols are extremely rare (Hildebrandt et al., 2020).

In this context, this study aims to tackle this issue by testing different microwave-assisted digestion protocols using a standard CRM along with different end-use plastic items. We firstly compared the digestion protocols for validation purposes using the CRM and the content of seven metal(loid)s. Then, we tested the analytical performances of these protocols on end-use conventional and compostable plastics, considering their increasing use in the market (Capolupo et al., 2023; Lin et al., 2023; Markowicz et al., 2019). Besides revealing the discrepancies between CRM and end-use plastics, this further comparison will explore the feasibility of a unified digestion method suitable for studying the selected metal(loid)s in both conventional and compostable plastic materials.

2. Materials and methods

2.1. Plastic materials selection and characterization

A comparison of the digestion protocols was first performed with the CRM: ERM®-EC681m (polyethylene (elements, high level)). This was purchased from the Joint Research Centre of the European Commission (JRC, Ispra, Italy) and comes as a green-colored pellet made of low-density polyethylene material (LDPE) spiked with metal-containing additives. Seven certified metal(loid)s were analyzed in the present work: As, Cd, Cr, Pb, Sb, Sn and Zn. Their concentrations in the CRM cover a range from 17.0 ± 1.2 to 1170 ± 40 mg kg⁻¹ ($U_{\text{certified}} k = 2$) (European Commission, 2015). Three end-use plastic samples (i.e., a commercially available LDPE and two compostable plastic materials) were also employed in the study to assess the performances of the validated digestion methods. The end-use LDPE originated from white bags, obtained from a grocery store. The compostable plastic materials also originated from grocery bags that were green and yellow in color (Fig. S1). These were made of a starch-based bioplastic blended with biodegradable polyesters, pursuant to the EN 13432 standard (Bouzi

et al., 2022; Paola Bracciale et al., 2024). Graphics and heat-sealed seams of these materials were not included in the sample that was digested to enhance sample homogeneity.

A Fourier transformed infrared (FTIR) spectroscope (Thermo Scientific™ (Waltham, MA, USA) Nicolet™ iS™ 10) operated in attenuated total reflectance (ATR) mode was applied to confirm the polymer composition. Thirty-two co-scans were collected for every sample in the 4000 cm^{-1} - 650 cm^{-1} spectral range, with a wavenumber resolution of 0.482 cm^{-1} . Prior to each measurement, a background spectrum was recorded. The obtained spectra were smoothed using the Savitzky–Golay filter, then normalized on the maximum absorbance peak.

2.2. Digestion protocols and metal(loid)s determination

Six different digestion protocols were tested (Table 1). These protocols include a digestion step with heating assisted by a microwave system (protocols 1, 2 and 3) and a further digestion step provided by H_2O_2 without any additional heating (protocols 1+H, 2+H and 3+H).

The choice of digestion reagents was based on commonly used conditions in the literature, with a primary focus on digestion protocols that are more frequently utilized to analyze environmental samples. Hence, HNO_3 was considered as a prevalent oxidizing agent, in combination with other auxiliary reagents, such as.

- H_2SO_4 (protocols 1 and 1+H), chosen for its potential to oxidize organic compounds (Eilola and Perämäki, 2009; Kalčíková et al., 2020; Lebbos et al., 2023);
- HCl (protocols 2 and 2+H), selected for its complexation and stabilization capacity towards some metal(loid)s (Link et al., 1998; Sastre et al., 2002);
- H_2O_2 (protocols 3 and 3+H), picked for its ability to enhance the role of HNO_3 and to contribute in the digestion as an O_2 source (Yáñez et al., 2016).

Operationally, the digestion of the plastic materials was obtained through microwave-assisted digestion in a closed system (ETHOS One, Milestone MLS) equipped with 10 polytetrafluoroethylene (PTFE)

Table 1
Summary of the protocols, conditions and acid mixtures applied in the current work for microwave-assisted acid digestions.

Protocol	Conditions	Acid mixture
1	Microwave-assisted heating (200 °C)	4 ml of 65% HNO_3 and 1 ml of 95% H_2SO_4
1+H	1) Microwave-assisted heating (200 °C)	1) 4 ml of 65% HNO_3 and 1 ml of 95% H_2SO_4
	2) Room temperature	2) 0.2 ml of 30% H_2O_2
2	Microwave-assisted heating (200 °C)	4 ml of 65% HNO_3 and 1 ml of 37% HCl
2+H	1) Microwave-assisted heating (200 °C)	1) 4 ml of 65% HNO_3 and 1 ml of 37% HCl
	2) Room temperature	2) 0.2 ml of 30% H_2O_2
3	Microwave-assisted heating (200 °C)	4 ml of 65% HNO_3 and 1 ml of 30% H_2O_2
3+H	1) Microwave-assisted heating (200 °C)	1) 4 ml of 65% HNO_3 and 1 ml of 30% H_2O_2
	2) Room temperature	2) 0.2 ml of 30% H_2O_2

vessels. Samples of each material were first cut using a ceramic knife into pieces with a size of ca. 5 mm and these were homogeneously mixed. Approximately 100 mg of sample were accurately weighed and inserted into each pre-cleaned vessel, together with the required mixture of acids. The materials were then digested applying a temperature ramp reaching 200 °C for 45 min, consisting of a 30 min heating and a 15 min holding time (European Commission, 2015).

Afterwards, a further digestion at room temperature was performed adding H_2O_2 after the initial digestion for the protocols 1+H, 2+H and 3+H (Table 1). Hence, 0.1 ml of H_2O_2 was added to each vessel and, following a gentle stirring, the reaction was allowed to continue for 30 min at room temperature, after which another 0.1 ml of H_2O_2 addition was made (Kalčíková et al., 2020; Lee et al., 2022; Pehlic et al., 2019; Reid et al., 1995). This further oxidation step with H_2O_2 was applied to ensure a complete digestion of the recalcitrant or partially digested polymer matrix. Additional heating at this stage was discarded to prevent uncontrolled reactions, ensure safety and maintain controlled conditions.

After the different digestion protocols, the vessels were left to cool to room temperature, then solutions were transferred to pre-cleaned low-density polyethylene (LDPE) bottles and diluted to 20 g with ultrapure water. These solutions were then filtered (0.22 μm PTFE filter), further diluted 20-fold and spiked with two internal standards (Rh and Re, respectively). Lastly, solutions were analyzed via ICP-MS using a He-collision cell in kinetic energy discrimination (KED) mode (Thermo Scientific ICAP Q). Settings, working parameters and determined isotopes are provided in Supplementary Materials (Table S3). External calibration was employed for element quantification. According to ERM®-EC681m, the analyzes were validated over the seven previously listed metal(loid)s (As, Cd, Cr, Pb, Sb, Sn and Zn; paragraph 2.1.) for which the content is certified.

2.3. Analysis of solid residuals

In the case of incomplete digestions where visible solid residuals were observed after the applied protocols, the solid residue was analyzed for morphology and main chemical composition. The associated solution was centrifuged at 5000 rpm for 10 min. Then, ca 200 μL of the solution with the residual was drop-casted onto sample holders (covered with a conductive carbon tape) for scanning electron microscope (SEM) imaging and dried in an oven at 60 °C for 60 min. Samples were subsequently coated with a gold layer using a Cressington (UK) 108 auto vacuum sputter coater to increase their conductivity. A field emission gun-SEM (Philips®, Netherlands) with a 20 keV beam under high vacuum conditions, coupled with energy dispersive X-ray spectroscopy (SEM-EDX) was then employed. This allowed the elemental content of insoluble substances after sample incomplete digestions to be semi-quantitatively analyzed.

2.4. Reagents, QA/QC procedures and data processing

All operations regarding sample and solution preparations were carried out under a laminar flow hood to avoid airborne contamination (aura HZ72T BIOAIR, Italy). Analytical grade reagents and ultrapure water (Milli-Q from Sartorius Arium® mini, Germany; resistivity: 18.8 $\text{M}\Omega\text{ cm}$; TOC: <5 ppb) were used. Ultrapure HNO_3 and HCl were produced by sub-boiling distillation (Monticelli et al., 2019) from commercial HNO_3 (Carlo Erba, 65% v/v) and HCl (Carlo Erba, 37% v/v) in a Milestone (USA) DuoPur system, whereas H_2SO_4 (Analytika, 95% v/v pure) and H_2O_2 (Fisher Chemical, 30–32% v/v for trace analysis) were employed as purchased. All LDPE containers (Nalgene®) employed for analytical solutions underwent a cleaning procedure: first, they were rinsed with ultrapure water and submerged in a 0.4% v/v detergent solution (Nalgene® L900) for one week; second, they were rinsed with ultrapure water and soaked in a 2% v/v HNO_3 solution for another week and, after rinsing with ultrapure water, they were left to dry at room

temperature under a laminar flow hood (Spanu et al., 2020). PTFE digestion vessels were pre-cleaned before each digestion cycle following a two-step procedure: they were first cleaned through a heating cycle (200 °C, 45 min) with 65% HNO₃ and then rinsed three times with ultrapure water (Link et al., 1998). Then, they were conditioned using another heating cycle with the acid mixtures used in the following protocol and again rinsed three times with ultrapure water. Multi-element standard solutions were applied for external calibration

of the ICP-MS measurements. These were prepared by diluting multi-elemental standard stock solutions (Merck KGaA (Germany); Sigma-Aldrich (USA)).

The metal(loid)s detected and quantified were As, Cd, Cr, Pb, Sb, Sn and Zn. Ti was added to the analytes list after SEM-EDX analysis of the elements in the residuals of end-use plastic sample digestion. The final metal(loid) concentrations were reported as milligrams of the extracted metal per kilogram of the dry sample (mg kg⁻¹). Uncertainty associated

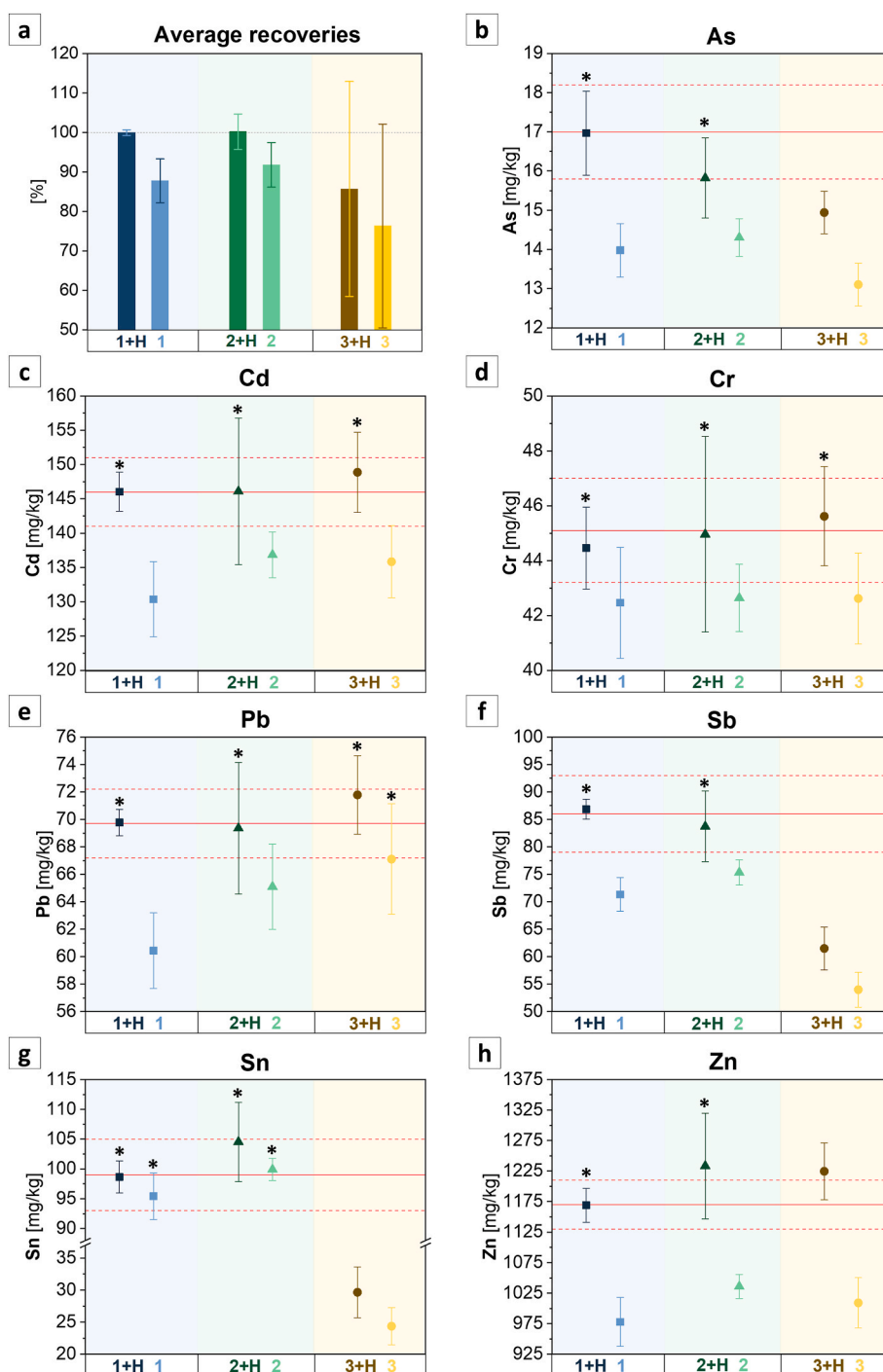


Fig. 1. Results of the seven selected metal(loid)s (As, Cr, Cd, Pb, Sb, Sn, and Zn, displayed from panel a to h, respectively) obtained by the application of the six digestion protocols (namely, 1+H, 2+H, 3+H, 1, 2, and 3) on ERM®-EC681m. Panel a displays the average recoveries provided by each single protocol, calculated considering all seven metal(loid)s collectively. For graphs b-h, the solid red line represents the certified value (unweighted mean) of each metal(loid), with the corresponding uncertainty displayed as dashed red lines (expanded uncertainty of the certified value with a coverage factor $k = 2$, corresponding to a level of confidence of 95 %). Measurement results are given with their average value ($n = 6$) and uncertainty (confidence interval at 95%). Asterisks (*) indicate results for which the evaluation proved no significant difference between the measurement and the certified value (paragraph 2.4.).

with the measurements was calculated after the digestion of 6 replicates and expressed as one standard deviation (European Commission, 2005). Method detection limits (MDLs) were estimated by means of method blanks: they were reported as the mean determined concentration plus three times the standard deviation of a set of 6 method blanks and expressed as mg kg^{-1} based on a 100 mg solid sample (Table S4). Potential contamination during laboratory procedures were assessed by including analytical blanks.

Calculations were carried out using Microsoft Excel spreadsheets. Statistical analysis concerning normality tests (Shapiro–Wilk test) and outlier evaluations (Grubbs test) was performed using the Origin 2018 software (OriginLab Corporation, Northampton, MA, USA). To quantitatively evaluate method performance, measurement results were compared against the certified values in compliance with the recommended guidelines (ISO/IEC GUIDE 98-3:2008E, 1995). ACD/Chem-Sketch molecular modelling software was used for structure drawing of polymer materials.

3. Results and discussion

3.1. Validation of digestion protocols with the CRM

The six different protocols for microwave-assisted digestions were first applied to digest the CRM ERM®-EC681m. The performance of the protocols was validated against the certified values of As, Cd, Cr, Pb, Sb, Sn and Zn and the completeness of the sample digestion was observed.

Protocols 1, 2 and 3 (i.e., protocols not involving an additional digestion step with H_2O_2 , Table 1) provided recoveries that ranged substantially, from $24.2 \pm 3.0\%$ (Sn with protocol 3) to $101.0 \pm 2.0\%$ (Sn with protocol 1), depending upon the specific protocol and metal (loid) (Table S1). The overall average recovery of all seven selected metal(loid)s was $87.8 \pm 5.6\%$ with protocol 1, $91.8 \pm 5.6\%$ with protocol 2 and $76.3 \pm 25.8\%$ with protocol 3 (Fig. 1a). For these three protocols, the only metal(loid)s whose measured concentrations were in alignment with the certified values were Pb with protocol 3 ($96.3 \pm 5.7\%$, Fig. 1e) and Sn with protocol 1 and 2 ($96.0 \pm 4.0\%$ and $101.0 \pm 2.0\%$, Fig. 1g). This demonstrated that protocols 1, 2 and 3 were not successful for effectively digesting the CRM for accurate determination of metal(loid) content, except for these three specific cases.

The lowest recoveries were observed for protocol 3, for both Sn ($24.2 \pm 3.0\%$, Fig. 1g) and Sb ($62.8 \pm 3.5\%$, Fig. 1f). Low values for Sb and Sn are linked to the absence of halogens in the digestion solution which may lead to losses of Sn and Sb due to the formation of hydrolysis products (Amaral et al., 2016; Lehtimäki and Väisänen, 2017). Our results are consistent with studies in which a combination of HNO_3 and HCl (similar to our protocol 2) was used to dissolve the same CRM assessed in this study (Hildebrandt et al., 2020).

Considering instead the protocols which involved an additional digestion step with H_2O_2 (i.e., 1+H, 2+H and 3+H in Table 1), nearly all provided concentrations were in agreement with the certified values for all metal(loid)s. The average recoveries for all seven selected metal(loid)s were $100.0 \pm 0.7\%$ for protocol 1+H, $100.2 \pm 4.5\%$ for protocol 2+H and $85.7 \pm 27.3\%$ for protocol 3+H (Fig. 1a). As shown, most of the protocols with H_2O_2 final addition yielded higher concentrations of metal(loid)s after digestion than protocols without a final H_2O_2 addition. Declines in recoveries between the corresponding protocols with and without H_2O_2 ranged from ca -4 to -18% , depending on the specific metal(loid) and protocol. The only exception was observed for protocol 3+H, where the observed values did not correspond well with the certified values: As ($87.9 \pm 2.9\%$, Fig. 1b), Sb ($71.5 \pm 4.7\%$, Fig. 1f), Sn ($30.0 \pm 4.0\%$, Fig. 1g) and Zn ($104.7 \pm 3.8\%$, Fig. 1h).

The results of the digestion and determination of metal(loid)s in the CRM helped to evaluate the importance of H_2O_2 as an auxiliary reagent in digestion protocols. Indeed, it is evident that H_2O_2 (used in protocols 1+H, 2+H and 3+H) played an important role in the digestion of the CRM and was effective even at room temperature. The combination of

H_2O_2 with other reagents during digestion is in fact known to enhance the oxidation of carbon to carbon dioxide, thereby improving digestibility (Yáñez et al., 2016; Bizzi et al., 2014). This process also helped to dissolve salts that potentially form during initial microwave-assisted digestion. For example, Pb concentrations obtained with protocols 1+H resulted in significantly higher values than with protocol 1 (i.e. $100.1 \pm 1.3\%$ compared to $86.7 \pm 3.7\%$, Fig. 1e). Protocol 1 can lead to the precipitation of lead sulphate salts, which may be dissolved by the application H_2O_2 in protocol 1+H. The only element which revealed similar recovery rates with both protocols – whether with or without H_2O_2 and regardless of the acid mixture used – was Sn: protocols 1+H and 1, and 2+H and 2 all yielded results that matched the certified value (Fig. 1g).

It is worth mentioning that the metal(loid) specific trends observed for protocols 1, 2 and 3 are also evident in protocols 1+H, 2+H and 3+H. Comparing the different reagents used in combination with HNO_3 (i.e., protocols 1+H, 2+H and 3+H, Table 1), both protocols 1+H (HNO_3 combined with H_2SO_4 and H_2O_2) and 2+H (HNO_3 mixed with HCl and H_2O_2) yielded results in line with the certified values for all metal(loid)s (Fig. 1 and Table S1). Specifically, protocol 1+H provided recovery rates ranging from $98.6 \pm 3.1\%$ for Cr (Fig. 1d) to $101.0 \pm 2.3\%$ for Sb (Fig. 1f), whereas for protocol 2+H the lowest recovery was $93.1 \pm 6.3\%$ for As (Fig. 1b), and the highest was $105.6 \pm 5.7\%$, observed for Sn (Fig. 1g and Table S1). The standard deviations relative to Cd, Pb and Cr provided by protocol 2+H varied from approximately 6.5 to 8.0%. This protocol also showed a higher standard deviation of Sb: this could be attributed to losses after the formation of volatile species that occur when Sb (III) species are complexed by chloride ions (Link et al., 1998). Protocol 3+H (HNO_3 mixed with H_2O_2) instead showed generally lower concentrations, especially for As, Sn and Sb: only Cd, Cr and Pb measurements agreed with the certified values, with recoveries of $102.1 \pm 4.1\%$, $101.1 \pm 3.8\%$ and $103.0 \pm 3.9\%$, respectively (Fig. 1 and Table S1). The recovery rate of Sb was $70.9 \pm 4.7\%$, while the lowest of $30.3 \pm 4.0\%$ was obtained for Sn.

The improved performance of protocol 1+H was presumably due to its more efficient digestion of the matrix, as its application consistently provided visibly clear solutions free from any noticeable precipitate. Our findings align with previous research revealing the benefits of H_2SO_4 (reagent used in protocol 1+H and 1) for polyethylene matrices (García-Poyo et al., 2015). Specifically, H_2SO_4 was shown to reduce digestion time and ensure complete digestion of the sample given its strong oxidizing properties and ability to effectively breakdown complex organic matrices (Eilola and Perämäki, 2009; Lebbos et al., 2023). Hindrances in the proper quantification of some analytes arising from this reagent (i.e., formation of insoluble sulphate salts or the potential generation of non-spectral interferences in ICP-MS) were not observed in the current work, at least for protocol 1+H: blank values and the corresponding MDLs were not statistically different from the values obtained for other reagents (Table S3) (Sakurai et al., 2006).

3.2. Analysis of end-use plastic materials

To test the wider relevance of the protocols validated with the CRM, we selected and analyzed three materials commonly available on the market (including one sample composed of LDPE and two compostable materials composed of polybutylene adipate terephthalate and thermoplastic starch (PBAT/TPS); Fig. S1) using the most efficient protocols. Their polymeric composition was verified using FTIR analysis (Fig. S2 and Fig. S3) (Bouzi et al., 2022; Paola Bracciale et al., 2024; Al-Itry et al., 2012).

Based on the more reliable results obtained for the CRM using protocols 1+H and 2+H (which included a final H_2O_2 addition; Paragraph 3.1.), these two protocols were selected for comparison in the analysis of end-use plastic materials (Fig. 2 and Table S2). Additionally, we also tested protocol 3+H: although this protocol was only validated with the CRM for 3 metal(loid)s, it is widely used for the acid digestion of plastic

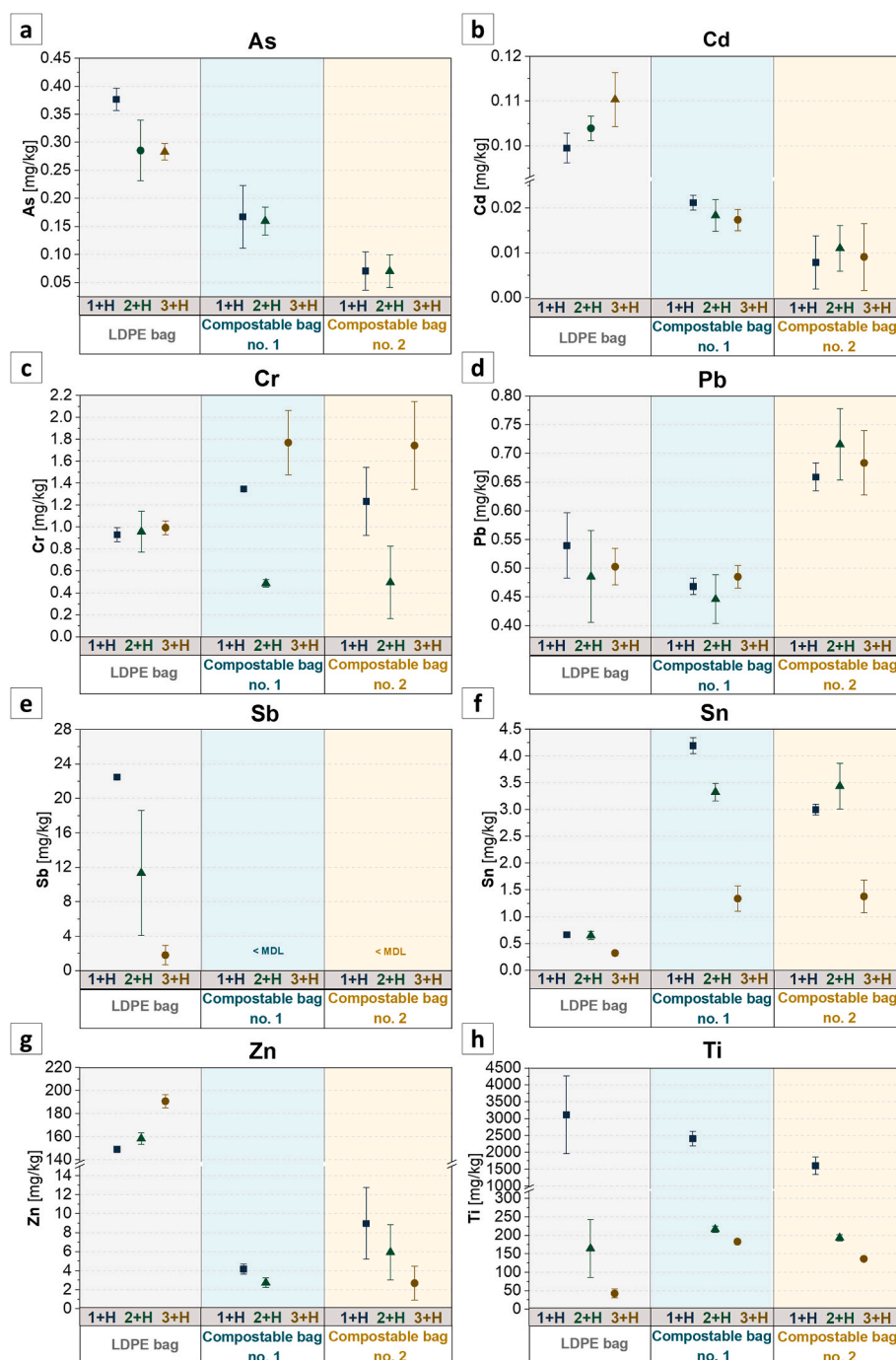


Fig. 2. Results of the analyzed metal(loid)s (from panel a to h) for end-use LDPE bag and compostable bags no. 1 and 2 obtained via the digestion protocols 1+H, 2+H and 3+H, respectively. Measurements are shown with their average value and uncertainty (confidence interval at 95%).

samples (Kutralam-Muniasamy et al., 2021; Lehtimäki and Väisänen, 2017) and therefore warrants investigation in this context.

Observing the concentrations observed for the LDPE sample, some differences arose between the three protocols. For example, Zn and Cd had higher concentrations with protocol 3+H (Zn: $190.8 \pm 5.8 \text{ mg kg}^{-1}$; Cd: $0.110 \pm 0.006 \text{ mg kg}^{-1}$; Fig. 2 and Table S2). For Sn, while concentrations with protocol 1+H and 2+H were similar ($0.66 \pm 0.04 \text{ mg kg}^{-1}$ versus $0.65 \pm 0.08 \text{ mg kg}^{-1}$), 3+H resulted in a lower concentration ($0.32 \pm 0.05 \text{ mg kg}^{-1}$, Fig. 2f) – the trend observed for this element is in line with what was already observed in the analysis of the CRM. The performance of the protocols for the analysis of Sb in the LDPE sample largely agreed with the results of the CRM: protocol 1+H gave

considerably higher values ($22.5 \pm 0.2 \text{ mg kg}^{-1}$) than 2+H ($11.3 \pm 7.3 \text{ mg kg}^{-1}$) and 3+H ($1.8 \pm 1.1 \text{ mg kg}^{-1}$) (Fig. 2e).

Importantly, the standard deviations of most metal(loid)s were minimized when protocol 1+H was applied. This was probably due to a more effective digestion of the matrix in comparison with the other protocols. The analysis of residuals performed with SEM clearly showed this phenomenon: protocols 2+H and 3+H showed diffused depositions and fragments of undigested plastic material (Fig. 3). Semi-quantitative determination of metal(loid)s in deposits through SEM-EDX revealed the presence of Ca and Ti as the main components of these deposits (Fig. S4). Ti was also quantified in the digestion solutions of the three protocols via ICP-MS, showing a great variance among digestion protocols:

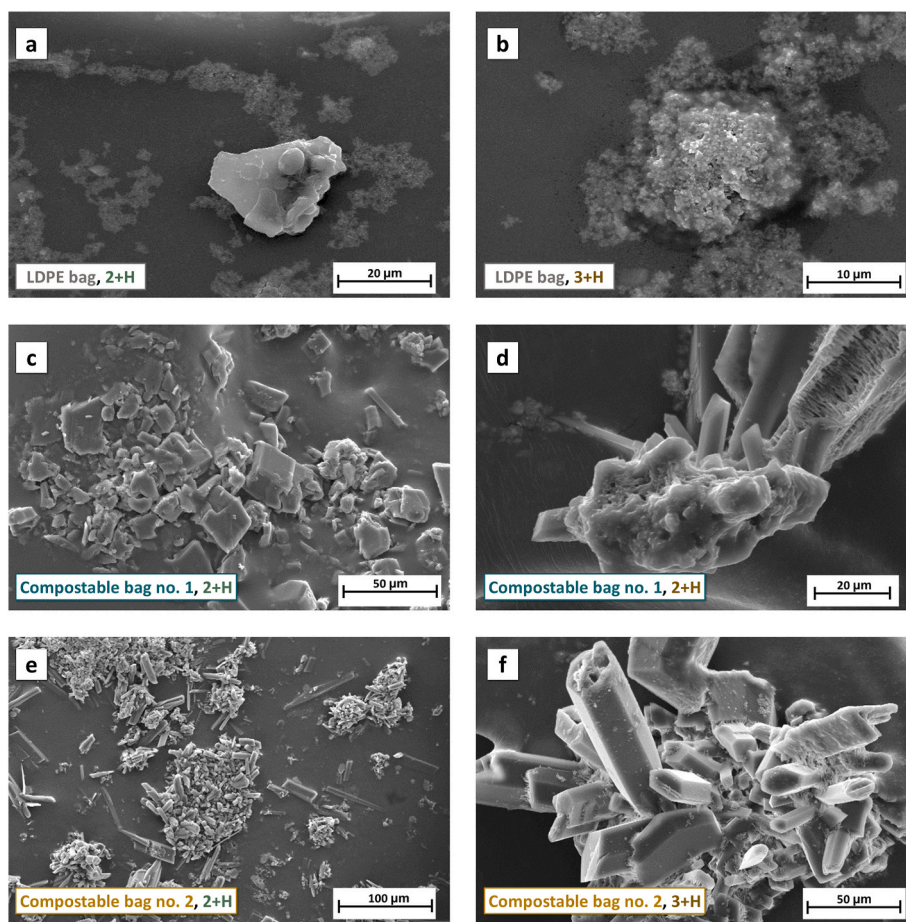


Fig. 3. SEM images of insoluble substances after incomplete digestions. Panels a and b display residuals of end-use LDPE bag, while c, d, e and f show the filtrates of the compostable plastic bag no. 1 and 2, respectively. Images refer solely to protocols for which evident residuals were observed.

protocol 1+H yielded a concentration of $3113.4 \pm 1152.5 \text{ mg kg}^{-1}$, while protocol 2+H gave $164.3 \pm 78.6 \text{ mg kg}^{-1}$ and 3+H resulted in $42.3 \pm 12.2 \text{ mg kg}^{-1}$ (Fig. 2h–Table S2).

The two compostable plastic samples showed even more pronounced differences in the concentrations of the selected metal(loid)s comparing the three protocols applied (Fig. 2 and Table S2). The metal contents were again generally higher when protocol 1+H was deployed in comparison to the others. The measured concentration of Zn was also slightly higher with 1+H for both materials (Fig. 2g). Concerning As, protocol 1+H offered similar results as 2+H ($0.17 \pm 0.06 \text{ mg kg}^{-1}$ with 1+H versus $0.16 \pm 0.02 \text{ mg kg}^{-1}$ with 2+H for compostable plastic bag no. 1, and $0.071 \pm 0.034 \text{ mg kg}^{-1}$ with 1+H versus $0.070 \pm 0.029 \text{ mg kg}^{-1}$ with 2+H for compostable plastic bag no. 2), whereas 3+H yielded concentrations below the MDL for both bags (Fig. 2a).

The higher concentrations yielded by protocol 1+H were again linked to a more efficient digestion of the sample matrix, which was evident observing the presence of undigested residuals: mixture 1+H always resulted in visibly clear solutions without the occurrence of deposits after the digestion of the two compostable plastic bags, whereas both mixture 2+H and 3+H left macroscopically evident residuals. These precipitates were investigated with SEM-EDX analysis (Fig. 3,

Fig. S4). This showed variable morphologies and chemical composition: they included particles with a major carbonaceous composition, possibly representing undigested polymer matrix, along with other inorganic particles that showed the presence of Ca, Ti and Pb. The latter probably originated from powders added to the polymer matrix during formulation. As in the case of the end-use LDPE, Ti in the compostable plastic bags also yielded different concentrations after using the three digestion protocols: for compostable plastic bag no. 1, the concentration obtained by protocol 1+H was $2408.3 \pm 213.5 \text{ mg kg}^{-1}$, while 2+H resulted in $216.3 \pm 8.8 \text{ mg kg}^{-1}$ and 3+H in $182.9 \pm 7.2 \text{ mg kg}^{-1}$. Similarly, for compostable plastic bag no. 2, protocol 1+H yielded a Ti concentration of $1603.1 \pm 259.0 \text{ mg kg}^{-1}$, 2+H gave $193.1 \pm 8.7 \text{ mg kg}^{-1}$ and 3+H resulted in $136 \pm 3.5 \text{ mg kg}^{-1}$ (Fig. 2h and Table S2).

Other metals instead showed less evident trends. For example, Cd concentrations fell within the same range for all protocols and for both bags (Fig. 2b). Pb resulted in similar values provided by all three protocols, with 1+H offering narrower standard deviations (Fig. 2d). Cr, instead, showed higher variability in comparison to the LDPE bag (Fig. 2c). This finding may be attributed to losses of Cr originating from the formation of chromium carbide during the digestion of the polymeric blend (Li and Jiang, 2006; Ritter et al., 2004).

3.3. Discrepancies between CRM and end-use plastics: challenges in metal(loid)s determination

The findings of this study revealed significant differences when applying the same digestion protocols to a CRM (specifically ERM®-EC681m) compared to end-use plastics, including those composed of the same polymers (i.e. CRM and end-use LDPE bag). These results indicated

that some discrepancies were related to the polymeric matrix of the materials analyzed, whereas others concerned the specific chemistry of each metal(loid).

A key observation is that even the protocols which provided high consistency with the CRM (e.g. protocols 1+H and 2+H) did not perform as reliably when applied to end-use plastics: end-use materials exhibited greater variance among replicates and protocols compared to the CRM. Unlike the CRM, which was entirely digested across all protocols, the end-use materials were more resistant to digestion, yielding results that greatly differed between the different protocols applied. Furthermore, metal(loid) concentrations of end-use materials displayed significantly greater variances compared to the CRM. This increased variability is largely attributed to the inherent heterogeneity of end-use plastics, where additives are unevenly distributed within the polymeric matrix. In contrast with CRMs, which are designed for homogeneity and assessed for minimal sample intake to ensure reliable measurements, end-use plastics lack uniformity – a feature that hinders measurements replicability (Nakashima et al., 2016).

Other differences presumably stem from the varying chemical speciation of additives in end-use plastics compared to the controlled composition of the CRM. The latter is produced for analytical purposes, with known and readily dissolvable additives. For instance, more readily dissolvable metal species (e.g., CaCrO₄ and SnS₂) replaced other less soluble metal oxides (e.g., Cr₂O₃ and SnO₂) in the formulation of the CRM used in this study (European Commission, 2015). In contrast, end-use plastics typically contain a complex cocktail of unknown additives, processing aids, unreacted monomers and contaminants, contributing to their heterogeneous matrix.

As a further note, in all the end-use plastic samples we detected abundant levels of Ti, as its presence is related to the use of pigments and UV absorbers, typically in the form of titanium dioxide (TiO₂) (Turner and Filella, 2023). However, we observed varying concentration values across the three methods (Fig. 2h), and diffused Ti was observed in the residuals of our samples (Fig. 3 and Fig. S4). TiO₂ is, in fact, not completely solubilized by HNO₃ alone, and other auxiliary acids (i.e., HF) are often used: this reagent requires specialized equipment for the subsequent ICP-MS analysis due to its corrosiveness (Pinna et al., 2022). In this study H₂SO₄ is observed to favor HNO₃ protonation, forming the nitronium ion, which reacts with the TiO₂ lattice structure and favors its dissolution. Our results align with previous studies showing that H₂SO₄ digestion yields high Ti recoveries (Mudunkotuwa et al., 2016; Watkins et al., 2018).

4. Conclusions and outlooks

This study reports a comprehensive comparison of different acid digestion protocols to determine metal(loid)s in different plastic samples, offering insights towards method harmonization. Among the protocols tested, we recommend the use of H₂SO₄, HNO₃ and H₂O₂ (protocol 1+H) for achieving a complete digestion and a precise quantification of As, Cd, Cr, Pb, Sb, Sn, Zn and Ti in end-use LDPE and PBAT/TPS plastic materials. This protocol stands as a sound compromise to alternative unconventional dissolution techniques requiring extremely high temperature or corrosive acids.

Our findings underline the challenges associated with the analysis of various polymers that constitute end-use plastics, along with their complex and heterogenous suite of inorganic additives. These issues likely extend to other types of polymers not covered in this study. Therefore, we support further research to assess the reliability of acid digestions for dissolving resistant and chemically stable matrices to ensure accurate extraction of all relevant metal(loid)s. Additionally, considering the significant role of the chemical properties of the inorganic additives, it is advisable to develop reference materials with additives that more accurately reflect the composition of plastics currently on the market.

Moreover, environmental plastics may be even more complex than

pristine end-use plastic materials. The concentrations of these enriched metal(loid)s may be significantly lower than those analyzed in this study, requiring robust and well-established methods (Carnati et al., 2023; Souza et al., 2022). For example, environmental plastics may undergo aging, leading to partial degradation of the polymeric matrix, enhanced leaching of additives, and potential changes in metal(loid) chemical speciation (Binda et al., 2024). These factors further complicate the application of analytical protocols and stress the need to also consider chemically aged polymers as CRMs.

In conclusion, we highlight the need for further comparative studies on different plastics to move towards harmonized and comparable data. This approach will ultimately improve our understanding of metal(loid)s in plastic materials and their environmental implications.

CRedit authorship contribution statement

Stefano Carnati: Writing – original draft, Investigation, Formal analysis. **Andrea Pozzi:** Supervision, Methodology, Data curation. **Daide Spanu:** Writing – review & editing, Methodology, Data curation. **Roberta Bettinetti:** Supervision, Data curation. **Luca Nizzetto:** Writing – review & editing, Funding acquisition, Formal analysis, Conceptualization. **Gabriela Kalčíková:** Writing – review & editing, Funding acquisition, Formal analysis. **Ludovica Botta:** Investigation. **Gilberto Binda:** Writing – review & editing, Formal analysis, Conceptualization.

Declaration of competing interest

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2024.143581>.

Data availability

All experimental data are available in Supplementary material.

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