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Development of a multi-element quantification method for technical polymers containing refractory oxides after microwave-assisted digestion using HBF_4

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Polymers used in packaging, medical devices, and construction often contain inorganic additives, including stabilizers, fillers, pigments, and antioxidants. Quantitative elemental analysis of these additives is essential for quality control, regulatory compliance, recycling, and the assessment of microplastics, but is complicated by refractory oxides (*e.g.*, TiO_2, Al_2O_3, ZrO_2) that are difficult to dissolve quantitatively. This study presents a two-step, microwave-assisted digestion method using tetrafluoroboric acid (HBF_4) for comprehensive elemental analysis of technical polymers containing such oxides. In the first step, the polymer matrix is oxidized using HNO_3 and H_2O_2 at 200 °C; and in the second step, HBF_4 is added and digestion continues at 180 °C to dissolve refractory oxides while avoiding the use of free HF. Method development was performed on polyethylene containing various oxides, and on polyvinyl chloride containing metal soaps, $CaCO_3$, and TiO_2. The protocol was benchmarked against HF-based digestions. The optimized conditions (4 mL HNO_3 + 1 mL H_2O_2, 75 min at 200 °C; 1 mL HBF_4, 45 min at 180 °C) gave recoveries typically between 90 and 105% for Al, Ca, Mg, Ti, and Zr with relative standard deviations ≤5% for most analytes. Limits of detection by inductively coupled plasma mass spectrometry (ICP-MS) were ≤2.6 mg kg^{-1} (LOQs ≤8.5 mg kg^{-1}) for most elements. Accuracy and applicability were confirmed for the polymer certified reference material ERM®-EC681k and for polycarbonate and acrylonitrile–butadiene–styrene masterbatches containing refractory oxides, demonstrating a robust, broadly applicable, and HF-free sample preparation strategy for elemental analysis of technical polymers and microplastics.

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1. Introduction

Polymers are used in a broad range of applications, spanning from food packaging to medical devices, electronics, and the construction industry.[1–3] To achieve this spectrum of applications, various organic, metal organic, and inorganic additives, such as stabilizers, fillers, pigments, and many others, are added to the polymers.[4,5] The quantification of these components in plastics is essential for quality control,[6,7] regulatory compliance,[8–10] recycling,[11] material sciences, and microplastic analysis.[12–14] For the identification and quantification of the elemental composition, plasma-based techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) are widely employed for solid samples following complete digestion.[15–19]

Numerous methods reported in the literature for element quantification in polymers rely on the decomposition of the polymer matrix by applying microwave-assisted acid digestion. Commonly, acid combinations such as nitric acid (HNO_3) with hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), or sulfuric acid (H_2SO_4) are employed (Table 1). These combinations are used to ensure the complete oxidation of the organic constituents. However, these acid mixtures are often insufficient to completely dissolve oxide-based pigments and other inorganic compounds commonly employed in polymers, such as ZnO, Fe_2O_3, Cr_2O_3, or TiO_2, which is additionally coated with SiO_2, Al_2O_3, or ZrO_2 for some applications.[4,5,20,21] The limitations of current digestion methods with respect to such refractory oxides manifest in several ways:

- Methods were developed and validated without explicitly including refractory oxides;[22–29]
- Residues after digestion have been reported to contain Ti and, in one case, Si, indicating incomplete digestion of these oxides;[24,26,27,30–32]

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Table 1 Overview of common digestion methods for polymers

Author	Polymers	Reagents for digestion	Reference material	Effectiveness against refractory oxides
Fordham *et al.*[22]	PE, PP, PET, PS	HNO_3/H_2SO_4 (initial charring) then HNO_3	—	No discussion of refractory oxides
Diemer and Heumann[25]	PE, PP	HNO_3/HF	—	The method was applied for Zr metallocene catalysts; no recovery rates were reported
Ernst *et al.*[23]	PE, PS, ABS, PC	H_2SO_4 (initial charring) then HNO_3 or H_2O_2 $HNO_3/HBF_4/H_2O_2/H_2O$	VDA 001-004	For samples with a higher filler content, complete digestion was reported; no values were provided for the corresponding elements
Skrzydlewska and Balcerzak[30]	PE, PP	HNO_3/H_2O_2	BCR-681	Undissolved TiO_2 was filtered off. Reference material did not contain refractory oxides
Sakurai *et al.*[31]	PE, PVC	HNO_3	BCR-680	White precipitate containing Ti and Si was observed after the digestion of PE
		HNO_3/H_2SO_4	BCR-680 BCR-681	Clear solutions were obtained; no refractory oxides were analyzed
Dimitrakakis *et al.*[24]	Waste electrical and electronic equipment plastics	HNO_3/H_2O_2	—	Sample solutions were filtered after digestion; no refractory oxides were analyzed
Pereira *et al.*[28]	PA66, PP, PET PE, PS, PEEK	HNO_3/HCl HNO_3	—	Although concentrations of Ti are presented, no evidence of the complete digestion of refractory oxides has been provided
Mello *et al.*[35]	Plastic components of a keyboard	HNO_3 HNO_3/HCl $HNO_3/H_2O_2/H_2SO_4$	ERM®-EC680k	The recovery for Cr in the reference material was 85%; digestion was performed with HNO_3/HCl
Imhof *et al.*[49]	Microparticles of PE, PP, and PS	$HNO_3/H_2O_2/H_2SO_4$	—	Although concentrations of Ti (presumably from TiO_2) are discussed, no evidence of the complete digestion of refractory oxides has been provided
Pereira *et al.*[26]	PVC	HNO_3	—	After digestion, a white, Ti-containing precipitate was observed
Lehtimäki and Väisänen[36]	PE, PP, PVC, ABS	HNO_3/H_2O_2	ERM®-EC681k NMIJ 8123-a NMIJ 8133-a BAM-H010	Diluting the ERM-EC681k sample after digestion resulted in a white suspension. The recovery rates of Sn and Cr were 57% and 46%, respectively. The recovery rate of Cr in BAM-H010 was 3%
Restivo *et al.*[34]	PE, PVC	HNO_3	ERM®-EC680k ERM®-EC681k	No refractory oxide analyzed
Kühn *et al.*[29]	Plastic waste, mainly PE and PP	HNO_3 HNO_3/HF	—	Ti concentrations are given for the digestion method that only used HNO_3, however, no evidence of complete digestion has been provided
Acosta-Coley *et al.*[12]	Microparticles, mainly PE and PP	HNO_3/HF	—	No discussion of refractory oxides
Hildebrandt *et al.*[37]	PE, PP, PVC, ABS	(1) HNO_3/HCl (2) HNO_3 (3) $HNO_3/HCl/H_2O_2$ (4) HNO_3/H_2O_2 (5) HNO_3/HBF_4	BAM-H010 ERM®-EC680m ERM®-EC681m NMIJ 8123-a NMIJ 8133-a PP CRM lead in Plastic-QC	The recovery rate of Cr in BAM-H010 varies significantly depending on the digestion temperature and the acid mixture used Digest. temp / Recovery Cr / Reagents 300 °C / 102–110% / 1–4 260 °C / 71% / 1 260 °C / 93% / 2 260 °C / 90% / 4 260 °C / 65% / 5 230 °C / 0.3% / 1
Klöckner *et al.*[33]	PP, PE, PVC, PET, SAN, PS, EPS, PUR, rubber	HNO_3/H_2O_2/HCl	ERM®-EC680m ERM®-EC681m	No discussion of refractory oxides
Klingenberg *et al.*[27]	PP	Dry ashing followed by HNO_3/HCl	—	After digestion, the solutions were centrifuged. Although concentrations of Ti (presumably from TiO_2) are discussed, no evidence of the complete digestion of refractory oxides has been provided
Poirier *et al.*[32]	Plastic waste	HNO_3/H_2O_2	—	After digestion, a white powdery residue containing Ti and Si was filtered off

• Many procedures rely on CRMs that either do not contain refractory oxides[23,30,31,33] or in which elements present as oxides were not targeted in the method evaluation;[34]

• They exhibit reduced recoveries for Cr when Cr_2O_3, is present.[35–37]

In particular, for ERM®-EC681k, ERM®-EC680k, and BAM-H010, which contain Cr introduced by Cr_2O_3, the certification reports themselves note that complete dissolution by acid digestion is highly challenging, and published methods confirm incomplete Cr recovery. Collectively, these observations show that many established protocols either do not consider refractory oxides, demonstrably leave residues containing such phases, or lack evidence that refractory oxide additives are fully brought into solution.

For the digestion of the comparably stable compounds, such as TiO_2, Al_2O_3, or ZrO_2, the addition of hydrofluoric acid (HF) is commonly required.[25] However, the use of HF introduces several drawbacks: its high acute toxicity and corrosiveness necessitate strict safety precautions[38] and HF-resistant sample introduction systems; excess fluoride can precipitate elements such as Al, Ba, Ca, Fe, Mg, and Sr as insoluble fluorides,[39,40] leading to lower recoveries and potential co-precipitation of other analytes such as rare earth elements.[41] A second processing step with boric acid (H_3BO_3) is therefore often employed to complex residual fluoride, but this increases the risk of contamination, may introduce additional spectral or matrix interferences in ICP-MS, and can require further dilution.[40,42]

Tetrafluoroboric acid (HBF_4) has been proposed as an alternative that provides F^- and boric acid upon hydrolysis, thereby enabling the dissolution of refractory oxides while simultaneously complexing excess fluoride.[43–45] HBF_4 has been successfully applied for the digestion of peat and plant samples,[46] soils and sediments,[47,48] and two reports describe the use for polymer digestion.[23,37] However, both polymer applications exhibit limitations.

Ernst *et al.*[23] combined HNO_3, H_2O_2, and HBF_4 in a power-controlled microwave program for waste plastics from electrotechnical applications and reported "complete digestion" for samples with elevated filler contents. Yet, the fillers and pigments present were not chemically characterized, and potential refractory oxides were neither explicitly identified nor quantified in the method evaluation. Consequently, it remains unclear whether the method effectively digests and quantitatively recovers typical refractory oxide additives. Hildebrandt *et al.*[37] compared a mixture of HNO_3 and HBF_4 with other acid mixtures using the CRM BAM-H010. At a digestion temperature of 260 °C, Cr recovery with HNO_3/HBF_4 was about 65%, while Pb introduced as stearate was not detected with the HBF_4-containing method. In contrast, quantitative Cr recovery was reported at 300 °C using HNO_3 alone. However, this protocol relies on digestion temperatures that are not accessible with all commonly used microwave systems, and it was not tested on real-world technical polymers with high pigment loadings (*e.g.*, TiO_2).

The aim of the present study is therefore not simply to introduce HBF_4 as an alternative fluoride source, but to develop and validate a temperature-controlled, microwave-assisted digestion protocol that explicitly targets refractory oxides in technical polymers. Method development is based on an in-house PE-based standard material spiked with a variety of oxide additives, as well as a commercial PVC compound with high filler and pigment loadings. This choice was necessary because available CRMs either contain no refractory oxides or include only Cr_2O_3, for which complete dissolution by acid digestion is known to be highly challenging, as discussed above. The use of these tailored materials, therefore, allows systematic evaluation of the digestion performance for a broader range of refractory oxides under realistic conditions. The performance of the digestions utilizing HBF_4 is compared directly to conventional HF-based digestion with respect to digestion completeness and recoveries for both major and trace elements. The general applicability of the procedure was further assessed using additional polymers, namely polycarbonate (PC) and acrylonitrile–butadiene–styrene (ABS), each containing refractory oxides. In addition, the accuracy and precision of the method were confirmed by analysis of the polymer CRM ERM®-EC681k, thereby providing a broadly applicable HBF_4-based digestion method for comprehensive elemental characterization of technical polymers and microplastics, including their refractory oxide additives.

2. Experimental

Method development studies were carried out collaboratively at the FH Münster and TU Hamburg. At the TU Hamburg, digestions were performed employing an established HF-containing acid mixture, providing a benchmark for complete digestion and quantitative recovery of elements, including those present as refractory oxides. At FH Münster, corresponding experiments were conducted using HBF_4-containing acid mixtures. These investigations systematically examined the influence of key process parameters, including digestion time and acid volume, on digestion efficiency.

2.1. Samples

A PE and a PVC sample were used for method development. The PE sample, a standard material produced in-house, was manufactured using high-density polyethylene (HDPE) powder (Eltex® A4040P, Ineos Olefins & Polymers, Cologne, Germany). This powder was mixed with PE-based master-batches containing various oxides (Al_2O_3, CaO, MgO, TiO_2, ZnO, and ZrO_2). The mixture was homogenized by extrusion (COLLIN TEACH LINE® ZK 25T, COLLIN Lab & Pilot Solutions, Maitenbeth, Germany) and processed into granules (COLLIN TEACH LINE® CSG 171T, COLLIN Lab & Pilot Solutions, Maitenbeth, Germany).

The PVC sample is a commercial compound in powder form, utilized for applications such as profile manufacturing. The powder contains various stabilizers based on Ca and Zn soaps and co-stabilizers that contain Al and Mg. The product is pigmented with TiO_2 (rutile), which is coated with Al_2O_3 and SiO_2. $CaCO_3$ is included in higher concentrations as filler.

The PE granulate was cryo-milled using liquid nitrogen and an ultra-centrifugal mill (ZM 200, Retsch, Haan, Germany) equipped with a 0.5 mm sieve. The PVC powder was not further ground.

The additive-free PE and a PVC powder (PVC S 67-04, Shin-Etsu PVC B.V., Hilversum, Netherlands) were also employed for preliminary tests to determine the required decomposition temperature.

For method verification, the CRM ERM®-EC681k (PE) was digested using the developed procedure without further sample preparation. To evaluate the general applicability of the method to other polymer types, a PC masterbatch granulate containing Al_2O_3 and an ABS masterbatch granulate containing Al_2O_3, $BaCO_3$, CdO, and ZnO were also digested with the optimized protocol. Reference values for the elemental concentrations in the PC and ABS materials were available from neutron activation analysis (NAA), allowing an independent comparison of recoveries. NAA was performed at the Helmholtz-Zentrum Berlin (Germany) using the BERII research reactor.

2.2. Instrumentation

2.2.1. TU Hamburg. A Multiwave 7000 (Anton Paar, Graz, Austria) microwave digestion system equipped with a magnetic stirring unit was used. The system allows digestions at temperatures up to 300 °C. The samples were weighed in TFM vessels with an internal volume of 10 mL.

An ICP-OES (Avio 550 Max, PerkinElmer) was employed to determine concentrations of the main elements Al, Ca, Mg, Ti, and Zn. Zr was determined using ICP-MS (ICP-MS 350D, PerkinElmer) in helium collision mode. The ICP settings are listed in the SI.

2.2.2. FH Münster. A Multiwave PRO (Anton Paar, Graz, Austria) microwave sample preparation system was employed for sample digestion. The system was equipped with a magnetic stirring unit and a 24-position rotor for TFM vessels with an internal volume of 50 mL (HVT50). Microwave power was 1000 W with a temperature limit of 205 °C when using HNO_3 and H_2O_2 or 185 °C for all digestions containing HBF_4. The microwave system was operated in temperature-controlled mode.

An ICP-MS (Agilent 8900, Agilent Technologies, Tokyo, Japan) coupled to an SPS 4 autosampler (Agilent Technologies, Tokyo, Japan) was used in the helium collision mode for the determination of element concentrations. ICP-MS instrument settings are listed in the SI.

2.3. Reagents and standards

2.3.1. TU Hamburg. All solutions and element standards were diluted with ultrapure water (18,2 MΩ cm, Milli-Q®, Merck, Darmstadt, Germany). For sample digestion, purified (Savillex DST 1000 subboiling systems) nitric acid (14 mol L^{-1}, VWR, Leuven, Belgium) was used. Hydrogen peroxide (Suprapur®, 30%, Merck, Darmstadt, Germany), hydrofluoric acid (Suprapur®, 40%, Merck, Darmstadt, Germany), and 40 g L^{-1} boric acid (Suprapur®, 99.9999%, Merck, Darmstadt, Germany) were employed for the digestions without further purification. Calibration solutions were prepared using 1 g L^{-1} single-element stock solutions (Cetripur®, Merck, Darmstadt, Germany).

2.3.2. FH Münster. Ultrapure water (18.2 MΩ cm, Arium Pro, Sartorius, Goettingen, Germany) was used for dilution and preparation of all standards and solutions. High-purity concentrated nitric acid (Suprapur®, 65%, Merck, Darmstadt, Germany), hydrogen peroxide (Suprapur®, 30%, Merck, Darmstadt, Germany), and tetrafluoroboric acid (ultra-pure, 38%, Chem-Lab, Zedelgem, Belgium) were utilized for the digestions. Multi element stock standard solution (Multi-element calibration standard IV for ICP, ARISTAR®, VWR Chemicals, Leuven, Belgium) as well as Ca (TraceCERT®, Sigma-Aldrich, Buchs, Switzerland), Ti, and Zr (both Cetripur®, Merck, Darmstadt, Germany) solutions containing 1 g L^{-1} of each element were employed to prepare calibration solutions.

2.4. Digestion procedures

For each digestion, 50 mg sample material was weighed into TFM digestion vessels, and PTFE-coated magnetic stir bars were added. In all digestion programs, the stirring speed was set to the maximum to ensure efficient mixing of the lightweight polymer particles with the acid mixture and to prevent adhesion or melting of the material on the vessel walls. The final digests were filtered (filter circles type 1025, particle retention 2–3 μm, Th. Geyer, Renningen, Germany), and diluted to a final volume of 50 mL. Prior to ICP analysis, aliquots were further diluted with ultrapure water as required. The specific acid mixtures and temperature programs used for each digestion protocol are summarized in Fig. 1.

2.4.1. HF-based digestions. As the polymer samples used in this study (the in-house PE standard material and the commercial PVC compound) are not CRMs, reference values for their elemental compositions had to be established independently. For this purpose, two HF-based digestion procedures were performed at TU Hamburg. In the first procedure, digestion was carried out with an acid mixture containing 4 mL HNO_3, 1 mL H_2O_2, and 0.5 mL HF without subsequent fluoride complexation. The samples were heated to 220 °C within 15 min, and this temperature was maintained for 60 min. In the second procedure, an additional complexation step with 5 mL H_3BO_3 was applied after digestion. The samples were heated within 10 min to 150 °C and maintained at this temperature for 15 min.

2.4.2. Fluoride-free digestions. Digestion experiments were performed without the addition of a fluoride source, using HNO_3 and H_2O_2, in order to assess whether refractory oxides can be dissolved under the maximum applicable digestion temperature of 200 °C, and to determine the minimum temperature required for complete decomposition of the polymer matrices prior to introducing HBF_4 into the method.

For the technical polymer samples containing oxide additives (PE and PVC), a digestion procedure with 4 mL HNO_3 and 1 mL H_2O_2 was applied, in which the temperature was ramped to 200 °C within 15 min and then held for 75 min.

In parallel, additive-free PE and PVC powders were digested under comparable conditions to determine the temperature required for the decomposition of the polymer matrices. For these experiments, 4 mL HNO_3 and 1 mL H_2O_2 were added to the samples. Three different maximum temperatures (180 °C,

190 °C, and 200 °C) were tested, each with a ramp time of 15 min and a hold time of 75 min.

These fluoride-free tests provided the basis for defining suitable temperature limits and designing a two-step digestion protocol involving HBF_4, taking into account the "SmartVent Technology" of the digestion vessels.

2.4.3. Method development of a two-step HBF_4-based digestion protocol. The HBF_4-based digestion protocol was developed as a two-step procedure. In step 1, the polymer matrix is decomposed with HNO_3 and H_2O_2 at 200 °C; in step 2, refractory oxides are dissolved after the addition of HBF_4 at a reduced maximum temperature. First, the holding times of step 1 and step 2 were varied while keeping the acid composition constant (4 mL HNO_3, 1 mL H_2O_2 in step 1; 4 mL HBF_4 in step 2). For both PE and PVC, three different holding times were investigated in step 1 (120 min, 90 min, and 75 min) and two in step 2 (45 min and 30 min), as summarized in Table 2.

In the subsequent stage of the method development, the volume of HBF_4 in step 2 was reduced in order to minimize polyatomic interferences and to prevent excessive sample dilution resulting from an elevated acid concentration, while maintaining the same amounts of HNO_3 and H_2O_2 in step 1. In step 2, HBF_4 volumes of 2 mL and 1 mL were evaluated (No. 5 and 6 in Table 2).

2.4.4. Digestion of ERM®-EC681k and application to other polymer types. For the assessment of accuracy and broader applicability, the optimized HBF_4-based protocol was applied to the certified reference material ERM®EC-681k and to the two additional technical polymer samples (PC and ABS masterbatches containing refractory oxides). For each material, digestions were carried out under the same conditions as defined for method no. 6 (Table 2), and the resulting solutions were analyzed by ICP-MS. For the CRM, measured concentrations were compared with the certified values. For the PC and ABS samples, results were evaluated against independently determined reference values obtained by NAA.

2.5. Data processing and method detection limits

2.5.1. Two-sample *t*-test for HF-based digestions. Statistical analysis was performed to compare mean concentrations from the reference methods at TU Hamburg. Outliers were identified using the Grubbs test ($\alpha = 0.05$) and excluded. Equality of variances was tested using the *F*-test ($\alpha = 0.01$). The two-sample *t*-test[50] ($\alpha = 0.01$) was used when equal variances were present. Welch's *t*-test[50] ($\alpha = 0.01$, df = 5) was applied to Ca data from the PE sample, which exhibited unequal variances.

2.5.2. Outlier analysis and confidence interval. Outlier analysis was performed using Dixon's *Q* test (Q_{crit}, $\alpha = 0.01$; $n = 6$). Error bars shown in the subsequent figures represent the confidence intervals of the mean values. These intervals were calculated according to DIN 62632 (ref. 51) applying the equation $CI = \bar{x} \pm t \times s/\sqrt{n}$ where t is the Student's t value ($\alpha = 0.05$, df $= n - 1$), s is the standard deviation, n is the number of digested samples, and $\bar{x}$ is the mean value.

2.5.3. Limits of detection and limits of quantification. Limits of detection (LOD) and limits of quantification (LOQ) were determined using 4 mL of HNO_3, 1 mL of H_2O_2, and 1 mL of HBF_4, following the digestion procedure described in Table 2, method no. 6. Solutions were prepared in the same manner as the analytical samples and subsequently analyzed. The calculation was carried out according to DIN 32645,[52] applying the following equations:

$$x_{LOD} = \Phi_{n;\alpha} \times \frac{s_B}{b} = 3 \times \frac{s_B}{b} \quad (1)$$

$$x_{LOQ} = k \times \Phi_{n;\frac{\alpha}{2}} \times \frac{s_B}{b} = 10 \times \frac{s_B}{b} \quad (2)$$

where Φ is a factor with n number of blank measurements ($n = 10$) and α the level of significance ($\alpha = 0.01$), s_B is the standard deviation of the blank measurements and b is the slope of the calibration curve; $k = 3$.

3. Results and discussion

3.1. HF-based digestions

Reference data for the PE and PVC samples were obtained using two independent HF-based digestion procedures. Both methods employed an $HNO_3/H_2O_2/HF$ mixture, with one including an additional post-digestion complexation step with H_3BO_3. The elemental mass fractions of Al, Ca, Mg, Ti, Zn (ICP-OES), and Zr (ICP-MS) determined for the samples are presented in Fig. 2.

The elemental mass fractions in the in-house produced PE sample span three concentration levels: a low level of 85 mg kg^{-1} for Zr, medium levels of approximately 650 mg kg^{-1} for Al and Ti, and high levels of around 3000 mg kg^{-1} for Ca, Mg, and Zn. In the commercial PVC compound, concentrations cover an even wider range. The lowest levels were measured for Zn (600 mg kg^{-1}) and Al (700 mg kg^{-1}), Mg showed an intermediate

Table 2 Microwave programs and HBF_4 volumes for the two-step digestion protocol

	Step 1			Step 2			
No.	Temp. (°C)	Ramp. (min)	Hold (min)	Temp. (°C)	Ramp. (min)	Hold (min)	HBF_4 volume (mL)
1	200	15	120	180	10	45	4
2			90			45	4
3			75			45	4
4			75			30	4
5			75			30	2
6			75			30	1

Table 3 Mean elemental mass fractions in PE and PVC applying HF-based digestions

	Mean mass fraction (mg kg^{-1}) ($n = 12$)	
Element	PE	PVC
Al	643.2 ± 46.6	720.8 ± 48.8
Ca	3069.0 ± 10.2[a]	37988.4 ± 929.9[b]
Mg	2857.4 ± 88.5	1919.8 ± 73.5
Ti	662.1 ± 20.3	15420.5 ± 346.4
Zn	3008.1 ± 79.5	619.9 ± 27.2
Zr	84.8 ± 1.1[c]	—

[a] $n = 5$. [b] $n = 11$. [c] $n = 8$.

concentration of about 2000 mg kg^{-1}, while very high concentrations were detected for Ti (15 g kg^{-1}, as TiO_2 pigment) and Ca (38 g kg^{-1}, as $CaCO_3$ filler). Thus, the two polymer samples together cover a broad and analytically relevant range of mass fractions, including the elements present as refractory oxides (Al_2O_3, TiO_2, ZrO_2).

Because the HF-based digestions were carried out both with and without a post-digestion complexation step using H_3BO_3, the resulting datasets were systematically compared to identify any statistically significant differences before defining reference values. For each element and matrix, outliers were first identified using the Grubbs test and removed (one outlier for Ca in PE with complexation and one for Ca in PVC without complexation). Homogeneity of variances between the two HF methods was then assessed; equal variances were found for all comparisons except Ca in PE. Accordingly, a two-sample *t*-test assuming equal variance was applied in all other cases, while Welch's *t*-test was used for Ca in PE.

For all elements except Ca in the PE sample, no statistically significant differences were observed between the HF digestion with and without H_3BO_3 complexation. In these cases, both datasets were therefore considered equivalent and were combined, and the mean of all valid measurements from both HF procedures was used to establish the reference mass fraction (Table 3).

For Ca in PE, Welch's *t*-test revealed a statistically significant difference between the two HF protocols. In this case, only the results obtained with the HF workflow, including the boric acid complexation, were used to define the reference value. The lower Ca mass fraction observed in the digestion without complexation is consistent with the formation of insoluble CaF_2 in HF media, which is known to be re-dissolved by complexation with boric acid. For the PVC sample, no significant difference between the two HF protocols was observed for Ca, possibly due to different solution equilibria in the presence of high chloride concentrations.

3.2. Fluoride-free digestions

To assess the performance of oxidizing acid mixture without fluoride and to define boundary conditions for later HBF_4-based digestions, two sets of experiments were carried out: digestion of technical polymers containing oxide additives and digestion of additive-free polymers.

When technical PE and PVC were digested with HNO_3 and H_2O_2 at 200 °C, the recoveries of Ca, Mg, and Zn in both matrices, and for Al in PVC, are in good agreement with the reference values (Fig. 3). This behaviour is consistent with the chemical properties of the substances employed. In the PE sample, Ca, Mg, and Zn were introduced as oxides. In the PVC sample, the elements originate from Ca and Zn soaps, as well as $Mg(OH)_2$ and hydrotalcite. All these species are readily soluble in concentrated nitric acid. In contrast, recoveries of Al and Zr in PE and of Ti in both PE and PVC are low, reflecting the fact that these elements were introduced as refractory oxides (Al_2O_3, TiO_2, ZrO_2). At the maximum applicable digestion temperature of 200 °C, these oxides could not be brought fully into solution in the absence of a fluoride source, demonstrating that

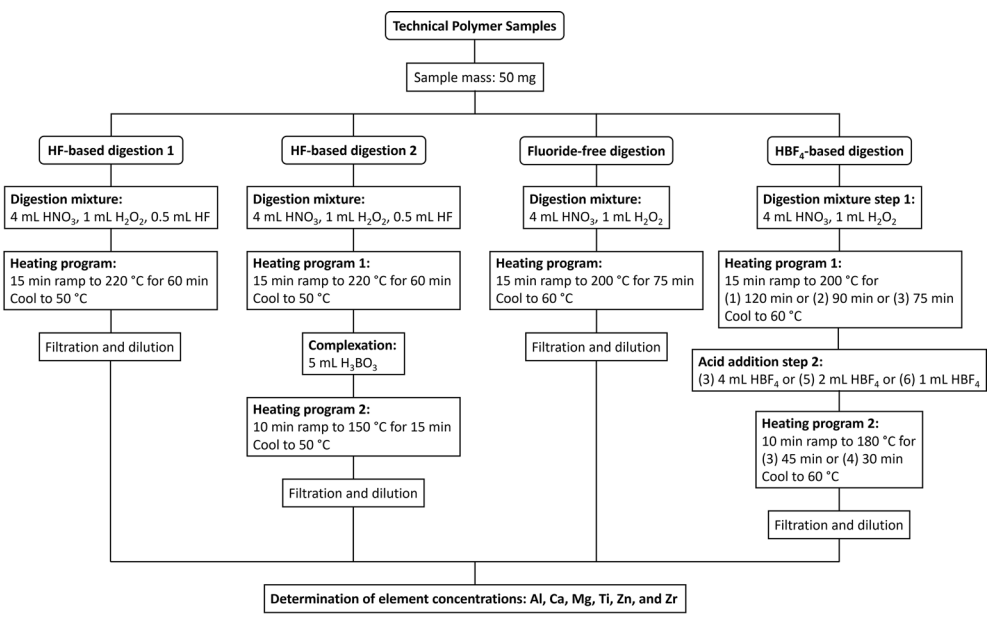

Fig. 1 Experimental conditions studied in this work for the digestion of technical polymers.

oxidizing acids alone are insufficient for quantitative digestion of the refractory oxide fraction.

To determine the minimum temperature required for the decomposition of the polymer matrices, additive-free PE and PVC powders were digested with the same HNO_3/H_2O_2 mixture at 180 °C, 190 °C, and 200 °C. At 180 °C and 190 °C, visible residues of polymer remained on the vessel walls for both materials. The residuals were weighed, yielding masses between 4 and 12 mg, which corresponds to approximately 8–23% of the original sample mass and suggests incomplete decomposition at these temperatures. Complete, residue-free digestion of the polymer matrix was attained at 200 °C for both samples.

These observations must be considered in the context of the digestion hardware. The vessels utilized in this study are equipped with the "SmartVent Technology", which vents automatically at elevated internal pressure. Venting, however, can lead to analyte and acid loss. Since the addition of HBF_4 in a closed vessel increases the pressure at elevated temperatures, the maximum operating temperature in the presence of HBF_4 had to be limited to 180 °C to avoid triggering the venting mechanism. The fluoride-free experiments, therefore, establish two critical constraints for the method development: refractory oxides cannot be quantitatively digested at 200 °C without a fluoride source, and complete decomposition of the polymer matrices requires 200 °C in an HNO_3/H_2O_2 medium, whereas the HBF_4-assisted dissolution of refractory oxides must be conducted at ≤180 °C to remain within the safe operating range of the "SmartVent" vessels. These findings were decisive for the development of a two-step digestion protocol, with matrix decomposition at 200 °C followed by the HBF_4-assisted dissolution of refractory oxides at 180 °C.

3.3. Method development of a two-step HBF_4-based digestion protocol

3.3.1. Variation of holding time in the first digestion step. Fig. 4 summarizes the elemental recoveries obtained for PE and PVC when the holding time in step 1 (200 °C, HNO_3/H_2O_2) was varied (120, 90, and 75 min), while step 2 was kept constant.

At 120 min, recoveries in PE for Ti, Zn, and Zr were between 90–97%, whereas Al, Ca, and Mg were lower (77–88%). Reducing the holding time to 90 min improved the accuracy, with recoveries between 95–103% for all elements. At 75 min, recoveries remained close to quantitative for most analytes, and the confidence intervals were markedly smaller (typically 1–3%), indicating improved precision. Only the recovery of Mg decreased slightly (88%), but within a narrow confidence interval (1.4%).

For PVC with a holding time of 120 min, Ca and Ti agreed reasonably with the reference values, but Al, Mg, and Zn exhibited larger deviations. At 90 min, Ca, Mg, Ti, and Zn lay close to the reference values (91–105%), but Al was slightly low (86%). At 75 min, most elements again remained within the range of 91–108%, only Ca showed a somewhat lower recovery (84%). However, when precision is also considered, the 75-min holding time yields improved confidence intervals for four out of the five elements compared to 90 min.

Overall, the 75-min holding time in step 1 provides the best compromise between accuracy and precision across both polymer matrices. It yields near-quantitative recoveries for all oxide-related elements with consistently small confidence intervals, while avoiding the overestimation and higher scatter observed at longer holding times. Consequently, 75 min at 200 °C was selected as the optimal step-1 holding time for the final two-step digestion protocol.

3.3.2. Variation of holding time in the second digestion step. The effect of the holding time in step 2 (180 °C, HBF_4) was evaluated using the optimized step-1 conditions. Holding times of 45 and 30 min were compared (Fig. 5).

Reducing the hold time from 45 to 30 min led to pronounced decreases in recoveries for Ca, Mg, and Al in the PE sample. Ca dropped to 51%, and Al and Mg fell below 82%. In PVC, the recovery of Al also decreased at 30 min, while the remaining elements were largely unaffected. The lowest recoveries were observed for elements known to form sparingly soluble

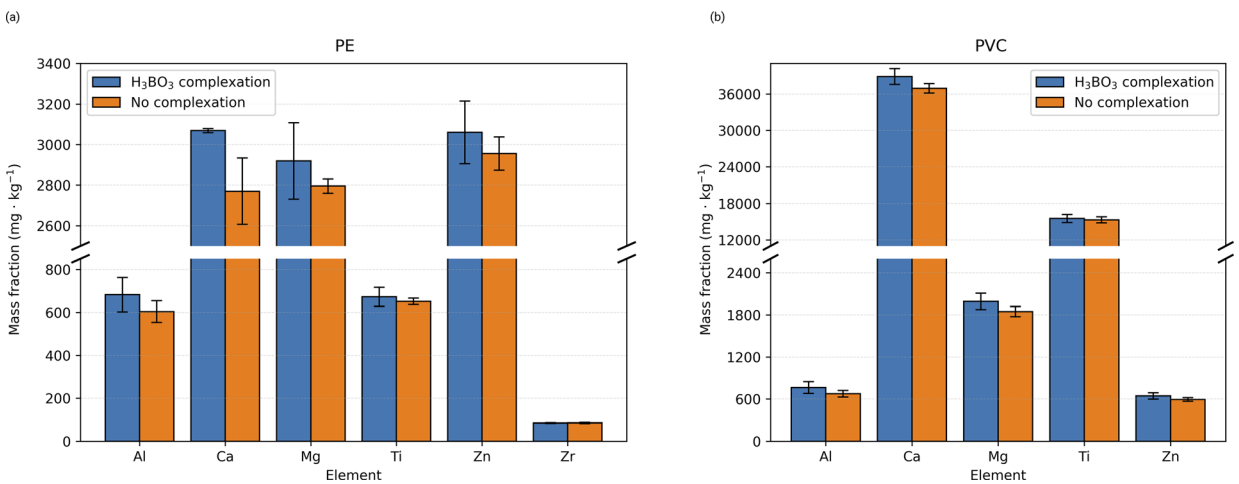

Fig. 2 Mass fractions of Al, Ca, Mg, Ti, Zn, and Zr in (a) PE and (b) PVC after digestion using HF with boric acid complexation and without complexation; error bars represent confidence intervals ($n = 5$ for Ca in PE with H_3BO_3 complexation; $n = 4$ for Zr in PE with both methods; $n = 5$ for Ca without complexation; $n = 6$ for all other elements).

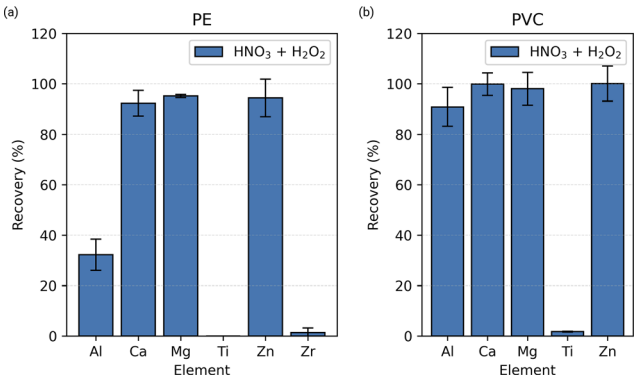

Fig. 3 Recovery of elements from (a) PE and (b) PVC using HNO_3 and H_2O_2 for digestion at 200 °C; error bars represent confidence intervals. Ti concentration in PE was below the detection limit ($n = 4$ for Zr in PE; $n = 6$ for all other elements).

fluorides. The higher recoveries of Al and especially Ca in PVC compared to PE can be attributed to the evolution of HCl during PVC decomposition, which may shift the solubility equilibrium of fluoride salts (*e.g.*, CaF_2) toward the dissolved state according to the reaction

$$CaF_{2(s)} + 2H_{(aq)}^{+} \rightleftharpoons Ca_{(aq)}^{2+} + 2HF_{(aq)}$$

by altering the complexation and pH value in the digestion medium.[53]

The sensitivity of Al, Ca, and Mg recoveries to the holding time in step 2 is likely linked to the hydrolysis behaviour of HBF_4. HBF_4 is known to hydrolyse stepwise *via* fluoro-hydroxyborate species, as illustrated by the following equation:

$$BF_4^- + nH_2O \rightleftharpoons [BF_{(4-n)}(OH)_n]^- + nHF$$

with $1 \leq n \leq 4$. The first hydrolysis step is reported to be comparatively slow, whereas the subsequent steps proceed rapidly and reversibly.[43,54] Shortening the holding time reduces the time available for these hydrolysis processes to reach a state in which free F^- is sufficiently bound and potentially precipitated fluorides can be redissolved or prevented from forming.

Taken together, these results indicate that a holding time of 45 min at 180 °C in step 2 is required to obtain robust recoveries for elements prone to fluoride precipitation while ensuring complete dissolution of refractory oxides. This condition was therefore selected for further optimization.

3.3.3. Variation of HBF_4 volume. In the final stage of method development, the volume of HBF_4 was reduced while applying the optimized holding times for steps 1 and 2. HBF_4 volumes of 4, 2, and 1 mL were compared. The aim was to minimize the acid load and potential polyatomic interferences (*e.g.*, $^{11}B^{16}O^+$, $^{10}B^{37}Cl^+$, or $^{11}B^{36}Ar^+$) while maintaining digestion efficiency.

As shown in Fig. 6, decreasing the HBF_4 volume to 1 mL still yielded quantitative recoveries for the refractory oxides. For both PE and PVC, recoveries of Al, Ti, and Zr remained in the range 99–108%. Importantly, no statistically significant changes in recovery were observed for the other elements with reduced HBF_4 volume, indicating that the digestion efficiency for these components remains unaffected under these modified conditions.

Based on these results, the final HBF_4-based protocol was defined with 4 mL HNO_3 and 1 mL H_2O_2 in step 1, followed by 1 mL HBF_4 in step 2, with holding times of 75 min at 200 °C and 45 min at 180 °C, respectively (method no. 6, Table 2).

Table 4 Comparison of relative standard deviations in PE and PVC following HF and optimized HBF_4-based digestions as a measure of precision

	RSD for PE (%)			RSD for PVC (%)		
Analytes	HF-based		HBF_4-based	HF-based		HBF_4-based
Al	11.2[a]	7.9[b]	2.8	10.4[a]	6.6[b]	2.3
Ca	0.3[a]	5.6[b]	1.9	3.1[a]	1.7[b]	6.4
Mg	6.2[a]	1.2[b]	0.5	5.5[a]	3.7[b]	7.6
Ti	6.2[a]	2.2[b]	1.5	4.1[a]	3.1[b]	2.9
Zn	4.8[a]	2.6[b]	1.3	6.8[a]	4.2[b]	4.7
Zr	1.3[a]	2.0[b]	1.9	—	—	—

[a] HF-based digestion with H_3BO_3 complexation. [b] HF-based digestion without H_3BO_3 complexation.

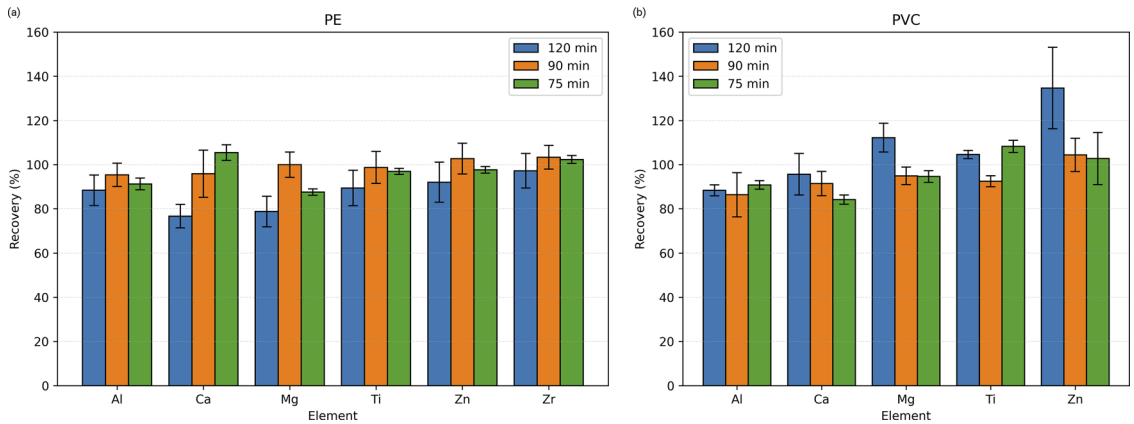

Fig. 4 Recovery of elements from (a) PE and (b) PVC with holding times of 120, 90, and 75 minutes in the first digestion step; error bars represent confidence intervals ($n = 5$ for Zr in PE for 75 min and Ti in PVC for 90 min; $n = 6$ for all other elements).

3.3.4. Precision of HBF_4-based *versus* HF-based digestions. The precision of the optimized HBF_4-based method was compared with that of the two HF-based procedures used to establish reference values. Table 4 summarizes relative standard deviations (RSDs) for both polymer matrices.

For the PE sample, the HBF_4-based digestion generally provided equal or better precision than either HF-based protocol. RSDs for the HBF_4 method were between 0.5–2.8%, compared with ranges of 0.3–11.2% for the HF-based digestions. In particular, the precision for Al, Mg, Ti, and Zn was improved with HBF_4 relative to at least one of the HF workflows.

For the PVC sample, the HBF_4 method exhibits lower RSDs than both HF digestions for Al (2.3% *vs.* 10.4/6.6%) and Ti (2.9% *vs.* 4.1/3.1%), and comparable precision for Zn (4.7% *vs.* 6.8/4.2%). For Ca and Mg, the HF-based methods yielded somewhat lower RSDs (Ca: 3.1/1.7% *vs.* 6.4%; Mg: 5.5/3.7% *vs.* 7.6%), although the HBF_4 precision for these elements remains reasonable for routine quantitative work. Overall, the HBF_4-based protocol provides precision that is at least comparable to, and in several cases better than, the established HF workflows.

3.4. Digestion of ERM®-EC681k and application to other polymer types

The optimized two-step HBF_4-based digestion procedure (method No. 6) was first evaluated using the polyethylene CRM ERM®-EC681k. As shown in Table 5, the measured mass fractions for Cd, Pb, and Zn were close to the certified values, with recoveries of 95.2%, 95.7%, and 91.6%, respectively. For Cr, the certified value (100 ± 5 mg kg^{-1}) represents the total Cr content, while the certification report additionally specifies a range for "acid-digestible Cr" (20–60 mg kg^{-1}), reflecting the known difficulty of completely dissolving Cr_2O_3 by acid digestion. Two HF-based procedures used during certification yielded 37.6 and 31.5 mg kg^{-1}, both below the total Cr content. The mass fraction obtained with the HBF_4-based method (27.9 ± 3.3 mg kg^{-1}) is also below the total certified value but lies within the acid-digestible Cr range. This demonstrates that, for Cr present as Cr_2O_3, the new protocol performs comparably to established HF workflows and achieves the expected level of "acid-digestible" recovery for this particularly challenging oxide form.

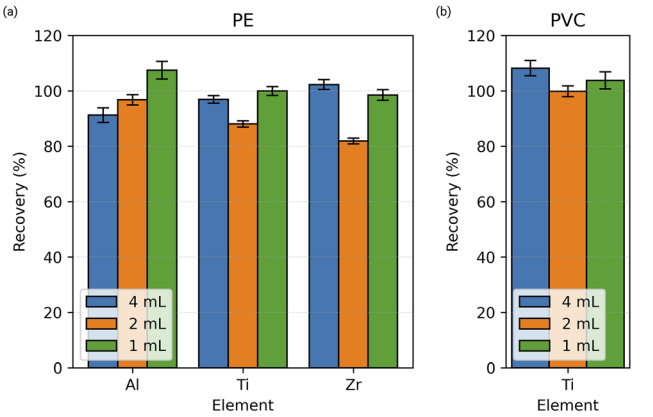

Fig. 6 Recovery of highly acid-resistant elements from (a) PE and (b) PVC with varying HBF_4 volume; error bars represent confidence intervals ($n = 5$ for Zr for 4 mL; $n = 6$ for all other elements).

Table 5 Determined element concentrations for ERM®-EC681k after optimized HBF_4-based digestion procedure

Analytes	Certified value (mg kg^{-1})	Measured value[b] (mg kg^{-1})	Recovery (%)
Cd	137 ± 4	130.4 ± 2.0	95.2
Cr	20–60[c]	27.9 ± 3.3	Within the given range
Pb	98 ± 6	93.8 ± 0.8	95.7
Zn	1.25 ± 0.07[a]	1.14 ± 0.06	91.6

[a] Indicative value in g kg^{-1}. [b] $n = 6$ for all elements. [c] Acid digestible.

Table 6 Determined element concentrations for ABS and PC after optimized HBF_4-based digestion procedure compared to NAA values

Polymer	Analytes	NAA values (mg kg^{-1})	Measured value[a] (mg kg^{-1})	Recovery (%)
ABS	Al	481 ± 34	493.7 ± 11.4	102.6
	Ba	460 ± 32	447.1 ± 3.1	97.2
	Cd	453 ± 32	403.6 ± 2.2	89.1
	Zn	447 ± 31	443.1 ± 9.5	99.1
PC	Al	2541 ± 252	2404.0 ± 55.2	94.6

[a] $n = 6$ for all elements.

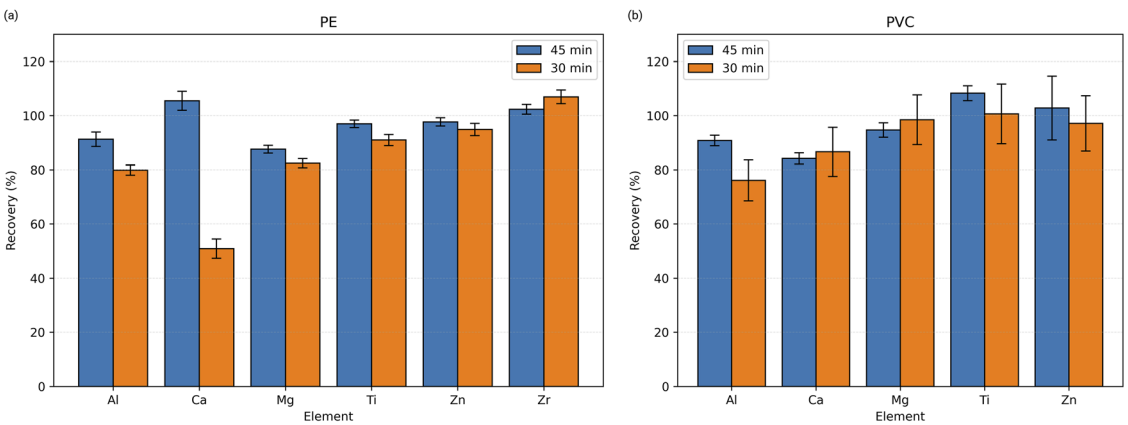

Fig. 5 Recovery of elements in (a) PE and (b) PVC with holding times of 45 and 30 minutes in the second digestion step; error bars represent confidence intervals ($n = 5$ for Ti in PVC for 45 min; $n = 6$ for all other elements).

Table 7 Limits of detection and limits of quantification for the optimized HBF_4-based digestion method

Analytes	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	Analytes	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
^{23}Na	3.9	12.8	^{59}Co	0.002	0.005
^{24}Mg	0.6	1.8	^{60}Ni	0.5	1.5
^{27}Al	1.1	3.6	^{63}Cu	0.5	1.5
^{39}K	8.9	29.6	^{66}Zn	2.5	8.4
^{44}Ca	13.4	44.8	^{88}Sr	0.01	0.05
^{47}Ti	0.1	0.3	^{90}Zr	0.01	0.05
^{52}Cr	0.06	0.19	^{111}Cd	0.004	0.013
^{55}Mn	0.03	0.08	^{137}Ba	0.02	0.07
^{56}Fe	1.8	5.9	^{208}Pb	0.03	0.10

To assess general applicability beyond PE and PVC, the optimized method was applied to an ABS masterbatch (containing Al_2O_3, $BaCO_3$, CdO, and ZnO) and a PC masterbatch (containing Al_2O_3). The results were compared with independently determined reference values from NAA (Table 6). For the ABS sample, recoveries were 102.6% (Al), 97.2% (Ba), and 99.1% (Zn), indicating good agreement with the NAA data. Only Cd showed a somewhat reduced recovery of 89.1%, while still remaining within a range acceptable for many practical applications. For the PC sample, Al was recovered at 94.6%, again in good agreement with the NAA value.

Unlike the PE and PVC materials used in method development, which were in powder form, the ABS and PC samples and the CRM were digested as granules with typical dimensions between 2.5 × 1.7 mm and 3.2 × 2.3 mm. The good agreement with the reference values across the granular samples indicates that the larger particle size did not negatively affect digestion efficiency under the optimized conditions. In practice, the main reason to reduce particle size for technical polymer products is often the sample homogeneity rather than the digestion efficiency itself.

Taken together, the results for ERM®-EC681k and for the ABS and PC masterbatches demonstrate that the optimized HBF_4-based digestion protocol provides reliable and broadly applicable quantitative data for a range of polymer types and additive systems, including those containing refractory oxides and elements subject to regulatory limits such as Cd and Pb.

3.5. Limits of detection and limits of quantification

LODs and LOQs were determined by ICP-MS using the final acid mixture (4 mL HNO_3, 1 mL H_2O_2, 1 mL HBF_4) and the complete digestion procedure (method no. 6, Table 2). The attained LODs and LOQs, summarized in Table 7, were calculated based on a sample mass of 50 mg and a dilution factor of 10, which was applied to compensate for the elevated acid concentrations.

The highest values were obtained for Ca, K, and Na (LODs between 13.4 and 3.9 mg kg^{-1}; LOQs between 44.8 and 12.8 mg kg^{-1}). These elements are often added as fillers, stabilizers, or processing aids and are typically present at elevated concentrations. Thus, the achieved values are appropriate for routine quality control and compositional verification. For Al, Fe, and Zn, LODs are below 2.6 mg kg^{-1} and LOQs below 8.5 mg kg^{-1}. For all remaining elements, LODs are ≤0.5 mg kg^{-1} and LOQs ≤1.9 mg kg^{-1}. Accordingly, the method is well-suited for compliance testing as well as for the determination of trace-level metallic impurities and catalyst residues. This is particularly relevant for transition metals, which are known to catalyze polymer degradation *via* the hydroperoxide decomposition pathway.[55,56]

4. Conclusions

This study addresses a gap in sample preparation for elemental analysis of technical polymers, namely the lack of digestion protocols that are explicitly developed and validated for common refractory oxide additives such as TiO_2, Al_2O_3, and ZrO_2 under realistic formulation conditions. By basing method development on an in-house PE standard and a highly filled PVC compound, both containing these oxides at technologically relevant mass fractions, and by comparing against HF-based digestion procedures, digestion completeness could be systematically and quantitatively assessed.

A two-step microwave-assisted digestion protocol was developed that decouples polymer matrix oxidation from oxide dissolution. Decomposition of the polymer is carried out at 200 °C in HNO_3/H_2O_2, while dissolution of the refractory oxides is performed in a second step at 180 °C in the presence of HBF_4, respecting the pressure limits of the digestion vessels. Within these constraints, the optimized protocol (4 mL HNO_3 + 1 mL H_2O_2, 75 min at 200 °C; 1 mL HBF_4, 45 min at 180 °C) provides recoveries close to 100% for Ti, Al, and Zr, as well as for other additive-related elements, over a broad concentration range and with good precision. This performance was confirmed not only for PE and PVC, but also for ABS and PC masterbatches and for a polymer CRM, demonstrating that the approach is applicable to various polymer matrices and additive systems.

Comparison with established HF workflows shows that, for most analytes, the HBF_4-based method provides comparable accuracy and equal or improved precision for most elements. For Cr present as Cr_2O_3, the method achieves an "acid-digestible" fraction within the range reported for HF-based procedures, which reflects the intrinsic limitations of acid digestion for this particular oxide rather than a shortcoming specific to the HBF_4 protocol. The achieved LODs and LOQs, including sub-mg kg^{-1} quantification limits for many elements and LOQs well below regulatory thresholds for Cd and Pb, are sufficient for the quantification of both typical additive levels and trace

impurities. This makes the protocol suitable for applications ranging from compounding control and failure analysis to recycling studies and microplastics characterization.

An additional practical benefit is that the use of HBF_4 avoids the need for free HF and a separate boric acid complexation step, thereby reducing health risks and lowering the overall chemical consumption, as the complexation step is eliminated.

Author contributions

S. K.: conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization, writing – original draft, writing – review and editing. B.-M. E.: data curation, investigation, methodology, writing – original draft, writing – review and editing. M. K.: funding acquisition, project administration, supervision, writing – original draft, writing – review and editing. U. E. A. F.: supervision, writing – original draft, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included in the main text and as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d6ja00169f.

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References

1 Conversio Marketing & Strategy, *Stoffstrombild Kunststoffe in Deutschland 2023 - Zahlen und Fakten zum Lebensweg von Kunststoffen*, Kurzfassung der Conversio Studie, 2024, https://plasticseurope.org/de/knowledge-hub/stoffstrombild-kunststoffe-in-deutschland-2023/, (accessed 28 April 2026).
2 Plastics Europe, *Plastics explained*, https://plasticseurope.org, (accessed 28 April 2026).
3 British Plastics Federation, *Plastics Applications*, https://www.bpf.co.uk/, (accessed 28 April 2026).
4 J. Murphy, *Additives for Plastics Handbook*, Elsevier science, Oxford (Royaume Uni), New York (N.Y.), Tokyo, 2nd edn, 2001.
5 R. Pfaendner, *Plastic Additives*, De Gruyter, Berlin, Boston, 2024.
6 S. Shawaphun, T. Manangan and S. Wacharawichanant, Thermo- and Photo-Degradation of LDPE and PP Films Using Metal Oxides as Catalysts, *Adv. Mater. Res.*, 2010, **93–94**, 505–508.
7 R. Yang, P. A. Christensen, T. A. Egerton and J. R. White, Degradation products formed during UV exposure of polyethylene–ZnO nano-composites, *Polym. Degrad. Stabil.*, 2010, **95**, 1533–1541.
8 European Parliament and Council, *Directive 2011/65/EU of 8 June 2011 on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment*, consolidated version of 01/01/2025.
9 European Parliament and Council, *Directive 94/62/EC of December 20, 1994, on Packaging and Packaging Waste*, 2018.
10 European Medicines Agency, ICH guideline Q3D (R2) on elemental impurities, 2022, https://www.ema.europa.eu/en/ich-q3d-elemental-impurities-scientific-guideline, (accessed 28 April 2026).
11 *Annex XVII to REACH*, 2024.
12 I. Acosta-Coley, D. Mendez-Cuadro, E. Rodriguez-Cavallo, J. de La Rosa and J. Olivero-Verbel, Trace elements in microplastics in Cartagena: A hotspot for plastic pollution at the Caribbean, *Mar. Pollut. Bull.*, 2019, **139**, 402–411.
13 O. H. Fred-Ahmadu, O. O. Ayejuyo and N. U. Benson, Dataset on microplastics and associated trace metals and phthalate esters in sandy beaches of tropical Atlantic ecosystems, Nigeria, *Data Brief*, 2020, **31**, 105755.
14 L. A. Holmes, A. Turner and R. C. Thompson, Adsorption of trace metals to plastic resin pellets in the marine environment, *Environ. Pollut.*, 2012, **160**, 42–48.
15 DIN German Institute for Standardization, *Determination of certain substances in electrotechnical products - Part 5: Cadmium, lead and chromium in polymers and electronics and cadmium and lead in metals by AAS, AFS, ICP-OES and ICP-MS (IEC 62321-5:2013); German version EN 62321-5:2014*, 2014, vol. 29.020,.
16 C. A. Gonzalez and S. J. Choquette, Certificate of Analysis - Standard Reference Material 2855 - Additive Elements in Polyethylene, 2019, https://www.nist.gov/image/srm-2855-additive-elements-polyethylene.
17 T. Linsinger, A. Liebich, E. Przyk and A. Lamberty, *The Certification of the Mass Fractions of As, Br, Cd, Cl, Cr, Hg, Pb, S and Sb and the Assignment of Indicative Values for Sn and Zn in Two Polyethylene Reference Materials, ERM-EC680k and ERM-EC681k*, Directorate-General Joint Research Centre; Institute for Reference Materials and Measurements EUR Report 22784 EN, 2007, https://publications.jrc.ec.europa.eu/repository/handle/JRC37540, (accessed 28 April 2026).
18 M. Ohata and A. Hioki, Development of PVC and PP resin pellet certified reference materials for heavy metal analysis with respect to the RoHS directive, *Anal. Sci.*, 2013, **29**, 239–246.
19 P. Quevauviller, Certified reference materials for the quality control of inorganic analyses of manufactured products (glass, polymers, paint coatings), *TrAC, Trends Anal. Chem.*, 2001, **20**, 446–456.
20 G. Buxbaum and G. Pfaff, *Industrial Inorganic Pigments*, Wiley-VCH, Weinheim, 3rd edn, 2010.

21 H. M. Smith, *High Performance Pigments*, Wiley-VCH, Weinheim, 2nd edn, 2009.

22 P. J. Fordham, J. W. Gramshaw, L. Castle, H. M. Crews, D. Thompson, S. J. Parry and E. McCurdy, Determination of trace elements in food contact polymers by semi-quantitative inductively coupled plasma mass spectrometry. Performance evaluation using alternative multi-element techniques and in-house polymer reference materials, *J. Anal. At. Spectrom.*, 1995, **10**, 303.

23 T. Ernst, R. Popp and R. van Eldik, Quantification of heavy metals for the recycling of waste plastics from electrotechnical applications, *Talanta*, 2000, **53**, 347–357.

24 E. Dimitrakakis, A. Janz, B. Bilitewski and E. Gidarakos, Determination of heavy metals and halogens in plastics from electric and electronic waste, *Waste Manag.*, 2009, **29**, 2700–2706.

25 J. Diemer and K. G. Heumann, Determination of zirconium traces in polymers by ICP-IDMS - a powerful and fast method for routine testing of zirconium residues in polyolefins, *Fresenius J. Anal. Chem.*, 1999, **364**, 421–423.

26 L. S. F. Pereira, M. F. Pedrotti, T. M. Miceli, J. S. F. Pereira and E. M. M. Flores, Determination of elemental impurities in poly(vinyl chloride) by inductively coupled plasma optical emission spectrometry, *Talanta*, 2016, **152**, 371–377.

27 P. Klingenberg, C. G. Schirmeister, M. Kappeler, A. Calean, H. Biester, E. Licht and B. Rapp, Quantification of regulated metals in recycled post-consumer polypropylene through comparative ICP-MS, AAS and LIBS analyses, *Polym. Test.*, 2024, **136**, 108480.

28 J. S. F. Pereira, C. L. Knorr, L. S. F. Pereira, D. P. Moraes, J. N. G. Paniz, E. M. M. Flores and G. Knapp, Evaluation of sample preparation methods for polymer digestion and trace elements determination by ICPMS and ICPOES, *J. Anal. At. Spectrom.*, 2011, **26**, 1849.

29 S. Kühn, A. van Oyen, A. M. Booth, A. Meijboom and J. A. van Franeker, Marine microplastic: Preparation of relevant test materials for laboratory assessment of ecosystem impacts, *Chemosphere*, 2018, **213**, 103–113.

30 E. Skrzydlewska and M. Balcerzak, Multi-elemental analysis of non-food packaging materials by inductively coupled plasma-time of flight-mass spectrometry, *Talanta*, 2004, **62**, 937–944.

31 H. Sakurai, J. Noro, A. Kawase, M. Fujinami and K. Oguma, Digestion of plastic materials for the determination of toxic metals with a microwave oven for household use, *Anal. Sci.*, 2006, **22**, 225–228.

32 L. Poirier, H.-K. Timken and F. Lopez-Linares, Application ICP-OES to Multielement Analysis on Plastic Waste and Blends with Vacuum Gas Oil: Developing a Sample Preparation Protocol, *Processes*, 2024, **12**, 2339.

33 P. Klöckner, T. Reemtsma and S. Wagner, The diverse metal composition of plastic items and its implications, *Sci. Total Environ.*, 2021, **764**, 142870.

34 T. Restivo, A. Thornton, B. Lockerman and M. Howe, *New Techniques for Preparing Plastics and Polymers by Microwave Sample Preparation*, CEM Corporation, Pittcon Plastics and Polymers, 2017, https://cem.com/de/new-techniques-for-preparing-plastics-and-polymers-by-microwave-sample-preparation, (accessed 28 April 2026).

35 P. A. Mello, L. O. Diehl, J. S. Oliveira, E. I. Muller, M. F. Mesko and E. M. Flores, Plasma-based determination of inorganic contaminants in waste of electric and electronic equipment after microwave-induced combustion, *Spectrochim. Acta B Atom Spectrosc.*, 2015, **105**, 95–102.

36 E. Lehtimäki and A. Väisänen, Determination of metal concentrations in certified plastic reference materials after small-size autoclave and microwave-assisted digestion followed with inductively coupled plasma optical emission spectrometry, *Spectrochim. Acta B Atom Spectrosc.*, 2017, **127**, 64–69.

37 L. Hildebrandt, M. von der Au, T. Zimmermann, A. Reese, J. Ludwig and D. Pröfrock, A metrologically traceable protocol for the quantification of trace metals in different types of microplastic, *PloS One*, 2020, **15**, e0236120.

38 Berufsgenossenschaft Rohstoffe und chemische Industrie, *M 005 – Fluorwasserstoff, Flusssäure und anorganische Fluoride (213-071)*, Jedermann-Verl., Heidelberg, 12th edn, 2012.

39 F. J. Langmyhr and K. Kringstad, An investigation of the composition of the precipitates formed by the decomposition of silicate rocks in 38-40% hydrofluoric acid, *Anal. Chim. Acta*, 1966, **35**, 131–135.

40 R. Bock, *Handbuch der analytisch-chemischen Aufschlussmethoden*, Wiley, 2001.

41 T. Yokoyama, A. Makishima and E. Nakamura, Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion, *Chem. Geol.*, 1999, **157**, 175–187.

42 M. Michaelis and A. Stadler, A Chemist's Guide to Sample Preparation. *Basics of Microwave-Assisted Acid Digestion in a Nutshell - How to Get Started with Anton Paar Instrumentation*, 2nd edn, 2021.

43 C. A. Wamser, Hydrolysis of Fluoboric Acid in Aqueous Solution, *J. Am. Chem. Soc.*, 1948, **70**, 1209–1215.

44 C. A. Wamser, Equilibria in the System Boron Trifluoride—Water at 25°, *J. Am. Chem. Soc.*, 1951, **73**, 409–416.

45 R. E. Mesmer, K. M. Palen and C. F. Baes, Fluoroborate equilibriums in aqueous solutions, *Inorg. Chem.*, 1973, **12**, 89–95.

46 M. Krachler, C. Mohl, H. Emons and W. Shotyk, Analytical procedures for the determination of selected trace elements in peat and plant samples by inductively coupled plasma mass spectrometry, *Spectrochim. Acta, Part B*, 2002, **57**, 1277–1289.

47 M. B. Javed, I. Grant-Weaver and W. Shotyk, An optimized HNO3 and HBF4 digestion method for multielemental soil and sediment analysis using inductively coupled plasma quadrupole mass spectrometry, *Can. J. Soil Sci.*, 2020, **100**, 393–407.

48 T. Zimmermann, M. von der Au, A. Reese, O. Klein, L. Hildebrandt and D. Pröfrock, Substituting HF by HBF4-an optimized digestion method for multi-elemental

sediment analysis via ICP-MS/MS, *Anal. Methods*, 2020, **12**, 3778–3787.

49 H. K. Imhof, C. Laforsch, A. C. Wiesheu, J. Schmid, P. M. Anger, R. Niessner and N. P. Ivleva, Pigments and plastic in limnetic ecosystems: A qualitative and quantitative study on microparticles of different size classes, *Water Res.*, 2016, **98**, 64–74.

50 D. L. Johnson, *Statistical Tools for the Comprehensive Practice of Industrial Hygiene and Environmental Health Sciences*, John Wiley & Sons, 2017.

51 DIN German Institute for Standardization, *Chemical Analysis - Guide to Quantification of Uncertainty in Measurement of Quantitative Test Results - Terms and Strategies*, 2019, 01.040.71, 71.040.01, 01.040.71, 71.040.01.

52 DIN German Institute for Standardization, *Chemical Analysis - Decision Limit, Detection Limit and Determination Limit under Repeatability Conditions - Terms, Methods, Evaluation*, 2008, vol. 71.040.01, 71.040.01.

53 M. E. Tarnopolskaia, A. Y. Bychkov, Y. V. Shvarov and Y. A. Popova, Experimental study of fluorite solubility in acidic solutions as a method for boron fluoride complexes studying, *Geochem. Int.*, 2017, **55**, 355–359.

54 S. Radosavljević, V. Ŝćepanović, S. Stević and D. Milojković, Effect of boric acid on tetrafluoroborate ion hydrolysis in solutions of tetrafluoroboric acid, *J. Fluorine Chem.*, 1979, **13**, 465–471.

55 C. Vasile, *Handbook of Polyolefins*, CRC Press, Boca Raton, 2000.

56 L. E. P. Real, *Weathering of Polymers and Plastic Materials*, Springer Nature Switzerland, Cham, 2023.

