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ARTICLE

Enhanced Microwave-Assisted Digestion Method for Accurate Trace-Level Analysis of Rare Earth Elements in Environmental Matrices

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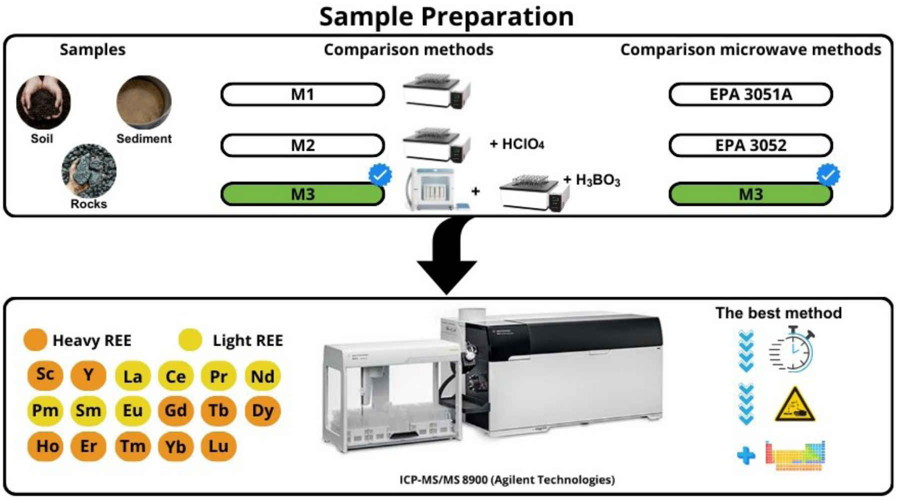

Rare Earth Elements (REEs) play an essential role in modern technologies, with soils and sediments often acting as the final repository for REE-containing products. This study evaluates sample preparation methodologies using digestion methods and triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ) for accurate REE quantification in soils, sediments, and rocks. Five digestion methods—differing in hydrofluoric acid (HF) usage and fluoride interference mitigation (Methods 1, 2, 3, USEPA 3052, and 3051)—were compared, identifying Method 3 as the optimal approach. Method 3, which includes 3.0 mL of HF, 3.5 mL of HCl, 1.5 mL of HNO_3, and boric acid (H_3BO_3) to neutralize fluorides, achieved REE recovery rates exceeding 84% across all certified reference materials (CRMs), including soil (TILL-3, NIST SRM 2709a), sediment (NIST SRM 8704), and rock (ITA-1 Friable Itabirite) samples. This method significantly reduces digestion time from 12 hours to 3 hours, minimizes acid consumption, and enhances sample throughput, offering a highly efficient workflow. In addition, Method 3 demonstrated high precision within a 95% confidence interval, excellent linearity, and minimal matrix interference for all REEs (except scandium). Detection limits (LOD: 0.0025–0.0610 $\mu g\ g^{-1}$) and quantification limits (LOQ: 0.0072–0.1448 $\mu g\ g^{-1}$) were markedly lower than previously reported values, enabling sensitive, trace-level REE analysis in complex environmental matrices. Overall, Method 3 stands

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out as an efficient, precise, and environmentally sustainable method for multi-element analysis, providing a rapid and reliable solution for REE quantification in soils, sediments, and rocks using ICP-MS/MS.

Keywords: rare earth elements, microwave digestion, soil, rocks, CRM, ICP-MS

INTRODUCTION

In recent decades, the global mining landscape has increasingly focused on a specific group of elements, the Rare Earth Elements (REEs), driven by a transition in the global energy matrix toward cleaner, renewable energy sources.[1] REEs are now central to raw material policies and critical for advanced industrial applications.[2]

According to the International Union of Pure and Applied Chemistry's (IUPAC) Nomenclature of Inorganic Chemistry, IUPAC Recommendations 2005, REEs include 17 metals from the periodic table: all 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) alongside scandium (Sc) and yttrium (Y). Among these, promethium (Pm) is a naturally radioactive and exceptionally rare element in the Earth's crust, predominantly produced as a byproduct of nuclear fission in reactors; thus, it is generally excluded from REE analysis. Sc and Y, while not lanthanides, are often categorized with REEs due to their frequent co-occurrence in mineral deposits and shared chemical properties.[3]

Quantifying REEs in soil, sediment, and rock samples is essential for understanding their environmental impacts and informing sustainable management strategies.[2] Highly sensitive and precise analytical methods are necessary to measure REE concentrations accurately in these complex matrices. Inductively coupled plasma mass spectrometry (ICP-MS), particularly the Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS/MS), has become the standard for REE quantification, offering high sensitivity and selectivity.[2] This method enables the detection and quantification of trace REE concentrations, overcoming the previous analytical challenges and costs associated with pre-separation techniques such as solvent extraction, ion exchange, and precipitation required for X-ray fluorescence or ICP optical emission spectrometry.[4,5]

Sample preparation remains a critical determinant of analysis quality, as ICP-MS typically requires samples in liquid form, a necessary condition for sample introduction, which is normally performed via pneumatic nebulization.[2,4] As found in the literature, the two main methods routinely used for REEs determinations are preconcentration in resins[6] and microwave-assisted digestion.[7] Additional approaches, including acid leaching[8] and alkaline fusion,[9] have also been explored. Some methods involve pre-concentration steps, such as solvent extraction, co-precipitation, or ion-exchange separation, to enhance detection limits.[6] However, these pre-concentration techniques are labor-intensive and time-consuming.

Microwave-assisted digestion typically utilizes concentrated acids like hydrofluoric acid (HF), nitric acid (HNO_3), and hydrochloric acid (HCl) to decompose soil matrices, releasing REEs for analysis. However, HF can lead to the formation of poorly soluble fluorides, including those of Al (III), Ca (II), Fe (III), Mg (II), and REEs, which can impair analytical accuracy. To address this, methods such as evaporate samples to dryness, boric acid (H_3BO_3) addition, or post-digestion treatment with perchloric acid ($HClO_4$) have been introduced to minimize fluoride formation, thereby enhancing REE measurement accuracy.[7,10-12]

The strategy of evaporating samples to dryness, while energy- and time-intensive, has shown high recovery rates. For example, Kasar et al. (2020) reported recovery rates exceeding 90% for 18 elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Sr, Cs, and U) using microwave digestion followed by evaporate samples to dryness.[12] Similarly, Ivanova et al. (2001) and other authors, demonstrated that REEs determination in soils via ICP-MS, using HF and HNO_3 with overnight digestion followed by HF and H_3BO_3 addition, resulted in recoveries exceeding 80%.[6,10,13–15] Other studies have applied HF, HCl, and HNO_3 for microwave digestion, recommending $HClO_4$ post-digestion to remove residual fluoride and achieve recoveries above 80%.[7,11]

A review of current literature highlights the lack of standardized methods for rare earth element (REE) analysis in geological samples, as well as the limited data on REE concentrations in soils, sediments, and rocks represents a key gap in supporting the development of international standards and geochemical baselines. To address this gap, it is essential to develop and implement standardized analytical methods and to establish comprehensive databases that consolidate data from various studies and regions. Additionally, there is a significant lack of REE data in waste materials, an emerging area of interest due to the environmental contamination risks associated with dam failures and electronic waste. To mitigate these risks, systematic studies should be conducted to quantify and monitor REE concentrations in industrial and electronic waste, promoting a proactive approach to waste management and enabling the development of more effective environmental regulations.

This work presents a systematic comparison of five microwave-assisted digestion methods to identify the most effective method for comprehensive REEs quantification. By optimizing triple quadrupole ICP-MS/MS detection conditions, we enhance measurement precision and selectivity across complex soil, sediment, and rock matrices. Using certified reference materials, this study aims to establish a reliable analytical framework for accurate REE analysis, contributing to standardized methods in environmental and geological sample assessment.

MATERIALS AND METHODS

Chemicals and reagents

All chemical reagents used were of analytical grade, ensuring minimal contamination and high reagent purity. Ultrapure deionized water (resistivity: 18 MΩ·cm) was obtained using a Millipore Nanopure system (Millipore, Bedford, MA, USA). Hydrochloric acid (37% HCl), nitric acid (65% HNO_3), and hydrofluoric acid (40% HF) were purified by sub-boiling using a Milestone DuoPur Quartz Acid Purification system (Milestone, Sorisole BG, Italy). Boric acid (99.6% H_3BO_3, Merck) and ACS-grade perchloric acid ($HClO_4$, Merck) were utilized for neutralizing residual HF and preventing the formation of REE fluorides.

Certified Reference Materials (CRM) were selected based on their REE content and representativeness of natural environmental matrices. These included multi-element REE standards (Sigma Aldrich, Buchs, Switzerland) and a 1000 mg L^{-1} Rhodium CRM (Inorganic Ventures, Christiansburg, USA) as an internal standard. The analytical curve was prepared with concentrations ranging from 2 to 65 ug L^{-1} in 2% HNO_3, with Rh added as an internal standard to control for instrumental drift.

Certified reference materials and quality control samples

This study employed two certified soil reference materials: TILL-3 (Canadian Soil CRM) and NIST SRM 2709a (San Joaquin Soil), as well as one sediment reference material, NIST SRM 8704 (Buffalo River Sediment). For quality control, a friable itabirite sample (ITA-1) sourced from Iron Quadrangle, Brazil, provided by the Federal University of Ouro Preto, served as a geological control to simulate rock matrix behaviour in REEs recovery assessment. The accuracy of each method was evaluated by calculating recovery rates based on certified values, while each CRM was measured in triplicate to ensure robustness in statistical assessments.

Digestion methods

To determine the most effective method for REE extraction, 3 microwave-assisted digestion methods were evaluated, each designed to optimize REEs solubilization in complex matrices. Each method used approximately 250 mg of sample and followed unique procedural steps. For the three initial methods focused on fluoride removal from digests to avoid poorly soluble fluoride formation, was used a standardized acid mix: 3.5 mL of 37% HCl, 1.5 mL of 65% HNO_3, and 3.0 mL of 40% HF, with a 3-hour of contact time.

1. **Method 1 (Evaporation to dryness):** Post 3 hours of contact time digestion, samples were evaporated to dryness at 90 °C, in a hot block (DigiBlock, Italy), followed by reconstitution with HCl and HNO_3 for two cycles. Total time: 48 hours.
2. **Method 2 ($HClO_4$ addition):** After the 3 hours of contact time digestion, 1 mL of $HClO_4$ was added and the samples were heated to 200 °C in a hot block (DigiBlock, Italy), dried, and reconstituted to eliminate HF interference. Total time: 24 hours.

3. **Method 3 (H_3BO_3 addition):** This method was processed in an ETHOS UP Microwave Digestion System with SR15 pressure vessels (Milestone, Belgium), using a ramp to 230 °C, followed by a 15-minute hold and cooling phase. To address HF complexation, 1.1 g of H_3BO_3 was added post-digestion, avoiding sample drying. This method aimed to neutralize HF and prevent fluoride precipitation without requiring evaporation. Total time: 6 hours.

The optimized method with superior accuracy and precision was then compared against two standardized microwave-assisted digestion methods by the U.S. Environmental Protection Agency (USEPA): USEPA 3051a and USEPA 3052.[23,24]

4. **USEPA 3051a (Pseudo-total digestion):** A standard method using 9.0 mL of HNO_3 and 3.0 mL of HCl at 175 °C for 4.5 minutes, designed for metals analysis in environmental samples.
5. **USEPA 3052 (Total digestion with HF and H_3BO_3):** This total digestion method included 9.0 mL of HNO_3, 3.0 mL of HF, with post-digestion addition of H_3BO_3, targeting complete REE recovery from silicate matrices.

For these two standardized methods, the digestion was processed in the same equipment ETHOS UP Microwave Digestion System with SR15 pressure vessels (Milestone, Belgium), using descripting ramp of both standardized methods.

Each sample batch was assigned a unique identifier to ensure traceability, and each digestion method was applied to all CRM samples in triplicate.

Instrumental analysis and ICP-MS/MS optimization

Sample analysis was performed using an Agilent 8900 ICP-MS/MS system (Agilent Technologies, Japan). The instrumental parameters are described in Table I.

Table I. Instrumental parameters for the determination of REE by ICP-MS/MS

Instrumental parameters	Operating conditions
Nebulizer	Mira Mist (peek)
Nebulization chamber	Scott double-pass (Quartz)
Torch	Quartz torch, 2.5 mm diameter
Sampling and Skimmer cones	Ni
Tygon® tubes	1.02 mm
Radiofrequency power (W)	1550
Sample flow (mL min^{-1})	0.4
Nebulization gas flow (L min^{-1})	1.07
Plasma gas flow (L min^{-1})	15.0
Auxiliary gas flow (L min^{-1})	0.90
Rinse time (s)	10
Peristaltic pump speed (rps)	0.5
Sample aspiration time (s)	30
Stabilization time (s)	20
Rising time (s)	10
Total time analysis (s)	120

Isotope selection was critical in mitigating isobaric interferences. By selecting non-interfering isotopes, we minimized the impact of overlapping signals from polyatomic ions, a technique that is consistently recommended in the literature to improve analytical specificity.[16] This approach allowed for more precise quantification of REEs, especially when analysing samples with complex matrix backgrounds that could otherwise lead to signal distortion. The isotopes selected for determination included ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, and ^{175}Lu. This method of interference reduction aligns with practices highlighted by Anders and Grevesse (1989) and Pradhan et al. (2015), who demonstrated that careful isotope selection enhances both sensitivity and selectivity in ICP-MS applications.[14,17] These tailored adjustments led to improved sensitivity and reproducibility in REE analysis, establishing a solid foundation for accurate and reproducible measurements in analytical applications.

The reaction cell was optimized, and a comparison was made between NO GAS and Helium (He) modes, with the He mode operated at a flow rate of 4.5 mL/min.

The Shapiro-Wilk test was applied to assess data normality, and ANOVA followed by Tukey's post-hoc test was used for normally distributed data at 0.05 significance level. For non-normal data, the Kruskal-Wallis test and Dunn's post-test were applied to compare group means. Method accuracy was determined through recovery percentage comparisons to CRM values using *t*-tests at 0.05 significance level.

For method validation, selectivity, linearity, repeatability, intermediate precision, accuracy/recovery, limit of detection (LOD), and limit of quantification (LOQ) were verified. Statistical tests employed included the Jackknife outlier test, Cochran's test for residue variance homogeneity, coefficient of determination, F-test, *t*-test, and coefficient of variation to evaluate these figures of merit.

Calibration curves were prepared in triplicate using seven multi-element standards with REE concentrations from 2 to 65 µg L^{-1}. To monitor signal consistency, an internal standard mix (^{103}Rh, ^{204}Tl) was added to all solutions, and the signal was correct using the ratio "signal analyte/signal internal standard" for all samples. Each batch analysis began and ended with calibration standards, with blank solutions interspersed every 5 to 7 samples to check system stability. After completion, trace element data were processed in MassHunter and corrected for instrumental drift. Quality control was verified by evaluating recoveries from multi-element standards and Certified Reference Materials (CRM).

Precision was measured through repeatability and intermediate precision tests. Repeatability, reflecting agreement in results under identical conditions, and intermediate precision, which measures consistency under variable conditions (e.g., across different days), were assessed. Both repeatability and intermediate precision were expressed as relative standard deviation (RSD).

LOD and LOQ were calculated based on ten replicate blanks (9 degrees of freedom), each subjected to the complete digestion process, to provide robust estimates for sensitivity.

RESULTS AND DISCUSSION

ICP-MS/MS optimization and minimization of interference

The analytical performance of the method was evaluated for a range of REEs under no-gas and helium (He) collision cell conditions. The coefficients of determination (R^2) in no-gas mode ranged from 0.9539 (Gd) to 0.9698 (Pr), while in He mode, all R^2 values were markedly improved, ranging from 0.9993 (Ce) to 0.9999 (Gd), indicating excellent linearity. In terms of precision, expressed as relative standard deviation (RSD%), the no-gas mode showed a wider variation, with values ranging from 1.0–38.4% depending on the element, such as 3.0–38.4% for Gd and 1.0–17.2% for Nd. In contrast, the He mode provided significantly better precision, with RSDs ranging from just 0.1% (La) to 3.4% (Lu). These results demonstrate that the use of He as a collision gas greatly enhances both signal stability and analytical accuracy for the determination of REEs by reducing interferences and improving repeatability. The implementation of the He mode, which utilizes helium as a collision gas, was essential in reducing these interferences. Literature supports the use of kinetic energy discrimination in the He mode to minimize oxide formation, which is essential for obtaining accurate results, particularly for elements such as Ce and Nd.[18]

Comparison of digestion Methods 1, 2 and 3 for SRM's soils

Figure 1 presents a comprehensive comparison of the mean concentrations (µg g^{-1}), standard deviations (µg g^{-1}) and recovery rates (%) for three analytical methods applied to both CRMs. Mean values (n = 3) followed by the same letter (A, B, or C) are not significantly different, whereas values followed by different letters indicate statistically significant differences. Statistical analysis was performed using one-way ANOVA, followed by Tukey's post-hoc test for parametric data, or using Kruskal-Wallis analysis of variance, followed by Dunn's test for non-parametric data at 0.05 significance level.

Table S1 (Supplementary Material section) presents the results of mean, standard deviation and recovery for the 3 methods and the two standardized methods USEPA 3051a and 3052, for the TILL-3 CRM of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu obtained after digestion (n = 3). The efficacy of each digestion method was analyzed with respect to REE recovery rates across diverse environmental matrices. This analysis allows for a deeper understanding of the complex factors influencing REE extraction and offers insights into the operational advantages and limitations of each method. The criteria used to determine acceptable recovery rates for the methods was a range of 80% to 120%.

Method 1 (Evaporation to dryness) showed limitations, especially with elements prone to forming stable, insoluble compounds, such as La, Ce, and Pr. Recovery rates for these elements, Figure 1, were below 50%, which is consistent with reports from Fedyunina et al. (2012) and Zimmermann et al. (2020), who observed that complete drying can lead to volatilization losses or incomplete solubilization.[6,15]

These findings suggest that the use of evaporation steps may not be suitable for matrices containing REEs, particularly those with a tendency to form volatile or refractory compounds. Additionally, the high standard deviations observed, Figure 1, indicate that the method's reproducibility is compromised, likely due to the partial crystallization of REE compounds, which can limit their redissolution during subsequent reconstitution steps.

Method 2 ($HClO_4$ addition) exhibited moderate recovery rates for specific REEs, such as Gd and Dy, achieving values above 80%, Figure 1. However, the recovery of La, Er, and other light REEs was particularly low, with values as low as 20% in some cases, Figure 1.

This trend may be attributed to the inability of $HClO_4$ alone to completely dissolve fluoride-bound REEs, especially those in highly resistant silicate phases, as documented by Balaram (2019).[2] $HClO_4$'s oxidative potential helps remove organic contaminants and some matrix interferences, but its lack of complexation ability with fluorides highlights a major limitation in recovering the full spectrum of REEs without additional treatments, as noted by Cotta and Enzweiler (2010).[4]

In fact, incomplete dissolution of fluoride-bound REEs is a recurring challenge in environmental samples, especially in matrices containing complex silicate structures.[16]

In contrast, Method 3 (H_3BO_3 addition) demonstrated a consistent and high recovery rate across all reference materials and REEs analyzed, Figure 1. This method achieved recovery rates exceeding 84% for most REEs, closely matching certified values in TILL-3, NIST SRM 2709a, NIST RM 8704 and ITA-1, Figure 2. The addition of boric acid post-digestion effectively neutralizes excess HF, preventing the formation of insoluble fluoride precipitates.[7] This approach aligns with the findings of Ebihara et al. (2020)[7] and Zimmermann et al. (2020),[15] who showed that boric acid acts as a fluoride scavenger, forming stable BF_4^- complexes that help maintain REE solubility. The efficiency of boric acid in eliminating fluoride interference is particularly notable with heavy REEs (HREEs), which are more prone to forming stable fluorides, thereby enhancing method consistency and reproducibility.

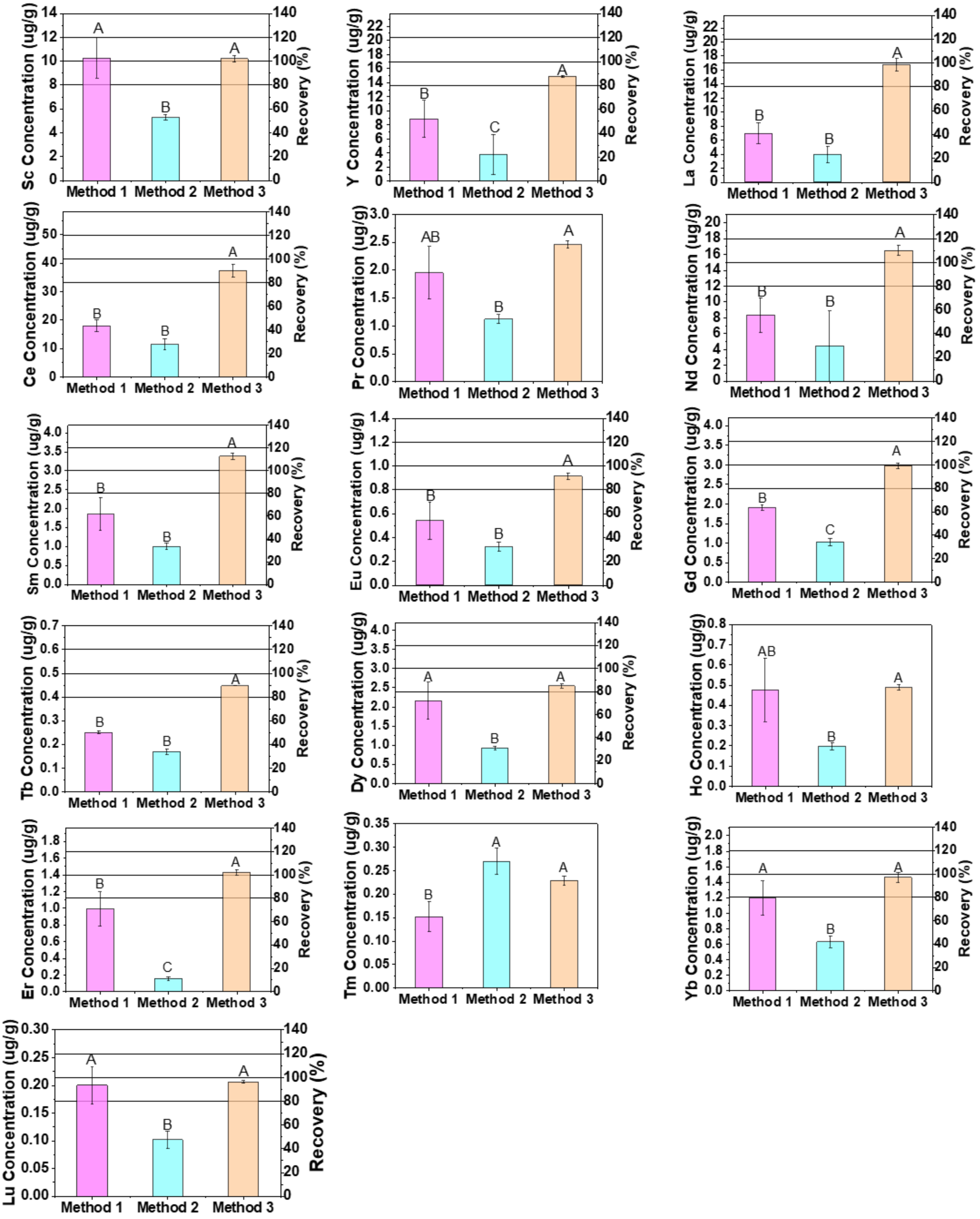

Figure 1. Comparison between microwave digestion of the 3 digestion methods, for concentration and recovery REEs in TILL-3 (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, and Lu), and NIST SRM 2709a (Gd and Dy), obtained after digestion (continuous lines correspond to 80, 100, and 120% of the certified value of the respective metal). Mean values (n = 3) followed by the same letter (A, B, or C) are not significantly different, whereas values followed by different letters indicate statistically significant differences. Statistical analysis was performed using one-way ANOVA, followed by Tukey's post-hoc test for parametric data, or using Kruskal-Wallis analysis of variance, followed by Dunn's test for non-parametric data at 0.05 significance level.

This study compared two open-vial digestion methods (Methods 1 and 2) with a closed-vial microwave-assisted digestion method (Method 3). The latter obtained significantly higher recoveries and a higher analytical frequency. It is worth noting that open-vial digestion methods have been shown to be more efficient than closed-vial methods, such as for the analysis of mercury in soils.[19]

Comparing these results with previous methods, Method 3's recovery rates for HREEs such as Lu and Yb were significantly higher, indicating that boric acid addition may be an optimal solution for complex matrices Figure 1. Studies by J. Ivanova et al. (2001), support these observations, as their work with boric acid-enhanced methods also reported improvements in REE recoveries, particularly for HREEs in geological matrices.[10] Comparing Method 3 with the proposed method by J. Ivanova et al. (2001),[10] it has the advantage of less time consumable and consequently higher analysis frequency, because of the reducing the sample contact time from 12 to 3 hours and no use of a second step of adding HF after microwave digestion. This finding highlights boric acid's dual role as both a stabilizing agent for REEs and a means of mitigating HF-related matrix interferences, thus promoting efficient solubilization and facilitating accurate quantification in ICP-MS/MS.

Comparison of microwave-assisted digestion Method 3 and standardized microwave-assisted digestion methods USEPA 3051a and USEPA 3052 for SRM's soils, sediments and QCM ITA-1

Figure 2 presents a comparison between Method 3 and two standardized methods, USEPA 3051a and 3052, across four reference materials: two soil standards (TILL-3 and NIST SRM 2709a), sediment reference material NIST RM 8704, and the Itabirito Rock Quality Control Material (QCM ITA-1). Similar to Figure 1, mean values (n = 3) followed by the same letter (A, B, or C) are not significantly different, whereas values followed by different letters indicate statistically significant differences. Statistical analysis was performed using one-way ANOVA, followed by Tukey's post-hoc test for parametric data, or using the Kruskal-Wallis analysis of variance, followed by Dunn's test for (non-parametric data) at 0.05 significance level. Tables S1, S2, S3 and S4 of the Supplementary Material section present the results of mean, standard deviation and recovery for the methods and the two standardized methods USEPA 3051a and 3052, for the TILL-3, NIST SRM 2709a, NIST RM9704 and ITA-1 samples CRMs; of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu obtained after digestion (n = 3).

The standardized USEPA methods (3051a and 3052), widely recognized for metals analysis, displayed partial efficacy in REEs recovery, Figure 2. USEPA 3052, which incorporates HF and post-digestion boric acid, yielded better results than 3051a, especially for silicate-rich matrices where REEs are more tightly bound.

However, neither method achieved the recovery consistency or levels observed with Method 3, Figure 2. These results are in line with studies by Sucharová and Suchara (2006), who observed that USEPA 3052 provided satisfactory recovery for some metals but was less effective for REEs due to fluoride complexation issues.[13] This limitation is particularly pronounced in matrices like soils and sediments, where REEs are often bound to mineral phases that resist complete dissolution in HF without additional complexing agents, such as boric acid, which are not explicitly recommended in the USEPA methods.[20]

Figure 2 also presents the results for the sediment CRM NIST SRM 8704. For this CRM as well, Method 3 outperformed Methods 3052 and 3051a in the digestion of the sediments, resulting in significantly higher mean concentrations and recovery rates across all rare earth elements (REEs). For example, scandium (Sc) recovery was 86.13% with Method 3, compared to 82.96% and 41.77% for Methods 3052 and 3051a, respectively.

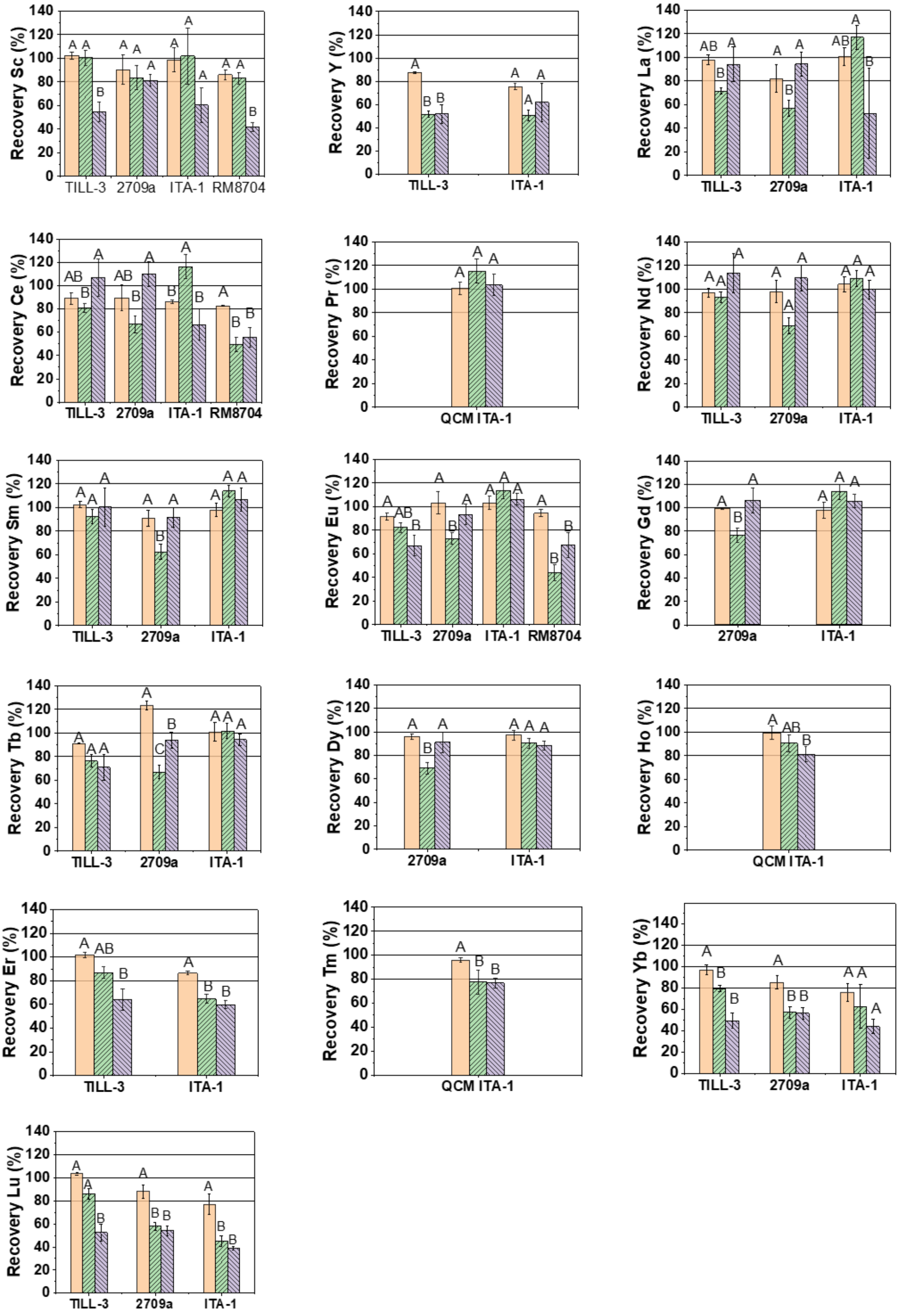

Figure 2. Comparison between microwave digestion of Method 3 (▭) and the two standardized methods USEPA 3052 (▨) and 3051a (▧), for concentration and recovery REEs certified in TILL-3, NIST SRM 2709a, RM8704 and QCM ITA-1 obtained after digestion. Continuous lines correspond to 80, 100, and 120% of the certified value of the respective metal. Mean values (n = 3) followed by the same letter (A, B, or C) are not significantly different, whereas values followed by different letters indicate statistically significant differences. Statistical analysis was performed using one-way ANOVA, followed by Tukey's post-hoc test for parametric data, or using Kruskal-Wallis analysis of variance, followed by Dunn's test for (non-parametric data) at 0.05 significance level.

Method 3 also delivered higher concentrations for elements like yttrium (Y), lanthanum (La), and cerium (Ce), suggesting more effective matrix digestion and reduced matrix interference. Furthermore, Method 3 provided particularly strong results for europium (Eu) with a recovery of 94.33%, surpassing the other methods by over 20%, Figure 2. These consistent improvements highlight Method 3's efficiency in quantifying REEs in sediment matrices, benefiting from lower acid consumption and higher analytical frequency.

Comparative performance in soil, sediment, and rock matrices

The efficacy of Method 3 was further confirmed by comparing its performance across different matrix types. In soil CRMs (TILL-3 and NIST SRM 2709a), Method 3 consistently achieved recovery rates close to certified values, with an average recovery range of 84–108% for TILL-3 and 82–105% for NIST SRM 2709a. In sediment CRM (NIST RM 8704) achieving recovery rates 83-84%. In rock samples (ITA-1), Method 3 achieved recovery rates within 76–111%, demonstrating its robustness even in silicate-rich matrices. The stability of recovery rates across these diverse matrices suggests that Method 3 offers matrix compatibility and adaptability, essential qualities for analytical methods in environmental geochemistry.

The matrix resilience observed with Method 3 is especially relevant given the diverse composition of environmental samples, which may contain a wide range of silicates, organic matter, and metal oxides. These complex matrices present significant challenges in REE quantification, as traditional methods often struggle to achieve high recovery rates across the REE spectrum.[20] The ability of Method 3 to maintain high recovery rates in both.

The higher temperature and extended digestion time of Method 3 likely contributed to its superior performance compared to USEPA 3052.[21] Method 3 also uses a smaller volume of HNO_3 but incorporates HCl, similar to aqua regia, which, combined with the higher temperature, improves efficiency, given that HF quantities are the same in both methods.[21,22]

Given these findings and the study's objective to achieve accurate and precise REE measurements in soil, sediments and rock samples, Method 3 met all required criteria. Figure 2 demonstrates that Method 3 was the only approach yielding over 84% recovery for all 13 REEs in soil CRMs and 13 of 16 REEs in QCM ITA-1. For the remaining three REEs (Y, Yb, and Lu), average recoveries with Method 3 were close to 80%, higher than those obtained with USEPA methods. Additionally, Method 3, compared to the USEPA methods, requires a smaller volume of acid than 3051a and 3052 and enables a higher analytical throughput.

Statistical validation and method consistency

Statistical comparisons with CRM certified values (using a *t*-test) are provided in Tables S1, S2, S3 and S4 (Supplementary Material). The statistical analysis of recovery rates provided robust validation of the digestion methods. Tukey's post-hoc test revealed that recovery rates obtained with Method 3 did not significantly differ from the certified values at 0.05 significance level for the majority of REEs across the TILL-3, NIST SRM 2709a, NIST RM9704 and ITA-1 samples. This result underscores Method 3's high accuracy, further supporting its adoption as a standardized approach for REE analysis.

The reproducibility of recovery rates across different CRMs demonstrates Method 3's reliability, consistent with studies by Fedyunina et al. (2012) that advocate for the use of boric acid as a stabilizing agent to maintain REE solubility.[6]

Table II reports the results for the selectivity, linearity, repeatability, intermediate precision, accuracy, LOD and LOQ for REEs in TILL-3 (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, and Lu), and NIST SRM 2709a (Gd and Dy), using Method 3 and comparison with other works in literature.

Table II. Results for the selectivity, linearity, repeatability, intermediate precision, accuracy, LOD and LOQ for REEs in TILL-3 (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, and Lu), and NIST SRM 2709a (Gd and Dy), using Method 3 and comparison with other works in literature

REEs	Linearity		Selectivity	Repeatability RSD (%)	Intermediate precision RSD (%)	Recovery (%)	This study LOD (µg g^{-1})	LOD (µg g^{-1})[25]	This study LOQ (µg g^{-1})	LOQ (µg g^{-1})[26]
	Solvent curve	Matrix Curve								
	Coefficient of Determination (R2)	Coefficient of Determination (R2)	F-test (residual variances) *t*-test (combined variances)							
Sc**	0.9996	0.9998	Homoscedastic - matrix effect	5.42	5.96	100	0.0701	-	0.1448	-
Y**	0.9998	0.9991	Homoscedastic - no matrix effect	4.27	4.91	87	0.0147	-	0.0424	-
La*	0.9997	0.9993	Homoscedastic - no matrix effect	6.83	6.84	84	0.0145	0.017	0.0299	0.010
Ce*	0.9993	0.9990	Homoscedastic - no matrix effect	7.02	7.78	90	0.0163	0.017	0.0210	0.029
Pr**	0.9996	0.9997	Homoscedastic - no matrix effect	5.66	7.01	-***	0.0055	0.006	0.0129	0.021
Nd**	0.9997	0.9997	Homoscedastic - no matrix effect	5.78	7.73	103	0.0128	0.013	0.0313	0.040
Sm**	0.9997	0.9997	Homoscedastic - no matrix effect	4.22	5.55	98	0.0070	0.023	0.0188	0.012
Eu**	0.9996	0.9997	Homoscedastic - no matrix effect	2.73	3.79	92	0.0055	0.007	0.0167	0.020
Gd**	0.9999	0.9995	Homoscedastic - no matrix effect	3.06	5.99	101	0.0610	0.023	0.0149	0.033
Tb**	0.9997	0.9997	Homoscedastic - no matrix effect	2.94	3.58	91	0.0042	0.005	0.0122	0.013
Dy**	0.9997	0.9997	Homoscedastic - no matrix effect	4.38	4.51	90	0.0066	0.022	0.0158	0.018
Ho**	0.9995	0.9997	Homoscedastic - no matrix effect	2.93	3.67	-***	0.0040	0.006	0.0121	0.018
Er**	0.9996	0.9997	Homoscedastic - no matrix effect	2.98	4.89	99	0.0033	0.007	0.0080	0.008
Tm**	0.9994	0.9995	Homoscedastic - no matrix effect	3.74	6.29	-***	0.0039	0.006	0.012	0.020
Yb**	0.9996	0.9997	Homoscedastic - no matrix effect	2.98	4.89	99	0.0025	0.008	0.0072	0.010
Lu**	0.9998	0.9997	Homoscedastic - no matrix effect	4.20	5.00	108	0.0027	0.013	0.0079	0.008

n=10 for all measurements; *No internal Standard; **Internal Standard Rh.

As observed in Table II, the selectivity of the Method 3 was evaluated using statistical comparison between the calibration curves and the certified reference materials. Among the 17 rare earth elements analyzed, only scandium (Sc) presented *t*-values exceeding the critical threshold, suggesting that its quantification may require matrix-matched calibration, especially in complex soil matrices (Table II). Regarding linearity, the method demonstrated excellent performance across all analytes. The data exhibited homoscedasticity, with no significant differences in residual variances, fulfilling this criterion for all calibration curves. Additionally, all coefficients of determination (R^2) exceeded 0.9990, confirming the method's strong and consistent linear response.

Method 3 showed consistently low relative standard deviations (RSDs) across all certified reference materials (CRMs), reinforcing the method's precision and repeatability. For the TILL-3 material, RSDs ranged from 2.79% to 7.12%; for NIST SRM 2709a, from 5.62% to 14.0%; and for ITA-1, from 1.75% to 11.5% (Table II). These values fall within acceptable limits for environmental analytical methods. Notably, the HorRat values remained below 2 for all analyses, in accordance with international guidelines, further supporting the method's precision. This level of reproducibility aligns with the recommendations of Zimmermann et al. (2020),[15] who emphasize that robust precision is a critical parameter for reliable analytical methods.

The method also demonstrated high sensitivity, with limits of detection (LOD) ranging from 0.0025 to 0.070 µg g^{-1} and limits of quantification (LOQ) from 0.0072 to 0.145 µg g^{-1} (Table II). These results indicate that Method 3 is suitable for trace-level detection of rare earth elements in soil matrices, ensuring its applicability in environmental monitoring and geochemical studies. These values are in agreement with studies by Coedo et al. (1998) and Fedyunina et al. (2012).[25,26] The LOD and LOQ values achieved were lower than or comparable to reported values in chondritic data, supporting the applicability of Method 3 in quantifying REE concentrations in TILL-3 and NIST SRM 2709a, as concentrations were below certification levels. The LOD and LOQ values achieved are suitable for REE quantification in environmental monitoring programs, where trace-level detection is essential for regulatory compliance and ecological assessments.

CONCLUSIONS

This study provides a comprehensive evaluation of five digestion methods for the analysis of Rare Earth Elements (REEs) in environmental matrices. The results demonstrate that Method 3, characterized by the addition of boric acid and optimization of time reaction, provides significant advantages over other methods in terms of recovery rates, precision, and applicability across diverse matrix types.

Recovery rates with Method 3 consistently exceeded 84% across all certified reference materials, showing minimal deviation from certified values. This high level of consistency confirms the method's reliability for accurate REE determination in soils, sediments, and geological materials. The effective use of boric acid played a key role in mitigating fluoride precipitation, ensuring complete digestion of refractory minerals and improving matrix compatibility, an important factor in environmental and geochemical studies.

In addition to recovery performance, Method 3 exhibited excellent sensitivity, with low limits of detection and quantification, and robust repeatability, as indicated by HORRAT values below 2. These results confirm its suitability for trace-level analyses, particularly in regulatory and ecological monitoring contexts where analytical reliability is essential.

Furthermore, the method's efficiency, reflected in reduced acid consumption, shorter reaction times, and compatibility with ICP-MS/MS instrumentation, supports its scalability for routine laboratory applications. Its environmentally conscious design also contributes to safer and more sustainable analytical workflows.

In conclusion, Method 3 provides a robust and reliable approach for comprehensive REE quantification in environmental matrices. Its combination of high recovery rates, matrix compatibility, and sensitivity aligns well with the needs of environmental monitoring and industrial applications, supporting its recommendation as a standardized method for REE analysis in complex environmental samples.

Conflicts of 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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REFERENCES

(1) International Energy Agency (IEA). *The Role of Critical Minerals in Clean Energy Transitions*. OECD Publishing Paris, 2021. Available at: https://iea.blob.core.windows.net/assets/ffd2a83b-8c30-4e9d-980a-52b6d9a86fdc/TheRoleofCriticalMineralsinCleanEnergyTransitions.pdf (accessed 2025-08-26).

(2) Balaram, V. Rare Earth Elements: A Review of Applications, Occurrence, Exploration, Analysis, Recycling, and Environmental Impact. *Geosci. Front.* **2019**, *10* (4), 1285–1303. https://doi.org/10.1016/j.gsf.2018.12.005

(3) Rare Earth Elements. In: Scott, R. A. Ed. *Encyclopedia of Inorganic and Bioinorganic Chemistry*. Wiley, 2005. https://doi.org/10.1002/9781119951438.eibd0664

(4) Cotta, A. J. B.; Enzweiler, J. Classical and New Procedures of Whole Rock Dissolution for Trace Element Determination by ICP-MS. *Geostand. Geoanal. Res.* **2012**, *36* (1), 27–50. https://doi.org/10.1111/j.1751-908X.2011.00115.x

(5) Zawisza, B.; Pytlakowska, K.; Feist, B.; Polowniak, M.; Kita, A.; Sitko, R. Determination of Rare Earth Elements by Spectroscopic Techniques: A Review. *J. Anal. At. Spectrom.* **2011**, *26* (12), 2373–2390. https://doi.org/10.1039/C1JA10140D

(6) Fedyunina, N. N.; Seregina, I. F.; Bolshov, M. A.; Okina, O. I.; Lyapunov, S. M. Investigation of the Efficiency of the Sample Pretreatment Stage for the Determination of the Rare Earth Elements in Rock Samples by Inductively Coupled Plasma Mass Spectrometry Technique. *Anal. Chim. Acta* **2012**, *713*, 97–102. https://doi.org/10.1016/j.aca.2011.11.035

(7) Ebihara, M.; Hayano, K.; Shirai, N. Determination of Trace Rare Earth Elements in Rock Samples Including Meteorites by ICP-MS Coupled with Isotope Dilution and Comparison Methods. *Anal. Chim. Acta* **2020**, *1101*, 81–89. https://doi.org/10.1016/j.aca.2019.12.031

(8) Drogobuzhskaya, S.; Frolova, M.; Shishov, A.; Tsvetov, N. Comparison of Extraction Abilities of Deep Eutectic Solvents and Aqueous Acid Solutions for Extraction of Rare Earths and Transition Metals. *J. Rare Earths* **2024**, *42* (6), 1157–1164. https://doi.org/10.1016/j.jre.2023.06.014

(9) Mnculwane, H. T. Rare Earth Elements Determination by Inductively Coupled Plasma Mass Spectrometry after Alkaline Fusion Preparation. *Analytica* **2022**, *3* (1), 135–143. https://doi.org/10.3390/analytica3010010

(10) Ivanova, J. On the Microwave Digestion of Soils and Sediments for Determination of Lanthanides and Some Toxic and Essential Elements by Inductively Coupled Plasma Source Mass Spectrometry. *Talanta* **2001**, *54* (4), 567–574. https://doi.org/10.1016/S0039-9140(00)00640-8

(11) Nandy, A. K.; Manjhi, J. K.; Roy, N. K. Stream Sediment and Soil Samples by Microwave Digestion Followed by ICP-MS Measurement. *At. Spectrosc.* **2008**, *29*, 115–123.

(12) Kasar, S.; Murugan, R.; Arae, H.; Aono, T.; Sahoo, S. K. A Microwave Digestion Technique for the Analysis of Rare Earth Elements, Thorium and Uranium in Geochemical Certified Reference Materials and Soils by Inductively Coupled Plasma Mass Spectrometry. *Molecules* **2020**, *25* (21), 5178. https://doi.org/10.3390/molecules25215178

(13) Sucharová, J.; Suchara, I. Determination of 36 Elements in Plant Reference Materials with Different Si Contents by Inductively Coupled Plasma Mass Spectrometry: Comparison of Microwave Digestions Assisted by Three Types of Digestion Mixtures. *Anal. Chim. Acta* **2006**, *576* (2), 163–176. https://doi.org/10.1016/j.aca.2006.06.004

(14) Pradhan, S.; Zhang, J.; Jianguo, Q.; Yun, X. Characterization of Geological Certified Reference Materials by Inductively Coupled Plasma-Mass Spectrometry. *Anal. Lett.* **2015**, *48* (13), 2136–2158. https://doi.org/10.1080/00032719.2015.1010123

(15) Zimmermann, T.; Von Der Au, M.; Reese, A.; Klein, O.; Hildebrandt, L.; Pröfrock, D. Substituting HF by HBF_4 – an Optimized Digestion Method for Multi-Elemental Sediment Analysis *via* ICP-MS/MS. *Anal. Methods* **2020**, *12* (30), 3778–3787. https://doi.org/10.1039/D0AY01049A

(16) Wu, S.; Zhao, Y.-H.; Feng, X.; Wittmeier, A. Application of Inductively Coupled Plasma Mass Spectrometry for Total Metal Determination in Silicon-Containing Solid Samples Using the Microwave-Assisted Nitric Acid–Hydrofluoric Acid–Hydrogen Peroxide–Boric Acid Digestion System. *J. Anal. At. Spectrom.* **1996**, *11* (4), 287–296. https://doi.org/10.1039/JA9961100287

(17) Anders, E.; Grevesse, N. Abundances of the Elements: Meteoritic and Solar. *Geochim. Cosmochim. Acta* **1989**, *53* (1), 197–214. https://doi.org/10.1016/0016-7037(89)90286-X

(18) Yamada, N. Kinetic Energy Discrimination in Collision/Reaction Cell ICP-MS: Theoretical Review of Principles and Limitations. *Spectrochim. Acta, Part B* **2015**, *110*, 31–44. https://doi.org/10.1016/j.sab.2015.05.008

(19) Souza, L. R. R.; Zanatta, M. B. T.; Da Silva, I. A.; Da Veiga, M. A. M. S. Mercury Determination in Soil and Sludge Samples by HR CS GFAAS: Comparison of Sample Preparation Procedures and Chemical Modifiers. *J. Anal. At. Spectrom.* **2018**, *33* (9), 1477–1485. https://doi.org/10.1039/C8JA00152A

(20) Langmyhr, F. J.; Kringstad, K. 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. https://doi.org/10.1016/S0003-2670(01)81639-1

(21) Mitra, S. (Ed.) *Sample Preparation Techniques in Analytical Chemistry*. J. Wiley, Hoboken, N.J, 2003. https://doi.org/10.1002/0471457817

(22) Sneddon, J.; Hardaway, C.; Bobbadi, K. K.; Reddy, A. K. Sample Preparation of Solid Samples for Metal Determination by Atomic Spectroscopy—An Overview and Selected Recent Applications. *Appl. Spectrosc. Rev.* **2006**, *41* (1), 1–14. https://doi.org/10.1080/05704920500385445

(23) United States Environmental Protection Agency (U.S. EPA). *Method 3051A (SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils*. Revision 1, 2007. Washington, DC.

(24) United States Environmental Protection Agency (U.S. EPA). *Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices*. Revision 0, 1993. Washington, DC

(25) Fedyunina, N. N.; Ossipov, K. B.; Seregina, I. F.; Bolshov, M. A.; Statkus, M. A.; Tsysin, G. I. Determination of Rare Earth Elements in Rock Samples by Inductively Coupled Plasma Mass-Spectrometry after Sorption Preconcentration Using Pol-DETATA Sorbent. *Talanta* **2012**, *102*, 128–131. https://doi.org/10.1016/j.talanta.2012.07.026

(26) Coedo, A. G.; Dorado, M. T.; Padilla, I.; Alguacil, F. J. Use of Boric Acid to Improve the Microwave-Assisted Dissolution Process to Determine Fluoride Forming Elements in Steels by Flow Injection Inductively Coupled Plasma Mass Spectrometry. *J. Anal. At. Spectrom.* **1998**, *13* (10), 1193–1197. https://doi.org/10.1039/a803932a

SUPPLEMENTARY MATERIAL

This supplementary material presents comparisons of rare earth element (REE) concentration, recovery, and relative standard deviation values obtained using the digestion methods M1, M2, and M3, and the standardized methods EPA 3052 and 3051a, applied to TILL-3, NIST SRM 2709, QCM ITA-1, and NIST RM 8704 matrices.

Table S1. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion methods M1, M2, M3, and the standardized methods USEPA 3051a and 3052 applied to the TILL-3 CRM (n = 3 for all REEs).

TILL-3							
REE	**Certified values (ug g^{-1})**		**M1**	**M2**	**M3**	**3052**	**3051**
Sc	10	Mean (ug g^{-1})	10.3±1.7 (NS)	5.303±0.022	10.21±0.30 (NS)	10.05±0.64	5.45±0.86 (NS)
		Recovery (%)	103	53.0	102.1	103.7	54.5
		RSD (%)	16.74	0.22	2.95	6.40	8.59
Y	17	Mean (ug g^{-1})	8.8±2.6	3.78±0.48	14.85±0.15	8.76±0.45	8.8±1.4
		Recovery (%)	51.9	22.2	87.4	51.5	51.6
		RSD (%)	15.46	2.84	0.89	2.67	8.08
La	21	Mean (ug g^{-1})	6.93±1.5	3.92±0.25	16.67±0.89 (NS)	15.02±0.62 (NS)	19.8±3.1
		Recovery (%)	33.0	18.7	98.1	71.7	94.2
		RSD (%)	7.04	1.19	4.24	2.97	14.73
Ce	42	Mean (ug g^{-1})	18.1±2.1	11.55±0.63	37.4±2.2 (NS)	33.86±1.5 (NS)	44.8±6.7
		Recovery (%)	43.0	27.5	89.0	82.4	106.7
		RSD (%)	8.45	1.49	5.17	3.65	15.98
Pr	-	Mean (ug g^{-1})	2.12±0.26	1.12±0.079	2.451±0.070	3.83±0.20	3.31±0.75
		Recovery (%)	-	-	-	-	-
		RSD (%)	23.97	7.09	2.86	5.04	22.74
Nd	16	Mean (ug g^{-1})	8.3±2.2	4.45±0.31	16.47±0.66 (NS)	14.92±0.71 (NS)	18.2±2.7 (NS)
		Recovery (%)	52.0	27.8	96.9	95.8	113.8
		RSD (%)	13.54	1.92	4.10	4.17	16.61
Sm	3.3	Mean (ug g^{-1})	1.85±0.44	1.003±0.087	3.374±0.086 (NS)	3.05±0.20 (NS)	3.31±0.54 (NS)
		Recovery (%)	56.1	30.4	102.2	93.8	100.4
		RSD (%)	13.18	2.65	2.62	5.90	16.32
Eu	<1.0	Mean (ug g^{-1})	0.54±0.16	0.32±0.039	0.913±0.029	0.822±0.040	0.669±0.084
		Recovery (%)	54.5	32.0	91.3	83	66.9
		RSD (%)	15.79	3.87	2.91	4.03	8.40
Gd	-	Mean (ug g^{-1})	2.00±0.73	1.024±0.09	2.758±0.072	2.67±0.23	2.49±0.41
		Recovery (%)	-	-	-	-	-
		RSD (%)	36.43	8.83	2.62	8.73	16.51
Tb	<0.5	Mean (ug g^{-1})	0.245±0.068	0.168±0.012	0.4466±0.0010	0.382±0.026	0.355±0.055
		Recovery (%)	51.0	33.6	91.1	80.7	71.1
		RSD (%)	13.65	2.36	0.19	5.27	11.05
Dy	-	Mean (ug g^{-1})	2.41±0.79	0.933±0.045	2.537±0.050	2.27±0.17	1.84±0.31
		Recovery (%)	-	-	-	-	-
		RSD (%)	32.72	4.87	1.98	7.58	16.53

(continued on next page)

Table S1. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion methods M1, M2, M3, and the standardized methods USEPA 3051a and 3052 applied to the TILL-3 CRM (n = 3 for all REEs). (continued)

			TILL-3				
REE	**Certified values (ug g^{-1})**		**M1**	**M2**	**M3**	**3052**	**3051**
Ho	-	Mean (ug g^{-1})	0.47±0.16	0.196±0.018	0.486±0.015	0.440±0.026	0.342±0.050
		Recovery (%)	-	-	-	-	-
		RSD (%)	33.11	9.38	3.11	5.83	14.71
Er	1.4	Mean (ug g^{-1})	0.99±0.20	0.162±0.021	1.427±0.033 (NS)	1.217±0.066	0.90±0.12
		Recovery (%)	70.7	11.6	101.9	89.1	64.3
		RSD (%)	14.60	1.49	2.33	4.74	8.88
Tm	-	Mean (ug g^{-1})	0.152±0.032	0.27±0.029	0.2290±0.0093	0.1912±0.0092	0.131±0.017
		Recovery (%)	-	-	-	-	-
		RSD (%)	20.98	10.65	4.07	4.82	12.75
Yb	1.5	Mean (ug g^{-1})	1.19±0.22	0.628±0.077	1.454±0.067 (NS)	1.188±0.046	0.74±0.10
		Recovery (%)	79.3	41.9	96.9	80.6	49.5
		RSD (%)	14.70	5.11	4.44	3.09	6.85
Lu	0.2	Mean (ug g^{-1})	0.200±0.033	0.102±0.016	0.2064±0.0023	0.1720±0.0093	0.105±0.015
		Recovery (%)	100.0	53.0	103.2	86.8	52.3
		RSD (%)	16.42	7.77	1.13	23.18	7.46

(NS) = Do not differ statistically ($p<0.05$) according to the *t*-test (n=3), n=3 for all measurements.

Table S2. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion method M3 and the standardized methods USEPA 3051a and 3052 applied to the NIST SRM 2709 (n = 3 for all REEs).

			NIST SRM 2709		
REE	**Certified values (ug g^{-1})**		**M3**	**3052**	**3051a**
Sc	11.1±0.1	Mean (ug g^{-1})	10.0±1.4 (NS)	9.3±1.2	9.03±0.58 (NS)
		Recovery (%)	90.3	79.8	81.3
		RSD (%)	9.7	10.5	5.3
Y	-	Mean (ug g^{-1})	13.74±0.56	8.2±0.81	12.9±1.10
		Recovery (%)	-	-	-
		RSD (%)	4.04	9.84	8.23
La	21.7±0,4	Mean (ug g^{-1})	17.8±2.5 (NS)	12.3±1.5	20.5±2.2 (NS)
		Recovery (%)	82.1	60.6	94.4
		RSD (%)	6.9	6.9	10.3
Ce	42±1	Mean (ug g^{-1})	37.5±4.7 (NS)	28.0±3.1 (NS)	46.1±4.6
		Recovery (%)	89.3	70.1	109.9
		RSD (%)	7.3	7.4	10.9
Pr	-	Mean (ug g^{-1})	2.01±0.17	3.01±0.36	3.37±0.52
		Recovery (%)	-	-	-
		RSD (%)	8.46	11.66	15.37

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Table S2. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion method M3 and the standardized methods USEPA 3051a and 3052 applied to the NIST SRM 2709 (n = 3 for all REEs). (continued)

NIST SRM 2709					
REE	**Certified values (ug g^{-1})**		**M3**	**3052**	**3051a**
Nd	17	Mean (ug g^{-1})	16.6±1.6 (NS)	11.7±1.2 (NS)	18.6±1.9
		Recovery (%)	97.9	70.8	109.3
		RSD (%)	9.3	7.5	11.1
Sm	4	Mean (ug g^{-1})	3.67±0.27 (NS)	2.49±0.26 (NS)	3.66±0.34
		Recovery (%)	90.96	62.27	91.56
		RSD (%)	6.69	6.54	8.38
Eu	0.83±0.02	Mean (ug g^{-1})	0.855±0.077 (NS)	0.604±0.040 (NS)	0.77±0.07
		Recovery (%)	103	73.2	93.1
		RSD (%)	9.26	4.86	8.64
Gd	3,0±0.1	Mean (ug g^{-1})	2.974±0.025 (NS)	2.28±0.19 (NS)	3.17±0.33
		Recovery (%)	99.1	76.2	105.6
		RSD (%)	0.82	6.21	10.84
Tb	0.5	Mean (ug g^{-1})	0.616±0.018	0.335±0.027	0.470±0.033 (NS)
		Recovery (%)	123.3	66.7	94.0
		RSD (%)	3.5	5.4	6.7
Dy	3	Mean (ug g^{-1})	2.871±0.070 (NS)	2.07±0.15 (NS)	2.73±0.27
		Recovery (%)	95.7	69.3	90.9
		RSD (%)	2.32	4.85	8.87
Ho	-	Mean (ug g^{-1})	0.602±0.050	0.412±0.033	0.511±0.040
		Recovery (%)	-	-	-
		RSD (%)	8.26	8.02	7.82
Er	-	Mean (ug g^{-1})	1.511±0.085	1.18±0.11	1.36±0.11
		Recovery (%)	-	-	-
		RSD (%)	5.62	9.34	8.01
Tm	-	Mean (ug g^{-1})	0.263±0.014	0.180±0.014	0.194±0.019
		Recovery (%)	-	-	-
		RSD (%)	5.47	7.54	9.55
Yb	2	Mean (ug g^{-1})	1.70±0.12	1.14±0.11	1.13±0.11
		Recovery (%)	85.1	57.7	56.3
		RSD (%)	5.99	5.53	5.23
Lu	0.3	Mean (ug g^{-1})	0.264±0.018 (NS)	0.174±0.010 (NS)	0.163±0.013 (NS)
		Recovery (%)	88.0	58.0	54.2
		RSD (%)	6.04	36.85	4.24

(NS) = Do not differ statistically ($p<0.05$) according to the *t*-test (n=3), n=3 for all measurements.

Table S3. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion method M3 and the standardized methods USEPA 3051a and 3052 applied to the QCM ITA-1 (n = 3 for all REEs).

QCM ITA-1					
REE	**Certified values (ug g^{-1})**		**M3**	**3052**	**3051a**
Sc	0.44±0.05	Mean (ug g^{-1})	0.50±0.13 (NS)	0.45±0.10 (NS)	0.265±0.064 (NS)
		Recovery (%)	113.9	91.9	60.2
		RSD (%)	3.6	23.6	14.5
Y	4.5±0.2	Mean (ug g^{-1})	3.38±0.12	2.27±0.21 (NS)	2.77±0.74
		Recovery (%)	75.1	49.3	61.6
		RSD (%)	2.6	4.7	16.5
La	1.9±0.04	Mean (ug g^{-1})	1.92±0.15 (NS)	2.22±0.20 (NS)	1.00±0.73 (NS)
		Recovery (%)	100.8	114.3	52.7
		RSD (%)	7.7	10.5	38.2
Ce	3.8±0.1	Mean (ug g^{-1})	3.266±0.057	4.42±0.40 (NS)	2.52±0.51
		Recovery (%)	85.9	113.5	66.3
		RSD (%)	1.5	10.6	13.4
Pr	0.47±0.01	Mean (ug g^{-1})	0.471±0.024 (NS)	0.540±0.048 (NS)	0.484±0.043 (NS)
		Recovery (%)	100.2	114.8	102.9
		RSD (%)	5.1	10.3	9.1
Nd	2.2±0.1	Mean (ug g^{-1})	2.30±0.14 (NS)	2.40±0.15 (NS)	2.19±0.18 (NS)
		Recovery (%)	104.1	108.4	99.6
		RSD (%)	6.1	8.3	8.2
Sm	0.58±0.02	Mean (ug g^{-1})	0.567±0.034 (NS)	0.663±0.029 (NS)	0.618±0.057
		Recovery (%)	97.8	116.4	106.5
		RSD (%)	5.80	4.9	9.9
Eu	0.200±0.004	Mean (ug g^{-1})	0.226±0.011 (NS)	0.227±0.013 (NS)	0.212±0.010 (NS)
		Recovery (%)	102.9	111.4	105.9
		RSD (%)	5.7	6.7	4.8
Gd	0.80±0.02	Mean (ug g^{-1})	0.781±0.055 (NS)	0.905±0.053 (NS)	0.843±0.044 (NS)
		Recovery (%)	97.7	109.5	105.3
		RSD (%)	6.9	6.6	5.5
Tb	0.120±0.002	Mean (ug g^{-1})	0.121±0.010 (NS)	0.1221±0.0078 (NS)	0.1135±0.0059 (NS)
		Recovery (%)	100.7	98.4	94.6
		RSD (%)	8.0	6.5	4.9
Dy	0.70±0.02	Mean (ug g^{-1})	0.679±0.028 (NS)	0.631±0.029	0.617±0.026 (NS)
		Recovery (%)	96.9	90.1	88.2
		RSD (%)	4.0	4.1	3.7
Ho	0.130±0.005	Mean (ug g^{-1})	0.1290±0.0073 (NS)	0.1173±0.0092	0.1053±0.0081 (NS)
		Recovery (%)	99.2	94.3	81
		RSD (%)	5.6	7.0	6.3
Er	0.39±0.02	Mean (ug g^{-1})	0.3376±0.0073	0.253±0.015	0.234±0.014
		Recovery (%)	86.6	65.1	59.9
		RSD (%)	1.7	3.9	3.5

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Table S3. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion method M3 and the standardized methods USEPA 3051a and 3052 applied to the QCM ITA-1 (n = 3 for all REEs). (continued)

QCM ITA-1					
REE	**Certified values (ug g^{-1})**		**M3**	**3052**	**3051a**
Tm	0.052±0.003	Mean (ug g^{-1})	0.0499±0.0011 (NS)	0.0404±0.0053	0.0399±0.0021 (NS)
		Recovery (%)	96	72.8	76.8
		RSD (%)	2.1	10.2	4.1
Yb	0.36±0.02	Mean (ug g^{-1})	0.272±0.029	0.225±0.073	0.158±0.023 (NS)
		Recovery (%)	75.7	51.7	44.0
		RSD (%)	8.0	20.4	6.4
Lu	0.058±0.003	Mean (ug g^{-1})	0.0446±0.0051	0.0260±0.0026	0.02±0.00093
		Recovery (%)	76.8	43.4	40.0
		RSD (%)	8.8	126.4	1.6

(NS) = Do not differ statistically ($p<0.05$) according to the *t*-test (n=3), n=3 for all measurements

Table S4. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion method M3 and the standardized methods USEPA 3051a and 3052 applied to the NIST RM 8704 (n = 3 for all REEs).

NIST RM 8704					
REE	**Certified values (ug g^{-1})**		**M3**	**3052**	**3051a**
Sc	11.26±0.19	Mean (ug g^{-1})	9.7±0.46	9.34±0.55	4.7±0.39
		Recovery (%)	86.13	82.96	41.77
		RSD (%)	4.10	4.88	3.43
Y	-	Mean (ug g^{-1})	25.33±0.95	12±1.6	13.7±2.3
		Recovery (%)	-	-	-
		RSD (%)	3.75	13.13	16.79
La	-	Mean (ug g^{-1})	24.91±0.72	14±2	14.8±2.3
		Recovery (%)	-	-	-
		RSD (%)	2.88	14.49	15.53
Ce	66.5±2	Mean (ug g^{-1})	54.96±0.22	32.8±4.2	37.1±5.6
		Recovery (%)	82.65	49.3	67.2
		RSD (%)	0.32	6.37	8.36
Pr	-	Mean (ug g^{-1})	5.52±0.18	3.99±0.54	2.88±0.8
		Recovery (%)	-	-	-
		RSD (%)	3.33	13.56	27.89
Nd	-	Mean (ug g^{-1})	26.59±0.58	16.2±2.2	18.8±3
		Recovery (%)	-	-	-
		RSD (%)	2.17	13.89	16.18
Sm	-	Mean (ug g^{-1})	5.88±0.23	3.73±0.38	4.37±0.72
		Recovery (%)	-	-	-
		RSD (%)	3.91	10.30	16.52

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Table S4. Results of mean concentration, standard deviation, recovery and relative standard deviation (RSD) obtained using the digestion method M3 and the standardized methods USEPA 3051a and 3052 applied to the NIST RM 8704 (n = 3 for all REEs). (continued)

NIST RM 8704					
REE	**Certified values (ug g^{-1})**		**M3**	**3052**	**3051a**
Eu	1.31±0.038	Mean (ug g^{-1})	1.236±0.039	0.818±0.075	0.88±0.14
		Recovery (%)	94.333	62.44	67.22
		RSD (%)	2.97	5.72	10.54
Gd	-	Mean (ug g^{-1})	5.29±0.16	3.43±0.4	4.07±0.75
		Recovery (%)	-	-	-
		RSD (%)	2.94	11.55	18.43
Tb	-	Mean (ug g^{-1})	0.781±0.024	0.522±0.046	0.586±0.096
		Recovery (%)	-	-	-
		RSD (%)	3.02	8.78	16.43
Dy	-	Mean (ug g^{-1})	4.98±0.16	3.81±0.65	3.16±0.54
		Recovery (%)	-	-	-
		RSD (%)	3.31	17.14	17.25
Ho	-	Mean (ug g^{-1})	0.944±0.034	0.602±0.065	0.58±0.1
		Recovery (%)	-	-	-
		RSD (%)	3.58	10.86	17.46
Er	-	Mean (ug g^{-1})	3.07±0.13	1.69±0.14	1.43±0.25
		Recovery (%)	-	-	-
		RSD (%)	4.19	8.25	17.73
Tm	-	Mean (ug g^{-1})	0.4157±0.0059	0.262±0.028	0.198±0.03
		Recovery (%)	-	-	-
		RSD (%)	1.41	10.71	15.14
Yb	-	Mean (ug g^{-1})	2.88±0.11	1.75±0.19	1.12±0.18
		Recovery (%)	-	-	-
		RSD (%)	3.73	10.75	15.73
Lu	-	Mean (ug g^{-1})	0.409±0.02	0.27±0.19	0.157±0.023
		Recovery (%)	-	-	-
		RSD (%)	4.81	69.42	14.54

(NS) = Do not differ statistically ($p<0.05$) according to the *t*-test (n=3), n=3 for all measurements.