

Simultaneous Measurement of $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ Ratios in Natural Geological Samples by MC-ICP-MS After One Stage Chemical Purification Using TODGA Resin

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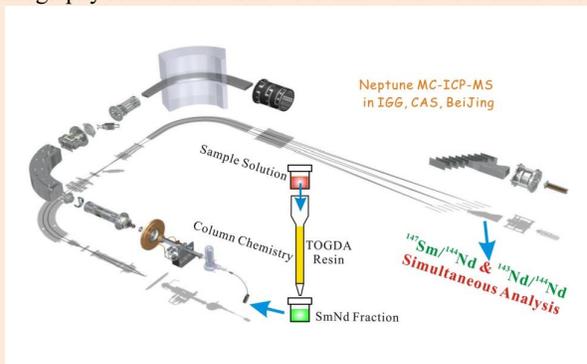
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ABSTRACT: We demonstrate the capability of simultaneous measurement of $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in natural geological samples by MC-ICP-MS after one stage chemical purification with TODGA resin as a potential alternative to the isotope dilution method. After sample digestion, one-step chemical isolation of Sm and Nd with almost 100% recovery from sample matrix elements was accomplished by using the TODGA extraction chromatography resin. The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were simultaneously determined through a single analytical session utilizing MC-ICP-MS. The present analytical protocol relies on the mathematical correction of isobaric interference, thus alleviating the separation of Nd and Sm from each other and utilizing enriched tracers. The feasibility of the present protocol was investigated by the reduplicate analyses of internationally certified reference materials (CRMs), which encompassed a wide range of chemical compositions and were of a similar order as those obtained through the isotope dilution method. This also reduced the cost and time consumption of both chemical preparation and mass spectrometric measurements.



INTRODUCTION

The isotope composition of radiogenic daughter nuclides (*e.g.*, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$) and the ratio of parent to daughter nuclides (*e.g.*, $^{87}\text{Rb}/^{86}\text{Sr}$, $^{147}\text{Sm}/^{144}\text{Nd}$, $^{176}\text{Lu}/^{177}\text{Hf}$) are generally required for both dating and tracing purposes in Earth and planetary sciences.¹ The classic ^{147}Sm - ^{143}Nd isotopic system (1.06×10^{11} yr, half-life) has been extensively utilized as a powerful tracer or chronometer since the 1970s.¹ Isotope dilution (ID) mass spectrometry, without doubt, is a well-known technique for its excellent precision and accuracy when properly utilized. Despite its tedious, time-consuming, restrictive, and extensive source filament and loading preparation procedure, isotope dilution thermal ionization mass spectrometry (ID-TIMS) is still regarded as a benchmark technique for Sm–Nd measurement.^{2,3} Recently,

isotope dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) has become a competitive technique for Sm–Nd analysis with high sample throughput and comparable precision to classical ID-TIMS.⁴

The classic isotope dilution method (ID-TIMS or ID-MC-ICP-MS) is usually associated with laborious two-step chemical purification and mass spectrometric measurement of Sm–Nd isotope ratios.^{3,4} The first step is to purify REEs from the sample matrix elements utilizing a standard cation exchange resin (AG50W-X8 or 12) after sample decomposition. Then, the Nd fraction must be separated from Sm as completely as possible utilizing extraction chromatography resin (*e.g.*, P204, P507, and Ln resin) to eliminate isobaric interference of ^{144}Sm (3.1%) on ^{144}Nd (23.8%). Finally, the Sm or Nd fraction must be determined separately for the Sm or Nd concentration and Nd composition

during mass spectrometric measurement.^{2–4}

Thus, it is important to develop methods that enable analysts to simultaneously measure $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. MC-ICP-MS has the potential to directly determine the isotope ratios of different elements because of its commercial advent in the mid-1990s.^{5–8} In early studies, several attempts have been made to measure the Sm/Nd ratio in geological samples utilizing quadrupole ICP-MS. However, these methods cannot compete with the ID method in terms of precision and accuracy.^{9–10} Luis *et al.*¹¹ and Yang *et al.*¹² have presented a rapid method for measuring the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of real geological samples after one-step chemical purification on a cation-exchange resin (AG50W-X8 or 12) utilizing MC-ICP-MS. Recently, Yang *et al.*¹³ have successfully demonstrated the simultaneous determination of $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of Sm–Nd mixtures utilizing MC-ICP-MS, comparable to isotopic dilution analysis.

We attempted to establish a rapid analytical method to simultaneously determine $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in natural geological samples utilizing MC-ICP-MS after one-step chemical purification. For such studies, ensuring the 100% recovery of Sm and Nd during their chemical separation of Sm and Nd from the sample matrix is critical. Here, we developed a one-stage TODGA method for the simultaneous separation of Sm, Nd, $^{147}\text{Sm}/^{144}\text{Nd}$, and $^{143}\text{Nd}/^{144}\text{Nd}$. Several internationally certified reference materials (CRMs) with wide ranges of Sm/Nd and bulk compositions have validated the robustness of this procedure. The proposed protocol greatly simplifies both chemical preparation and mass spectrometric measurement, greatly reducing the experimental cost and improving efficiency and is a potential alternative to isotope dilution analysis in isotope geosciences.

EXPERIMENTAL

Chemical reagent and materials. The electrical resistivity of Milli-Q H_2O is $18.2\ \text{M}\Omega\ \text{cm}$ at $25\ ^\circ\text{C}$ from Millipore (Elix-Millipore, USA). HF, HCl, and HNO_3 from the Beijing Institute of Chemical Reagents were purified by the SavillexTM DST-1000 sub-boiling distillation system (Minnetonka, USA). Without additional purification, we directly utilized 70% HClO_4 and high-purity H_3BO_3 obtained from Acros Organics Belgium. The TODGA extraction chromatography resin was procured from Eichrom Technologies (Darien, IL, USA). A reservoir with $4\ \text{cm} \times 5\ \text{mm}$ dimension and 10-mL extension were packed with $\sim 1\text{-mL}$ TODGA resin (50–100 μm particle mesh size). Certified multi-element standard mixture solutions were obtained from SPEX CertiPrep, which included 10 mg/L of 17 elements—Y, Sc, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th. The international CRMs for rock powder (BCR-2, BIR-1, AGV-2, W-2, and GSP-2) were obtained from the United States Geological

Survey.

Sample digestion. Samples were prepared in Class 100 (ISO-class 5) horizontal laminar airflow hoods inside a Class 1000 (ISO-class 6) over-pressured clean laboratory. Approximately 100 mg of basaltic to granodioritic CRMs of rock powder was weighed into a 7-mL round-bottom SavillexTM Teflon-PFA screw-cap capsule. The mixed concentrated HF– HNO_3 – HClO_4 (2 mL–1 mL–0.2 mL) was added and sealed on a hot plate for one week. After complete dissolution, the capsule was opened and evaporated to fumes at *ca.* $190\ ^\circ\text{C}$ to remove HF, converting insoluble fluorides into soluble compounds. The residues were completely dissolved in 3 mL 3% H_3BO_3 solution in 3 M HCl at $100\ ^\circ\text{C}$ on a hotplate overnight. The 3% H_3BO_3 solution completely dissolved the formed fluorides. After the sample completely dried, 5 mL of concentrated HNO_3 was added to the residue. This procedure was repeated until a complete dissolution was achieved. Finally, the residue was dissolved in 5 mL of 3.5 M HNO_3 and sealed overnight on a hot plate before column chemistry.

Column chemistry. The sample solution was collected in 5 mL of 3.5 M HNO_3 and centrifuged for 10 min at 5000 rpm. The 1-mL TODGA resin was preconditioned with 20 mL of 0.05 M HCl to remove residual REEs from the resin, followed by 10 mL of Mill-Q water and 10 mL of 3.5 M HNO_3 to convert to the loading acid solution. The loading sample solution was first eluted with 10 mL of 3.5 M HNO_3 to remove bulk matrix elements (*e.g.*, Fe, Mg, Al, K, Na, Ti, Cr, and Ba). Then, residual major (*e.g.*, Ca) and transition elements were further washed in 25 mL of 12 M HNO_3 .^{14–15} Finally, all REEs were thoroughly stripped in 30-mL 0.05 M HCl and collected into 50-mL clean PFA Teflon vials.^{16–18} The REEs fraction was gently evaporated and taken up with 2% HNO_3 for Sm–Nd isotope analyses by MC-ICP-MS. Prior to the analyses, further dilution was performed to obtain an appropriate beam intensity during the mass spectrometric measurement. The total procedural blanks for this technique were $<20\ \text{pg}$ each of Nd and Sm. The recovery of Sm and Nd in this one-step isolation was 100%, which is essential and prerequisite for $^{147}\text{Sm}/^{144}\text{Nd}$ isotope ratios, and will be discussed later.

Mass spectrometry. A Neptune MC-ICP-MS device (Thermo Scientific, USA) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), was utilized for simultaneous Sm–Nd measurement. Sample introduction was via a self-aspirating *ca.* $50\ \mu\text{L}\ \text{min}^{-1}$ PFA concentric nebulizer (Table 1). After measurement, the sample introduction system was rinsed with 2% HNO_3 for 5 min to minimize memory effects. $^{147}\text{Sm}^+$ and $^{149}\text{Sm}^+$ were monitored to assess potential isobaric interferences from $^{144}\text{Sm}^+$, $^{148}\text{Sm}^+$, and $^{150}\text{Sm}^+$ on $^{144}\text{Nd}^+$, $^{148}\text{Nd}^+$, and $^{150}\text{Nd}^+$, respectively (Table 2). The Nd isotope analyses comprised nine blocks of six cycles per block with an integration time of 8 s per cycle. For sample analysis, a SPEX CertiPrep REEs mixture was repeatedly measured for every five samples for the external

Table 1 Typical instrumental operating conditions and data acquisition parameters

Neptune MC-ICP-MS	
RF forward power	1280 W
Cooling gas	16 L/min
Auxiliary gas	0.8 L/min
Sample gas	~1.10 L/min (optimized daily)
Extraction	-2000 V
Focus	-645 V
Detection system	Nine Faraday collectors
Interface cone	Nickel (standard sample and H cone)
Mass resolution	400 (Low)
Acceleration voltage	10 kV
Spray chamber	Glass cyclonic
Nebulizer type	Micromist PFA nebulizer
Sample uptake rate	50 μ L/min
Uptake mode	Self-aspiration
Sensitivity on ^{146}Nd	8 V/ppm (10^{11} Ω resistors)
Sampling mode	9 blocks of 6 cycles
Integration time	8 s
Baseline determination	ca. 1 min on peak in 2% HNO_3

calibration for $^{147}\text{Sm}/^{144}\text{Nd}$ ratio.¹³ Over the analytical session of this study, 30 analyses of JNdi-1 yielded a $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.512110 ± 18 (2SD), identical to the recommended value. Meanwhile, 15 analyses of SPEX CertiPrep REEs gave a $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.511090 ± 16 (2SD).

For data reduction, raw data were exported and reduced offline to correct for instrumental mass bias and isobaric interference. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ utilizing the exponential law, where isobaric interference correction of ^{144}Sm on ^{144}Nd was performed with an interference-free $^{147}\text{Sm}/^{149}\text{Sm} = 1.08680$ ratio for Sm mass fractionation.^{19,20} Data reduction was also performed by a computer utilizing a self-written Excel Visual Basic for Applications macro program, within which interference corrections were made, followed by a mass fractionation correction utilizing the exponential law. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratios were obtained in two steps. First, $^{147}\text{Sm}/^{144}\text{Nd}$ ratio was calculated from the corrected ^{144}Nd and measured ^{147}Sm intensity utilizing an exponential law, assuming the same mass bias as Sm. Second, it was externally calibrated with the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the SPEX CertiPrep REEs mixture for every five samples.

RESULTS AND DISCUSSION

Purity, yield, and procedural blank. Generally, the analyte of

interest has to be isolated or removed from the matrix element of the sample as completely as possible, employing ion exchange chromatography before its mass spectrometric measurement.^{2,3,21,22} Considering that our goal is to simultaneously measure $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in a single sample solution with MC-ICP-MS, it is necessary to obtain a solution containing Sm and Nd present in the sample without mutual fractionation of these elements during chemical isolation, but with high purity. This implies that the ion exchange resin technique has to yield Sm and Nd cuts with 100% recovery. The sample solution was processed in a single step on a TODGA extraction chromatography resin.^{14, 15}

To test the recovery of REEs, an aliquot of the multi-element standard solution (~10 ppm) was added to concentrated HF, HNO_3 , and HClO_4 and processed through sample dissolution and extraction chromatography, similar to that for real geological samples. Compared with certified values, the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios demonstrated the quantitative recovery of the elements of interest. For conventional Sm–Nd isotopic analysis, the 100-mg sample utilized for most geological samples was sufficient (more than 100 ng) for Sm and Nd.²³ Total procedural blanks, including sample dissolution and column chemistry, were less than 20 pg for Sm and Nd, which is <0.02% of Sm–Nd processed and thus considered to be negligible.

Our previous experiment indicated that although standard cation resin could obtain 100% Sm and Nd recovery with 30 mL of 6 M HCl after eluting major elements, Rb, Sr, and most Ba usually were collected in REEs fractions, in which $^{130}\text{Ba}^{16}\text{O}^+$ interference $^{146}\text{Nd}^+$.²²⁻²⁵ Therefore, we do not utilize standard cation resin here.^{18, 26}

Simultaneous Sm–Nd isotopic measurement. To simultaneously obtain $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in an analyse for the sample solution, great care must be taken to correct the contribution of the isobaric interference of ^{144}Sm on the ^{144}Nd signal. This study adopted an approach ($^{147}\text{Sm}/^{149}\text{Sm} = 1.08680$ and $^{144}\text{Sm}/^{149}\text{Sm} = 0.22332$) similar to *in situ* Nd isotopic analysis of enriched LREEs accessory minerals.^{27,28} First, the measured $^{147}\text{Sm}/^{149}\text{Sm}$ ratio was utilized to obtain the Sm mass bias factor, and then utilized $^{147}\text{Sm}/^{144}\text{Sm}$ ratio to calculate the ^{144}Sm value considering the more abundant ^{147}Sm than ^{149}Sm in nature. Next, the interference-corrected $^{146}\text{Nd}/^{144}\text{Nd}$ ratio was employed to calculate the Nd mass bias factor. Finally, the correct $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ ratios were exponentially normalized with the obtained Nd mass bias factor. Moreover, our obtained

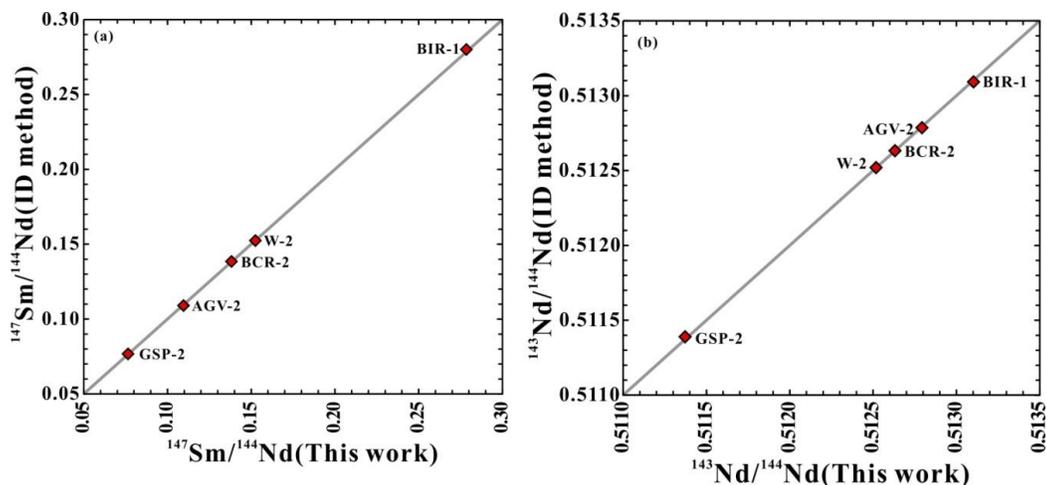
Table 2 Faraday cup configuration for simultaneous Sm–Nd isotopic measurement

Faraday cup	L4	L3	L2	L1	Center	H1	H2	H3	H4
Measured element	$^{142}\text{Nd}^+$	$^{143}\text{Nd}^+$	$^{144}\text{Nd}^+$	$^{145}\text{Nd}^+$	$^{146}\text{Nd}^+$		$^{148}\text{Nd}^+$		$^{150}\text{Nd}^+$
Interference element	$^{142}\text{Ce}^+$		$^{144}\text{Sm}^+$			$^{147}\text{Sm}^+$	$^{148}\text{Sm}^+$	$^{149}\text{Sm}^+$	$^{150}\text{Sm}^+$

Bolded text indicates masses utilized to determine mass fractionation.

Table 3 $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ data for CRMs measured here and literature values

CRMs	$^{147}\text{Sm}/^{144}\text{Nd}$		This work ($\pm 2\sigma_m$)	$^{143}\text{Nd}/^{144}\text{Nd}$		This work ($\pm 2\sigma_m$)
	This work	Reference Value (ID method)		Reference Value (ID method)	This work	
BCR-2	0.1380	0.1379~0.1401 ^{3,4,18,21-23,26}	0.512628(07)	0.512601~0.512642 ^{3,4,16-18,21-23,26}	0.348413(05)	
	0.1377		0.512630(05)		0.348415(03)	
BIR-1	0.2780	0.2764~0.2864 ^{3,4,18,21-22,31}	0.513099(11)	0.513084~0.513107 ^{3,4,21-22,31}	0.348412(07)	
AGV-2	0.1096	0.1086~0.1093 ^{3,18,23,26}	0.512793(09)	0.512765~0.512811 ^{3,16-18,23,26}	0.348414(05)	
W-2	0.1522	0.1514~0.1532 ^{3,4,21-23,26}	0.512526(08)	0.512490~0.512537 ^{3,4,21-23,26}	0.348418(06)	
	0.1528		0.512510(10)		0.348414(07)	
GSP-2	0.0764	0.0767 ³	0.511372(10)	0.511353~0.511389 ³	0.348416(06)	

**Fig. 1** Comparison of (a) $^{147}\text{Sm}/^{144}\text{Nd}$ and (b) $^{143}\text{Nd}/^{144}\text{Nd}$ data of international CRMs between simultaneous measurement here and classic isotope dilution method (Table 1). Error bars are greatly smaller than symbols in all cases and are not presented on this scale.

$^{145}\text{Nd}/^{144}\text{Nd}$ ratios of CRMs (Table 3) after isobaric interference correction agreed well with the recommended value of 0.348415 obtained by TIMS.²⁹ The detailed data reduction procedure can be found elsewhere.^{12,13} Fisher et al.²⁸ recently adopted our revised values of Sm isotope ratios, further confirming the correctness of the present protocol.

In addition to the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is also important for classic Sm-Nd isotopic tracing to get the initial Nd (ϵ_{Nd}) composition or dating of geological samples, particularly in relatively old age (e.g., Archean) sample with elevated $^{147}\text{Sm}/^{144}\text{Nd}$.³⁰ Generally, the reproducibility of $^{147}\text{Sm}/^{144}\text{Nd}$ ratio by ID-TIMS or MC-ICP-MS is ca. 1% for inter-laboratory comparison, which is rational for geochronological and geochemical studies.⁴ Here, external calibration with a known $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of REEs mixture measured by ID method can be utilized to correct $^{147}\text{Sm}/^{144}\text{Nd}$ ratio in real CRM solution after the above-mentioned single chemical purification.

Analytical results of international rock reference materials. To estimate the robustness of our protocol, one or two aliquots of CRM rock powder were subjected to a chemical procedure, considering the well-known sample heterogeneity of natural

geological samples. The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios obtained here were compared with literature data, which were determined by classic ID-TIMS or ID-MC-ICP-MS.^{2-4,9,22,23,31} As illustrated in Table 3 and Fig. 1. The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of real geological reference materials from this work were within the analytical uncertainties of the literature values, indicating our present procedure's overall capability and validity. Based on these data, our methodology is suitable and feasible for Sm-Nd isotope geochemical studies.

Advantages over isotope dilution method. Compared with the classic ID-MS method, the present simultaneous measurement offers several improvements in chemical purification and mass spectrometric measurement.^{2-4,9,22,23,31} Specifically, 1) chemical separation is greatly simplified from two- to one-step procedures after sample dissolution, which makes Sm-Nd separation unnecessary and reduces the time and effort required. 2) Mass spectrometry measurements are shortened from two to one after chemical isolation, which doubles the sample throughput. The present protocol for simultaneous analysis is highly efficient, with only 10 min per sample.¹³ 3) The time-consuming spike calibration preparation for costly isotopically enriched tracers is avertable, in which the reverse isotope dilution method for

concentration and isotopic composition calibration before its usage has been eliminated.^{29,31} Considering the different isotopic compositions of enriched tracers from natural samples, it is very difficult to calibrate mass fractionation during mass spectrometric measurement before usage.³² 4) Considering the relatively wide mixture ratio of samples and tracers, over- or under-spiking during the ID method is unavoidable and usually occurs for Sm. Therefore, our present protocol alleviates the interference of some of the measured isotopes from the enriched spike introduction during previous Nd concentration and isotopic composition measurements in a single-mass spectrometric run.^{4,29} In summary, in terms of simplicity, feasibility, and rapidity, our developed protocol has obvious advantages over previous ID-TIMS or ID-MC-ICP-MS methods, as illustrated by the highly reproducible data determination of CRMs (Table 3 and Fig. 1).

CONCLUSION

A simple and rapid analytical protocol for simultaneous determination of $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in geological samples utilizing MC-ICPMS is established, which can be an alternative to classic isotope dilution analysis. One-stage chemical purification of REEs with 100% recovery was performed with TODGA extraction chromatography resins. Meanwhile, single-time mass spectrometric measurement was required by relying on the mathematical correction of isobaric interferences, which alleviates the separation of Nd and Sm from each other or other REEs, and utilizing an enriched tracer. The accuracy and precision of the present protocol, based on duplicate analyses of international CRMs encompassing a wide range of bulk compositions, were found to be of similar order as those obtained by employing the isotope dilution method. Our developed methodology greatly simplifies chemical preparation and mass spectrometric measurements, reducing experimental costs and improving efficiency.

AUTHOR INFORMATION



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Notes

The authors declare no competing financial interest.

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