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Direct determination of rare earth elements in atmospheric precipitation using a membrane desolvation ICP-MS/MS with N₂O as the reaction gas

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Analyzing rare earth elements (REEs) in atmospheric precipitation can reveal their sources and migration patterns. However, their direct determination in atmospheric precipitation using ICP-MS/MS remains challenging owing to low (sub-ng L⁻¹) levels and mass spectral interference. This study established a reliable ICP-MS/MS method using a membrane desolvation system to enhance the sensitivity of REEs detections and employing N₂O as the reaction gas to eliminate spectral interference for the direct measurement of REEs in atmospheric precipitation. The production rates of REE monoxides were significantly enhanced when using N₂O as the reaction gas instead of O₂. In particular, the yield of EuO⁺ increased to 64.9%, while that of YbO⁺ increased to 39.5%. A regular 10% signal suppression of REE⁺ was observed in the presence of matrix using membrane desolvation and employing ¹⁸⁵Re as an internal standard effectively improved the results by >98%. The instrumental detection limits of the proposed method ranged from 0.001 ng L⁻¹ for Lu to 0.022 ng L⁻¹ for Nd. The results for REEs in the certified reference material (SLRS-6) at a 1:10 dilution was consistent with the values reported in the literature. Thus, the proposed method was employed to analyze atmospheric precipitation samples. The accuracy of the results demonstrated that this method has the potential for routinely measuring sub ng L⁻¹ levels of REEs in freshwater samples, offering advantages regarding sample throughput and reduced handling.

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1. Introduction

Rare earth elements (REEs) are crucial for tracing natural and human-induced processes in water owing to their unique chemical and physical properties.¹⁻⁴ Research has indicated that the atmospheric inputs of particles and rainwater significantly contribute to the presence of REEs in the oceans and often surpass river inputs.⁵⁻⁷ However, the distribution of REEs in natural systems and their migration pathways remain insufficiently studied, particularly concerning atmospheric precipitation.⁸ Accurately determining the presence of REEs in atmospheric precipitation is essential to understand their sources and migration patterns. However, currently employed methods to measure REE concentrations in atmospheric

precipitation require 30-fold⁹ to 200-fold^{10,11} preconcentration, rendering the direct determination of REEs challenging.

Currently, quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) is an excellent method for REE quantification in waters owing to its high sensitivity and multi-elemental measurement. However, directly measuring REEs in natural waters remains challenging for two main reasons. First, the extremely low concentration of REEs (sub-ng L⁻¹) in natural waters, is often below the detection limit of the Q-ICP-MS system.^{3,12} Second, oxide and hydroxide interference are generated by Ba (such as BaO⁺ on Eu⁺ and BaH⁺ on La⁺) and light REEs oxides and hydroxides on heavy REEs.¹³ Therefore, the separation and pre-concentration of REEs from matrix elements are typically required before obtaining Q-ICP-MS.¹³⁻¹⁷ These sample pretreatment processes are time-consuming, labor-intensive, and require large sample volumes, and the risk of sample contamination increases. Developing a convenient, rapid, and cost-effective method for REEs determination would significantly enhance the quantification analysis of these elements in water samples.

The direct Q-ICP-MS analysis of natural water enables analysts to minimize sample manipulation and reduce the potential for blank contamination. For example, Lawrence *et al.*¹⁸ proposed a method for directly determining REEs in

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natural water using Q-ICP-MS. However, this method was only suitable for analyzing water samples with high REE concentrations. Specialized sample introduction systems, such as ultrasonic nebulization and microflow nebulization/desolvation, can be used in conjunction with sector field (SF)-ICP-MS to enhance the signal response and reduce polyatomic spectral interference, enabling the direct analysis of REEs in water samples.^{19–25} Despite its high sensitivity, there is an increased risk of interference. For example, barium hydroxide and lanthanum oxide can affect the $^{155}\text{Gd}^+$ signal by 20%, with 13% and 7% contributed by $^{138}\text{Ba}^{16}\text{O}^{16}\text{H}^+$ and $^{139}\text{La}^{16}\text{O}^+$, respectively.¹⁹ After connecting to the membrane desolvation device, Q-ICP-MS still has a poor detection limit (1–3 ng L⁻¹).²⁰ SF-ICP-MS with a membrane desolvation is the most sensitive method for ultra-trace REEs analysis, however, its high cost (over US \$600,000) limits its use.^{19,25}

Recently, inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) has attracted attention owing to its efficient and direct approach for ultra-trace level analysis. Moreover, it can effectively reduce spectrochemical and isobaric interferences.^{26–30} Several studies have reported the determination of REEs using ICP-MS/MS.^{31–35} These studies utilized a mass-shift mode that enabled each REE isotope to react with oxygen gas (O₂) or nitrous oxide gas (N₂O) to form monoxide ions. This process effectively removes spectral interference, enabling the accurate determination of REEs without requiring a correction for interferences. Zhu *et al.*³⁶ developed a method to directly measure REEs in natural water using O₂ as the reaction gas. However, the sensitivities for Eu and Yb were lower due to the conversion efficiency of REE⁺ to REEO⁺, which was lower (14% to 20%) for Eu and Yb.^{34,36} Notably, the formation of REEO⁺ was enhanced using N₂O instead of O₂ as a reaction gas, resulting in improved sensitivity and limits of detection, and the significant enhancement of Eu and Yb oxides sensitivity.^{32,37–39}

This study aims to develop a reliable method for the accurate and direct determination of sub-ng L⁻¹ REEs in atmospheric precipitation using ICP-MS/MS. This method employed N₂O as an oxidizing reaction gas to selectively eliminate possible spectral interferences of the analytes. Additionally, it used a membrane desolvation sample introduction system to enhance the sensitivity of the measurements. The validity of the proposed method was confirmed by the direct analysis of REEs in the river water certified reference material SLRS-6 at a 1 : 10 dilution. Determination of REEs was also carried out for atmospheric precipitation samples. Finally, REE concentrations in real atmospheric precipitation samples collected from Xizang and Yunnan provinces were determined, and the distribution patterns of the REEs were compared.

2. Experimental

2.1 Instrumentation

In this study, a NexION 5000 Multi-Quadrupole ICP-MS Instrument (PerkinElmer Inc., Shelton, CT, USA) was used, equipped with platinum cones and a hyper skimmer, as previously described.⁴⁰ A CETAC Aridus 3 membrane desolvation

system (Omaha, NF, USA) was used to enhance the sensitivity of REEs, incorporating a 100 μL min⁻¹ microconcentric nebulizer. The conditions for ICP-MS/MS (Table 1) ensured optimal performance in measuring REEs with high sensitivity and low limit of quantification (LOQ). The quantification process utilized external calibration with ^{185}Re as the internal standard to correct for signal drift.

2.2 Reagents and standards

Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Millipore, France) and used throughout the experiments. High-purity nitric acid (HNO₃) was purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China) and purified twice using a sub-boiling distillation system (DST-1000, Savillex) prior to use. High-purity oxygen (O₂, 99.999%) and nitrous oxide (N₂O, 99.999%) gases were sourced from Beijing Hongba Gas Technology Co., Ltd and used as cell gases. Single-element standard solutions (1000 mg L⁻¹) of REEs, Ba, K, Na, Ca, and Mg, were obtained from the National Institute of Metrology, China. The REE stock standard solution (10 mg L⁻¹) was obtained from PerkinElmer, Inc. (Shelton, CT, USA). To confirm the accuracy of the proposed method, certified reference materials (CRMs, SLRS-6) for river water was purchased from the National Research Council of Canada and analyzed at a 1 : 10 dilution.

2.3 Analytical measurement

To eliminate interferences in REE⁺ determination, the mass-shift method was employed, which involved oxidizing REE⁺ to REEO⁺ using N₂O or O₂, resulting in a 16 amu shift for accurate measurement. The signal intensities of REEO⁺ were measured over the range of 0–2 mL min⁻¹ gas flows of N₂O or O₂, and the maximum signal intensity of REEO⁺ was observed at 1.2 mL min⁻¹ for N₂O or O₂. Before each measurement, the cell was

Table 1 Optimized conditions for the ICP-MS/MS and Aridus 3 membrane desolvation system

Instrument parameters	Value
RF power (W)	1600
Plasma gas flow (L min ⁻¹)	16
Nebuliser gas flow (L min ⁻¹)	1.10
Auxiliary gas flow (L min ⁻¹)	1.4
QID fixed voltage (V)	–12
Hyper skimmer park voltage (V)	13
Omniring park voltage (V)	–210
Inner target lens voltage (V)	4
Outer target lens voltage (V)	–1
Deflector exit voltage (V)	–8
Differential aperture voltage (V)	–3.5
Cell gas	N ₂ O
Reaction gas flow rate (mL min ⁻¹)	1.2
Analytical mode	Mass-shift
Internal standard	^{185}Re
PFA spray chamber (°C)	110
Membrane (°C)	140
Membrane sweep gas (L min ⁻¹)	3.5
Nitrogen addition gas (mL min ⁻¹)	5.0



flushed for about 10 min with the respective reaction gas (O_2 or N_2O).

2.4 Sample preparation

Six atmospheric precipitation samples were collected from Yunnan and Xizang Province, respectively. To avoid the influence of dry precipitation, rainwater samples were collected half an hour after the start of each rain event using a polyethylene bucket with a polyethylene lid. The collector and container were pre-cleaned with 5–7 N HNO_3 , rinsed with ultrapure water, and dried. To prevent contamination from dry deposition, the lid was immediately removed before the rain began. The water samples were filtered using 0.45 μm membrane filters immediately after sampling and acidified to 2% (v/v) HNO_3 for storage.

3. Results and discussion

3.1 Comparison of REE oxidation yields using O_2 and N_2O

High yields of REE oxides are crucial to improve the sensitivity of REE measurements using the ICP-MS/MS mass-shift method. Thus, this study compared the REE oxidation yields obtained from the ICP-MS/MS mass-shift method using O_2 and N_2O , as shown in Fig. 1. The REE oxidation yields were <60% when using O_2 as the cell gas. These values were lower than those reported by Yang *et al.*³³ and Ding *et al.*³⁵ (>80%), except for Eu and Yb. The yields of EuO^+ and YbO^+ were 15.3% and 8.6%, respectively, which were significantly lower than those (21% for Eu and 36% for Yb, respectively) reported by Yang *et al.*³³ However, the O-binding energy of N_2O is lower than that of O_2 . As a result, the reaction enthalpies for REE^+ with N_2O can be reduced compared to those with O_2 , which can improve the formation rates of REE^+ and enhance sensitivity.^{38,41} In this study, the yields of EuO^+ and YbO^+ increased to 64.9% and

39.5%, respectively, when using N_2O compared to that for O_2 . For the other REEs, the oxidation yields were exceeding 60% when using N_2O as the cell gas than O_2 , except for La and Ce, which were comparable to those reported by Sugiyama.⁴² Therefore, N_2O was used as the reaction cell gas in this study.

3.2 Matrix effect on REE sensitivities

Although ICP-MS/MS offer high sensitivity, the mass-shift mode ($REE^+ REEO^+$) was insufficient to directly measure all REEs at low concentrations in atmospheric precipitation samples. Therefore, a membrane desolvation sample introduction system (MD-ICP-MS/MS) was used to further enhance the REEs' sensitivity. This technique can effectively introduce samples by using a polytetrafluoroethylene (PTFE) membrane to separate solvent vapors from the sample aerosol, improving transport efficiency, increasing ion signal intensity, and minimizing the formation of oxides and hydroxides. Because of these advantages, membrane desolvation has been successfully employed in numerous trace and ultra-trace element studies.^{44,45} To quantify the possible matrix effects to determine REEs in water, three solutions containing REE + 2% HNO_3 , REE + matrix + 2% HNO_3 , and REE + matrix + ^{185}Re + 2% HNO_3 were applied. The matrix induced effects were expressed as the ratio of the signals for REE + matrix + 2% HNO_3 to those obtained for REE + 2% HNO_3 , as shown in Fig. 2. The introduced sample matrix had a signal suppression effect on all REE^+ species,^{18,20} and a regular 10% signal suppression for all REE^+ species was observed, consistent with the 15% suppression reported by Chung *et al.*²¹ but lower than the 30–60% reported by Gabrielli *et al.*¹⁹ This signal reduction could be effectively compensated using ^{185}Re as the internal standard (Fig. 2), achieving an improvement of >98%. Therefore, the precision and accuracy of REE determination were improved using MD-ICP-MS/MS method.

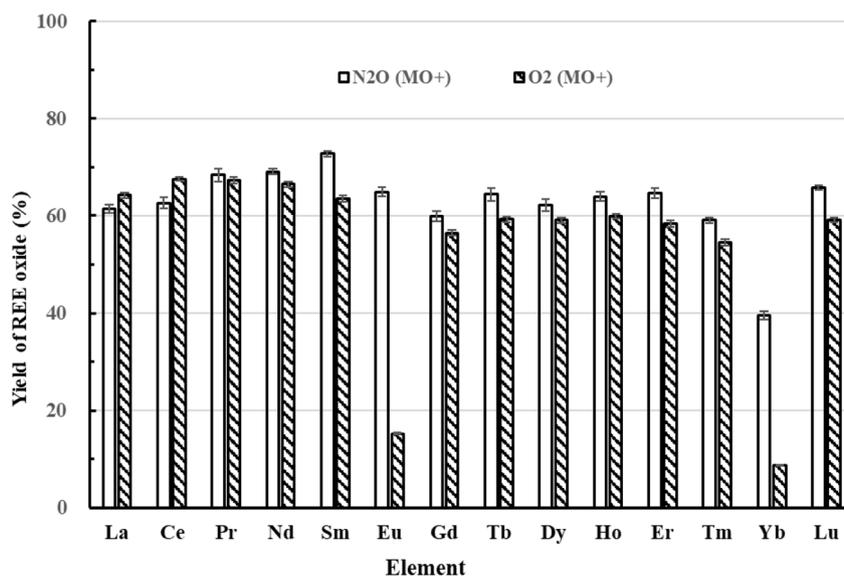


Fig. 1 Yields of REE oxides using the ICP-MS/MS mass-shift method with O_2 or N_2O as the cell gas. The flow rate of O_2 or N_2O was 1.2 mL min^{-1} , and the concentration of REE was $1 \mu\text{g L}^{-1}$.



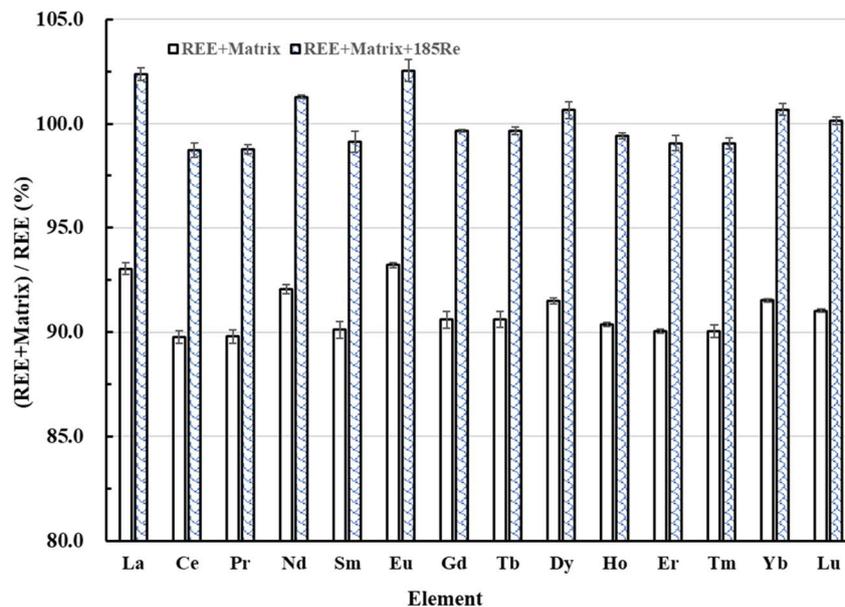


Fig. 2 Comparison of the matrix effects between REE⁺ signals caused by a matrix with or without ¹⁸⁵Re as the internal standard. The matrix comprised 10, 5, 5, and 1 mg L⁻¹ Na, Ca, Mg and K, respectively, and the concentration of REEs was 0.2 μg L⁻¹.

3.3 Performance of the proposed method

Under optimized conditions, the blank equivalent concentration (BEC) and instrument detection limit (IDL) values were obtained by measuring 2% HNO₃, while sensitivity was determined by measuring 1 μg L⁻¹ REE in the same solution using MD-ICP-MS/MS (Table 2). Using our proposed method, the BEC and IDL values of REEs were lower than those obtained by Zhu *et al.*³⁶ using ICP-MS/MS directly. Moreover, the sensitivity for each REE was improved by 2.6–9.7 times, with Eu and Yb showing improvements of 9.7 and 6.2 times, respectively. Therefore, the proposed method can be used to directly and effectively determine low concentrations of REEs.

3.4 Measurement results of REEs in SLRS-6 and atmospheric precipitation samples

To confirm the accuracy of the proposed method, the river water CRM SLRS-6 was used following dilution 10 times. As shown in Table 3, REE concentrations ranged from 1.70 to 288.5 ng L⁻¹, which were consistent with the literature-reported values of 1.79–292.7 ng L⁻¹.⁴³ The proposed method was also applied to determine REEs in atmospheric precipitation samples collected from the Yunnan and Xizang provinces, and the results are presented in Table 3. The concentrations of REEs in atmospheric precipitation significantly varied, with the MT region in the Xizang province exhibiting the lowest levels, ranging from

Table 2 BEC, IDL, and sensitivity values for REEs measured using the proposed method

Element	Present work			Ref. 36		
	BEC ng L ⁻¹	IDL ng L ⁻¹	Sensitivity CPS mL ng ⁻¹	BEC ng L ⁻¹	IDL ng L ⁻¹	Sensitivity CPS mL ng ⁻¹
La	0.005	0.006	966 000	0.24	0.15	268 000
Ce	0.012	0.009	965 816	0.14	0.13	268 000
Pr	0.004	0.007	1 221 966	0.03	0.08	312 000
Nd	0.012	0.022	461 511	0.11	0.26	56 000
Sm	0.013	0.011	347 535	0.03	0.01	47 000
Eu	0.009	0.002	622 913	0.023	0.007	64 000
Gd	0.008	0.004	255 608	0.03	0.009	52 000
Tb	0.001	0.001	1 085 937	0.009	0.06	343 000
Dy	0.014	0.005	286 438	0.017	0.005	92 000
Ho	0.001	0.002	977 734	0.017	0.07	356 000
Er	0.005	0.002	323 943	0.014	0.004	114 000
Tm	0.0008	0.001	868 418	0.009	0.06	336 000
Yb	0.001	0.003	184 686	0.05	0.014	30 000
Lu	0.0008	0.001	893 204	0.009	0.06	340 000



Table 3 Analytical results of REEs in SLRS-6 and atmospheric precipitation samples, ng L⁻¹

	SLRS-6 reported ⁴¹	SLRS-6 this study	GGQ-S	GGQ-W	LZ-S	LZ-W	MT-S	MT-W
La	248.3 ± 12.1	244.3 ± 10.2	1.32 ± 0.12	1.13 ± 0.11	0.75 ± 0.08	0.55 ± 0.08	0.30 ± 0.09	0.22 ± 0.06
Ce	292.7 ± 15.1	288.5 ± 12.3	2.50 ± 0.20	2.10 ± 0.12	1.43 ± 0.21	0.83 ± 0.14	0.43 ± 0.10	0.24 ± 0.04
Pr	59.1 ± 1.9	58.3 ± 1.1	0.31 ± 0.06	0.29 ± 0.04	0.19 ± 0.04	0.12 ± 0.02	0.068 ± 0.008	0.043 ± 0.009
Nd	227.8 ± 9.4	225.3 ± 5.6	1.29 ± 0.10	1.17 ± 0.15	0.82 ± 0.08	0.52 ± 0.10	0.27 ± 0.06	0.19 ± 0.03
Sm	39.5 ± 1.7	38.7 ± 1.1	0.23 ± 0.05	0.21 ± 0.06	0.16 ± 0.05	0.10 ± 0.02	0.056 ± 0.010	0.037 ± 0.009
Eu	7.26 ± 0.35	7.20 ± 0.21	0.054 ± 0.010	0.050 ± 0.011	0.037 ± 0.008	0.026 ± 0.003	0.017 ± 0.004	0.013 ± 0.004
Gd	31.6 ± 2.5	30.1 ± 2.2	0.21 ± 0.04	0.20 ± 0.05	0.15 ± 0.03	0.093 ± 0.010	0.061 ± 0.009	0.042 ± 0.07
Tb	4.07 ± 0.27	3.89 ± 0.22	0.033 ± 0.011	0.031 ± 0.008	0.023 ± 0.005	0.015 ± 0.005	0.010 ± 0.003	0.007 ± 0.001
Dy	21.9 ± 1.1	21.1 ± 0.9	0.22 ± 0.05	0.21 ± 0.06	0.16 ± 0.02	0.10 ± 0.02	0.051 ± 0.006	0.039 ± 0.004
Ho	4.3 ± 0.3	4.15 ± 0.2	0.04 ± 0.007	0.04 ± 0.004	0.03 ± 0.004	0.017 ± 0.003	0.009 ± 0.002	0.007 ± 0.002
Er	12.4 ± 0.7	11.9 ± 0.7	0.12 ± 0.03	0.12 ± 0.03	0.091 ± 0.006	0.057 ± 0.005	0.029 ± 0.003	0.019 ± 0.003
Tm	1.79 ± 0.18	1.70 ± 0.13	0.018 ± 0.005	0.017 ± 0.004	0.013 ± 0.003	0.008 ± 0.002	0.004 ± 0.001	0.003 ± 0.001
Yb	11.2 ± 0.7	11.7 ± 0.4	0.12 ± 0.03	0.11 ± 0.03	0.086 ± 0.008	0.056 ± 0.006	0.034 ± 0.003	0.021 ± 0.003
Lu	1.91 ± 0.23	1.86 ± 0.21	0.018 ± 0.005	0.017 ± 0.004	0.013 ± 0.002	0.008 ± 0.001	0.005 ± 0.001	0.003 ± 0.001

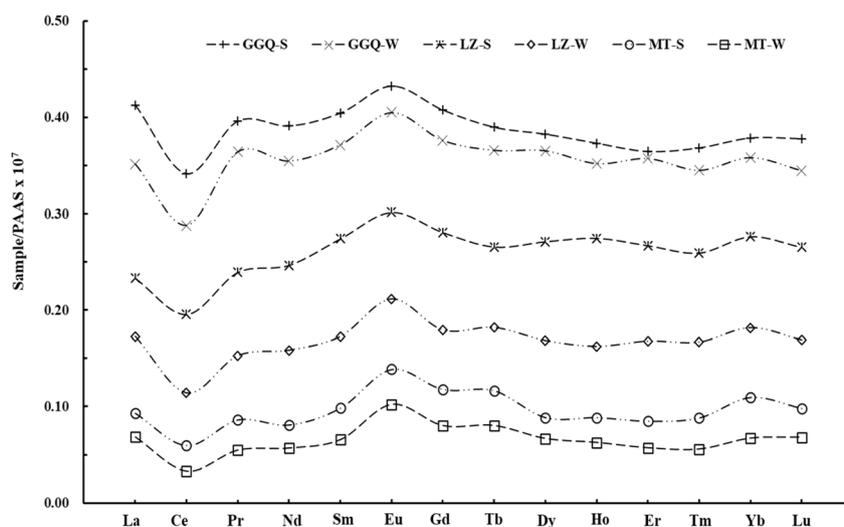


Fig. 3 Patterns of shale-normalized REEs in atmospheric precipitation from the Yunnan and Xizang provinces.

0.003 to 0.24 ng L⁻¹ for Lu to Ce. These values were higher than the BEC and IDL values presented in Table 2. Therefore, the proposed method could successfully determine the low concentrations of REEs in these samples.

Shale-normalized REE patterns can assist in identifying the sources of atmospheric precipitation. Four primary types of shale-normalized patterns emerged from the analysis of dissolved REEs: (1) middle rare earth elements (MREE)-enriched (Sm to Dy); (2) Flat REE patterns; (3) heavy rare earth elements (HREE)-enriched (Ho to Lu); and (4) light rare earth elements (LREE)-enriched (La to Nd). These patterns provided insights into the origins of REEs in atmospheric precipitation. The shale-normalized REE distribution patterns for these samples are plotted in Fig. 3, and were enriched in MREE. MREE enrichment can result from the interaction of water and airborne particles which occurs through the dissolution or leaching of these particles when they interact with water.⁴⁶

4. Conclusion

This study presents an alternative method for the direct measurement of REEs in atmospheric precipitation samples using MD-ICP-MS/MS. Spectral interferences were eliminated using ICP-MS/MS in the mass-shift mode, employing N₂O as the reaction cell gas. This approach shifted the mass-to-charge ratio (*m/z*) of the target analyte by 16 amu.³⁸ The use of membrane desolvation was beneficial for directly measuring ultra-trace REEs in atmospheric precipitation samples, eliminating the need for tedious, contamination-prone preconcentration and matrix separation procedures. The analytical results for REEs using SLRS-6 were consistent with those of previous studies, confirming the reliability of the proposed method for measuring REEs in atmospheric precipitation samples. This method shows promise for routinely measuring sub ng L⁻¹ levels of REEs in freshwater samples, offering advantages in terms of multi-element capability, sample throughput, and reduced handling.



Data availability

Data will be made available upon request.

Author contributions

Jiang-yi Zhang: writing – original draft, review & editing, methodology, data curation; Wen-jing Liu: review & editing, methodology, data curation, resources; Di Liu: methodology, data curation; Guang-liang Wu: investigation, data curation; Zhi-fang Xu: review & editing, methodology, resources, supervision, project administration.

Conflicts of interest

The authors have no conflicts of interest to declare.

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