

Determination of Sulfur Isotope Ratios ($^{34}\text{S}/^{32}\text{S}$) in Atmospheric Precipitation Samples by Triple Quadrupole ICP-MS

Jiang-yi Zhang,^{a,c,d} Wen-jing Liu,^{b,c,d,*} Zhi-fang Xu,^{b,c,d} and Guang-liang Wu^{a,c,d}

^a Institutional Center for Shared Technologies and Facilities, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, P. R. China

^b State Key Laboratory of Lithospheric and Environmental Coevolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, P. R. China

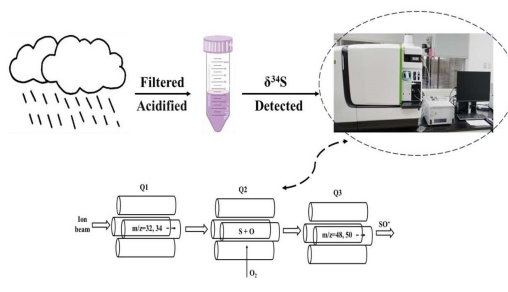
^c Innovation Academy for Earth Science, Chinese Academy of Sciences, Beijing 100029, P. R. China

^d College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Received: July 31, 2024; Revised: September 21, 2024; Accepted: October 26, 2024; Available online: October 26, 2024.

DOI: 10.46770/AS.2024.157

ABSTRACT: The direct determination of sulfur isotope ratios $^{34}\text{S}/^{32}\text{S}$ ($\delta^{34}\text{S}$), in atmospheric precipitation by triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS) is challenging owing to intense interference from polyatomic species of mass that affects all sulfur isotopes. Additionally, high background levels of sulfur often pose a challenge for accurately determining $\delta^{34}\text{S}$ at low concentrations in atmospheric precipitation samples. To address these challenges, a reliable method based on mass shift ICP-MS/MS was developed in this study. The $\delta^{34}\text{S}$ ratio was determined at m/z 48 and 50 instead of at m/z 32 and 34 by using O_2 as a reactive gas to shift the $^{32,34}\text{S}^+$ ions to $^{32,34}\text{S}^{16}\text{O}^+$, thus avoiding on-mass interferences at m/z 32 and 34. The sulfur concentration in the background blank, which mainly originated from the Ar and O_2 gas used during analysis, was reduced from 22.1 $\mu\text{g L}^{-1}$ to 0.82 $\mu\text{g L}^{-1}$ by purifying Ar and O_2 using a gas trap. The $\delta^{34}\text{S}$ measurements were not significantly affected by the sulfur concentration of the sample between 200 and 1000 $\mu\text{g L}^{-1}$, and the atmospheric precipitation matrix did not affect $\delta^{34}\text{S}$ determination using ICP-MS/MS. Therefore, the proposed method does not require strict matrix and concentration matching, simplifying the analytical process. The results obtained from atmospheric precipitation using the proposed method are consistent with those obtained by isotope ratio mass spectrometry, thereby validating the proposed method.



INTRODUCTION

Acid deposition by acid rain is regarded to pose a severe threat to the aquatic environment and surrounding ecosystems.^{1,2} Sulfate ions (SO_4^{2-}) is a significant contributor to acid rain pollution and is the primary sulfur-containing ion found in precipitation.^{3,4} Generally, sulfate present in the atmosphere primarily arises from natural sources such as volcanic eruptions, sea spray, soil or mineral dust, and biogenic emissions, as well as human activities such as the combustion of fossil fuels and coal, smelting of metal sulfides, and the production of sulfuric acid⁵⁻⁸. Sulfur that originates from different sources shows distinct isotope compositions, which are particularly useful in identifying and

understanding the sources of dissolved sulfate in rainwater.⁹⁻¹¹ Therefore, the determination of such isotope ratios could help assess the influences of emission reduction measures on the various sources of sulfur.

Sulfur exhibits four naturally occurring isotopes: ^{32}S (94.99%), ^{33}S (0.75%), ^{34}S (4.25%), and ^{36}S (0.01%);¹² the $^{34}\text{S}/^{32}\text{S}$ ratio is commonly used to characterize a sample. Traditionally, $^{34}\text{S}/^{32}\text{S}$ ratios in natural water samples are measured by gas source isotope ratio mass spectrometry (IRMS). However, this method requires a sufficiently high sulfate concentration or a high sample volume to precipitate barium sulfate (BaSO_4) on the milligram scale before converting S to SO_2 gas for analysis,¹³⁻¹⁵ approximately 30 μg of sulfur may achieve a precision of 0.4‰ (2SD).¹⁶ Therefore,

preparing samples of natural water for isotopic analysis by IRMS is complicated and time-consuming with a low sample throughput. Given that the amount of rainwater collected is usually small and contains low concentrations of dissolved sulfate, the resulting amount of BaSO₄ precipitate is insufficient for sulfur isotope analysis.¹⁷ Therefore, the IRMS method cannot overcome the routine challenges presented when analyzing rainwater samples.

Multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is an alternative method for measuring the sulfur isotope composition in water samples with high precision (approximately 0.1‰).^{17–20} It is superior for analyzing small quantities of dissolved sulfate (~70 ng of sulfur)^{12,21} and limited sample volumes,²² especially samples with minute differences in the isotope abundance. However, this method necessitates the separation of sulfur from the sample matrix prior to obtaining isotope ratio measurements, which involves time-consuming chemical purification steps. In addition, MC-ICP-MS is high-cost and complex, limiting its suitability for most experiments.^{23–31}

As interest in sulfur isotope analysis expands, there is a growing need for fast and accurate methods for detection that require less chemical purification and provide a more direct analytical approach.^{32–34} Since sulfur isotopes display considerable ³⁴S/³²S ratio variations in nature (–50‰ to +40‰),³⁵ high-precision techniques are not necessarily required. Therefore, a single, rapid, and easy-to-use technique would benefit large-scale environmental surveying. You *et al.*³⁶ and Prohaska *et al.*³⁷ have reported rapid, sensitive, and precise methods for determining sulfur isotope ratios in water samples using sector field (SF)-ICP-MS. However, sample purification prior to analysis is required to circumvent the possible metal isobaric interferences caused by ⁶⁴Ni²⁺, ⁶⁴Zn²⁺ or ⁶⁸Zn²⁺. Alternatively, the sulfur species in aqueous solutions were first separated and pre-concentrated, then measured ³⁴S/³²S at m/z 48 and 50 instead of at m/z 32 and 34 by oxidizing 17 mg L⁻¹ sulfur with O₂ using single quadrupole (Q)-ICP-MS.³⁸ This method eliminates interference from ¹⁶O¹⁶O⁺, ¹⁴N¹⁸O⁺, ¹⁵N¹⁶O¹H⁺, ³³S¹H⁺, ¹⁶O¹⁸O⁺, ¹⁶O¹⁷O¹H⁺, ¹⁶O¹⁶O¹H₂⁺, and ¹⁵N¹⁸O¹H⁺ ions at m/z 32 and 34. However, interference from ^{48,50}Ti⁺, ⁴⁸Ca⁺, ³⁶Ar¹²C⁺, ³¹P¹⁶O¹H⁺, ⁵⁰Cr⁺, ⁵⁰V⁺, ³⁸Ar¹²C⁺, and ³⁶Ar¹⁴N⁺ may arise at m/z 48 and 50 if directly measuring. Additionally, the sensitivity of SO⁺ may potentially decrease following the collision/reaction process.³² Mason *et al.*³⁹ reported the use of Xe gas to reduce background noise from O₂⁺ ions and measured sulfur isotope ratios using Q-ICP-MS. However, in this method, the sulfur content in the sample should be greater than 10 mg L⁻¹, which limits the effectiveness of this technique for trace sulfur analysis.

The rapid determination of ³⁴S/³²S ratios by triple quadrupole ICP-MS (ICP-MS/MS) has received extensive attention recently because it provides a solution to the constraints of reaction mode

techniques on single quadrupole and bandpass ICP-MS, and can effectively mitigate spectrochemical interference from ions of similar m/z as the targeted ³⁴S/³²S ions for detection. Prohaska and co-workers⁴⁰ evaluated the performance of ICP-MS/MS for the first time in measuring natural sulfur isotope ratios, including limits of detection, measurement precisions, within-lab reproducibility, instrumental isotopic fractionation, combined measurement uncertainty and deviation of the measured value from the certified value. Using the MS/MS mode, the ³⁴S/³²S ratio was measured as ³⁴S¹⁶O⁺/³²S¹⁶O⁺ molecular analogs. This approach effectively separated the targeted ³⁴S/³²S analyte from the interference derived from polyatomic species from the matrix,^{41,42} thus eliminating the need for time-consuming chemical purification steps. Furthermore, precise sulfur isotope ratios were obtained with standard deviation (SD) less than 0.9‰ (1SD).⁴³ Leyden *et al.*⁴⁴ have reported a new method for tracking seawater intrusion in coastal areas, which involves utilizing ICP-MS/MS to determine ³⁴S/³²S ratios in complex natural water samples in a rapid and straightforward manner with an uncertainty in δ³⁴S of approximately 1.1–1.5‰ (1SD). However, this method required sulfur concentrations of 2 µg mL⁻¹ or greater, which is much higher than the sulfur concentration in rainwater.^{45,46} As a result, samples containing lower sulfur content must be pre-concentrated prior to ICP-MS/MS analysis.

The aim of this study was to develop an ICP-MS/MS method that can directly analyze sulfur isotopes in atmospheric precipitation at low sulfur concentrations. Rather than measuring the ³⁴S/³²S ratios, this approach entails determining the ³⁴S¹⁶O⁺/³²S¹⁶O⁺ isotope ratios by ICP-MS/MS following sulfur oxidation using O₂ as the reactive gas, inspired by reports from Leyden *et al.*⁴⁴ The results obtained from analyzing samples from atmospheric precipitation were found to be consistent within the expected error range with those obtained by IR-MS, thus validating the method reported herein.

EXPERIMENTAL

Instrumentation. A NexION 5000 Multi-Quadrupole ICP-MS instrument (PerkinElmer Inc., Shelton, Connecticut, USA) was employed for ³⁴S¹⁶O⁺/³²S¹⁶O⁺ analysis, and the instruments mass-bias was corrected using the sample-standard bracketing (SSB) method. The ICP-MS/MS was equipped with a SMARTintroTM Ultra High Purity quartz torch, a fixed 2.0 mm injector, a SilQ spray chamber, Pt cones, a Pt hyper skimmer, and a PFA ST3 self-aspirating nebulizer. Oxygen (O₂, 99.999%) gas was used for sulfur oxidation. A gas trap with a 40 mm inner diameter and a length of 280 mm, featuring a 1/4-inch interface, was utilized to purify Ar and O₂ gas for trapping sulfur dioxide (SO₂). The trap is filled with activated carbon and activated alumina to adsorb SO₂. During trapping, SO₂ molecules undergo electrostatic interaction

Table 1. Typical operating parameters of the instrument

ICP-MS/MS instrument	PerkinElmer NexION 5000
RF power	1600 W
Nebulizer gas flow rate	0.94 L min ⁻¹
Auxiliary gas flow rate	1.2 L min ⁻¹
Plasma gas flow rate	16 L min ⁻¹
QID fixed voltage	-12 V
Hyper skimmer park voltage	4 V
Omniring park voltage	-200 V
Axial field voltage	150 V
Reaction gas flow rate	0.95 mL min ⁻¹
Sweeps per reading	100
Reading per replicate	30
Replicates	10
Dwell time	15 ms
Detector dead time	35 ns
Sample analysis time	15.6 min

Table 2. Potential source of sulfur contamination and equivalent concentration

Potential Source	Signal intensity of ³² S ¹⁶ O ⁺ , cps	S equivalent concentration, μg L ⁻¹
Ar and O ₂ before purification	828640 ± 13092	22.1 ± 0.3
Ar and O ₂ after purification	30720 ± 614	0.82 ± 0.02
100 μg L ⁻¹ sulfur in 1% HNO ₃	3751732 ± 9379	--
Ultra-purity water 1% HNO ₃	39618 ± 475	1.1 ± 0.01
Cleaned pipette tip	44142 ± 380	1.2 ± 0.01
	--	0

and van der Waals forces with the activated carbon, leading to efficient adsorption. Additionally, the hydroxyl group on the surface of activated alumina reacts with the oxygen in SO₂ to form sulfate ions. The activated carbon and activated alumina were obtained from Sichuan Southwest Super Energy New Materials Co., Ltd. The typical operating parameters of the instrument used in this study are summarized in Table 1.

Reagents and standards. Ultra-pure water (18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Millipore, France) and was used throughout this study. Single-element stock solutions of titanium, calcium, chromium, and vanadium with concentrations of 1 mg L⁻¹ were purchased from the National Center for Analysis and Testing of Steel Material, P. R. China. Sodium sulfate (Na₂SO₄, 99.99%) and potassium sulfate (K₂SO₄, 99.99%) were obtained from Shanghai Aladdin Biochem Technology Co., Ltd., China. High-purity nitric acid (HNO₃) was purchased from Sinopharm Chemical Reagent Co. (Beijing, China) and purified by sub-boiling distillation prior to use. Sulfur-certified reference materials (CRMs) IAEA-S-1 ($\delta^{34}\text{S}_{\text{V-CDT}} = -0.3 \pm 0.03\%$) and IAEA-S-2 ($\delta^{34}\text{S}_{\text{V-CDT}} = 22.62 \pm 0.08\%$), were obtained from the International Atomic Energy Agency (IAEA) in Vienna, Austria. A seawater sample of the Atlantic Ocean water standard was obtained from the International Association for the Physical Sciences of the Ocean (IAPSO) and used to validate the methods for sulfur detection.

Sample preparation. 10 mg of each IAEA-S-1 and IAEA-S-2 standard was added into separate 15 mL Savillex™ PFA acid-cleaned vials. Thereafter, HNO₃ (5 mL) was added to each vial, following which the vials were capped and heated on a hotplate at 140 °C for two days. The solutions were then evaporated to dryness, and the dry residues were redissolved in ultra-pure 2% HNO₃ and transferred into 250 mL Teflon acid-cleaned beakers. The total sulfur concentration was 5.2 mg L⁻¹ for both ‘stock reference solutions’ IAEA-S-1 and IAEA-S-2, respectively.

Atmospheric precipitation samples were collected from Beijing, Hangzhou, and Changdu City in China. The samples were filtered through a 0.45 μm membrane filter, acidified to pH < 2 with HNO₃ and subsequently stored at 4°C prior to analysis.

RESULTS AND DISCUSSION

Sources of sulfur contamination and blank measurements.

The sulfur content in background blank samples can significantly impact the accuracy when determining sulfur isotope ratios, especially for samples with sulfur concentrations below 1000 ng mL⁻¹.^{21,44} Therefore, determining sulfur isotope ratios in atmospheric precipitation samples by ICP-MS/MS is challenging. High background levels are often caused by sulfur contamination from various laboratory components. In our study, multiple sources of contamination were apparent during sample processing, such as purified HNO₃, ultra-pure water, pipette tips, and Ar and O₂ gas (Table 2). Among these, Ar and O₂ were the most significant sources of sulfur contamination, leading approximately 22.1 μg L⁻¹ of sulfur. Therefore, Ar and O₂ gas were purified prior to delivery to the instrument to remove sulfur-containing impurities from the gases. Fortunately, using a SO₂ trap proved effective for removing sulfur from Ar and O₂ gas with an adsorption rate of 96%, reducing the sulfur content in the blank samples to 0.82 μg L⁻¹. Ultra-pure water was another primary source of sulfur contamination (1.1 μg L⁻¹) throughout the experiment. Sulfur contamination from HNO₃ was considered negligible because the contribution from 1% HNO₃ is 1.2 μg L⁻¹. Therefore, sulfur contamination from 5 mL of HNO₃ when added to 10 mg of the IAEA-S-1 and IAEA-S-2 standards during digestion can also be considered negligible. The pipette tip, which is also considered a potential source of sulfur contamination, was cleaned prior to transferring 1% HNO₃ for analysis. Furthermore, the signal intensity was indistinguishable from that of 1% HNO₃. Therefore, the pipette tips were considered negligible sources of contamination. In summary, the sulfur content in the background blank samples was approximately 2 μg L⁻¹, and the 1% sulfur content in the background blank samples did not impact the sulfur isotope analysis.⁴⁴ Therefore, for accurate determination of the sulfur isotope ratios by the proposed method, the minimum sample sulfur content should be 200 μg L⁻¹.

Table 3. Comparison of measured $\delta^{34}\text{S}_{\text{VCDT}}$ values with recommended values in reference material using ICP-MS/MS (n=10)

Sample	Certified Value of $\delta^{34}\text{S}_{\text{VCDT}}$ (‰,1SD)	Measured Value by ICP-MS/MS (‰,1SD)	Measured Value by EA-IRMS (‰,1SD)
IAEA-S-1	-0.3 ± 0.03	-0.3 ± 0.8	--
IAEA-S-2	22.62 ± 0.08	22.1 ± 1.0	--
Na_2SO_4	--	1.3 ± 0.8	1.5 ± 0.15
K_2SO_4	--	-1.2 ± 0.9	-1.5 ± 0.12

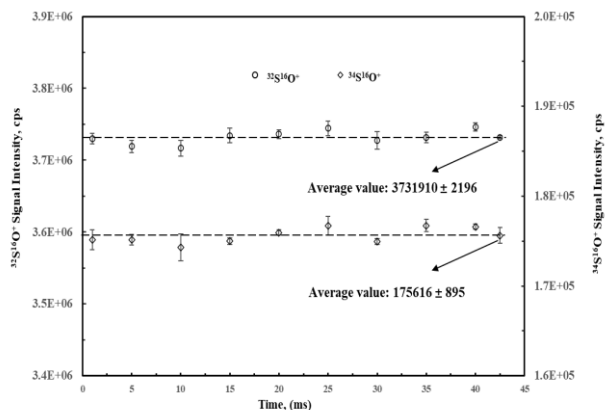


Fig. 1 Effect of dwell time on the reaction rate between the S and SO.

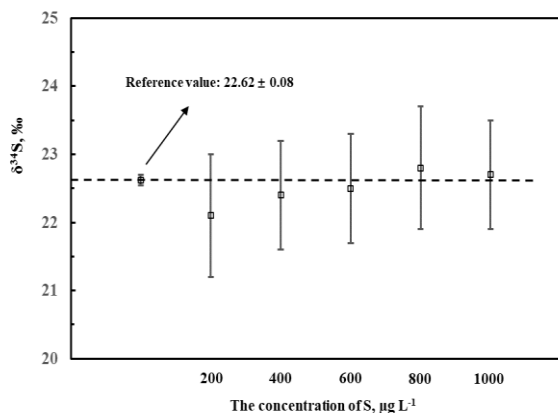


Fig. 2 Effect of sulfur concentration of the sample on $\delta^{34}\text{S}$ measurement (n=5).

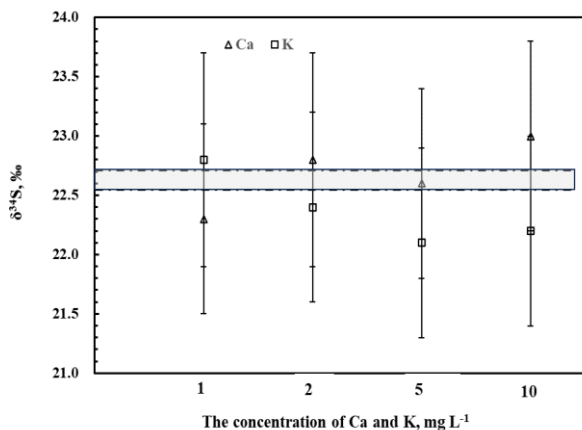


Fig. 3 Effect of different concentrations of Ca and K on $\delta^{34}\text{S}$ measurement.

Eliminating interference using ICP-MS/MS to accurately determine $\delta^{34}\text{S}$. The novel approach of reacting S with O_2 to form SO^+ has provided an avenue for accurately measuring $\delta^{34}\text{S}$ at m/z 48 and 50, eliminating interference from ions of similar m/z as the dominant sulfur isotopes ($m/z = 32$ and 34). This study evaluates the effects of eliminating matrix interference on the accuracy of $\delta^{34}\text{S}$ determination using ICP-MS/MS by a mass-shift approach. Standard solutions of IAEA-S-1 and IAEA-S-2 with sulfur concentrations of $400 \mu\text{g L}^{-1}$ and containing potential matrix elements such as $100 \mu\text{g L}^{-1}$ of titanium, chromium, and vanadium, and 5mg L^{-1} of calcium, were used as unknown samples. The SSB method was employed to breaking the standard samples IAEA-S-1 and IAEA-S-2. The standard samples were analyzed 10 times independently and the measured values of $\delta^{34}\text{S}$ were consistent with the certified values (Table 3), indicating that the proposed method could effectively eliminate interference from matrix elements for $\delta^{34}\text{S}$ determination. To further ensure the reliability of the proposed method, we prepared Na_2SO_4 and K_2SO_4 solutions with sulfur concentrations of $400 \mu\text{g L}^{-1}$ and measured them using the proposed method alongside elemental analysis combined with isotope ratio mass spectrometry (EA-IR-MS); the results from both methods were consistent.

Effect of dwell time on the reaction rate between the S and SO.

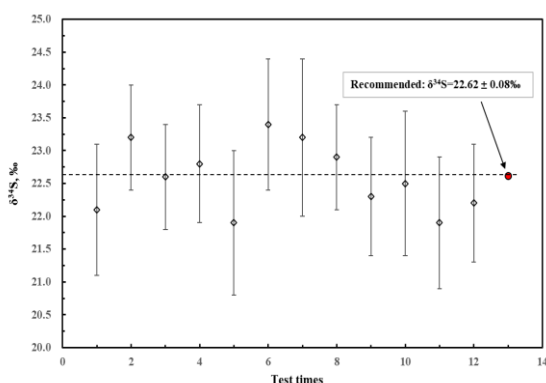
The reaction rate between S and SO was a critical factor for determining the precision of the $\delta^{34}\text{S}$ isotope, which was investigated at different dwell times with $100 \mu\text{g L}^{-1}$ S concentration, as shown in Fig. 1. There was no difference in the reaction rate between S and SO at different dwell times due to their same signal intensity, with the average value being 3721910 ± 2196 for $^{32}\text{S}^{16}\text{O}^+$ and 175616 ± 895 for $^{34}\text{S}^{16}\text{O}^+$, respectively.

Effect of sulfur concentration in samples.

When using the SSB method to correct mass bias, the concentration of a sample and breaking the isotope standard should be matched. To evaluate the effect of the sulfur concentration of the sample on $\delta^{34}\text{S}$ measurements, IAEA-S-2 was employed as an unknown sample prepared with sulfur concentrations ranging from 200 to $1000 \mu\text{g L}^{-1}$, and a sample of IAEA-S-1, which contained $400 \mu\text{g L}^{-1}$ S, was used for bias correction; the results are shown in Fig. 2. The measured $\delta^{34}\text{S}$ values ranged from 22.1 ± 0.9 to 22.8 ± 0.9 (1SD), with an average of 22.5 ± 0.3 (1SD) when the sulfur concentration was between 200 and $1000 \mu\text{g L}^{-1}$. These values are consistent with the reference value of 22.62 ± 0.08 , indicating that the sulfur concentration in the samples did not significantly impact the $\delta^{34}\text{S}$ measurements obtained using the proposed method.

Table 4. Results of $\delta^{34}\text{S}$ and matrix composition determination in- atmospheric precipitation samples

Samples	Cl ⁻	SO ₄ ²⁻	K	Na	Mg	Ca	$\delta^{34}\text{S}$ (‰ _{VCDT})	
	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	ICP-MS/MS	IRMS
BJR-1	2.1	3.8	0.3	0.4	0.7	2.9	3.6±0.8	3.82
BJR-2	1.7	4.6	0.1	0.1	0.7	2.9	3.5±0.9	--
BJR-3	1.6	3.7	0.1	0.1	0.6	2.5	3.8±0.9	--
BJR-4	1.8	4.3	0.1	0.2	0.7	2.9	1.7±0.8	1.94
BJR-5	1.9	2.8	0.1	0.3	0.6	1.5	2.7±1.0	2.98
BJR-6	1.7	4.4	0.1	0.1	0.6	2.5	3.8±1.0	--
HZR-1	0.8	7.7	0.5	0.2	0.2	3.6	4.0±0.9	--
HZR-2	1.6	7.8	0.3	0.7	0.3	5.8	7.4±0.8	7.08
HZR-3	1.1	5.4	0.4	0.7	0.2	3.4	6.2±0.9	--
HZR-4	5.1	8.5	0.9	2.6	0.5	5.5	8.7±1.0	8.29
HZR-5	2.0	7.8	0.4	0.7	0.2	4.9	6.0±0.8	--
HZR-6	2.3	7.4	0.3	1.2	0.2	2.9	4.1±0.9	3.75
CDR-1	0.5	0.9	0.4	0.4	0.2	1.8	5.1±0.9	--
CDR-2	0.2	0.7	0.1	0.2	0.1	1.1	5.9±1.0	--
CDR-3	0.4	0.8	0.1	0.2	0.2	2.0	5.4±0.8	--
CDR-4	0.4	0.6	0.1	0.2	0.1	3.1	5.6±0.9	5.39

**Fig. 4** Long-term stability of measured $\delta^{34}\text{S}$ for reference materials IAEA-S-2 using the proposed method.

Influence of sample matrix on $\delta^{34}\text{S}$ measurement. The sample matrix can affect vaporization and ionization efficiency in plasma, causing bias in the measured $\delta^{34}\text{S}$ values^{19,47}. Therefore, a matrix-matched bracketing standard was used to correct for matrix effects. However, the extent of sample matrix effects on $\delta^{34}\text{S}$ values in atmospheric precipitation samples remains uncertain. These samples typically contain potassium (K⁺), sodium (Na⁺), calcium (Ca²⁺), and magnesium (Mg²⁺) cations and chloride (Cl⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻) anions, all within a lower concentration range, which adds to the complexity of the study. In this work, the effect of the NO₃⁻ concentration on $\delta^{34}\text{S}$ was not considered because 2% HNO₃ was used as the measurement matrix for the standards and the samples. The effects of Na⁺ and Cl⁻ on $\delta^{34}\text{S}$ were also not considered because in a previous study conducted by Lin *et al.*,¹⁸ it was observed that 100 mg L⁻¹ NaCl only produced an error of 0.74‰, which is within the typical uncertainty range using ICP-MS/MS (1.1–1.5‰ (1SD))⁴⁴. Additionally, Hanousek *et al.*¹⁷ did not observe any significant bias in measured $\delta^{34}\text{S}$ in samples containing up to 49.7 mg L⁻¹ of chloride anions, but observed a negative isotopic deviation when the concentration of Na⁺ reached

25 mg L⁻¹. Meanwhile, no significant isotopic bias was observed with a Mg²⁺ concentration of 12.8 mg L⁻¹.

Notably, these concentrations were far above the range found in the analyzed samples. Therefore, only the effects caused by Ca²⁺ and K⁺ from the sample matrix on determining $\delta^{34}\text{S}$ were considered for this study. The IAEA-S-2 standard was measured with varying concentrations of these elements, and the results are shown in Fig. 3. No differences in sulfur isotopes were observed within the range of concentrations investigated, even at 10 mg L⁻¹ of Ca²⁺ or K⁺. To further investigate the effects of the sample matrix on $\delta^{34}\text{S}$ determination, IAPSO seawater diluted 1000-fold was used, which contained 10781.4 mg L⁻¹ of Na⁺, 1283.7 mg L⁻¹ of Mg²⁺, 412.1 mg L⁻¹ of Ca²⁺, 399.1 mg L⁻¹ of K⁺, 19352.7 mg L⁻¹ of Cl⁻, and 2712.4 mg L⁻¹ of SO₄²⁻, respectively.⁴⁸ The measured value of $\delta^{34}\text{S}$ was 21.1 ± 1.0‰, consistent with the reference value of 21.45 ± 0.20.⁴⁴ This indicates that the matrix elements present in lower concentration do not affect $\delta^{34}\text{S}$ determination using ICP-MS/MS.

The long-term stability of the proposed method. Under optimized conditions, 500 µg L⁻¹ IAEA-S-2 solution was measured multiple times over three months, with IAEA-S-1 used as the bracketing standard for instrument quality discrimination correction, and the results are shown in Fig. 4. The average determination value of $\delta^{34}\text{S}$ for IAEA-S-2 was 22.6 ± 0.5‰ (1SD, n=12), consistent with the recommended value of 22.62 ± 0.08‰. The long-term precision of $\delta^{34}\text{S}$ measured by the proposed method was 0.8‰–1.2‰ (1SD), aligning with the reported range of 1.1–1.5‰ (1SD).⁴⁴

Determining $\delta^{34}\text{S}$ in atmospheric precipitation samples. The proposed method was employed for determining $\delta^{34}\text{S}$ in samples of atmospheric precipitation. The results of $\delta^{34}\text{S}$ and the matrix composition are shown in Table 4. The sample matrix concentration was considered negligible due to low concentrations

of Cl^- , Ca^{2+} , K^+ , Mg^{2+} , and Na^+ . The concentration of SO_4^{2-} and composition of $\delta^{34}\text{S}$ in atmospheric precipitation samples from different regions varied from one another. The SO_4^{2-} concentration ranged from 0.6 to 8.5 mg L^{-1} , and the $\delta^{34}\text{S}$ values ranged from $1.7 \pm 0.8 \text{‰}$ to $8.7 \pm 1.0 \text{‰}$. The results determined by the proposed method were validated by IR-MS, and were found to be consistent (Table 4), indicating that the proposed method is viable for the direct determination of $\delta^{34}\text{S}$ in atmospheric precipitation samples.

CONCLUSION

An effective method for directly determining $\delta^{34}\text{S}$ in atmospheric precipitation samples that with low sulfur concentrations by ICP-MS/MS has been developed in this study, which is improvement over the process previously established by Leyden *et al.*⁴⁴. To accurately analyze $\delta^{34}\text{S}$ in rainwater samples with low sulfur concentrations, minimizing the sulfur content in the background blank is crucial. This was achieved by utilizing a gas trap to purify Ar and O_2 , as both gases were the main sources of sulfur contamination. The proposed method is straight-forward and fast, eliminating the need for conventional and time-consuming chemical purification steps prior to sulfur isotope analysis, thereby reducing the time required for sample handling and analysis. Notably, the proposed method does not require strict matrix and concentration matching, simplifying analysis while avoiding sample contamination, and thus significantly improving the efficiency of the analytical process. The method proposed here-in combined with that which has been reported by Leyden *et al.*⁴⁴ will enable the direct determination of $\delta^{34}\text{S}$ in various natural water environments, offering insight into sulfur cycling, especially for extensive sample surveys, and thereby enhancing our understanding of environmental processes and sulfur remediation strategies.

However, this method has limitations on precision compared to MC-ICP-MS, restricting its use in isotope geochemistry and environmental chemistry, which often require higher precision. Knowing the sulfur concentrations and signal intensity of ^{32}S and ^{34}S in unknown samples is essential before conducting ICP-MS/MS analysis to avoid P/A factor effects on S isotope ratio measurements.

AUTHOR INFORMATION



Wen-Jing Liu received her BSc in 2007 from China University of Geosciences, China, and M.A. in 2010 from Institute of Geochemistry, Chinese Academy of Sciences, and PhD in 2013 from the Institute of Geochemistry, Chinese Academy of Sciences. She is a professor of geochemistry at the Institute of Geology and Geophysics, CAS. Her major research interests are Chemical weathering and

carbon cycling, Stable metal isotope (Li, Mg, Ca, and Fe isotope systems) and cosmogenic nuclide (^{10}Be , ^{26}Al) applications in Earth's surface process (mainly continent weathering and erosion). She was awarded the International Postdoctoral Exchange Fellowship by the China Postdoctoral Council in 2014 and the Youth Innovation Promotion Association Fellowship by the Chinese Academy of Sciences in 2019. Wen-Jing Liu is author or co-author of over 50 articles published in peer-reviewed scientific journals.

Corresponding Author

* W. J. Liu

Email address: liuwenjing@mail.iggcas.ac.cn

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (2023YFC3710600 and 2020YFA0607700), the National Natural Science Foundation of China (42273050 and 42422303), the Instrument Function Development of Chinese Academy of Sciences, and the Key Research Program of the Institute of Geology & Geophysics, CAS (IGGCAS-202204). Wenjing Liu acknowledges support from the Youth Innovation Promotion Association CAS (Y2023014).

REFERENCES

1. A. Bytnerowicz, O. Badea, F. Popescu, R. Musselman, M. Tanase, I. Barbu, W. Fraczek, N. Gembasu, A. Surdu, F. Danescu, D. Postelnicu, R. Cenusu, and C. Vasile, *Romania. Environ. Pollut.*, 2005, **137**, 546-567. <https://doi.org/10.1016/j.envpol.2005.01.040>
2. Y. Wu, W. J. Liu, Y. F. Xu, Z. F. Xu, X. D. Zhou, and L. Zhou, *Environ. Pollut.*, 2021, **288**, 117770. <https://doi.org/10.1016/j.envpol.2021.117770>
3. G. Likens, C. Driscoll, D. Buso, M. Mitchell, G. Lovett, S. Bailey, T. Siccama, W. Reiners, and C. Alewell, *Biogeochemistry*, 2002, **60**, 235-316. <https://doi.org/10.1023/A:1020972100496>
4. M. Zheng, D. Song, D. Zhang, and Z. Zhao, *Atmos. Environ.*, 2024, **317**, 120185. <https://doi.org/10.1016/j.atmosenv.2023.120185>
5. D. E. Canfield, *Rev. Mineral. Geochem.*, 2001, **43**, 607-636. <https://doi.org/10.2138/gsrmg.43.1.607>
6. C. W. Mandeville, J. D. Webster, C. Tappen, B. E. Tayler, A. Timbal, A. Sasaki, E. Hauri, and C. R. Bacon, *Geochim. Cosmochim. Acta*, 2009, **73**, 2978-3012. <https://doi.org/10.1016/j.gca.2009.01.019>
7. N. McArdle, P. Liss, and P. Dennis, *Eire. J. Geophys. Res-Atmos.*, 1998, **103**, 31079-31094. <https://doi.org/10.1029/98JD01664>
8. G. X. Zhu, Q. G. Guo, T. B. Chen, Y. C. Lang, M. Peters, L. Y. Tian, H. Z. Zhang, and C. Y. Wang,

- Environ. Sci. Pollut. Res.*, 2016, **23**, 5507-5515.
<https://doi.org/10.1007/s11356-015-5746-2>
9. Z. Y. Guo, Q. J. Guo, S. L. Chen, B. Zhu, Y. L. Zhang, J. H. Yu, and Z. B. Guo, *Atmos. Res.*, 2019, **217**, 198-207.
<https://doi.org/10.1016/j.atmosres.2018.11.009>
 10. Y. Kim, I. Lee, C. W. Lim, J. Farquhar, S. M. Lee, and H. Kim, *Environ. Pollut.*, 2018, **237**, 878-886.
<https://doi.org/10.1016/j.envpol.2017.12.112>
 11. Z. L. Yan, X. K. Han, Y. C. Lang, Q. J. Guo, and S. L. Li, *Environ. Pollut.*, 2020, **267**, 115444.
<https://doi.org/10.1016/j.envpol.2020.115444>
 12. G. Paris, *Geostand. Geoanal. Res.*, 2024, **48**, 29-42.
<https://doi.org/10.1111/ggr.12535>
 13. N. V. Grassineau, D. P. Matthey, and D. Lowry, *Anal. Chem.*, 2001, **73**, 220-225. <https://doi.org/10.1021/ac000550f>
 14. D. A. Yang, G. Landais, N. Assayag, D. Widory, and P. Cartigny, *Rapid Commun. Mass Spectrom.*, 2016, **30**, 897-907.
<https://doi.org/10.1002/rcm.7513>
 15. K. Takahashi, Y. Nakai, Y. Motizuki, T. Ino, S. Ito, S. B. Ohkubo, T. Minami, Y. Takaku, Y. Yamaguchi, M. Tanaka, and H. Motoyama, *Rapid Commun. Mass Spectrom.*, 2018, **32**, 1991-1998. <https://doi.org/10.1002/rcm.8275>
 16. A. Giesemann, H. J. Jaeger, A. L. Norman, H. R. Krouse, and W. A. Brand, *Anal. Chem.*, 1994, **66**, 2816-2819.
<https://doi.org/10.1021/ac00090a005>
 17. O. Hanousek, T. W. Berger, and T. Berger, *Anal. Bioanal. Chem.*, 2016, **408**, 399-407. <https://doi.org/10.1007/s00216-015-9053-z>
 18. A. J. Lin, T. Yang, S. Y. Jiang, *Rapid Commun. Mass Spectrom.*, 2014, **28**, 750-756. <https://doi.org/10.1002/rcm.6838>
 19. X. P. Bian, T. Yang, A. J. Lin, and S. Y. Jiang, *Talanta*, 2015, **132**, 8-14. <https://doi.org/10.1016/j.talanta.2014.08.053>
 20. M. Martinez, J. I. Garcia-Alonso, C. Parat, J. R. Encinar, and I. L. Hécho, *Anal. Chem.*, 2019, **91**, 10088-10094.
<https://doi.org/10.1021/acs.analchem.9b02038>
 21. S. L. Schurr, F. Genske, H. Strauss, and A. Stracke, *Chem. Geol.*, 2020, **558**, 119869.
<https://doi.org/10.1016/j.chemgeo.2020.119869>
 22. G. Paris, A. L. Sessions, A. V. Subhas, and J. F. Adkins, *Chem. Geol.*, 2013, **345**, 50-61.
<https://doi.org/10.1016/j.chemgeo.2013.02.022>
 23. N. Lv, Z. A. Bao, K. Y. Chen, Y. Zhang, and H. L. Yuan, *Atom. Spectrosc.*, 2023, **44**, 418-426.
<https://doi.org/10.46770/AS.2023.282>
 24. H. M. Yin, J. Lin, H. M. Yu, and F. Huang, *Atom. Spectrosc.*, 2022, **43**, 437-442. <https://doi.org/10.46770/AS.2022.135>
 25. W. Zhang, Z. C. Wang, Z. C. Hu, Q. He, Y. H. Li, Y. T. Feng, H. Liu, and X. J. Zhang, *Atom. Spectrosc.*, 2022, **43**, 60-69.
<https://doi.org/10.46770/AS.2022.007>
 26. Y. S. Cheng, Y. F. Du, K. Y. Chen, C. L. Zong, J. Zhao, and L.-H. Chen, *Atom. Spectrosc.*, 2022, **43**, 236-245.
<https://doi.org/10.46770/AS.2022.105>
 27. A.-Y. Sun, Y.-S. He, Z.-N. Wang, R.-Y. Yang, P.-J. Wang, Q. S. Shi, Y.-C. Zhang, Y. Wang, and Y. Wang, *Atom. Spectrosc.*, 2022, **43**, 337-345. <https://doi.org/10.46770/AS.2022.020>
 28. R. Lin, K. Q. Zong, J. Lin, A. Yang, K. Chen, Z. C. Hu, and Y. H. Liu, *Atom. Spectrosc.*, 2022, **43**, 396-402.
<https://doi.org/10.46770/AS.2022.188>
 29. X. Li, Y. S. He, S. Ke, A.-Y. Sun, Y.-C. Zhang, Y. Wang, R.-Y. Yang, and P.-J. Wang, *Atom. Spectrosc.*, 2022, **43**, 164-173.
<https://doi.org/10.46770/AS.2022.062>
 30. Q. Dong, C. L. Xiao, W. H. Cheng, H. M. Yu, J. B. Shi, Y. H. Yin, Y. Liang, and Y. Cai, *Atom. Spectrosc.*, 2022, **43**, 145-153.
<https://doi.org/10.46770/AS.2021.1109>
 31. X. J. Nie, Z. A. Bao, P. Liang, K. Y. Chen, C. L. Zong, and H. L. Yuan, *Atom. Spectrosc.*, 2022, **43**, 117-125.
<https://doi.org/10.46770/AS.2021.910>
 32. J. G. Martínez-Sierra, O. G. S. Blas, J. M. M. Gayón, and J. I. G. Alonso, *Spectrochim. Acta B*, 2015, **108**, 35-52.
<https://doi.org/10.1016/j.sab.2015.03.016>
 33. P. A. Penanes, A. R. Galán, G. Huelga-Suarez, J. Á. Rodríguez-Castrillón, M. Moldovan, and J. I. G. Alonso, *J. Anal. At. Spectrom.*, 2022, **37**, 701-726.
<https://doi.org/10.1039/D2JA00018K>
 34. Y. Zhu, *Atom. Spectrosc.*, 2023, **44**, 267-281.
<https://doi.org/10.46770/AS.2023.187>
 35. T. B. Coplen, J. K. Böhlke, P. De Bièvre, T. Ding, N. E. Holden, J. A. Hopple, H. R. Krouse, A. Lamberty, H. S. Peiser, K. Revesz, S. E. Rieder, K. J. R. Rosman, E. Roth, P. D. P. Taylor, R. D. Vocke, Jr. and Y. K. Xiao, *Pure Appl. Chem.*, 2002, **74**, 1987-2017. <https://doi.org/10.1351/pac200274101987>
 36. C. F. You and M. D. Li, *J. Anal. At. Spectrom.*, 2005, **20**, 1392-1394. <https://doi.org/10.1039/B510042A>
 37. T. Prohaska, C. Latkoczy, and G. Stingeder, *J. Anal. At. Spectrom.*, 1999, **14**, 1501-1504. <https://doi.org/10.1039/A901973A>
 38. A. A. Menegario, M. F. Gine, J. A. Bendassolli, A. C. S. Bellato, and P. C. O. Trivelin, *J. Anal. At. Spectrom.*, 1998, **13**, 1065-1067.
<https://doi.org/10.1039/A801129J>
 39. P. R. D. Mason, K. Kaspers, and M. J. van Bergen, *J. Anal. At. Spectrom.*, 1999, **14**, 1067-1074.
<https://doi.org/10.1039/A902037C>
 40. O. Hanousek, M. Brunner, D. Pröfrock, J. Irrgeher, and T. Prohaska, *Anal. Methods*, 2016, **8**, 7661-7672.
<https://doi.org/10.1039/C6AY02177H>
 41. L. Balcaen, G. Woods, M. Resano, and F. Vanhaecke, *J. Anal. At. Spectrom.*, 2013, **28**, 33-39.
<https://doi.org/10.1039/C2JA30265A>
 42. S. J. Christopher, D. L. Ellisor, and W. C. Davis, *Talanta*, 2021, **231**, 122363. <https://doi.org/10.1016/j.talanta.2021.122363>
 43. E. McCurdy, G. Woods, B. Georg, and N. Sugiyama, *Spectroscopy*, 2020, **35**, 27-34.
<https://www.spectroscopyonline.com/view/accurate-low-level-sulfur-analysis-by-icp-ms-using-ms-with-oxygen-reaction-cell-gas>
 44. E. Leyden, J. Farkas, S. Gilbert, J. Hutson, and L. M. Mosley, *Talanta*, 2021, **235**, 122708.
<https://doi.org/10.1016/j.talanta.2021.122708>
 45. Á. Keresztesi, I. A. Nita, R. Boga, M. V. Birsan, Z. Bodor, and R. Szép, *Environ. Res.*, 2020, **188**, 109872.
<https://doi.org/10.1016/j.envres.2020.109872>
 46. X. Zhou, Z. Xu, W. Liu, Y. W. T. Zhao, H. Jiang, X. Zhang, J. Zhang, L. Zhou, and Y. Wang, *Sci. Total Environ.*, 2019, **662**, 218-226. <https://doi.org/10.1016/j.scitotenv.2019.01.096>
 47. X. K. Zhu, A. Makishima, Y. Guo, N. S. Belshaw, and R. K. O'Nions, *Int. J. Mass Spectrom.*, 2002, **220**, 21-29.
[https://doi.org/10.1016/S1387-3806\(02\)00767-4](https://doi.org/10.1016/S1387-3806(02)00767-4)
 48. F. J. Millero, R. Feistel, D. G. Wright, and T. J. McDougall, *Deep Sea Res. Part I Oceanogr.*, 2008, **55**, 50-72.
<https://doi.org/10.1016/j.dsr.2007.10.001>