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Article

Precise Determination of Sulfur Isotopes in Organic Matters with 300 nmol Sulfur by An Improved Elemental Analyzer - Isotope Ratio Mass Spectrometry (EA-IRMS)

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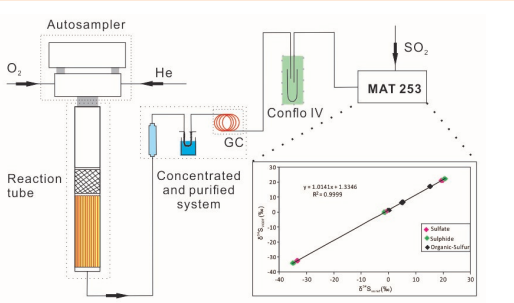
ABSTRACT: Elemental analyzer - isotope ratio mass spectrometry (EA-IRMS) is the most popular method for the measurement of sulfur isotopes in various samples including sulfide, sulfate and organosulfur compounds. The precision of ~±0.3‰ (1σ) can be achieved for samples with ~100 μg S. However, for samples with low sulfur content, or organic matter in particular (*e.g.*, animal bone collagen), the precise and accurate sulfur isotope analysis remains challenging, with typical $\delta^{34}S$ precision ranging from ±0.3‰ to ±1‰. In this study, we applied an improved EA-IRMS with a custom-built cryofocus device for the analysis of sulfur isotopes in organic matter. After sample combustion, all the product gases were transferred into a cold trap by a fast helium flow (100 mL/min). SO_2 was then separated from other gases through a packed gas chromatographic (GC) column at lower flow rate (10 mL/min). The sample size of this method is ~300 nmol S, which is only 1/10 of that required by the conventional method. Lowered sample size allows fully oxygen isotope homogenization of sample SO_2 with oxygen buffers during combustion. With this method, the $\delta^{34}S$ precision from the measurement of organosulfur standards was better than ±0.3‰.



INTRODUCTION

Sulfur (S) is an element exhibiting numerous forms (such as sulfates, sulfides, elemental sulfur and organosulfur compounds) with multiple valence states (from -2 to +6) in nature. They are involved in a variety of geological and biogeochemical processes and have left unique isotope fingerprints, which are widely applied in Earth and environmental sciences.[1-11] Following pyrite, organosulfur compounds represent the second largest reservoir of reduced sulfur,[12] and is a key component of the biogeochemical cycle of S. Therefore, sulfur isotope signal in organic matter is a sensitive tracer of S cycle in the present and past. For instance, the migration history of ancient human can be investigated through the $\delta^{34}S$ of animal collagen.[13,14]

The measurement of S isotopes started from the classical dual-inlet method with SO_2 conversion.[15] With the development of continuous-flow technique, elemental analyzer-isotope ratio mass spectrometry (EA-IRMS) has become the most popular method for S isotope measurements. The analytical precision for routine $\delta^{34}S$ measurement is ~±0.3‰.[16] However, when measuring samples with low S content (<1%) such as organic matter, this method has some limitations. First, the measurement of organic S isotopes requires large sample size (1-4 μmol S). Furthermore, the combustion of a large sample produces considerable amount of CO_2 and N_2, which may (1) saturate or even overload the gas chromatographic (GC) column, causing incomplete separation of SO_2; (2) influence the peak shape of SO_2 (peak tailing and minor peaks),[17] resulting in low precision and accuracy; (3) speed up the accumulation of ash and call for frequent replacement of ash tube, causing low sample throughput; (4) cause overpressure and deactivation of the ion source. Second, $^{32}S^{18}O^{16}O^{+}$ interferes with the measurement of $^{34}S^{16}O^{16}O^{+}$. The ^{18}O interferences may come

Table 1. Sulfur content and sulfur isotopic composition of the standards used in this study

Sample	Sample type	Sulfur conc (%)	Recommended $\delta^{34}S_{VCDT}$ (‰)	Distributor
B2155	Protein (Casein)	0.75 ±0.08	+6.32 ±0.80	Elemental Microanalysis Ltd
B2215	Gelatin	0.51 ±0.03	+1.21 ±0.24	Elemental Microanalysis Ltd
B2222	Bovine gelatin	0.43 ±0.01	+6.79 ±0.08	Elemental Microanalysis Ltd
B2219	Fish gelatin	0.43 ±0.01	+17.05 ±0.07	Elemental Microanalysis Ltd
NBS127	Sulfate	13.7	21.12 ±0.05	U.S. Geological Survey
IAEA-SO-5	Sulfate	13.7	0.51 ±0.09	International Atomic Energy Agency
IAEA-SO-6	Sulfate	13.7	-34.05 ±0.09	International Atomic Energy Agency
GBW04414	Sulfide	13.0	-0.07±0.13	IMR CAGS
GBW04415	Sulfide	13.0	22.15±0.14	IMR CAGS
IAEA-S-3	Sulfide	13.0	-32.49±0.08	International Atomic Energy Agency

from the O_2 during the combustion [18-20], as well as the oxygen from the organic compounds themselves.[18]As a result, $\delta^{34}S$ values measured from direct combustion by EA-IRMS were shifted by a few permil from those obtained via barium sulfate ($BaSO_4$) conversion ,[21] and ±1‰ to ±2‰ biases were observed when calibrating organic S isotopes using inorganic standards.[18] Therefore, the incorporation of oxygen isotope buffer is essential to minimize the influence of oxygen from the organosulfur molecules.[22,23] Recent advances in EA-IRMS have enabled precise determination of S isotope compositions in low-sulfur content materials. Spangenberg *et al.* (2022) developed a method, by which toxic sulfide samples were converted to SO_2 *via* offline combustion, then oxidized and precipitated as $BaSO_4$ and finally analyzed by EA-IRMS.[24] Wu *et al.* (2024) introduced an improved standard addition method capable of analyzing samples with S concentrations between 0.81–3.47 ppm.[25] These methods, however, require either offline preparation of sample $BaSO_4$, or replicated measurement of sample-standard mixtures at different mixing ratio, significantly lowered the sample throughput.

An alternative approach becoming popular in recent decades for S isotope analysis is the multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS).[26-30] However, samples with low S content in solution must be performed sulfur purification using anion exchange chromatography. Meanwhile, low recovery (normally <95%) during the wet chemical pretreatment may cause low reproducibility and accuracy.[26] For the bulk S isotope ratios measurement in solid matters, Horst *et al.* (2024) coupled an EA to MC-ICP-MS and achieved high-precision $\delta^{34}S$ measurements in various materials with a minimal sulfur content of 3.5 μg. However, samples with less than 100 μg S showed large discrepancy (~±3‰) against the "true" value, showing clear non-linearity.[27]

In this study, we improved the EA-IRMS method in previous studies, [31,32] and performed sulfur isotope measurements on organosulfur samples. A custom-built cryofocus device and a slow injection flow (~10 mL/min) were applied to collect and concentrate SO_2. The oxygen isotope homogenization was effectively achieved during the sample combustion. In addition, we simulated the measurement of organosulfur compound by doping dextrose,[19] carbonate, and NH_4Cl into a sulfate standard (NBS127), and found that $\delta^{34}S$ values were not affected by other gases generated by combustion. Our method reduced the sample size required for measurement by an order of magnitude, and improved the precision and accuracy through an effective oxygen isotope homogenization and a reduced memory effect. The measurement of four organic sulfur standards proved that the precision of this method was better than ±0.3‰.

EXPERIMENTAL

Materials. We used B2155, B2215, B2222 and B2219 as standards for sulfur isotope composition in organic matter, NBS127, IAEA-SO-5 and IAEA-SO-6 as standards for sulfate, and GBW04414, GBW04415 and IAEA-S-3 as standards for sulfides. The sulfur content and sulfur isotope composition of all standards are presented in Table 1. Additionally, dextrose, NH_4Cl, carbonate powder (GBW04417, ~200 mesh) and silica powder (~200 mesh) were prepared for doping experiments.

EA-IRMS instrumentation. All measurements were conducted at the Institute of Mineral Resources, Chinese Academy of Geological Sciences (IMR CAGS). Our EA-IRMS was composed of a Flash 2000HT elemental analyzer (Thermo Fisher Scientific), a custom-built cryofocus device, a Conflo IV continuous interface (Thermo Fisher Scientific) and a MAT 253 continuous-flow IRMS (Thermo Fisher Scientific). A 3×10^8 Ω and a 3×10^{10} Ω resistor were registered to faraday cups receiving *m/z* 64 and 66 signals, respectively.

The reactor of EA was as same as the setup for conventional sulfur measurement, with tungsten oxide (WO_3), reduced copper and quartz wool packed in a quartz tube. A 1 m-long packed GC column (PoraPLOT Q; packed in 1/16" O.D. Teflon tubing) was applied instead of the original shorter column used for sulfur measurement. The cryofocus device was consisted of a cold trap (1/8" O.D. stainless steel tubing) and a six-port valve and a heating device, which enables the cryogenic collection of CO_2 and SO_2, the switching of flow rate and the complete release of frozen

Table. 2 Time sequence of organic matter sulfur isotope measurements

Time (s)	Autosampler	R1	R2	R3	Cold trap	6PV
0	On	-	-	-	-	-
5	-	-	-	-	-	Load
10	-	-	-	-	Descond	-
40	-	On	-	-	-	-
60	-	Off	-	-	-	-
80	-	-	On		-	-
100	-	-	Off		-	-
120	-	-	-	On	-	-
140	-	-	-	Off	-	-
240	-	-	-	-	Ascend	Inject
750	-	-	-	-	-	Load
800	Finished					

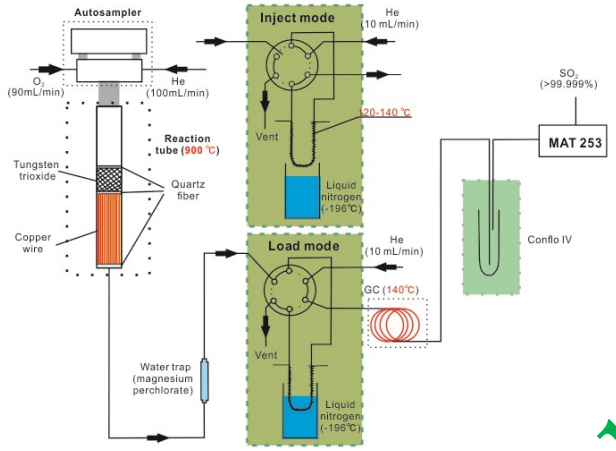


Fig. 1 The schematic of our EA-IRMS for the organic matter sulfur isotope analysis.

analyte gas. With the switching of flow rate from an initial flow of ~100 mL/min to an injection flow of ~10 mL/min, the concentration of sample gas was increased by an order of magnitude. Therefore, the sample size can be reduced accordingly. When preparing samples, tin capsules with large size (9 mm × 9 mm) were recommended in order to ensure effective flashover.

Analytical procedure. We used an analytical procedure modified from the previous study.[24] Briefly, organosulfur standards (~1300-2400 μg, equivalent to 5.6-18 μg S) and ComAid vanadium pentoxide (V_2O_5) were wrapped in a tin capsule with mixing ratio of 1:3. Sample was dropped into the reactor, where carbon, nitrogen and sulfur in sample were oxidized in an oxygen flow (150 mL/min) and converted into CO_2, N_2, and SO_2 at 900 °C. Gas products were then flushed with the initial fast helium (He) flow (100 mL/min) through the water trap (filled with magnesium perchlorate) and into the cold trap. The six-port valve was set to "Load mode" and the cold trap was immersed in liquid nitrogen (-196 °C) (Table 2; Fig. 1) during the combustion. Meanwhile, three injections of SO_2 reference gas were introduced into the IRMS via a dual-inlet system. The cryogenic collection lasted for 230 s. Afterwards, the six-port valve was set to "Inject mode" (Table 2; Fig. 1) while the cold trap was elevated and the automatic heating device (120-140 °C) was activated simultaneously. Subsequently, sample gas was transferred via an injection He flow (10 mL/min) to the GC column, where SO_2 and other gases were separated and entered the IRMS through the high-flow (HF) port of the Conflo IV (Fig. 1). The entire acquisition was completed in ~800 s. See Table 2 for the outlined analytical procedure.

RESULTS

Results from the measurements of four organic standards are shown in Table 3. The standard deviations (1 σ) for the measurements of all standards were better than ±0.28‰, consistent to that of routine measurement on samples with higher sulfur content such as sulfide and sulfate.[33,34] When calibrated by sulfide and sulfate, the biases between measured $\delta^{34}S$ values and their recommended values are less than ±0.4‰. The results of doping experiments are presented in Table S1. With the addition of dextrose, carbonate power and NH_4Cl into the sulfate standard (NBS127), the precisions of measurement were better than ±0.4‰.

DISCUSSION

Influence of system blank on experimental results. For sulfur measurement, the shift of blank (or memory effect) may affect the quality of data significantly, particularly for samples with low sulfur content. These samples must be loaded with weight >10 mg and are difficult to be combusted completely.[23] In addition, SO_2 is highly viscous and tend to stick in the tubing system. Previous studies have indicated that when samples with $\delta^{34}S$ difference >30‰ were measured in a row, a pronounced "memory effect" can be observed in the latter sample.[16] Memory effect can be observed from the increase of instrumental background as well. In this study, the *m/z* 64 signal of the system blank was observed to be approximately 20 mV after multiple sample analyses, which is almost identical to the instrument background before the first measurement. Such low blank accounts for less than 2% of the sample signal (>1200 mV) and is negligible. The low blank may be resulted from (1) the reduced sample size, which is reduced by ~90% in comparison with the conventional method; (2) the help of cryogenic trap and the heating device, which removed SO_2 from the tubing and the reactor more effectively. Therefore, after the full detection of sample peak (at ~700 s), an additional purge for 100 s is long enough to drawdown the system blank to background level. It is noteworthy that a previous study from our laboratory utilized a double-trap cryofocus system with a lower final injection flow (1 mL/min).[35] Indeed, such setup enables the measurement of smaller sample (50-80 nmol). However, the blank signal after one

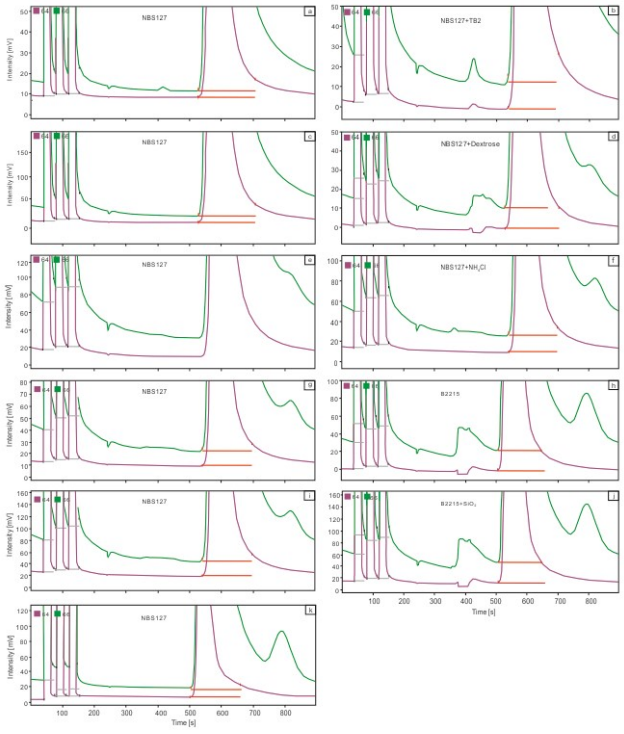


Fig. 2 The pop-up of sample SO_2 peak shape during the doping experiments. Panel a, c, e, g, i and k are NBS127; b, d and f are NBS127 mixed with carbonate power, Dextrose and NH_4Cl, respectively; h and j are B2215 and B2215+SiO_2, respectively.

measurement was as high as ~300 mV, and remained at ~100 mV after three blank measurements, showing contribution from either capsule or sample residue. Therefore, we changed the setup to one-trap with a higher injection flow.

Effect of gaseous contaminants on the $\delta^{34}S$. A series of doping experiments were conducted, in which dextrose, carbonate power and NH_4Cl were added into the sulfate standard (NBS127) at different mixing ratios (see Table S1), in order to simulate the combustion product of organic samples (CO_2, N_2, H_2O and SO_2). For comparison, a series of analyses were conducted on organic standard B2215 (gelatin) and mixtures of B2215 and SiO_2 (1:1). NBS127 was inserted after each set of doping experiment. The measurement sequence was as followed: NBS127, (NBS127+ carbonate power) × 6, NBS127, (NBS127+dextrose) × 6, NBS127, (NBS127+NH_4Cl) × 3, NBS127, B2215 × 3, NBS127, (B2215+SiO_2) × 3, NBS127. The results are presented in Table S1 and Fig. 2. No contaminant peak can be observed in the initial NBS127 measurement (Fig. 2a). In contrast, a small peak was observed prior to the SO_2 peak in the NBS127+carbonate mixture (Fig. 2b). From the ratio and the peak shape we speculate that this peak is actually SO_2 occurred in the position of CO_2 peak (Table S1). This is due to the overload of the GC column by large amount of CO_2 (11.9 μmol at maximum) and the resulted incomplete separation of SO_2 and CO_2. Similarly, this small SO_2 peak was observed from results of other doping experiments and organic standards as well. When water vapor was abundant in the product, the *m/z* 64 and 66 peaks are somehow inclined and asynchronous. Generally, the small peak was separated nicely from the major peak, and will not affect the result. A minor peak with only *m/z* 66 signal occurred after the major peak. However, the signal integration was already finished prior to this peak. Therefore, it will not affect the calculation. In summary, doping experiment and the measurement of organic standards showed that with the 1-m long GC column, gaseous impurities will not influence the quality of SO_2 measurement.

Interference with oxygen isotopes. Besides $^{34}S^{16}O^{16}O$, $^{32}S^{16}O^{18}O$ is another SO_2 isotopologue with nominal mass 66 and is the isobaric interference in the measurement of sulfur isotopes in SO_2. The major source of $^{32}S^{16}O^{18}O$ for sulfide measurement is through the combustion with $^{16}O^{18}O$ in oxygen flow and the oxygen isotope exchange with buffers. For sulfate and organosulfur, however, the ^{18}O in product SO_2 also comes from the structure of the molecule, whose $\delta^{18}O$ values may have a wide range over 40‰.[36] Ury *et al.* (2002) proposed an ^{18}O correction using the equation:[19]

$$\delta^{34}S = 1.089 \times {}^{66}\delta - 0.09 \times \delta^{18}O \qquad (1)$$

where $^{66}\delta$ is the δ value of the beam ratio (*m/z* 66 / *m/z* 64) measured by the IRMS. Assuming the natural abundances of ^{34}S and ^{18}O to be 4% and 0.2%, extreme natural variation in oxygen isotope could lead to over 3‰ biases in measured $\delta^{34}S$ values. To minimize the influence of oxygen isotopes, it is essential to homogenize the oxygen isotopes in the analyte SO_2 with oxygen buffer to make sure that the oxygen isotope of sample SO_2 is identical to that generated from sulfur isotope standards. Molecular oxygen (O_2), V_2O_5, quartz wool or quartz chips usually serve as the oxygen buffer during the conventional sulfur measurement. In practice, however, doping of dextrose in sulfate has been demonstrated to result in a shift in $\delta^{34}S$ value by 2‰.[20] For organosulfur measurement, the discrepancy in $\delta^{34}S$ values between a direct EA-IRMS measurement made on organic sample and on $BaSO_4$ by chemical conversion was as high as ~3‰.[18] These results showed that the oxygen buffer used in these study is insufficient to diminish the bias caused by oxygen isotope heterogeneity in their sample and standard.

In this study, the oxygen isotope homogenization may not be a major problem, because the sample size for measurement was decreased by 90% and the oxygen buffer used in this study (quartz wool, V_2O_5 and O_2) is capable to homogenize the oxygen isotope in SO_2. To prove the efficiency of oxygen buffer, we calibrated the sulfate standards (NBS127, IAEA-SO-5 and IAEA-SO-6) using sulfide standards (GBW04414, GBW04415 and IAEA-S-3). The results are presented in Table S2. The biases between their calibrated

Table 3. Results of four organic standards calibrated by sulfide, sulfate and organosulfur, respectively

Sample	Sample size		$\delta^{34}S_{VCDT}$ (‰) corrected by organosulfur	Average $\delta^{34}S_{VCDT}$ (‰)	$\delta^{34}S_{VCDT}$ (‰) corrected by sulfide	$\delta^{34}S_{VCDT}$ (‰) corrected by sulfate	Recommended $\delta^{34}S_{VCDT}$ (‰)
	Total (μg)	Sulfur (μg)					
B2215	2000	10.2	0.87	1.14±0.27	1.25±0.27	1.16±0.26	1.21 ±0.24
	1400	7.1	1.46				
	2400	12.2	1.5				
	2300	11.7	0.97				
	2000	10.2	1.01				
	1300	6.6	1.0				
B2155	2400	18	6.15	6.52±0.28	6.39±0.28	6.28±0.28	6.32 ±0.80
	2400	18	6.74				
	2000	15	6.8				
	1400	10.5	6.64				
	2400	18	6.63				
	2200	16.5	6.19				
B2222	2000	8.6	6.38	6.54±0.21	6.53±0.21	6.42±0.21	6.79 ±0.08
	1500	6.5	6.75				
	2300	9.9	6.66				
	2400	10.3	6.59				
	2000	8.6	6.66				
	1400	6.0	6.18				
B2219	2400	10.3	17.05	16.99±0.13	16.75±0.13	16.61±0.21	17.05 ±0.07
	2000	8.6	17.08				
	1300	5.6	17.07				
	2400	10.3	16.97				
	2400	10.3	16.77				

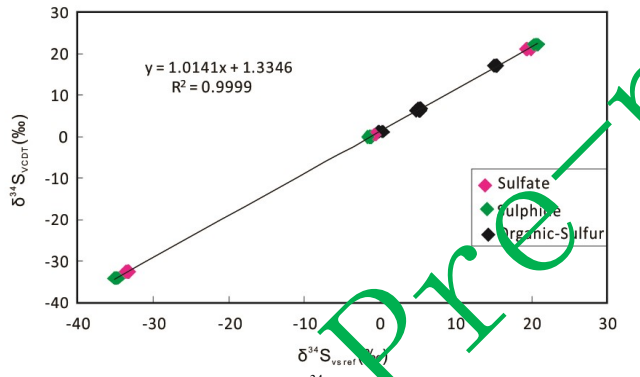


Fig. 3 The universal calibration of $\delta^{34}S$ among sulfide, sulfate and organic matter samples.

and recommended values were less than ±0.1‰ (Table S2). Moreover, for the dextrose doping experiment with O/S ratio (ranging from 29.2-73.5) much greater than sulfate (4), the calibrated $\delta^{34}S$ value is 21.52±0.39‰, biased from its recommended value (21.12‰) by only ±0.4‰, close to those achieved by previous studies with additional oxygen buffer reactor installed.[17,19] Thus, we demonstrate that when measuring small organosulfur samples (~300 nmol S), reactor for conventional sulfur measurement is sufficient for the oxygen isotope homogenization.

Precision and accuracy of sulfur isotope measurements in organic matters. As shown in Table 3, the precision of organosulfur measurements for four organic matter standards in this study are better than ±0.3‰ (1 σ, n = 6). When calibrated with sulfide or sulfate standards, the bias between measured $\delta^{34}S$ values and their recommended values are less than ±0.3‰ (Table 3). In recent decade, organosulfur measurements were done by IRMS with newly developed EA, such as the vario ISOTOPE tube equipped with the "purge and trap" chromatography (Elementar, Germany) and the EA-Isolink (Thermo Fisher Scientific, Germany) working at low flow rate.[16,17] These studies showed that good precision (±0.3-0.4‰) can be obtained for organosulfur isotope measurement on samples with 5-120 μg S. With an imporved old-fashioned EA, our measurement can achieve the same precision and accuracy for organosulfur, with a slightly larger sample size (~10 μg S). Moreover, measured $\delta^{34}S$ values of sulfide, sulfate and organosulfur fall on the same regression line when plotted against their recommended values (slope = 1.0141, R^2 = 0.9999; Fig. 3), showing no obvious matrix effect in our method. Therefore, our method may be applied in sulfur isotope analysis in other matrix, such as the direct measurement sulfur isotopes in whole rock sample.

CONCLUSION

In this study, an EA-IRMS with a custom-built cryofocus device was applied to the measurement of sulfur isotopes in organic matter with sulfur content of ~300 nmol (~10 μg). As a result of smaller sample size, the oxygen buffer was capable to homogenize the oxygen isotope in sample SO_2 in such small sample, and the

interference of ^{18}O on ^{34}S was reduced. With the help of cryogenic trap and the heating device, the system blank was greatly decreased. From doping experiments, we showed that with the lengthened GC column, SO_2 was effectively separated from other gas impurities. Measurement on multiple organosulfur standards showed that the precision of this method was better than ±0.3‰, and the biases between the calibrated values from their recommended values were less than ±0.3‰. Sulfide, sulfate and organosulfur present no obvious matrix effect in our experiments. Moreover, this method can be applied to carbon isotope analysis in samples with very low carbon content, *e.g.*, trace carbonate in silicate rocks.

ASSOCIATED CONTENT

The supporting information (Tables S1-S1) is available at https://www.at-spectrosc.com.

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Notes

The authors declare no competing financial interest.

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