

Sulfur isotope fractionation analysis in mineral waters using an Agilent 8900 ICP-QQQ

Application note

Food safety, geochemistry

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Introduction

Stable isotope geochemistry is a branch of geology that investigates the age of natural materials, their origin and the processes they have undergone since formation [1]. Stable isotope analysis is also used in biogeochemical studies to monitor element cycling in ecosystems [2] and to identify geographical/regional differences for food provenance and archaeology. Of the elements of interest in stable isotope studies (hydrogen, carbon, nitrogen, oxygen and sulfur), only sulfur is accessible using aqueous solution analysis by ICP-MS, and even sulfur is difficult to measure by conventional quadrupole ICP-MS.



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The relative abundance of the two major stable isotopes of sulfur, ^{32}S (94.99% abundance) and ^{34}S (4.25%), varies significantly in nature, so the $^{34}\text{S}/^{32}\text{S}$ ratio can be used to characterize a sample. In sulfur stable isotope analysis, the variation in the $^{34}\text{S}/^{32}\text{S}$ isotope ratio is calculated and reported as a deviation or delta (δ) in ^{34}S abundance relative to a standard material, the troilite (iron sulfide) mineral from the Canyon Diablo meteorite, referred to as δVCDT (Vienna Canyon Diablo Troilite). Natural variations in ^{34}S abundance, expressed in parts per thousand or "per mil" (‰), can be of the order of -50‰ to +40‰ (and occasionally much greater), due to redox reaction. Examples of some values for natural S isotope fractionation are given in Table 1 [3].

Table 1. Sulfur isotope distribution in nature.

Source	$\delta^{34}\text{S}$ (‰) relative to VCDT
Igneous rocks	0
Sedimentary rocks	-40 to +40
Seawater SO_4	+21
Atmospheric SO_4	-30 to +30
Surface water/groundwater SO_4	-22 to +135
Soil (organic sulfur)	-30 to +30
Vegetation (organic sulfur)	-34 to +32
Animals (organic sulfur)	-10 to +22
Fossil fuels (organic sulfur)	-11 to +28

Sulfur isotope ratio (IR) analysis has been mostly done by gas phase isotope ratio mass spectrometry (IRMS) but recent developments in ICP-MS technology have vastly improved its ability to measure sulfur accurately at low levels. In this work, we investigated the performance of a new, high sensitivity ICP-MS instrument, the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ), for low level S IR analysis of mineral waters. Spectral interferences on S arising from O_2^+ can be removed by operating the ICP-QQQ in MS/MS mode, allowing both sulfur isotopes to be measured and potentially offering a faster and simpler S isotope analysis technique.

Experimental

Sulfur IR analysis method: mass-bias correction, matrix effects and background control

For accurate and precise IR analysis by ICP-MS, the instrumental mass bias must be corrected, and the effect of the sample matrix must be controlled.

As is typical for isotope ratio analysis by ICP-MS, instrumental mass-bias was corrected using sample-standard bracketing. A standard solution of known S isotope composition was measured before and after each sample, and the sample IR was corrected by the average IR of the two standard measurements. A 0.5 ppm solution of IAEA-S-1 was used as the mass bias correction standard [4].

The sample matrix can also affect the relative transmission of different mass ions in ICP-MS, and consequently the mass bias and the measured IR. To overcome this effect, a chelation technique can be used to remove the sample matrix before analysis [5]. Alternatively, the variation in sample matrix composition can be reduced by diluting all samples and standards in a consistent matrix. In this work, the mass bias standard and samples were diluted using a solution which contained 50 ppm calcium (Ca) and 100 ppm sodium chloride (NaCl). Use of this diluent reduced the matrix variation that could otherwise have caused fluctuations in the mass bias. The S concentration in the matrix blank was around 0.7 ppb which was low enough not to affect the accuracy of the IR analysis.

Sample dilution in a consistent matrix avoided the necessity for time consuming matrix removal. The matrix dilution approach was made possible by the high sensitivity and low S background of the 8900 ICP-QQQ. Sulfur is ubiquitous in laboratory consumables, supplies, and many of the materials used in instrument components, typically leading to a high elemental background signal. To minimize the contribution from the ICP-MS hardware, key components of the argon gas flow path of the 8900 #100 (Advanced Applications configuration) ICP-QQQ have been replaced using more inert materials. This has successfully reduced the background signal for S (and Si), allowing a detection

limit specification of < 50 ppt for S, Si (and P) to be quoted¹. In a recent study, S was measured with a sensitivity of 10⁴ cps/ppb using the 8900 #100 ICP-QQQ to achieve a background equivalent concentration (BEC) of less than 100 ppt S in ultrapure water [6].

Instrumentation

An Agilent 8900 ICP-QQQ (#100, Advanced Applications configuration) equipped with the standard Ni cones and x-lens was used. The standard glass concentric nebulizer was replaced with a PFA nebulizer, run using self-aspiration for better signal precision.

The two most abundant isotopes of S, ³⁴S and ³²S, were measured using the Agilent 8900 #100 in MS/MS mass-shift mode with O₂ cell gas [6]. The polyatomic interference from ¹⁶O₂⁺ on the primary isotope of S, ³²S⁺ at *m/z* 32, and from ¹⁶O¹⁸O⁺ on the minor ³⁴S isotope at *m/z* 34 were avoided by shifting S⁺ to a new mass. S⁺ reacts readily with O₂ cell gas to form the product ion SO⁺, while the O₂⁺ interference does not react in the same way with the O₂ cell gas. Consequently, the SO⁺ product ions can be measured free of interference at M + 16 amu (*m/z* 48 for the primary ³²S¹⁶O⁺ isotope product ion and *m/z* 50 for ³⁴S¹⁶O⁺). Tuning conditions and method parameters are summarized in Table 2.

Table 2. Agilent 8900 ICP-QQQ tuning and method conditions

	Tuning parameter	Value
Plasma	RF power (W)	1550
	Sampling depth (mm)	8.0
	Nebulizer gas flow rate (L/min)	0.90
	Make up gas flow rate (L/min)	0.30
Lens	Extract 1 (V)	-80
	Extract 2 (V)	-150
	Omega (V)	10.0
	Omega bias (V)	-120
Cell	Octp Bias (V)	-5.0
	Axial Acceleration (V)	2.0
	KED (V)	-8.0
	Cell gas	Oxygen
	Cell gas flow rate (mL/min)	0.45

	Method parameter	Value
Data acquisition	Integration time (s)	1 and 5 for ³² S and ³⁴ S
	Number of sweeps	1000
	Number of replicates	10
Rinse	1% HNO ₃ rinse (s)	20
	50 ppm Ca/100 ppm NaCl rinse (s)	30
Peripump	Uptake time (s)	30
	Stabilization time (s)	30

The high sensitivity and low background of ³²S and ³⁴S can be clearly seen in Figure 1, which shows a spectrum of sulfur obtained using the MS/MS method.

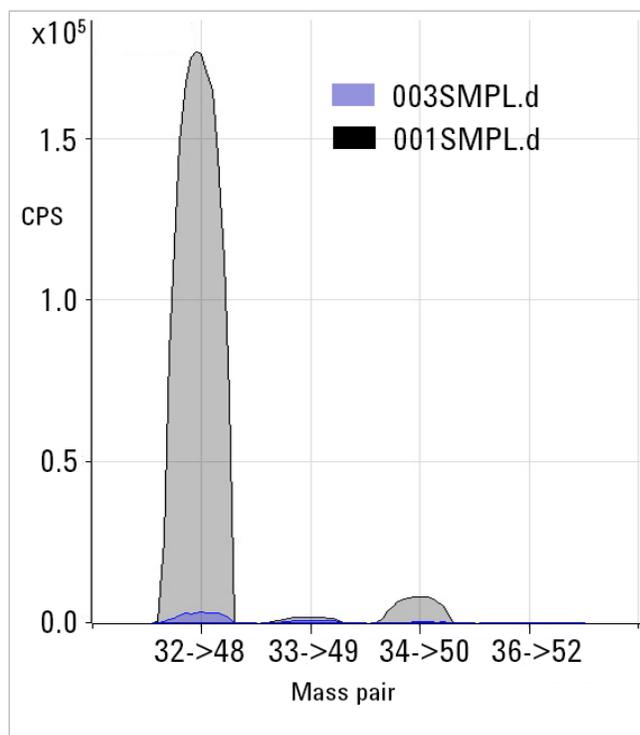


Figure 1. MS/MS spectrum of 10 ppb sulfur solution (grey) and blank (blue)

1. This specification is verified on every Agilent 8900 Advanced Applications and Semiconductor configuration instrument during factory testing

Sample and sample preparation

Sulfur isotope certified reference materials (CRMs) IAEA-S-1 ($^{34}\delta_{\text{VCDT}} = -0.3\text{‰}$) and IAEA-S-2 ($^{34}\delta_{\text{VCDT}} = +22.7\text{‰}$) were purchased from National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA. Each CRM was gently dissolved in diluted nitric acid and diluted to the appropriate concentration. A matrix blank was prepared with 50 ppm Ca (SPEX Certiprep, US) and 100 ppm NaCl (Wako Pure Chemical Industries Ltd, Japan) in 1% nitric acid (Tama Pure 100: Tama Chemicals Co. Ltd, Japan). This solution was also used to dilute the standards and samples.

The seawater and mineral water samples were diluted between 10 and 2000 times to give a S concentration in the range 0.2 to 0.8 ppm. Concentration matching contributed to accurate isotope ratio analysis because, at these levels, ^{32}S is measured in analogue mode and ^{34}S in pulse counting mode. Concentration matching also removes any potential errors caused by detector dead time (the instrument default dead time was 36.3 ns for mass 32).

Results and discussion

Synthetic sample analysis

Sulfur isotope CRMs IAEA-S-1 and IAEA-S-2 and two mixes of the two CRMs were prepared to give four samples with theoretical $^{34}\delta_{\text{VCDT}}$ values of -0.3, 5.4, 11.2 and 22.6. Each blend was prepared at a S concentration of 0.5 ppm. The S IRs were measured six times (standard corrected as described previously).

Figure 2 shows the raw IR data for the IAEA-S-1 mass bias standard and the corrected IR data for the CRM blend samples. The average $^{34}\delta$ values and errors (two times the standard deviation) were determined for the four CRM mixes, and these measured values were plotted against the theoretical values for each mixed standard. The results can be seen in Figure 3, demonstrating the good linearity obtained.

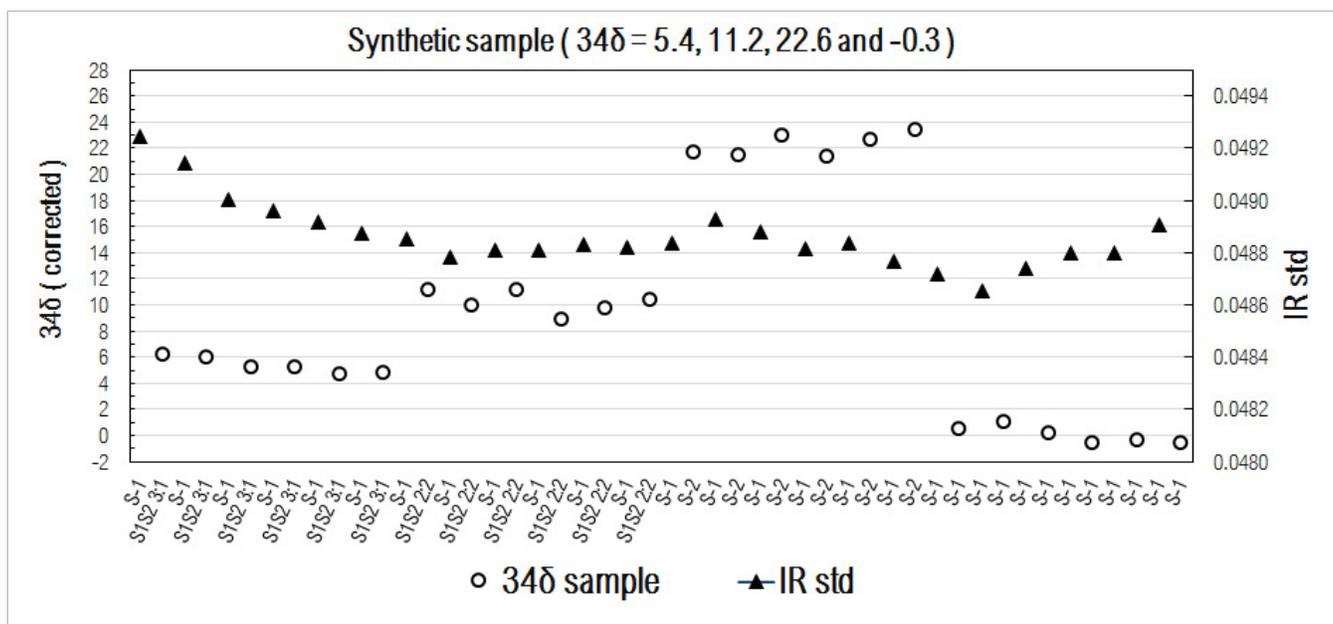


Figure 2. Raw IR analysis of bracketing mass bias standard IAEA-S-1 (triangles) and corrected S IRs of six separate measurements of each of four isotope CRM blends (points)

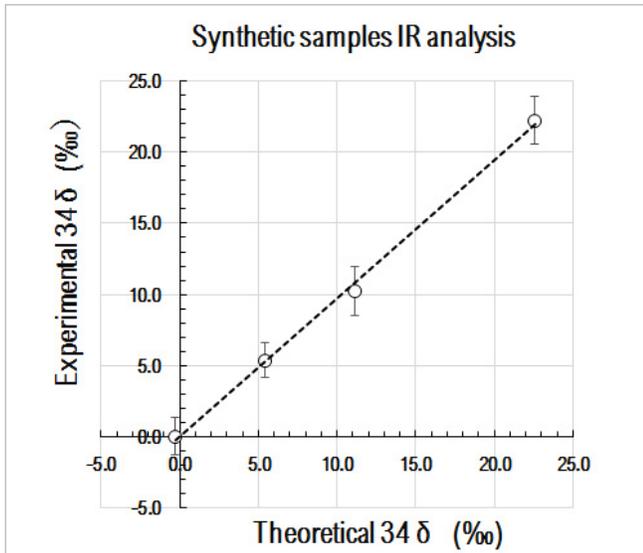


Figure 3. Average of Sulfur IR analysis of the four IAEA CRM blends.

Water sample analysis

Three different brands of mineral water were purchased at a local store in Tokyo, Japan. The mineral water samples were prepared for analysis, together with samples of; JSAC 0301, a Japanese river water CRM (from the Japan Society for Analytical Chemistry); a spring water collected from the IKAHO hot spring in the north of Japan; a NASS 5 seawater CRM (National Research Council, Canada); and Tamapure-AA 100 high purity sulfuric acid (Tama Chemicals Co., Ltd.).

Before the IR measurements were undertaken, the sulfur concentration of each sample was checked to determine the appropriate dilution factor. The dilution factors applied to the samples are given in Table 3. Each sample was measured 10 times and the average and the standard deviation were calculated. Figure 4 shows the average IR and the error (as two times standard deviation) of the IR.

Table 3. Dilution factors

Sample	Dilution factor
Mineral water A	10
Mineral water B	10
Mineral water C	1000
JSAC 0301: Japanese river water CRM	10
IKAHO hot spring water	1000
NASS 5	2000
High purity sulfuric acid	50000

The results show a clear difference in the S IRs for all of the samples, including between the 3 brands of mineral water. The $^{34}\delta$ value of +21.5‰ determined in the seawater reference material agrees well with the global average oceanic seawater value of +21‰ for seawater sulfate (see Table 1 and reference 3).

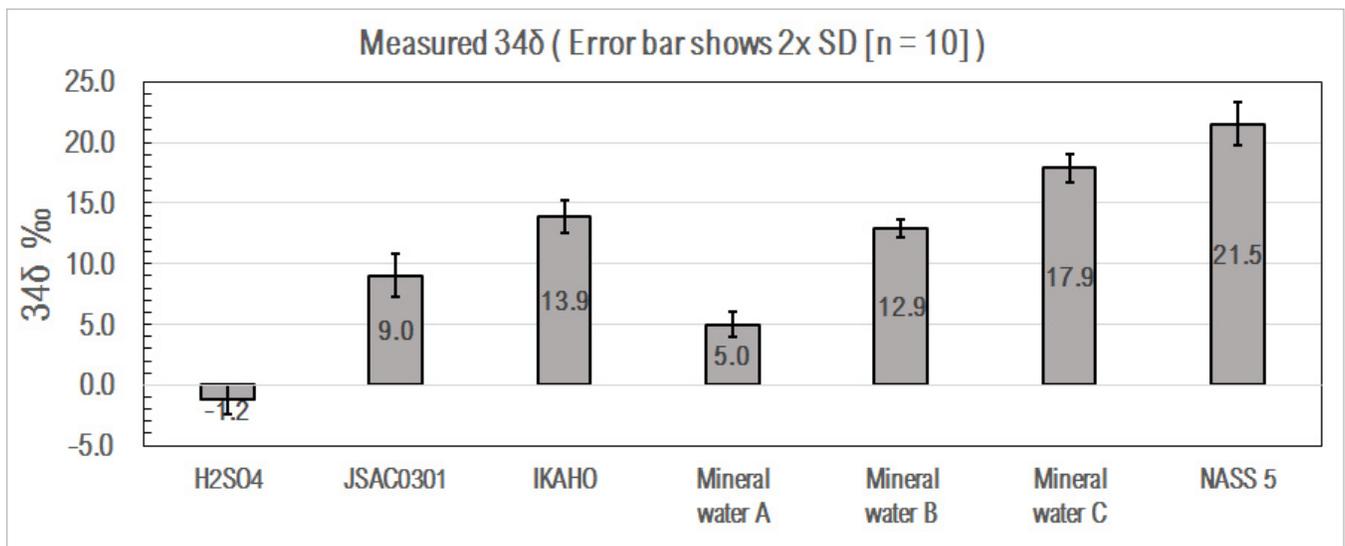


Figure 4. Measured sulfur IR for sulfuric acid, river water CRM, spring water, 3 commercial mineral waters (brands A, B and C) and seawater CRM

The new, fast ICP-QQQ method for sulfur isotope analysis could be useful in identifying the natural characteristics of a water-source, monitoring seasonal and biogeochemical variations, and also for determining the impact of man-made sources of sulfur on the environment.

Conclusions

The Agilent 8900 Advanced Applications configuration ICP-QQQ is ideally suited to $^{34}\text{S}/^{32}\text{S}$ isotope ratio analysis, which can provide valuable information for sample characterization in natural systems or to monitor anthropogenic impact. The 8900 ICP-QQQ provides a low background and high sensitivity for sulfur, which enabled a method to be developed that simply required the sample to be diluted with the matrix blank before analysis. Sample/standard bracketing was used to correct for any instrumental mass-bias or drift.

By operating the 8900 ICP-QQQ in MS/MS mode with O_2 cell gas, problematic spectral interferences due to O_2^+ overlaps on $^{32}\text{S}^+$ and $^{34}\text{S}^+$ were successfully avoided. The S IR analysis method was applied to various samples including three mineral waters, a river CRM, a seawater CRM, a hot spring water, and high purity sulfuric acid. The precision of the IRs achieved was excellent at 1-1.5 ‰ (as two times the standard deviation).

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