

# Precise sulfur isotope ratio measurements in trace concentration of sulfur by inductively coupled plasma double focusing sector field mass spectrometry†

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Sulfur isotope ratios ( $^{34}\text{S}/^{32}\text{S}$ ) were determined by means of inductively coupled plasma double focusing sector field mass spectrometry (ICP-SMS) operated in the medium resolution mode ( $m/\Delta m = 4000$ ) using a torch with a platinum guard electrode and a microconcentric nebulizer combined with a membrane desolvation unit. The guard electrode together with the nebulizing unit increased the signal intensity of the measured isotopes by two orders of magnitude. The use of the membrane desolvation unit decreased the signal intensity of the corresponding interference (mainly oxygen containing species) significantly. Detection limits in solution of  $0.01 \text{ ng g}^{-1}$ , limited only by blank levels, could be achieved. Moreover, sulfur isotope ratios could be determined at concentration levels down to  $1 \text{ ng g}^{-1}$  with a precision of better than 0.1% relative standard deviation (RSD) ( $n = 10$ ). A precision of 0.04% RSD could be achieved at higher concentration levels. ICP-SMS has been shown to be an excellent tool for fast and precise isotope ratio measurements in combination with a high sample throughput and minimum sample preparation prior to analysis.

## Introduction

Sulfur isotope ratios ( $\delta^{34}\text{S}$  values) are known to vary significantly in nature (more than 30‰<sup>1,2</sup>) and are therefore currently used as important tracers for geochemical,<sup>3–7</sup> biological,<sup>8–12</sup> environmental<sup>13–17</sup> and industrial<sup>18–20</sup> studies or even to trace life on Mars.<sup>21</sup> Usually, sulfur isotope ratios are expressed as  $\delta\text{S}$  values ( $\delta^{34}\text{S} = \{[(^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{standard}}] - 1\} \times 1000$ ), which are differences in isotopic ratio with respect to the standard Canyon Diablo Troilite (CDT). To standardize the  $\delta\text{S}$  values, the Commission of Atomic Weights and Isotopic Abundances recommends that relative  $^{34}\text{S}/^{32}\text{S}$  ratios of all sulfur bearing substances be expressed on the VCDT scale, defined by assigning a  $\delta^{34}\text{S}$  value exactly to the silver sulfide reference material IAEA-S1.<sup>22,23</sup> Moreover, precise isotope ratio measurements are a prerequisite for the accurate determination of sulfur contents via isotope dilution mass spectrometry even in difficult chemical matrices. A precision of 0.1% RSD can be expected to be sufficient for most investigations, but a fast, precise and accurate analytical method for sulfur isotope ratio measurements is required.

Conventionally, sulfur isotopes are measured by means of gas source mass spectrometry using  $\text{SO}_2$  or preferably  $\text{SF}_6$  as a gaseous sulfur source. The method includes an exhausting sample preparation step.<sup>24</sup> Sulfur is evolved as  $\text{H}_2\text{S}$ , trapped as  $\text{Ag}_2\text{S}$  and finally  $\text{SO}_2$  or  $\text{SF}_6$  is produced for isotopic analysis.<sup>25</sup> The precisions obtained are usually better than 0.05% RSD. Alternatively, Fourier transform infrared spectrometry has been employed for sulfur isotope ratio measurements.<sup>26</sup> Other methods include ion microprobe

measurements<sup>27</sup> and secondary ion mass spectrometry, which has become relatively routine.<sup>28–30</sup> The main disadvantages are the high instrumental effort and marked matrix effects on instrumental mass bias. The reported precision is about 0.1–0.2% RSD.

The inductively coupled plasma is increasingly being implemented as a tool for fast, precise and accurate isotope ratio measurements.<sup>31,32</sup> Measurement of sulfur by ICP-MS is hampered by spectral interferences (polyatomic oxygen species) found for  $^{32}\text{S}$  and  $^{34}\text{S}$  and by the low ion formation yield. Therefore, sulfur isotope ratios are usually measured by ICP-MS at the  $m/z$  of polyatomic sulfur containing ions (e.g.  $^{32}\text{S}^{16}\text{O}^+$ ), resulting in relatively poor detection limits for sulfur and an isotope ratio precision of about 1% RSD.<sup>33</sup>

High mass resolution is known to resolve most spectral interferences by applying mass resolutions up to  $m/\Delta m = 10\,000$ .<sup>34</sup> All the major interferences on sulfur can be resolved easily by applying a mass resolution of about  $m/\Delta m = 4000$  (Table 1), which is available in the medium resolution mode of a Finnigan MAT Element sector field ICP-MS instrument.

Introduction systems which incorporate membrane desolvation units are reported to reduce oxygen containing interferences significantly.<sup>35,36</sup> Therefore, a combination of high

Table 1 Spectral interferences at  $m/z$  32 and 34

Isotope	Abundance	Interference	$m/\Delta m$
$^{32}\text{S}$	95.0	$^{16}\text{O}-^{16}\text{O}$	1801
		$^{14}\text{N}-^{18}\text{O}$	1061
		$^{15}\text{N}-^{16}\text{O}-^1\text{H}$	1040
		$^{14}\text{N}-^{16}\text{O}-^1\text{H}-^1\text{H}$	770
$^{34}\text{S}$	4.2	$^{33}\text{S}-^1\text{H}$	2977
		$^{32}\text{S}-^1\text{H}-^1\text{H}$	1711
		$^{16}\text{O}-^{18}\text{O}$	1297
		$^{16}\text{O}-^{17}\text{O}-^1\text{H}$	1000
		$^{16}\text{O}-^{16}\text{O}-^1\text{H}-^1\text{H}$	904

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mass resolution and membrane desolvation can contribute significantly to the interference free measurement of sulfur by ICP-MS as reported in this paper, which demonstrates the method to be an effective tool for fast and precise sulfur measurements.

## Experimental

An inductively coupled plasma double focusing sector field mass spectrometer (Finnigan MAT Element, Finnigan MAT, Bremen, Germany) was used for all experiments. The mass separator consists of a magnetic and electrostatic sector field aligned in reversed Nier Johnson geometry. The instrument was equipped with a torch in combination with a Pt guard electrode (CD1, Finnigan MAT). In the present configuration a microconcentric nebulizer equipped with a heated PTFE spray chamber and a membrane desolvation system (MCN-6000, Cetac Technologies, Omaha, NE, USA) was used. A conventional T-type microconcentric nebulizer (MCN-100, Cetac Technologies) in combination with a double pass Scott type spray chamber cooled at 4 °C was used for comparison studies.

All isotope ratio measurements were accomplished at a medium mass resolution setting ( $m/\Delta m=4000$ ) using the fast electrostatic scanning mode. Here, the acceleration voltage is scanned while the magnetic field is kept constant. This procedure allows rapid switching between the peaks, which are therefore measured 'quasi-simultaneously'. The scan conditions and nebulizing conditions were adjusted in order to obtain optimum precision, and are discussed later. Typical ICP-MS operating parameters are listed in Table 2.

All chemical preparations were conducted in special class 100 metal-free clean benches and analytical measurements were performed in a class 10 000 clean room laboratory.

A 1000  $\mu\text{g g}^{-1}$  stock standard solution was prepared gravimetrically from Suprapur sulfuric acid (Merck, Darmstadt, Germany) and further diluted to the required concentration. Sphalerite reference standard NIST SRM 123 (IAEA, Seibersdorf, Austria) was dissolved by microwave digestion (MLS 1200-Mega, Milestone MLS, Leutenkirch, Germany) using  $\text{HNO}_3$  (analytical reagent grade, Janssen Chimica, Geel, Belgium) and subsequently diluted using ultrapure water. In all analytical work, nitric acid prepared by double sub-boiling distillation in a sub-boiling apparatus made of ultrapure quartz (Milestone MLS) of analytical reagent grade (Janssen Chimica) and purified water were used. Water was purified in a three stage process, comprising a reverse

osmosis step, followed by passage through a laboratory-reagent grade water system (F + L, Vienna, Austria) and finally by sub-boiling distillation (Milestone MLS). All working solutions were stored at 4 °C in polyethylene bottles (Semadeni, Ostermüdingen, Switzerland).

## Results and discussion

### High resolution measurements and membrane desolvation

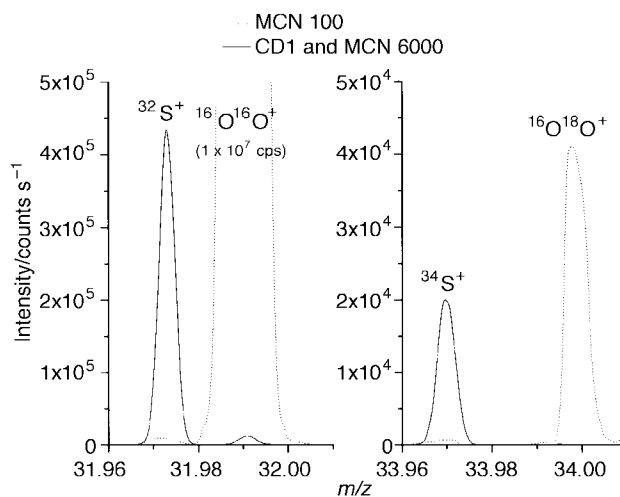
Low mass resolution spectra ( $m/\Delta m=300$ ) at  $m/z$  32 and 34 show significant interference by oxygen containing polyatomic ions (Table 1). The spectral interferences cannot be corrected by blank correction alone, since polyatomic ion formation depends significantly on the matrix composition and plasma conditions and therefore quantification of sulfur using  $m/z$  32 leads to limits of detection of more than 500  $\text{ng g}^{-1}$  using low mass resolution. Further interferences caused by doubly charged ions ( $^{64}\text{Ni}^{2+}$ ,  $^{64}\text{Zn}^{2+}$ ,  $^{68}\text{Zn}^{2+}$ ) have to be taken into account depending on the chemical composition of the sample. Fig. 1 shows unequivocally that the interfering species can be separated from the sulfur isotopes at  $m/z$  32 and 34 by applying a mass resolution of  $m/\Delta m=4000$ . The mass spectrum is acquired using a conventional microconcentric T-type nebulizer, a cooled glass spray chamber and a torch without a Pt guard electrode. It is obvious that the adjacent oxygen interference is significantly higher than the sulfur peak and still interferes owing to the poor abundance sensitivity obtained with magnetic sector field instruments.

The use of a microconcentric nebulizer in combination with a membrane desolvation unit shows oxide formation rates of <0.01% (CeO/Ce), owing to a significant reduction in the solvent load transported to the plasma, achieved by desolvation through a porous membrane.<sup>35</sup> Therefore, oxygen interferences at  $m/z$  32 and 34 could be reduced significantly. Moreover, the high efficiency of the nebulization unit and the formation of a dry aerosol lead to an increase in the signals of the isotopes of interest ( $^{32}\text{S}$  and  $^{34}\text{S}$ ) by a factor of 5–8.<sup>35</sup> Therefore, the peak of interest becomes more dominant with respect to the adjacent interference.

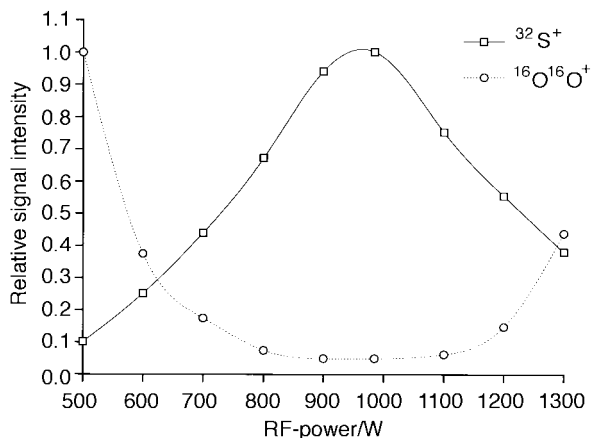
Additionally, the use of a shielded torch increases the signals of the isotopes of interest by a further order of magnitude. Rf power, nebulizer gas flow rate and sampling depth interact extensively and have to be adapted accordingly. The microconcentric nebulizer had to be operated at maximum flow rate

**Table 2** Operating parameter settings for the Finnigan MAT Element optimized for sulfur measurements and sulfur isotope ratio measurements

<i>General setup—</i>	
Rf power	950 W
Sample gas flow rate	1.10 $\text{L min}^{-1}$
Sample uptake rate	60 $\mu\text{L min}^{-1}$
Sampling and skimmer cones	Nickel
Guard electrode	Platinum (on)
Acquisition mode	E-Scan
$m/\Delta m$	4000
<i>Parameter for isotopic measurements—</i>	
Mass window	20%
Settling time	1 ms
Sample time	1 ms ( $^{32}\text{S}$ ) 5 ms ( $^{34}\text{S}$ )
Number of samples	2 × 20
Runs and passes	980 × 1
Analysis time	2 min
Replicate measurements	10
Deadtime	23 ns
Mass bias factor	0.7% per u



**Fig. 1** Mass spectrum with medium mass resolution,  $m/\Delta m=4000$ , at  $m/z$  32 and  $m/z$  34 (sulfur concentration of 1  $\text{ng g}^{-1}$ ) using a conventional setup (MCN-100; torch without guard electrode) and a setup using a torch with a Pt guard electrode and a microconcentric nebulizer combined with membrane desolvation (MCN-6000).



**Fig. 2** Influence of the rf power on the  $^{32}\text{S}^+$  and  $^{16}\text{O}-^{16}\text{O}^+$  signal using a torch in combination with a Pt guard electrode.

( $1.26 \text{ L min}^{-1}$ ). Hence the rf power was adjusted to reach maximum intensities on the sulfur isotopes and minimum intensities on oxygen interferences as shown in Fig. 2.

Fig. 1 also shows the spectrum at  $m/z$  32 and 34 obtained at  $m/\Delta m=4000$  using a microconcentric nebulizer in combination with a membrane desolvation unit as the sample introduction system and additionally a shielded torch with a Pt guard electrode, after optimization of the system. It can be clearly seen that the signal intensity of the  $^{32}\text{S}$  and  $^{34}\text{S}$  peaks could be increased by up to two orders of magnitude and the signal intensity for the interfering species could be minimized significantly compared with a conventional setup.

Therefore, limits of detection (LODs) ( $3\sigma$ ) could be reduced to about  $0.01 \text{ ng g}^{-1}$  (only limited by the blank level). Table 3 reports the decrease in LODs by using both high mass resolution and novel instrumentation. Moreover, the signal intensities for sulfur are still high enough for the accurate determination of sulfur isotope ratios on  $1 \text{ ng g}^{-1}$  sulfur.

### Isotope ratio determination

In order to obtain optimum instrumental conditions, parameters influencing isotope ratio determinations such as sampling time, settling time of the magnet, segment duration, number of samples (measured channels per peak), mass window and total scan duration were carefully optimized according to previous studies<sup>32</sup> and are listed in Table 2. Isotope ratios were performed using a mass window of 20%. Sample times were optimized with respect to the signal abundance of the selected isotopes, *i.e.* 1 ms for  $^{32}\text{S}$  and 5 ms for  $^{34}\text{S}$ . Since optimum sample times are not necessarily inversely proportional to the abundance,<sup>37</sup> they have to be adapted iteratively to obtain maximum precision. A minimum settling time of 1 ms was selected.<sup>32</sup> The main problem when using high resolution instruments for isotope ratio measurements in the high mass resolution mode is the need for the mass calibration to be highly stable and for there to be no significant drift of the peak maximum in the mass table. This can only be performed by establishing a maximum stable temperature equilibrium within the instrument in a thermally stable labora-

**Table 3** Detection limits of sulfur in combination with different instrumental setups

$m/\Delta m$	Nebulizer	Guard electrode	Detection limit/ $\text{ng g}^{-1}$ ( $3\sigma$ )
300	MCN-100	No	500
4000	MCN-100	No	10
4000	MCN-6000	Yes	0.01

**Table 4** Isotope ratio measurements of  $^{34}\text{S}/^{32}\text{S}$

Concentration/ $\text{ng g}^{-1}$	$^{34}\text{S}/^{32}\text{S}$ (deadtime and mass bias corrected)	RSD (%) ( $n=10$ )
100	0.04226	0.04
10	0.04225	0.06
1	0.04221	0.09

tory environment. As documented by Finnigan MAT, problems of thermal instability have been overcome in the redesign of the Element high resolution instrument, the new Finnigan MAT Element2.<sup>38</sup> Thus, a minimum mass window down to 5% can be selected, which ensures that the measurement is performed solely on the peak maximum.

By using the optimized setup, precisions for 10 replicate measurements of  $^{34}\text{S}/^{32}\text{S}$  ratios of 0.04, 0.06 and 0.09% could be achieved on 100, 10 and  $1 \text{ ng g}^{-1}$  total sulfur, respectively, using a total time of 2 min per measurement (Table 4). Higher concentration levels would lead to a significant increase in the influence of the detector deadtime or even lead to an overload of the detector using the selected setup. Thus the optimum concentration range is between 10 and  $100 \text{ ng g}^{-1}$ . A deadtime of 23 ns was selected for deadtime correction. This deadtime was determined by a method proposed by Russ and Bazan<sup>39</sup> over the whole mass table using  $^{24}\text{Mg}/^{25}\text{Mg}$ ,  $^{58}\text{Ni}/^{60}\text{Ni}$ ,  $^{86}\text{Sr}/^{88}\text{Sr}$ ,  $^{137}\text{Ba}/^{138}\text{Ba}$  and  $^{207}\text{Pb}/^{208}\text{Pb}$  ratios. Since the deadtime was found to be stable over the whole mass range,<sup>40</sup> the same deadtime could be applied for  $^{32}\text{S}/^{34}\text{S}$ . The mass bias factor was determined using the NIST SRM 123 standard and was found to be 0.7% per mass unit.

The accuracy found for different dilutions of the NIST SRM 123 standard was  $<0.1\%$ . To avoid circular reasoning, the samples were prepared and diluted independently for applying the calibration and checking the accuracy, respectively. To investigate the accuracy more precisely, the accurate determination of the mass bias without any influence by deadtime has to be performed. This would require an enriched standard reference material with an isotopic ratio of approximately 1, which was not available at the time of the measurements.

### Conclusions

Sulfur measurements using the current setup resulted in limits of detection of  $<0.01 \text{ ng g}^{-1}$  (limited solely by the blank levels). A precision of better than 0.1% RSD for 10 successive measurements was achieved for sulfur concentrations down to  $1 \text{ ng g}^{-1}$ . A total analysis time of 2 min for a single measurement was required. For the first time, stable sulfur isotope ratio measurements of  $^{32}\text{S}/^{34}\text{S}$  for very low concentrations of sulfur have been achieved using ICP-MS. The reported precision is suitable for many applications and can be used directly for differential measurements. Therefore, the method presented opens the door for measurements on numerous different samples, by using a universal, commercially available method, in combination with high sample throughput both for isotope ratio measurements in tracer studies and isotope dilution measurements for accurate quantification in various matrices, *e.g.* soil, biological matrices, oil and sludge. The accuracy of the values must be tested individually on available reference materials. The availability of certified spiked sulfur solutions will furthermore extend this technique to provide accurate isotope dilution concentration measurements of quality comparable to that of other methods.

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