

On-Line Sulfur-Isotope Determination Using an Elemental Analyzer Coupled to a Mass Spectrometer

A. Giesemann,^{†,‡} H.-J. Jäger,[†] A. L. Norman,^{†,§} H. R. Krouse,[§] and W. A. Brand^{||}

Institut für Pflanzenökologie, Justus Liebig Universität Giessen, Heinrich-Buff-Ring 38,

35392 Giessen, Germany, Department of Physics, The University of Calgary, 2500 University Drive NW,

Calgary, Alberta, Canada T2N 1N4, and Finnigan MAT GmbH, Barkhausenstrasse, 2-28197 Bremen, Germany

An on-line method for S-isotope analysis is described. Samples are combusted in an elemental analyzer. SO₂ is separated from other combustion gases by gas chromatography, and the gases enter the ion source of the mass spectrometer through a split interface. Integrated peak areas for ³²SO₂⁺ and ³⁴SO₂⁺ are compared to the response for a standard gas sample to determine the δ³⁴S value. δ³⁴S values of samples analyzed using the on-line method correspond linearly with those achieved from the same sample prepared off-line, where Kiba reduction followed by oxidation of the sulfur to SO₂ is carried out prior to S-isotope analysis against a known standard. With the described on-line method, the amount of sulfur necessary for S-isotope analysis is reduced to about 10 μg of S per analysis. The time needed for on-line preparation and measurement is less than one-third of the off-line procedure.

Stable sulfur-isotope analysis is often associated with many problems concerning sample preparation and mass spectrometric determination. The ³⁴S/³²S ratios are most commonly determined after SO₂ has been generated out of natural materials. Sample preparation always requires several chemical transformation steps to finally produce SO₂ out of the S-containing compounds. The standard preparation techniques used for most sulfur-bearing samples start with conversion of all sulfur to BaSO₄, which is then reduced to H₂S by one of the following three procedures: graphite reduction at 1000 °C,¹ reduction with tin(II)-strong phosphoric acid (Kiba's reagent) at 300 °C in a stream of nitrogen,² or application of a HI-H₃PO₄-HCl reduction solution.³ The generated H₂S is converted to Ag₂S, which is finally oxidized to SO₂. One major disadvantage of these methods is that they all need relatively large amounts of the original material to obtain sufficient sulfur as the numerous chemical processes require rather high amounts of sulfur (3–7 mg of S). Although

for some sulfides and sulfates thermal decomposition with a mixture of V₂O₅-SiO₂ is possible, the amount of S needed is about 640 μg or more.^{4,5} Smaller samples can be analyzed using SF₆, but preparation of such samples is rather dangerous as highly reactive fluorinating agents have to be used.⁶

Sulfur isotopes fractionate in biological, geochemical, and chemical processes, and fractionation is to be expected during sample preparation, especially when a reaction is carried out incompletely. Therefore great care must be taken to ensure complete conversion with every preparation step. Consequently, as few preparation steps as possible during sample preparation for S-isotope analysis are desirable. Preliminary investigations of on-line systems for S-isotope analysis have been carried out by Pichlmayer and Blochberger,⁷ who described a system where an elemental analyzer is interfaced to a high-precision isotope ratio mass spectrometer, and Haystead,⁸ who used Dumas elemental analysis mass spectrometers. In this paper we describe a method where small amounts of sulfur (down to 20 μg of S) extracted from plant or soil material through one single chemical conversion step are combusted and the S-isotopic composition of the SO₂ is determined directly from the combustion gas. Results achieved with this method have been published preliminarily during a workshop on sulfur transformation in soil ecosystems, Saskatoon, SK, Canada.⁹

EXPERIMENTAL SECTION

1. Off-Line Preparation and S-Isotope Analysis. Off-line isotope ratio mass spectrometry of sulfur involved two distinct steps: sample preparation and mass spectrometric measurement.

Sample preparation for such an off-line analysis of the S-isotopic composition in plant and soil material started with oxidation of all sulfur in the samples through either Parr bomb

[†] Justus Liebig Universität Giessen.

[‡] Current address: Institute for EcoToxicology, Forschungsanstalt für Landwirtschaft, Bundesallee 50, 38116 Braunschweig, Germany.

[§] The University of Calgary.

^{||} Finnigan MAT GmbH.

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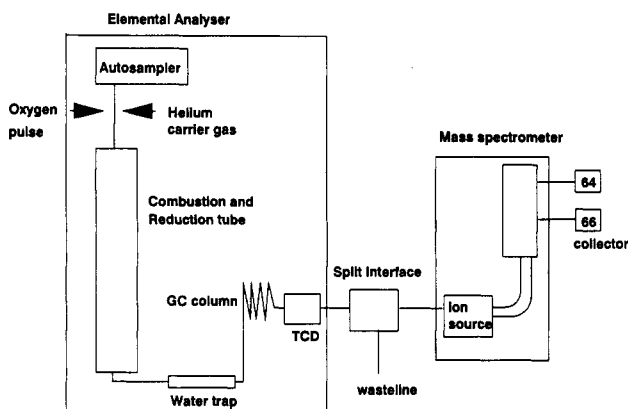


Figure 1. Schematic of coupled elemental analyzer and mass spectrometer.

oxidation¹⁰ or Eschka reduction¹¹ followed by precipitation of the sulfur as BaSO₄ with a 0.5 M BaCl₂ solution. An aliquot of BaSO₄ containing about 7 mg of S was then reduced to H₂S using Kiba's reduction mixture.² The evolved H₂S was trapped in a cadmium acetate solution (15 g/L cadmium acetate + 0.5 mL of glacial acetic acid GRA) and converted to Ag₂S through addition of silver nitrate solution (0.1 M). Dried Ag₂S was mixed with V₂O₅ (ratio 4.25:10) and sealed off in evacuated quartz vials. SO₂ was generated in these vials by heating them to 1000 °C for 90 s in a muffle oven.

The mass spectrometric determination of the sulfur-isotope ratios was carried out on a Finnigan MAT Delta S using a dual-inlet system with two gas bellows connected to the changeover valve on the ion source. The ion current of masses 66 and 64 in the sample gas was compared to the corresponding ion currents of a reference gas produced from our laboratory CdS standard that was treated by the procedure described above. The ³⁴δ value (11.0‰ vs CDT) of the CdS standard was calibrated vs CDT independently.

2. On-Line Analysis. For on-line analysis, a Carlo Erba NA 1500 elemental analyzer was connected to the Finnigan MAT Delta S mass spectrometer through a split interface (Figure 1). The samples (BaSO₄ or Ag₂S, respectively) were wrapped together with 0.1 mg of V₂O₅ in tin capsules. Then they were combusted at 1100 °C in a 5-mL pulse of oxygen (grade 4.5) in a Carlo Erba NA 1500 elemental analyzer. All gases produced during the combustion were carried on in a stream of helium (grade 5.6, 60 mL/min flow rate) through an oxidation–reduction reactor filled with tungstic anhydride, copper oxide, and reduced copper as recommended by Carlo Erba. Through sweeping all gases over heated CuO and reduced Cu, the reduction of traces of SO₃ produced during the reaction was ensured and the surplus of oxygen trapped. Water vapor was removed in a desiccant trap containing anhydrous Mg(ClO₄)₂. Finally, the combustion gases passed over a Poropak QS column (heated to 80 °C), where CO₂ and N₂ were separated from the SO₂.

A 0.1% portion of the GC column effluent was transferred via a split interface and a capillary into the ion source of the mass spectrometer. Reference gas for isotopic calibration

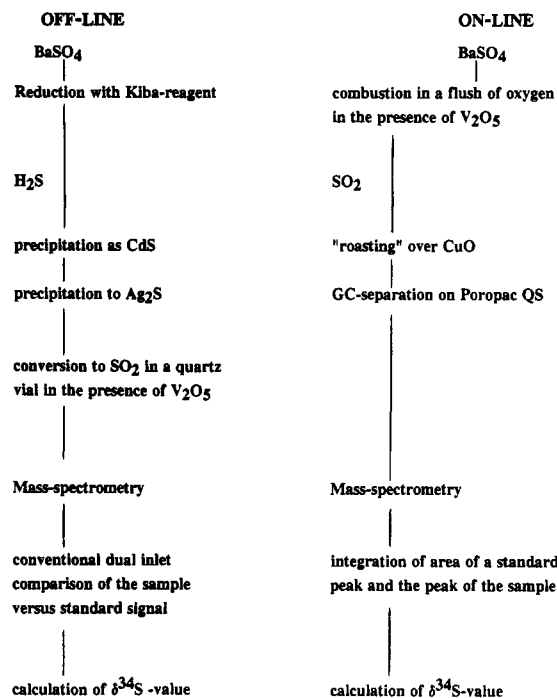
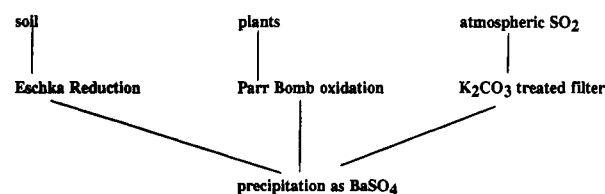


Figure 2. Comparison of the methods for off-line and on-line combustion preparation of SO₂ and subsequent stable isotope mass spectrometry.

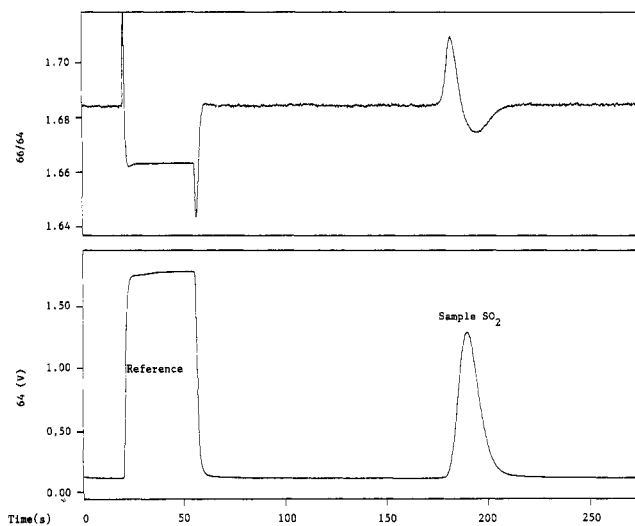


Figure 3. Mass 64 ion current (lower trace) and 66/64 ion current ratio from SO₂ gas which derives from the standard pulse or from SO₂ originating from sample combustion followed by GC separation.

was supplied from a SO₂ bottle by injecting a pulse of this SO₂ into the carrier gas between the elemental analyzer and split interface. The MS system was differentially pumped so that a pressure of 1 × 10⁻⁶ mbar—read on the ionization manometer—was maintained in both the ion source and the analyzer. The ion currents of masses 64 and 66 were recorded over the time the gas spent in the source, and the areas underneath these peaks were integrated. Comparison of these areas to corresponding peak areas of a standard gas was carried

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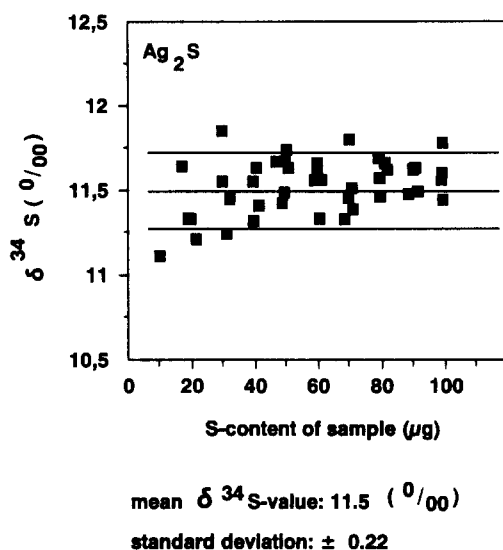
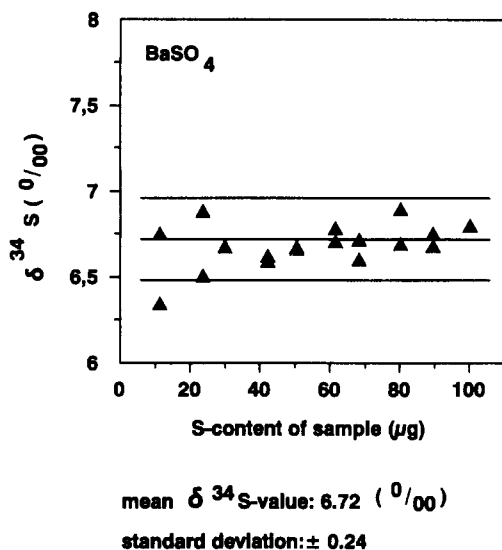


Figure 4. Correlation of S content and S-isotope composition in on-line S-isotope analysis of Ag_2S and BaSO_4 , respectively. The horizontal lines represent the statistical mean \pm one standard deviation.

out to determine the isotope ratio. These calculations were done using the Finnigan MAT Isodat software, version 5.0.

All results from both on-line and off-line procedures are expressed as $\delta^{34}\text{S}$ notation, giving the difference between the S-isotopic composition of a sample and a standard relative to the corresponding isotopic composition of this standard:

$$\delta^{34}\text{S} = \left(\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} - 1 \right) \times 10^3 \text{ (‰)}$$

All results are reported vs Cañon Diabolo troilite (CDT).

RESULTS AND DISCUSSION

The major differences that exist between off-line and on-line S-isotope analysis (Figure 2) are the way to produce SO_2 and the measurement technique in the mass spectrometer. During off-line analysis, sample and standard gas are measured directly against each other at constant pressure and current when pure SO_2 gas is supplied from the variable volumes which are part of a conventional dual-inlet system connected to a changeover valve. The vacuum inside the mass spectrometer was read as 2×10^{-7} mbar on the ionization manometer for such off-line applications. During on-line analysis, the vacuum inside the mass spectrometer was reduced to a reading of 1×10^{-6} mbar, due to helium passing through the ion source. The standard gas used for on-line analysis is injected as a pulse of SO_2 into the helium stream and is exposed to the mass spectrometer for a time span of 35 s. Then the standard SO_2 is turned off, and the gas leaves the source within the helium stream. About 200 s later, the SO_2 produced during sample combustion in the elemental analyzer reaches the ion source.

Combustion of a sample followed by chromatographic separation of the combustion gases leads to a slight separation of the isotopes. The trace of the 66/64 ratio (upper trace in Figure 3) rises first and then falls steeply, indicating that the beginning of the SO_2 peak leaving the GC column is enriched in ^{34}S while the end is depleted. Slight differences in S-isotopic

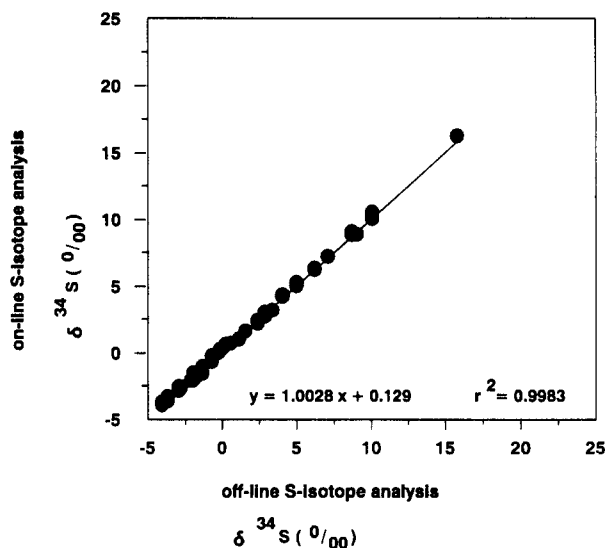


Figure 5. S-isotope composition of Ag_2S samples determined in off-line and on-line analyses.

composition of the standard gas could also be observed at the beginning and the end of the SO_2 pulse injected, with the start being enriched in ^{34}S . Such chromatographic isotope effects are well-known, especially with C-isotope analysis.^{12,13}

SO_2 leaves the GC column as a peak and hence the SO_2^+ current in the ion source is not constant over time. The primary parameter checked in the on-line procedure was the linear correspondance of the ion current ratio with intensity over the range present in the ion source throughout the analysis. Hence, a linearity calibration was carried out in the range of 0.5–2 V ion current using the Finnigan MAT Isodat software, version 5.0.

The results showed that, with a well-focused ion source, changes in $\delta^{34}\text{S}$ values were less than 0.01‰ per 1-V change of signal (1 V = 3.3 nA). Therefore, nonlinear response of the ratio can be ruled out safely.

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Table 1. Calculation of $\delta^{34}\text{S}$ for a Sample vs CDT after On-Line S-Isotope Analysis against Bottle SO_2 as Working Standard

- (1) determination of $^{66}\delta$ of the working standard (SO_2) by combusting an Ag_2S with known $^{34}\delta_{\text{CDT}}$ value:^a
 $^{66}\delta_{\text{SO}_2/\text{CDT}} = ^{66}\delta_{\text{SO}_2/\text{Ag}_2\text{S}} + ^{66}\delta_{\text{Ag}_2\text{S}/\text{CDT}} + [^{66}\delta_{\text{SO}_2/\text{Ag}_2\text{S}} ^{66}\delta_{\text{Ag}_2\text{S}/\text{CDT}}]/1000$ (1)
- (2) determination of $^{66}\delta$ of an unknown sample (SA) vs CDT using the working standard (SO_2) as mediator:
 $^{66}\delta_{\text{SA}/\text{CDT}} = ^{66}\delta_{\text{SA}/\text{SO}_2} + ^{66}\delta_{\text{SO}_2/\text{CDT}} + [^{66}\delta_{\text{SA}/\text{SO}_2} ^{66}\delta_{\text{SO}_2/\text{CDT}}]/1000$ (2)
- (3) oxygen correction of the sample analyzed:^b
 $^{34}\delta_{\text{SA}/\text{CDT}} = ^{34}\delta_{\text{SO}_2/\text{CDT}} + ^{66}\delta_{\text{SA}/\text{SO}_2}[1 + ^{34}\delta_{\text{SO}_2/\text{CDT}}/1000 + 2^{18}\text{R}_{\text{SMOW}}/^{34}\text{R}_{\text{CDT}}]$ (3)

^a Please note that $^{66}\delta_{\text{SO}_2/\text{CDT}}$ is determined by preparing Ag_2S and CDT separately into SO_2 and measuring their difference without correcting for the ^{18}O contribution. In practice, this value may be obtained from the known $^{34}\delta$ of the Ag_2S reference material by applying formula 3 in reverse order.
^b The last expression $2^{18}\text{R}_{\text{SMOW}}/^{34}\text{R}_{\text{CDT}}$ amounts to 0.0904.

The next question considered was whether the $\delta^{34}\text{S}$ value changed with the amount of sulfur combusted in the elemental analyzer. Different amounts of sulfur—between 10 and 100 μg of S—were combusted as either pure Ag_2S or BaSO_4 . Down to 20 μg of S, very good reproducibilities of $\pm 0.22\%$ for Ag_2S and $\pm 0.24\%$ for BaSO_4 were achieved (Figure 4).

Finally, the comparability of the results achieved with this on-line method to those achieved with off-line procedures was tested. Aliquots of Ag_2S whose S-isotopic composition had been determined off-line were analyzed on-line. Sample giving off-line $\delta^{34}\text{S}$ values within the range of -5 to $+20\%$ were combusted. A good linear correlation ($r^2 = 0.9983$) was achieved, and replicate analysis of the samples gave reproducible results in the mean range of $\pm 0.2\%$ (Figure 5).

During on-line analysis, the standard gas used derives from a bottle and hence is likely to show an O-isotopic composition different from the one of SO_2 resulting from the combustion procedure. This working standard has to be used as a mediator whose S-isotopic composition was determined as $^{66}\delta$ without an oxygen correction. The S-isotopic composition of the samples was determined as $^{66}\delta$ against this working standard. To calculate the $\delta^{34}\text{S}$ values, oxygen correction is applied in the very last step using the $^{66}\delta$ of the sample (Table 1).

The major aim of this on-line method was to reduce the time- and chemical-consuming preparation of sulfur from soil and plant samples as far as possible. It had to be checked whether BaSO_4 , the result of oxidation of all S in the samples followed by precipitation, gave identical $\delta^{34}\text{S}$ values in on-line analysis as Ag_2S which had been prepared out of the BaSO_4 during off-line preparation. Table 2 gives the results of this comparison. The $\delta^{34}\text{S}$ values were identical within the standard deviation range of the method. Statistical analysis of the comparison (χ^2 test, F test, Duncan test) showed that the results of both analysis series were identical at the 99.9% and 99% levels.

Summarizing, the multistep preparation necessary for the off-line (conventional) S-isotope determination could be reduced to one single preparation step, which is oxidation of all sulfur in the sample and precipitation of this sulfur as BaSO_4 . As a consequence, reduction in preparation time could be achieved. While about 4.5 h is necessary to prepare SO_2 in quartz vials for off-line analysis via the Kiba reduction process and consecutive S-isotope analysis on the mass

Table 2. Comparability of On-Line Determination of S-Isotope Composition in BaSO_4 and in Ag_2S Prepared from BaSO_4 Through the Kiba Reduction Procedure^a

sample	on-line $\delta^{34}\text{S}$ values (‰)	
	BaSO_4	Ag_2S
$(\text{NH}_4)_2\text{SO}_4$	15.94	15.75
MgSO_4	6.44	6.63
soil	5.71	5.66
litter	4.16	4.07

^a S of all samples was extracted in one preparation step as described in the text. Triplicate analyses of each sample gave a range of better than $\pm 0.25\%$. Statistical analysis of the difference between both series (χ^2 test, F test, and Duncan test) proved no difference at the 99.9% and 99% significance levels.

Table 3. Comparison of Time Requirements (In Minutes) for Off-Line and On-Line Preparation and S-Isotopic Composition in Plant Samples

	off-line	on-line
oxidation of all S in plant samples, pptn as BaSO_4	30	30
Kiba reduction and pptn as Ag_2S	90	nn ^a
filtration of Ag_2S	15	nn
transfer to quartz vials	40	nn
sealing of vials	90	nn
SO_2 production in vials	2	nn
MS analysis	15	nn
filling of tin capsules	nn	10
coupled combustion of sample to SO_2 and MS analysis	nn	15
total	272	55

^a nn, indicates that these procedures are not necessary for the described method.

spectrometer, on-line analysis requires less than 1 h to obtain the $\delta^{34}\text{S}$ value of a sample (Table 3).

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