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

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An on-line method for S-isotope analysis is described. Samples are combusted in an elemental analyzer. SO$_2$ 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 $^{32}$SO$_2^+$ and $^{34}$SO$_2^+$ are compared to the response for a standard gas sample to determine the $^{34}$S/$^{32}$S value. $^{34}$S/$^{32}$S 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 SO$_2$ 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 $^{34}$S/$^{32}$S ratios are most commonly determined after SO$_2$ has been generated out of natural materials. Sample preparation always requires several chemical transformation steps to finally produce SO$_2$ out of the S-containing compounds. The standard preparation techniques used for most sulfur-bearing samples start with S-containing compounds. The standard preparation for such an off-line analysis of the S-isotopic composition in plant and soil material started with oxidation of all sulfur through either Parr bomb for some sulfides and sulfates thermal decomposition with a mixture of V$_2$O$_5$–SiO$_2$ is possible, the amount of S needed is about 640 µg or more. Small samples can be analyzed using SF$_6$, but preparation of such samples is rather dangerous as highly reactive fluorinating agents have to be used.

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, who described a system where an elemental analyzer is interfaced to a high-precision isotope ratio mass spectrometer, and Haystead, 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 a single chemical conversion step are combusted and the S-isotopic composition of the SO$_2$ 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. A. Giesemann, A.; Jäger, H.-J.; Norman, A. L.; Krouse, H. R. On-line analysis of S-isotope distribution in small samples. In Sulfur Transformations in Soil Ecosystems; NHRI Symposium 11; Saskatoon, SK, Canada, 1993; pp 73–86.

**EXPERIMENTAL SECTION**

1. **Off-Line Preparation and S-Isotope Analysis.** Off-line isotopic 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


999-2700/94/0336-2816$04.50/0 © 1994 American Chemical Society
oxidation\textsuperscript{10} or Eschka reduction\textsuperscript{11} followed by precipitation of the sulfur as BaSO\textsubscript{4} with a 0.5 M BaCl\textsubscript{2} solution. An aliquot of BaSO\textsubscript{4} containing about 7 mg of S was then reduced to H\textsubscript{2}S using Kiba’s reduction mixture.\textsuperscript{2} The evolved H\textsubscript{2}S was trapped in a cadmium acetate solution (15 g/L cadmium acetate + 0.5 mL of glacial acetic acid GRA) and converted to Ag\textsubscript{2}S through addition of silver nitrate solution (0.1 M). Dried Ag\textsubscript{2}S was mixed with V\textsubscript{2}O\textsubscript{5} (ratio 4.25:10) and sealed off in evacuated quartz vials. SO\textsubscript{2} 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 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 $\delta^{34}S$ 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 (BaSO\textsubscript{4} or Ag\textsubscript{2}S, respectively) were wrapped together with 0.1 mg of V\textsubscript{2}O\textsubscript{5} 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 SO\textsubscript{3} produced during the reaction was ensured and the surplus of oxygen trapped. Water vapor was removed in a desiccant trap containing anhydrous Mg(ClO\textsubscript{4})\textsubscript{2}. Finally, the combustion gases passed over a Porapak QS column (heated to 80 °C), where CO\textsubscript{2} and N\textsubscript{2} were separated from the SO\textsubscript{2}.

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 was supplied from a SO\textsubscript{2} bottle by injecting a pulse of this SO\textsubscript{2} into the carrier gas between the elemental analyzer and split interface. The MS system was differentially pumped so that a pressure of 1 × 10\textsuperscript{-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


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 \( \delta^{34}S \) notation, giving the difference between the S-isotopic composition of a sample and a standard relative to the corresponding isotopic composition of this standard:

\[
\delta^{34}S = \left( \frac{^{34}S/^{32}S}_{\text{sample}} - 1 \right) \times 10^3 \quad \text{%}
\]

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 \( \times \) 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 \( \times \) 10\(^{-4}\) 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 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 correspondence 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 \( \delta^{34}S \) 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.


\(^{13}\) Ricci, M. F.; Merrit, D. A.; Freeman, K. H.; Hayes, J. M., Org Geochem., in press.
whether BaSO₄, the result of oxidation of all sulfur in the sample and precipitation of this sulfur as BaSO₄ during off-line preparation. Table 1 gives the results of this comparison. The δ³⁴S values were identical within the standard deviation range of the method. Statistical analysis of the comparison (χ² test, F test, and Duncan test) showed that the results of both analysis series were identical at the 99.9% and 99% significance 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 BaSO₄. As a consequence, reduction in preparation time could be achieved. While about 4.5 h is necessary to prepare SO₂ in quartz vials for off-line analysis via the Kiba reduction process and consecutive S-isotope analysis on the mass spectrometer, on-line analysis requires less than 1 h to obtain the δ³⁴S value of a sample (Table 3).

**ACKNOWLEDGMENT**

All research work was carried out at the Institute of Ecotoxicology, Federal Research Centre for Agriculture, Braunschweig, Germany, and we thank the head of this institute, Prof. Dr. H. J. Weigel, for his support. Work was partially financed by a grant from PEF, Baden-Württemberg to H.-J.J. and was part of the German/Canadian Technology Transfer Programme of the GKSS, Geesthacht, Germany.

Received for review January 3, 1994. Accepted May 19, 1994.

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**Table 1. Calculation of δ³⁴S for a Sample vs CDT after On-Line S-Isotope Analysis against Bottle SO₂ as Working Standard**

1. determination of δ⁶⁶S of the working standard (SO₂) by combusting an Ag₂S with known δ³⁴S₀₂ value:

\[
δ^{34}S_{SO_2/CDT} = \frac{δ^{34}S_{Ag_2S} + δ^{34}S_{SO_2}}{δ^{34}S_{Ag_2S}} × 1000 \quad (1)
\]

2. determination of δ⁶⁶S of an unknown sample (SA) vs CDT using the working standard (SO₂) as mediator:

\[
δ^{34}S_{SA/CDT} = \frac{δ^{34}S_{Ag_2S} + δ^{34}S_{SO_2}}{δ^{34}S_{Ag_2S}} × 1000 \quad (2)
\]

3. oxygen correction of the sample analyzed:

\[
δ^{34}S_{SA/CDT} = \frac{δ^{34}S_{SO_2/CDT} + δ^{34}S_{SO_2}(1 + \delta^{34}S_{SO_2/CDT}/1000)}{1 + \delta^{34}S_{SO_2/CDT}} \quad (3)
\]

* Please note that δ⁶⁶S₀₂/CDT is determined by preparing Ag₂S and CDT separately into SO₂ and measuring their difference without correcting for the δO contribution. In practice, this value may be obtained from the known δ⁶⁶S of the Ag₂S reference material by applying formula 3 in reverse order.

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**Table 2. Comparability of On-Line Determination of S-Isotope Composition in BaSO₄ and in Ag₂S Prepared from BaSO₄ Through the Kiba Reduction Procedure**

<table>
<thead>
<tr>
<th>sample</th>
<th>BaSO₄</th>
<th>Ag₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>15.94</td>
<td>15.75</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>6.64</td>
<td>6.66</td>
</tr>
<tr>
<td>soil</td>
<td>5.71</td>
<td>5.66</td>
</tr>
<tr>
<td>litter</td>
<td>4.16</td>
<td>4.07</td>
</tr>
</tbody>
</table>

* 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 ±0.25%.

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

<table>
<thead>
<tr>
<th>process</th>
<th>off-line</th>
<th>on-line</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxidation of all S in plant samples, pptn as BaSO₄</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Kiba reduction and pptn as Ag₂S</td>
<td>90</td>
<td>nn</td>
</tr>
<tr>
<td>filtration of Ag₂S</td>
<td>15</td>
<td>nn</td>
</tr>
<tr>
<td>transfer to quartz vials</td>
<td>40</td>
<td>nn</td>
</tr>
<tr>
<td>sealing of vials</td>
<td>90</td>
<td>nn</td>
</tr>
<tr>
<td>SO₂ production in vials</td>
<td>2</td>
<td>nn</td>
</tr>
<tr>
<td>MS analysis</td>
<td>15</td>
<td>nn</td>
</tr>
<tr>
<td>filling of tin capsules</td>
<td>nn</td>
<td>10</td>
</tr>
<tr>
<td>coupled combustion of sample to SO₂ and MS analysis</td>
<td>nn</td>
<td>15</td>
</tr>
<tr>
<td>total</td>
<td>272</td>
<td>55</td>
</tr>
</tbody>
</table>

* nn indicates that these procedures are not necessary for the described method.