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A simple and reliable method reducing sulfate to sulfide for multiple sulfur isotope analysis

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Rationale:
Precise analysis of four sulfur isotopes of sulfate in geological and environmental samples provides the means to extract unique information in wide geological contexts. Reduction of sulfate to sulfide is the first step to access such information. The conventional reduction method suffers from a cumbersome distillation system, long reaction time and large volume of the reducing solution. We present a new and simple method enabling the process of multiple samples at one time with a much reduced volume of reducing solution.

Methods:
One mL of reducing solution made of HI and NaH2PO2 was added to a septum glass tube with dry sulfate. The tube was heated at 124°C and the produced H2S was purged with inert gas (He or N2) through gas-washing tubes and then collected by NaOH solution. The collected H2S was converted into Ag2S by adding AgNO3 solution and the co-precipitated Ag2O was removed by adding a few drops of concentrated HNO3.

Results:
Within 2–3 h, a 100% yield was observed for samples with 0.2–2.5 μmol Na2SO4. The reduction rate was much slower for BaSO4 and a complete reduction was not observed. International sulfur reference materials, NBS-127, SO-5 and SO-6, were processed with this method, and the measured against accepted δ34S values yielded a linear regression line which had a slope of 0.99 ± 0.01 and a R2 value of 0.998.

Conclusions:
The new methodology is easy to handle and allows us to process multiple samples at a time. It has also demonstrated good reproducibility in terms of H2S yield and for further isotope analysis. It is thus a good alternative to the conventional manual method, especially when processing samples with limited amount of sulfate available.
Stable sulfur isotopes have been widely used to trace a range of biogeochemical processes. The discovery in 2000 of the mass-independent isotopic fractionations of sulfur isotopes (S-MIF) in sulfate and sulfide in Archean rocks showed the potential of the S-MIF signals for tracking the oxygenation of the atmosphere 2.4 Gy ago, and the geochemical evolution of Mars. The S-MIF signals in ice-core sulfate have also been observed and demonstrated to be useful for tracking the sulfur cycle in today's stratosphere and they serve as a unique proxy of large volcanic eruptions that inject sulfate into the stratosphere and thus have global climate impacts. Multiple sulfur isotope compositions can also help to constrain the oceanic sulfur cycle (e.g.,). In summary, it seems that the best composition of the reducing solution would be a mixture of 0.13 g NaH2PO2 in 1 mL HI (57%), and the amount of water in the reduction experiment should be limited. The latter requirement suggests dry sulfate samples are a better choice as the starting material. Typically, barium sulfate (BaSO4) is the preferred sulfate form for the four-sulfur isotopes analysis because it is the natural form found in major geological samples or can be readily prepared from natural samples containing soluble sulfate (e.g., sea water) by precipitation with excess BaCl2 solution. BaSO4 has very low solubility (= 0.02 mg/L at 20°C) and this may inhibit the reaction efficiency and speed, especially when the volume of the reducing solution is small. Alternatively, soluble sulfate in natural samples can also be extracted and purified by other methods such as using an ion-exchange resin and this can yield dry Na2SO4 by evaporating the eluent. We thus conducted tests with both BaSO4 and Na2SO4 to explore the reaction efficiency of the reduction process with respect to different sulfate forms. In this report, we present a series of experiments where we used a reducing solution comprising NaH2PO2 and HI (57% by weight) to process dry sulfate samples (both Na2SO4 and BaSO4). To avoid the cumbersome distillation apparatus, we tested a simple flow system with only sealed glass tubes connected by PEEK tubes and explored the possibility of processing multiple samples at one time. The reproducibility for H2S yield and for further sulfur isotope analysis is reported.

2 | EXPERIMENTAL

2.1 | Reagents

The new reducing solution was made of 100 mL concentrated hydriodic acid (HI, 57% by weight) and 13 g sodium hypophosphite (NaH2PO2). The reducing solution was prepared in a fume hood, where 100 mL HI and 13 g NaH2PO2 were added to a flask. The flask was placed on a hot plate magnetic stirrer and a magnetic stir bar was used to mix the liquid and the salt. Because HI is easily oxidized by O2, helium (He) or another inert gas stream (e.g., N2) was introduced by a PEEK tube into the flask to purge the mixture. While purging with He, the hot plate temperature was set at 130°C. The flask was heated at 130°C for at least 1 h to reduce any sulfur compounds into H2S (that was flushed away from the reagents) and to reduce traces of I2 (in the form of I3−) by NaH2PO2. The solution started with a deep color and became colorless with time. After being heated for 1 h, the solution was allowed to cool down under the He stream and then stored in a sealed brown bottle. The reducing solution may become oxidized over time; this is indicated by a light yellow color, which may become deeper depending on the degree of oxidation.

In the reducing solution of Thode et al., high concentrations of HI seem to be the most important component of the reducing agent for complete sulfate reduction, and the presence of H2PO2 or NaH2PO2 increases the reduction speed by maintaining a high hydriodic acid to iodine ratio which is one of the factors favoring the reduction. HCl is only of secondary importance and its presence is suggested to increase the acidity and volume, and reduce the use of relatively expensive HI. However, Gustafsson found the presence of water to be detrimental for the reduction because water tends to dilute and thus lower the concentration of HI, and at lower HI concentration, side products (viz. SO2 and elemental S) will be formed. In this regard, mixing 50% H2PO2 and concentrated HCl with the concentrated HI may have drawbacks for the reduction efficiency, because both H2PO2 (50%) and concentrated HCl (37%) contain more than 50% water by weight. To avoid additional water in the reducing solution, the H2PO2 can be replaced with dry NaH2PO2 salt, and HCl can be omitted. Gustafsson and Davis and Lindstrom have used a reducing solution containing only HI (57%) and NaH2PO2 salt, and found a good reduction yield. In particular, Davis and Lindstrom found that the optimum composition of the reducing solution for complete and fast sulfate reduction is 0.13 g NaH2PO2 in 1 mL HI (57%). In these studies, aqueous sulfate samples were processed and a cumbersome distillation apparatus was used.

In summary, it seems that the best composition of the reducing solution would be a mixture of 0.13 g NaH2PO2 in 1 mL HI (57%), and the amount of water in the reduction experiment should be limited. The latter requirement suggests dry sulfate samples are a better choice as the starting material. Typically, barium sulfate (BaSO4) is the preferred sulfate form for the four-sulfur isotopes analysis because it is the natural form found in major geological samples or can be readily prepared from natural samples containing soluble sulfate (e.g., sea water) by precipitation with excess BaCl2 solution. BaSO4 has very low solubility (= 0.02 mg/L at 20°C) and this may inhibit the reaction efficiency and speed, especially when the volume of the reducing solution is small. Alternatively, soluble sulfate in natural samples can also be extracted and purified by other methods such as using an ion-exchange resin and this can yield dry Na2SO4 by evaporating the eluent. We thus conducted tests with both BaSO4 and Na2SO4 to explore the reaction efficiency of the reduction process with respect to different sulfate forms. In this report, we present a series of experiments where we used a reducing solution comprising NaH2PO2 and HI (57% by weight) to process dry sulfate samples (both Na2SO4 and BaSO4). To avoid the cumbersome distillation apparatus, we tested a simple flow system with only sealed glass tubes connected by PEEK tubes and explored the possibility of processing multiple samples at one time. The reproducibility for H2S yield and for further sulfur isotope analysis is reported.

The isotopic analysis is conventionally performed by reducing sulfate (SO42−) to hydrogen sulfide (H2S), converting H2S into silver sulfide (Ag2S), and fluorinating Ag2S to sulfur hexafluoride (SF6) for isotopic composition analysis by isotope ratio mass spectrometry (IRMS). The reduction from SO42− to H2S is mainly achieved by two different reducing agents: tin(II) (Sn2+) solutions and hydriodic acid (HI)/hypophosphorous acid (H3PO2) mixtures. The Sn2+ solution is mainly applied to solid samples (e.g., minerals) with an optimum reaction temperature between 280 and 300°C, and the HI reducing solution can be applied to aqueous samples at 100–125°C. Currently, the most widely used reducing method in sulfur isotope geochemistry follows the reducing agent recipe (500 mL concentrated HI, 816 mL concentrated HCl, and 245 mL 50% H2PO2) of Thode et al., and uses a distillation apparatus similar to that described in Forrest and Newman.

In the reducing solution of Thode et al., high concentrations of HI seem to be the most important component of the reducing agent for complete sulfate reduction, and the presence of H2PO2 or NaH2PO2 increases the reduction speed by maintaining a high hydriodic acid to iodine ratio which is one of the factors favoring the reduction. HCl is only of secondary importance and its presence is suggested to increase the acidity and volume, and reduce the use of relatively expensive HI. However, Gustafsson found the presence of water to be detrimental for the reduction because water tends to dilute and thus lower the concentration of HI, and at lower HI concentration, side products (viz. SO2 and elemental S) will be formed. In this regard, mixing 50% H2PO2 and concentrated HCl with the concentrated HI may have drawbacks for the reduction efficiency, because both H2PO2 (50%) and concentrated HCl (37%) contain more than 50% water by weight. To avoid additional water in the reducing solution, the H2PO2 can be replaced with dry NaH2PO2 salt, and HCl can be omitted. Gustafsson and Davis and Lindstrom have used a reducing solution containing only HI (57%) and NaH2PO2 salt, and found a good reduction yield. In particular, Davis and Lindstrom found that the optimum composition of the reducing solution for complete and fast sulfate reduction is 0.13 g NaH2PO2 in 1 mL HI (57%). In these studies, aqueous sulfate samples were processed and a cumbersome distillation apparatus was used.

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Different from what can be found in the literature, in this study we used sodium hydroxide (NaOH, 0.1 M) as the trapping solution to
collect the reduction product H₂S. Conventional trapping solutions, cadmium (or zinc) acetate (Cd(CH₃CO₂)₂, 0.1 M) and/or silver nitrate (AgNO₃, 0.01 M) were also investigated, and the results were compared with that from the NaOH trapping solution. As detailed below, using NaOH as the trapping solution allows direct quantification of the sulfur concentration by UV absorption spectroscopy, which is faster and more reliable than gravimetric techniques.

2.2 | Apparatus

The reduction train is sketched in Figure 1. The main parts of the apparatus are four 15-mL glass tubes each with a nitrile/PTFE septum and a block heater. Reaction tube ‘a’, two gas washing tube ‘b1’ and ‘b2’ and the collection tube ‘c’ were connected with PEEK tubes (1/16” ID) directly through the septum. Alternatively, a drying cartridge filled with potassium perchlorate (KClO₄) and a cryogenic trap (whose internal temperature can be controlled between −200°C and −80°C) can be placed between the trap ‘b2’ and the collection tube to test the possibility of using pure H₂S as the working gas for isotope analysis. The drying cartridge and the cryogenic trap allow us to purify H₂S without any loss. The dry sulfate sample (i.e. Na₂SO₄) and 1 mL reducing solution were introduced into glass tube ‘a’, which was placed on a block heater and purged with a He flow for 20 minutes before turning the heater to a temperature of 124°C. The purge before the heating stage is necessary to remove traces of I₂, especially when the reducing solution has a light yellow appearance over time due to slight oxidation.

The He gas was supplied from a tank. In practice, we used a home-made flow distributor to distribute the He gas to eight reaction train flows, as shown in Figure 2. Each flow was then guided to an individual reduction train, and the flow rate (~2 mL/min) of each reduction train was controlled by a micro-flow meter (ref: P-446, IDEX Health & Science, Sainte-Foy-La-Grande, France). In this way, multiple samples can be processed simultaneously.

2.3 | Testing samples

We used the above-mentioned reducing solution and apparatus to process dry sulfate samples in the forms of barium sulfate (BaSO₄) and sodium sulfate (Na₂SO₄). The Na₂SO₄ samples were prepared from a 1 mM Na₂SO₄ solution (0.142 g Na₂SO₄ in 1 L Milli-Q water; Millipore SAS, Molsheim, France), and then the desired volume of the Na₂SO₄ solution (e.g., 0.2 or 0.5 mL) was added to a pre-cleaned reaction tube. The reaction tube was allowed to completely dry in a 100°C oven, and the sample was then stored for later use.

In order to prepare the BaSO₄ samples, the desired volume (e.g., 0.2 or 0.5 mL) of the 1 mM Na₂SO₄ solution was added to the reaction tube, and a drop of 1 M HCl solution was then added to remove any carbonate in the solution. After storage overnight, a drop of 0.1 M BaCl₂ solution was added to the reaction tube to precipitate BaSO₄. After the BaSO₄ had precipitated, the samples were divided into two sets, which were then processed differently. One set of BaSO₄ samples was dried completely in an oven at 100°C, so the dry samples contain BaSO₄, BaCl₂ and NaCl. We termed this set of samples BaSO₄-EB (BaSO₄ with excess BaCl₂). The other set of BaSO₄ samples was centrifuged and the supernatant was removed. The remained solids were rinsed with Milli-Q water and then separated from the rinsing water by centrifuging. This step was repeated three times before the sample was placed in the oven to dry. This set of samples was termed P-BaSO₄ (pure BaSO₄).

In addition, international reference materials (in the form of BaSO₄), IAEA-SO-5 (δ³⁴S = (0.5 ± 0.2) ‰), IAEA-SO-6 (δ³⁴S = (−34.1 ± 0.2) ‰) and NBS-127 (δ³⁴S = (20.3 ± 0.4) ‰) were prepared by weighing ~ 0.5 mg of the BaSO₄ standards into reaction tubes. After reduction, these samples were further converted into SF₆ for isotope analysis. We note that the reference materials were not weighed precisely because of the capability of our balance (0.1 mg precision).
However, the purpose of processing these samples is to test potential sulfur isotope fractionation during the reduction, rather than to assess the reduction yield (which can be assessed from the samples made from drying Na₂SO₄ solution with accurate measurement of sulfur content, or precipitating BaSO₄ from the same Na₂SO₄ solution).

2.4 Quantification

The yield of the reduction from sulfate (SO₄²⁻) to sulfide (S²⁻) can be directly assessed by determining the quantity of H₂S released in the NaOH trapping solution. Hydrogen sulfide (H₂S) solution is known to absorb UV light with a peak absorbance at 230 nm. Guenther et al.22 have shown that in alkaline solutions with pH >8, H₂S is present nearly 100% in the form of the bisulfide ion (HS⁻), and that they found that at pH ~8, UV determination of HS⁻ yields are accurate because precise estimates of total sulfide concentration in the solution can be achieved. Thus, with NaOH as the trapping solution, the yield of the reduction can be directly assessed by measuring HS⁻ in the solution with optical methods. In comparison, the conventional trapping solution (cadmium acetate or silver nitrate) collects H₂S as a precipitate, which makes it difficult to directly quantify the reduction yield.

In this study, we used a UV spectrophotometer (model 6850; Jenway, Stone, UK) to determine the concentration of H₂S in the NaOH trapping solution. The calibration standards were made by mixing sodium sulfide nonahydrate (Na₂S·9H₂O, >99.99% purity; Sigma-Aldrich, St Louis, MO, USA) with 0.1 M NaOH solution. A few crystals of Na₂S·9H₂O were quickly rinsed on Kimwipes® disposable wipers to remove surface oxidation products, dried and weighed directly. A stock solution of 0.01 M HS⁻ was made by mixing 0.0125 g of pre-cleaned Na₂S·9H₂O in 5 mL 0.1 M NaOH solution. A set of working standards, 0.0 μM, 20 μM, 50 μM and 100 μM, was then made by diluting 0.002, 0.005 and 0.1 mL of the stock solution into the required volume of 0.1 M NaOH to obtain a 10-μL standard solution. The stock solution should be stored in a sealed brown bottle and flushed with He before storage, since sulfide is easily oxidized by O₂ once in contact with air. Even when the stock solution was flushed before storage, we noticed significant loss of sulfide after 2–3 days. Guenther et al.22 made the stock solution in a glass aspirator bottle purged with N₂ and stated that the solution should be stable for about 1–2 weeks. In practice, we prepared a fresh stock solution once every 2 days, and working standards every day.

2.5 Procedure

Prior to the reduction, all glassware, caps, septum and PEEK tubes were cleaned with Milli-Q water. The PEEK tubes have to be flushed to ensure that there is no water left inside them; otherwise the water will block the flow of the carrier gas in the reduction line.

In a fume hood, 1 mL of reducing solution was added to a pre-prepared reaction tube to a known amount of dry sulfate. In the reaction tube, the reducing solution was purged with He for 20 min at room temperature to remove any I₂ and O₂. The gas washing tubes (‘b1’ and ‘b2’ in Figure 1) and the collection tube (‘c’ in Figure 1) were prepared by adding 12 mL Milli-Q water and 12 mL 0.1 M NaOH, respectively. After the reducing solution had been purged for 20 min, the reduction train was assembled (Figure 1) and the reaction tube was placed in the block heater and heated at 124°C. At lower temperatures the reduction speed will be slow, while if the temperature is too high, an excessive amount of phosphine (PH₃) will be produced from the decomposition of NaH₂PO₂.14 For the alternative setup, the drying agent was in-line with the cryogenic system, and the latter was set at −200°C to trap the reaction products. When the reaction was over, the temperature of the cryogenic trap was raised to −120°C when the produced H₂S was released and trapped in the collection tube.

The collection tube was removed from the reduction train after the reaction was complete. The concentration of H₂S in the trapping solution was first measured by UV spectrophotometry as described in section 2.4, in order to assess the yield. Then 1 mL of 0.01 M AgNO₃ was added to the collection solution to precipitate Ag₂S and Ag₂O. After gentle shaking, a few drops of concentrated HNO₃ (68%) were added to the suspension. Following thorough shaking, the Ag₂O dissolved and only Ag₂S remained in the solid phase. The tube was allowed to settle, and a plastic laboratory dropper was used to remove the supernatant. The solid was then rinsed three times with Milli-Q water, transferred to an aluminum boat and dried prior to fluorination.

2.6 Isotope analysis

To explore potential sulfur isotope fractionation during the reduction, we processed the international sulfate reference materials IAEA-SO-5, IAEA-SO-6 and NBS-127, following the procedure mentioned in section 2.5. The reference materials were weighed, and approximately 0.5 mg was added to the reaction tube. The reaction was stopped after ~5 h.

After being converted into Ag₂S as described in section 2.5, the reference materials were transported to the Stable Isotope Geochemistry Laboratory at IPG-Paris (Institut de Physique du Globe, Paris, France) for sulfur isotope analysis. At IPG, the samples were dried, transferred to an aluminum boat and then weighed. Due to the small amount (~0.3 mg Ag₂S or less) of the sample, we found it is very difficult to transfer the dry Ag₂S from the collection tube to the Al boat. As an alternative, we transferred the solid together with a small amount of water from the tube to the Al boat, and then dried the samples. Under these circumstances we found that, after drying, the inside wall of the Al boat became light-brown in color, and the mass of the dried Al boat plus the sample exceeded the sum of the sample and the Al boat, indicating the gain of extra mass during the drying process. This is probably due to the development of a thin layer of Al₂O₃ on the Al metal surface when Al contacts with water at the drying temperature (70°C). This is consistent with the observation that, after drying an Al boat with Milli-Q water at 70°C, a brown layer was formed on the inner surface of the Al boat and the mass of the Al boat was increased. Nevertheless, the fluorination yields and the sulfur isotopic analysis results suggested this influences neither the fluorination procedure nor the isotopic composition.

The dried Ag₂S samples were fluorinated in nickel bombs under approximately 37 kPa of fluorine gas (F₂) at 250°C overnight. The evolved SF₆ was purified cryogenically and then by gas chromatography. Because of the small amount of samples (~0.5 mg Ag₂S), a microvolume cold finger of an isotope ratio mass spectrometer (MAT 253; Thermo
Scientific, Bremen, Germany) working in dual-inlet mode was used to concentrate the sample gas for isotope analysis. The analytical uncertainty (1σ) for the instrument was 0.25% for δ24S values, 0.010% for Δ32S and 0.062% for Δ34S obtained by replicate analysis (N = 4) of IAEA-S-1 over a period of 4 weeks (once a week) when the processed sulfate standards were also measured for sulfur isotopic composition.

3 | RESULTS AND DISCUSSION

3.1 | H2S collection agents

The reduction product, H2S, has to be collected and converted into Ag2S before fluorination for isotope analysis. As mentioned above, Cd(CH3CO2)2 and AgNO3 have both been shown to be able to efficiently trap H2S by forming CdS and Ag2S precipitates, respectively. The CdS precipitate is further converted into Ag2S by adding AgNO3 solution.16,17

The conventional reducing solution commonly contains phosphorous acid (H3PO3) or hypophosphorous acid (H3PO2),13 and phosphine (PH3) is produced when the reducing solution is heated.18 Once PH3 comes in contact with AgNO3, it reduces Ag+ to Ag0 and this leads to excess precipitate in addition to Ag2S.17 To prevent this, Thode et al16 and Forrest et al17 used Cd(CH3CO2)2 as the trapping solution. In particular, Forrest et al17 flushed the Cd(CH3CO2)2 solution with N2 for 15 min after the CdS precipitated and prior to adding AgNO3. This step was found to effectively remove PH3 and thus no excess precipitate formed. However, Arnold et al13 found that when using AgNO3 as the trapping solution, the excess Ag precipitate in the trap is not detrimental to the final isotope analysis of the sulfur content after fluorination. Because of this, AgNO3 appears to be the better reagent for the collection of H2S, given the environmentally toxic nature of Cd2+.

In this study, we first employed 0.01 M AgNO3 as the trapping solution. However, we observed spuriously high precipitates in the trap as soon as the reducing solution was heated, and the trapping solution turned completely dark in a few minutes, even when there was no sulfate added to the reducing solution. At the same time, we noticed an apparent silver mirror on the inside wall of the collection tube, indicating reduction of Ag+ to Ag0. This severe reduction of the AgNO3 solution is probably due to the high production of PH3 from our reducing solution. Different from the conventional reducing solution, our reducing solution used NaH2PO2 instead of H3PO3/H3PO2. NaH2PO2 starts to decompose and produce PH3 at 90°C, while H3PO2 effectively decomposes to yield PH3 at 200°C. Therefore, at the temperature of the reduction experiment (i.e., 124°C), our reducing solution was presumably producing much more PH3 than the conventional reducing solution. To remove the excess precipitate other than Ag2S caused by PH3, we used 1 M HNO3 followed by 1 M NH4OH to wash the precipitate formed in the AgNO3 trapping solution. Only part of the precipitate was removed after these treatments and there was still more precipitate than expected. Thus, AgNO3 is not a good choice as the trapping solution, as least for our reducing solution.

To avoid the reduction of Ag+ by PH3, we next tested 0.1 M Cd(CH3CO2)2 as the trapping solution and following the strategies described in Forrest et al.17 Despite this, excess precipitation was still frequently observed after AgNO3 was added to the trapping solution for conversion of CdS into Ag2S. In particular, we noticed that during the collection of H2S, yellow material was accumulating at the wall directly above the surface of the Cd(CH3CO2)2 solution, indicating the formation of CdS. However, at the same time, the entire Cd(CH3CO2)2 solution became light brown and the brown color became deeper with increasing trapping time. When AgNO3 was added after the collection, the trapping solution turned dark with extensive precipitate at the same time. Obviously, there were still interferences between the trapping solution and/or AgNO3 with the volatile product(s) of the reducing solution. Similarly, excess precipitate remained after washing with 1 M HNO3 and 1 M NH4OH. This, together with the toxic nature of Cd2+, made us decide to abandon Cd(CH3CO2)2 as the trapping solution in our system.

Instead, we used 0.1 M NaOH as the trapping solution to collect H2S. At a pH of 13, the trapped H2S mainly existed in the form of H5S−, as shown in Figure 3A. Since the NaOH trapping solution was purged with He, under this condition the dissolved O2 concentration was very low and thus the trapped sulfide was stable. The use of NaOH as the trapping solution has two advantages: (1) the trapped H2S can be precisely quantified in real-time using UV spectrophotometry, as described in section 2.4, and thus the progress toward to complete reduction of a sulfate sample can be monitored; and (2) no reaction occurs between PH3 and AgNO3 thus avoiding the production of excessive mass interference.

After sample collection, 1 mL 0.01 M AgNO3 was added to the trap to produce Ag2S. AgOH was produced at the same time, and this quickly changed to Ag2O. The suspension was allowed to settle for 10–20 min after thorough shaking, and a few drops of 68% HNO3 were then added to acidify the trapping solution. Ag2O was readily dissolved in the acidified solution and only Ag2S remains.

3.2 | H2S yield

In the 0.1 M NaOH trapping solution, sulfide was mainly present in the form of HS− (Figure 3A). Figure 3B shows the typical absorbance spectra of two Na2S working standards (in 0.1 M NaOH matrix) and two NaOH trapping solutions after 2 h collection of H2S and, as expected, the absorbance spectra peak was at ~230 nm, consistent with that from Guenther et al.22 Figure 3C shows the plot of the average of the calibration curve over 3 days of analyzing working standards.

As described in section 2.3, three different sulfate samples were processed using our system, Na2SO4, BaSO4-EB and P-BaSO4, and the time-resolved H2S yields from these three materials are plotted in Figure 4. The real-time production of H2S was monitored by UV determination of HS− in the trapping solution every 15–20 min. Once the produced H2S reached the amount expected from the starting sulfate, or no longer increased with time, the block heater was turned off and the reduction train was flushed with He for a further 20 min after the reaction tube had cooled to room temperature.

In general, Na2SO4 was reduced faster than P-BaSO4 and much faster than BaSO4-EB. Regardless of the quantity of the starting sulfate, after 1 h of reduction an average H2S yield of 85.7 ± 10.3% was reached when Na2SO4 was the starting material. In comparison,
the H₂S yield after 1 h of reduction was 63.9 ± 2.1% for BaSO₄-EB and only 18.5 ± 0.04% for P-BaSO₄. After 2 h, a 99.5 ± 3.7% yield was reached for Na₂SO₄, indicating the completion of the reduction. However, after 2 h, it appeared that no more H₂S was produced for BaSO₄-EB and P-BaSO₄, and the yield remained at 80.4 ± 0.75% for BaSO₄-EB and 28.5 ± 0.09% for P-BaSO₄ after 4 or 5 h. For two of the BaSO₄-EB samples, we let the reaction continue overnight, and the yield increased from 41.7% and 34.5% at 5 h to 58.3% and 86.5%, respectively.

The final yields (yield after stopping the reaction) of Na₂SO₄, BaSO₄-EB and P-BaSO₄ sample with different quantities of sulfate are plotted in Figure 5. Overall, Na₂SO₄ was often 100% reduced within 2 h regardless of the starting quantity, even when the drying agent and the cryogenic trap were put in-line, while a 100% yield for BaSO₄-EB and P-BaSO₄ was never observed even after overnight heating.

The different apparent reaction speeds and yields of H₂S between Na₂SO₄, BaSO₄-EB and P-BaSO₄ and the reducing solution probably reflect the effect of the sulfate salt solubility. Na₂SO₄ is soluble in water, while BaSO₄ has a very low solubility of 0.01 μmol/mL in water at 20°C and less than 0.02 μmol/mL at ~120°C. Given the small volume of the reducing solution used (1 mL), there would be less than 2% of the added BaSO₄ (if 1 μmol is added) dissolved. Our observations clearly point to the sulfate ion (SO₄²⁻) or sulfuric acid...
(H2SO4) as the reactive species with the reducing acids, i.e. the sulfate salt has to be dissolved first in order to produce H2S. This explains why the BaSO4 samples reacted so slowly with the reducing solution relative to Na2SO4. In addition, if there is an excess of Ba2+ ions in the solution (due to the dissolution of the excess BaCl2 used to precipitate BaSO4 from Na2SO4), this will inhibit the dissolution of BaSO4 as the dissociation equilibrium of BaSO4 will be pushed to the BaSO4 side, following Le Chatelier’s principle. This probably explains why the reducing reaction with P-BaSO4 was faster than that with BaSO4-EB.

To confirm the effect of excess Ba2+ ions on the reduction of BaSO4, we prepared a few BaSO4 samples with considerably more Ba2+ by adding 1 mL of 0.1 M BaCl2 to 1 mL of 1 mM Na2SO4 solution. These samples were then directly dried without removing the supernatant from the precipitate. For these samples, after the reduction started, we measure the trapping solution every hour for 7 h, and no H2S was detected at any time.

Therefore, the solubility of the sulfate salt largely affects the reduction speed and the overall yield. We thus recommend extracting and converting sulfate in natural samples into Na2SO4 whenever possible when applying our reducing solution. The extraction of sulfate can be conducted using the IC method described in Geng et al.26 or the anion-exchange resin method described in Le Gendre et al.21 If the use of BaSO4 is unavoidable, excess Ba2+ should be removed after precipitating BaSO4 with BaCl2, while increasing the volume of the reducing solution (e.g., using 10 mL instead of 1 mL) and/or the reaction time may improve the yield.

### 3.3 Isotope analysis of the standard materials

Since the overall goal of reducing sulfate to sulfide is to perform the four-sulfur isotopes analysis, we processed three different barium sulfate standards, IAEA-SO-5, IAEA-SO-6 and NBS-127, which were equivalent to P-BaSO4 samples. Unfortunately, there are no international standards in sodium sulfate form and thus a strict comparison of the isotopic precision of the reduction step for the two chemical forms is impossible. Even a simple comparison of the salt from an identical sulfate batch is not possible, as BaSO4 reduction will never reach full decomposition. The fluorination yields from Ag2S to SF6 and sulfur isotopic compositions measured from these standards are listed in Table 1. The fluorination yield range is from 84.6 to 113.5% with an average of 101 ± 7.5%, except for one standard with a low yield of 26.1%. Regardless of the fluorination yield, the measured isotopic ratios of all the processed sulfate standards are statistically consistent with their accepted values, including the one with relatively low yield (26.1%). The measured δ34S(‰)VCDT values of all standards with different quantities of sulfur (0.34–2 μmol in SF6) versus their accepted δ34S(‰)VCDT values are plotted in Figure 6. A least-squares linear regression gives a slope of (0.99 ± 0.01), suggesting good reproducibility and the conservation of sulfur isotopic composition during the reduction of sulfate to sulfide using our reducing system, despite the reduction yields of these standard materials not being 100%. This is not a surprise. In fact, if any sulfur isotope fractionation occurs during the reduction, it would be between the solid BaSO4 and the dissolved HSO4− (the form of SO42− in concentrated acid solution), but not in the step(s) from SO42− to H2S because the dissolved part is

### TABLE 1 Fluorination yields and measured isotopic ratios of the sulfate standards processed with this system

| Standards       | Ag2S (mg) | SF6 yield (%) | Δ33S values vs CDT (‰) | Δ34S values vs CDT (‰) | Accepted Δ34S* values vs CDT (‰) |
|-----------------|-----------|---------------|------------------------|------------------------|----------------------------------|
| NBS-127         | 0.20      | 101.7         | 0.015                  | 0.025 ± 0.010          | 19.8                             |
|                 | 0.10      | 105.3         | 0.018                  |                        | 22.4                             |
|                 | 0.08      | 93.7          | 0.033                  |                        | 22.8                             |
|                 | 0.12      | 98.2          | 0.034                  |                        | 21.4                             |
| IAEA-SO-5       | 0.51      | 104.6         | 0.063                  | 0.097 ± 0.071          | 0.7                               |
|                 | 0.52      | 101.6         | 0.052                  |                        | 0.7                               |
|                 | 0.62      | 26.1          | 0.203                  |                        | 0.8                               |
|                 | 0.21      | 99.3          | 0.067                  |                        | 0.5                               |
| IAEA-SO-6       | 0.41      | 112.5         | 0.077                  | 0.086 ± 0.020          | -34.0                            |
|                 | 0.46      | 106.9         | 0.065                  |                        | -33.5 ± 0.6                      |
|                 | 0.13      | 102.0         | 0.110                  |                        | -32.9                            |
|                 | 0.15      | 84.6          | 0.090                  |                        | -32.9                            |

The values of Δ34S are not reported as when the samples were measured the mass spectrometer had a high background of mass 131 (15 to 50 mV) and thus the Δ34S data were discarded. The initial masses of the BaSO4 standards were only approximately weighed, and the mass(es) in Ag2S form were obtained according to the measured H2S production after ~5 h of reduction.

*aAccepted values are taken from Halas and Szaran.28

![FIGURE 6](image-url) Measured versus accepted δ34S (‰)VCDT values of IAEA-SO-5, IAEA-SO-6 and NBS-127. The reduction of these sulfate standards to H2S were conducted using the protocol described in this study.
100% converted into H2S. Kusakabe and Robinson\textsuperscript{27} found that the sulfur isotope fractionation between solid BaSO\textsubscript{4} and the dissolved HSO\textsubscript{4}\textsuperscript{−} in the BaSO\textsubscript{4}−HSO\textsubscript{4}−−H\textsubscript{2}O system is very small (less than 0.4\% in the temperature range from 110 to 350°C), which could explain why the solubility effect seems to not affect the isotopic measurements.

For these standards, we also reported the Δ\textsuperscript{33}S values and they are all not distinct from what can be expected from mass-dependent fractionation. However, we did not include the Δ\textsuperscript{32}S values as, when these standards were measured, the mass spectrometer had a high and variable background at m/z 131 up to 50 mV which caused the $\delta^{36}$S values to drift and made them unreliable.

4  CONCLUSIONS

We present a simple and reliable reducing method modified from the literature for the conversion of sulfate into sulfide for four-sulfur isotopes analysis. This system is simple to set up, easy to replace and cheap to acquire and is made from sealed test tubes and PEEK flow lines (metal part, e.g. needle, in contact with the hot reducing solution is not allowed). This method uses a reducing solution made of 100 mL 57% HI and 13 g NaH\textsubscript{2}PO\textsubscript{2}, and a very small amount (1 mL) of reducing isotope analysis. This system is simple to set up, easy to replace and operated at a time, making it easier to process multiple samples simultaneously. The use of NaOH as the trapping solution allows the assessment of reduction yield directly from UV determination of HS\textsuperscript{−} simultaneously. The use of NaOH as the trapping solution allows the assessment of reduction yield directly from UV determination of HS\textsuperscript{−} in the trapping solution.

This new approach was demonstrated to produce H\textsubscript{2}S very rapidly with a 100\% recovery when soluble sulfate salt was used (e.g., Na\textsubscript{2}SO\textsubscript{4}), as opposed to BaSO\textsubscript{4} for which the kinetic was slow and conversion never reached 100\% even after overnight reaction. However, despite the relatively low reduction yield for BaSO\textsubscript{4}, there was no significant isotope fractionation effect induced by the reduction. As it is the dissolved part of the sulfate salt that reacts with the reducing solution, this method is most suitable for natural samples containing soluble sulfate (e.g., aerosol, snow and ice core), which can be extracted (e.g., by the resin method) and converted into Na\textsubscript{2}SO\textsubscript{4}. The use of the barite precipitate method for sulfate extraction and purification is not recommended as the salt solubility inhibits the reduction speed and yield. If BaSO\textsubscript{4} is the main form of sulfate (e.g., barite), increasing the volume of the reducing solution and/or the reaction time may improve the H\textsubscript{2}S yield although there is no guarantee of a complete conversion. While poor conversion and fluorination yields do not seem to introduce isotope fractionations, poor yield reduces the sensitivity of the method to sample sizes above a few micromoles of sulfate and it may also have consequence on the mass-dependent slopes between the sulfur isotope ratios as the $^{33}S/^{32}S$ ratios of the international standards have never been calibrated.

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