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International Journal of Mass Spectrometry 242 (2005) 309–318

www.elsevier.com/locate/ijms

Determination of sulfur isotope abundance ratios for SI-traceable low sulfur concentration measurements in fossil fuels by ID-TIMS

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Received 16 September 2004; accepted 14 October 2004
Available online 15 December 2004

Abstract

The present work describes the development of an existing TIMS procedure to a reference procedure for low sulfur concentration measurements in fossil fuels. With this enhanced procedure SI-traceable sulfur mass fractions below 10 mg kg^{-1} can be obtained. The achieved detection limit is approximately 0.2 mg kg^{-1}. The procedure was validated by certified reference materials. The procedure was already applied to candidate reference materials and to samples analysed within projects of the "Comité Consultatif pour la Quantité de Matière – CCQM".

Additionally the influence of the isotopic composition on the results and its corresponding uncertainty was studied. Reference data published in the literature on the isotopic composition of sulfur were assessed.

Keywords: TIMS; IDMS; Low sulfur; Fossil fuel; Reference procedure

1. Introduction

In terms of ecological aspects sulfur is of paramount importance. Sulfur is part of all fossil fuels and is being released when burning fossil fuels. The so released sulfur can be found in the environment mainly in form of sulfurous acid and sulfates, which are responsible for the so called "acid rain", whose consequences and after-effects are well-known. But also in industry sulfur can cause problems, because sulfur is toxic for nearly all catalysers. Therefore it is necessary to know, at which concentration sulfur is present, when performing process optimization. On this reasons the determination of sulfur will always be an issue, especially in the low mg kg^{-1} range.

With growing environmental awareness the limits of all contaminants are lowered continuously and so they do for sulfur. To reduce environmental and health risks the limits for sulfur concentration in fossil fuels drop worldwide. Current limits exist already in the European Union, in North America and especially in Germany, which are fixed in national and international directives (Table 1). In these countries the limits of sulfur will be reduced to 15 mg kg^{-1} or below within the next years. Legal regulations will become more stringent and the need for effective control will rise. This requires suitable analytical reference procedures and reference materials for the determination of sulfur in the low mg kg^{-1} range.

Due to its impact on environment and health the accuracy and reliability of sulfur measurements are of utmost importance. Routinely X-ray fluorescence or high-temperature combustion followed by infrared or fluorescence detection are used for the determination of sulfur in fossil fuels down to approximately 5 mg kg^{-1} with corresponding uncertainties in the range of 30–100%. These methods, however, require sulfur standards and matrix reference materials for calibration and validation. The certification of these materials in turn requires reference procedures offering smallest possible uncertainties.

Paulsen and Kelly [1] published in 1984 a new procedure for the determination of sulfur in metals by applying the isotope dilution technique in combination with thermal

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doi:10.1016/j.ijms.2004.10.024

Table 1
Current and future sulfur limits for diesel and gasoline (petrol)

Region	Sulfur limitation in mg kg^{-1}		Directive
	Diesel	Gasoline	
Current			
European Union	350	150	98/70/EC [13]
Germany	10[a]	10[a]	10. BImSchV, MinöStG [14,15]
United States	500	300	40 CFR Part 80 [16]
Year 2005			
European Union	50 (10)[b]	50 (10)[b]	2003/17/EC [17]
Germany	10[a]	10[a]	10. BImSchV, MinöStG [14,15]
United States	500		40 CFR Part 80 [16]
Year 2007			
European Union	50 (10)[a]	50 (10)[a]	2003/17/EC [17]
Germany	10[a]	10[a]	10. BImSchV, MinöStG [14,15]
United States	15	15	40 CFR Part 80 [18]
Year 2009			
European Union	10	10	2003/17/EC [17]
Germany	10	10	10. BImSchV [14]
United States	15	15	40 CFR Part 80 [18]

[a] The limitation of 50 mg kg^{-1} is mandatory according to EC regulation, but petrol and diesel with sulfur levels above 10 mg kg^{-1} are rated by an extra tax, so that only fuels below 10 mg kg^{-1} are marketed in Germany.

[b] Fuels of 10 mg kg^{-1} must be marketed and available from January 1, 2005, from January 1, 2009 all petrol and diesel marketed must be below 10 mg kg^{-1}.

ionization mass spectrometry (ID-TIMS). The sulfur isotope abundance ratios were calculated from the corresponding AsS$^+$ ion currents (^{75}As^{32}S$^+$, ^{75}As^{34}S$^+$). The chemical sample preparation, which includes a digestion in Carius tubes and further treatment in the reduction apparatus, is rather time consuming and additionally bears some risks in the digestion step caused by uncontrolled breaking of the tubes. In 1994, Kelly et al. [2] applied this procedure to the determination of sulfur in fossil fuels. The concentration range of the investigated samples was between 4.7% (47 g kg^{-1}) and 0.015% (150 mg kg^{-1}) sulfur. Within the last decade inductively coupled plasma mass spectrometry (ICPMS) showed a rapid development. Consequential, high resolution ICPMS (HR-ICPMS) was successfully combined with isotope dilution mass spectrometry (IDMS) and was applied to the determination of sulfur in fossil fuels [3,4]. The reported measurement ranges reach just under the 10 mg kg^{-1} limit, which at present is a kind of sonic barrier for sulfur in fuel analysis. In HR-ICPMS the S$^+$ ions can be detected directly. The HR-ICPMS procedure is not based on the time-consuming chemical sample treatment like the TIMS procedure. But the undisturbed measurement of the ^{32}S$^+$, ^{33}S$^+$ and ^{34}S$^+$ ion currents requires a medium mass resolution mode. The ion current of ^{36}S$^+$, however, is still disturbed by the isobaric interference of ^{36}Ar$^+$ such that corrections are needed for accurate measurements.

Performing SI-traceable measurements of highest possible metrological quality the isotopic composition and the blank level of the reagents more and more affect the accuracy of the results and therefore need to be considered. Especially for low sulfur levels at around 10 mg kg^{-1} the blank level becomes significant. Even if the required reagents (NH_3, As_2O_3, HCl, HNO_3, H_2O) were used at highest available purity, a blank of 0.2–0.3 μg sulfur can hardly be under-run. When digesting a sample mass of 300 mg of fossil fuel with a sulfur mass fraction of 10 mg kg^{-1}, the blank mass already ranges between 7 and 10% of the total analyte mass. To reach highly accurate results or small combined uncertainties the blank contribution need to be under control. In contrast to the blank contribution the isotopic composition of sulfur in the sample affects the accuracy of the results at each sulfur concentration level. Isotopic abundance variations for sulfur in nature are demonstrated in several publications. Coplen et al. [5,6] recently reported on isotopic abundance variations of several elements. According to these publications the isotopic abundance variation of sulfur in total ranges between $\delta(^{34}\mathrm{S}) = -55‰$ and $\delta(^{34}\mathrm{S}) = +135‰$. For fossil fuels a variation between $\delta(^{34}\mathrm{S}) = -12‰$ and $\delta(^{34}\mathrm{S}) = +28‰$ has been observed. This large variation requires the determination of the isotopic composition and the molar mass of sulfur in the sample, which in turn requires the determination of all sulfur isotopes. For the determination of sulfur isotopic composition, reference materials with SI-traceable sulfur isotopic composition are necessary to correct for fractionation and/or discrimination effects caused by the mass spectrometer. The influence of the applied sulfur isotopic composition on the final result as well as varying data of the available sulfur isotopic reference materials are discussed in this work.

The parameter $\delta(^{34}\mathrm{S})$ expressed in ‰ is defined as:

$$\delta(^{34}\mathrm{S}) = \left(\left(\frac{R(^{34}\mathrm{S}/^{32}\mathrm{S})_{\mathrm{Sample}}}{R(^{34}\mathrm{S}/^{32}\mathrm{S})_{\mathrm{Standard}}}\right) - 1\right) \times 10^3.$$

δ-values are commonly used to express isotopic abundance variations. In the case of sulfur it quotes the relative deviation of the measured isotope abundance ratio to the standard V-CDT (Vienna-Canyon Diablo Troilite) in ‰.

IDMS offers the possibility of a reference procedure for the determination of sulfur in fossil fuels. In combination with TIMS a highly selective and well-understood technique can be applied as reference procedure with the potential of providing smallest combined uncertainties. Different materials have been examined within this work to prove the described potentials for the here presented ID-TIMS procedure. In parallel different samples from projects run under the auspices of the “Comité Consultatif pour la Quantité de Matière – CCQM” have been analysed. CCQM is the consultative committee for chemical analysis within the International Metre Convention. The Key Comparison CCQM-K35 as well as the Pilot Study CCQM-P26.1 are projects of the Inorganic Analysis Working Group of CCQM and are intended to demonstrate the capability of National Metrological Institutes (NMI) for low sulfur measurements in fossil fuels. These international activities on

Table 2
Analysed sample materials

Sample	Description	Nominal sulfur mass fraction in mg kg^{-1}
CCQM-K35	Low sulfur in diesel fuel	50
CCQM-P26.1	Very low sulfur in kerosene	10
LGC-3021	Diesel for sulfur content	10[a]
LGC-3022	Diesel for sulfur content	30[a]
LGC-3023	Diesel for sulfur content	52.4 (1.3)[b]
SRM-1624d	Sulfur in diesel	4000[a]
SRM-2723a	Sulfur in diesel oil	10.0 (1.1)[c]

[a] Candidate reference material, not yet certified.

[b] Certified value, expanded uncertainty U in parentheses, applying to the last two digits; $U = ku_c$ with $k = 4.3$.

[c] Certified value, expanded uncertainty U in parentheses, applying to the last two digits; $U = ku_c$ with $k = 2.2$.

harmonization of sulfur measurements stress the importance and necessity of accurate and reliable sulfur measurements in fossil fuels.

The materials investigated are displayed together with their nominal sulfur mass fractions in Table 2. CCQM-K35 and CCQM-P26.1 were organized by the National Institute of Standards and Technology (NIST). The projects are still ongoing, so that final results cannot be published yet. The determination of sulfur in the samples LGC-3021, -3022, -3023 and SRM-2723a was carried out to optimize the chemical sample preparation and the TIMS measurements as well as for validation purposes. The primary aim was to gain small reproducibilities of the sulfur mass fraction and the blank level.

2. Experimental

2.1. Materials and reagents

In contrast to trace metals the determination of sulfur demands for the use of glass labware, as some sulfur species can be adsorbed or even absorbed in polymers. On this reason only Duran® or quartz glass was used for sample preparation. Only high-purity reagents and sulfur standards in which sulfur only is present as sulfate and therefore do not adsorb on container walls were stored in PFA-bottles. The determination of sulfur in the low mg kg^{-1} level requires clean working conditions and specialized sample handling equipment in order to keep the blank contribution and contamination risks small. Only precleaned perfluoralkoxy (PFA)- and glassware was used, only pipette tips consisted of polypropylene (PP). The cleaning procedure has been published previously [7].

As already mentioned above blank levels are an issue especially for the determination of low sulfur. To account for this all reagents were used of highest available purity. Additionally ultrapure water (Seral Reinstwassersysteme, Ransbach-Baumbach, Germany), nitric acid and hydrochloric acid (all Merck KgaA, Darmstadt, Germany) were checked for their sulfur blank level. Due to the expected low sulfur concentration the water samples were analysed by HR-ICPMS with external calibration. The acid samples, 5 mL each, were analysed by ID-TIMS. The stated uncertainties are expanded ($k = 2$) and were calculated from comparable blank measurements. The results (Table 3) clearly demonstrate that further purification of the ultrapure water was not necessary, because the reached blank level already was negligible compared to the other reagents. Subboiled hydrochloric acid (starting material p.A. grade) offers the lowest sulfur blank level, whereas in the case of nitric acid no real enhancement was detected for the subboiling procedure. Remarkable is that even two bottles of the same purity and the same lot show larger difference in the sulfur blank level than different purity grades. Based on these findings Ultrapure water, subboiled hydrochloric acid and nitric acid Suprapur® grade were used for all subsequent measurements.

Ammonia solution (Suprapur®) and hydrogen peroxide (Ultrapur®) were obtained from Merck KgaA (Darmstadt, Germany). Arsenic-(III)-oxide (99.999%) was obtained from MaTecK GmbH and nitrogen (>99.999 vol.%) was obtained from Messer (Griesheim, Germany). The reagents for the reduction solution, hydriodic acid (Merck KgaA, Darmstadt, Germany) and phosphinic acid (Fluka) were purchased p.A. grade only, as the reduction solution (75 mL 50% H_3PO_2, 255 mL 32% HCl, 155 mL 67% HI) was refluxed for 5 h to

Table 3
Sulfur blank levels of the core reagents

Reagent	Purity	Lot	Method	Sulfur mass fraction in µg kg^{-1}[a]
Deionised water	Approximately 1 MΩ cm	–	HR-ICPMS	27 (2)
Ultrapure water	>18 MΩ cm	–	HR-ICPMS	21 (2)
Hydrochloric acid 32%	p.A.	Z721919326	ID-TIMS	225 (35)
Hydrochloric acid 32%	Subboiled p.A.	Z721919326	ID-TIMS	126 (35)
Hydrochloric acid 30%	Suprapur®	ZH082318206	ID-TIMS	195 (35)
Hydrochloric acid 30%	Ultrapur®	B812614	ID-TIMS	208 (35)
Nitric acid 65%	p.A.	K32171456325	ID-TIMS	153 (35)
Nitric acid 65%	Subboiled p.A.	K32171456325	ID-TIMS	138 (35)
Nitric acid 65%	Suprapur®	ZU486841212	ID-TIMS	111 (35)
Nitric acid 65%	Suprapur®	ZU486841212	ID-TIMS	137 (35)
Nitric acid 60%	Ultrapur®	B962418145	ID-TIMS	131 (35)

[a] Expanded uncertainty with $k = 2$ is given in parenthesis and applies to the last one or two digits, respectively.

Table 4
Survey of solutions prepared from assay, spike and isotopic reference materials

Element	Chemical form	Supplier and product	Purity (%)	Isotopic composition	Isotope ratio		S mass fraction in mg kg^{-1}
					Ratio	Value	
S	SO_4^{2-} solution	SRM-3154[a]	–	Natural	$^{32}S/^{34}S$	22.555 (26)[b]	104.00 (30)[b,c]
S	SO_4^{2-} solution	SRM-3154[a]	–	Natural	$^{32}S/^{34}S$	22.555 (26)[b]	84.94 (25)[b,c]
S	Ag_2S, solid	IAEA-S-1[d]	–	Natural	$^{32}S/^{34}S$	22.6504 (20)[e]	∼138[c]
S	Elemental	Chemotrade	99.844[c,f]	^{34}S, 99.8%[f]	$^{32}S/^{34}S$	0.002120 (56)[b]	90.09 (19)[b,g]

[a] National Institute of Standards and Technology, Gaithersburg, USA.
[b] Measurement results with expanded uncertainty ($k = 2$).
[c] Mass fraction of total sulfur.
[d] International Atomic Energy Agency, Vienna, Austria.
[e] Data from [9].
[f] Data stated by producer, no certified values.
[g] Mass fraction of ^{34}S.

remove all sulfur. The sulfur species were reduced to hydrogen sulfide, which then was evaporated through the reflux condenser.

Sulfur, enriched in ^{34}S (Chemotrade, Duesseldorf, Germany) was dissolved in HNO_3 to prepare the ^{34}S enriched spike solution. The ^{34}S solution was characterized using two back-spike solutions. For details about the assay, spike and isotopic reference materials as well as solutions prepared thereof, see Table 4.

2.2. Sample preparation

The chemical sample preparation was divided into two major steps: the sample digestion and the formation of As_2S_3. The sample digestion was performed using a high pressure asher system – HPA (Anton Paar GmbH Graz, Austria) equipped with a heating block holding five quartz digestion vessels of 90 mL volume. The fossil fuel samples (approximately 300 mg) were exactly weighed into the vessel. An exactly weighed amount of spike solution (approximately 1 g) and 5 mL HNO_3 and 1 mL H_2O_2 were added. For the determination of the sulfur isotopic composition in the sample as a matter of course no spike was added. The vessels were closed with a quartz cylinder and Teflon ribbon and were put into the HPA. Then the digestion program started, which worked for 4 h at a maximum temperature of 320 °C and a maximum pressure of approximately 120 bar. The detailed time programme is displayed in Fig. 1. Several attempts have been carried out to increase the maximum sample weight for the HPA digestion and to reduce the duration of the heating program, but none of them proved successful for more than some single trials, the corresponding recoveries ranged between 93 and 97%.

For the reduction of the SO_4^{2-}, gained by the HPA digestion, to H_2S a modified and enhanced version of the apparatus suggested by Paulsen and Kelly [1] was used. Basically this apparatus consisted of a 100 mL three-necked round-bottom flask, a heating device and a magnetic stirrer. The flask was equipped with a thermometer, a port for the nitrogen supply and a reflux condenser. This was connected with a 100 mL gas washing bottle (frit of porosity 1), which in turn was lined up with a tube equipped with a pipette tip at the end. The pipette tip dunked into a 50 mL Falcon® tube filled with an ammoniacal solution of arsenic-(III)-oxide (1000 mg kg^{-1}). When running the reduction process the flask was filled with 35 mL of the reduction solution (see above). After refluxing for 30 min the solution was cooled down to 30 °C and then the sample was added. Then the whole mixture was refluxed for 45 min with a stirring speed of 350 rpm. The so formed H_2S bubbled through the ammoniacal arsenic solution by means of a nitrogen stream, which was kept constant at 340 mL min^{-1} by applying a gas flow meter (Vögtlin Instruments, Germany). The formed oxo-thio-arsenate(III) was precipitated as arsenic-(III)-sulfide by adding HCl (subboiling quality). After centrifuging (8000 rpm, 12 min), washing with 1 mL ultra pure water and again centrifuging (8000 rpm, 12 min), the precipitate was dissolved in ammonia solution (25%) to yield a resulting concentration of 3 μg μL^{-1}, which was required for the TIMS measurements. The whole reduction procedure was optimized thoroughly to get reproducible conditions. Especially the co-evaporation of the reduction solution and the transport thereof to the arsenic solution was a critical part. Varying amounts of reduction solution being introduced into the arsenic solution required varying amounts of HCl for the precipitation, which lead to varying procedural blank levels.

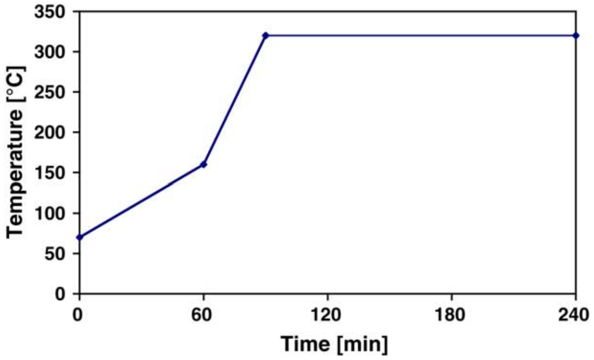

Fig. 1. HPA heating program for the digestion of fossil fuels.

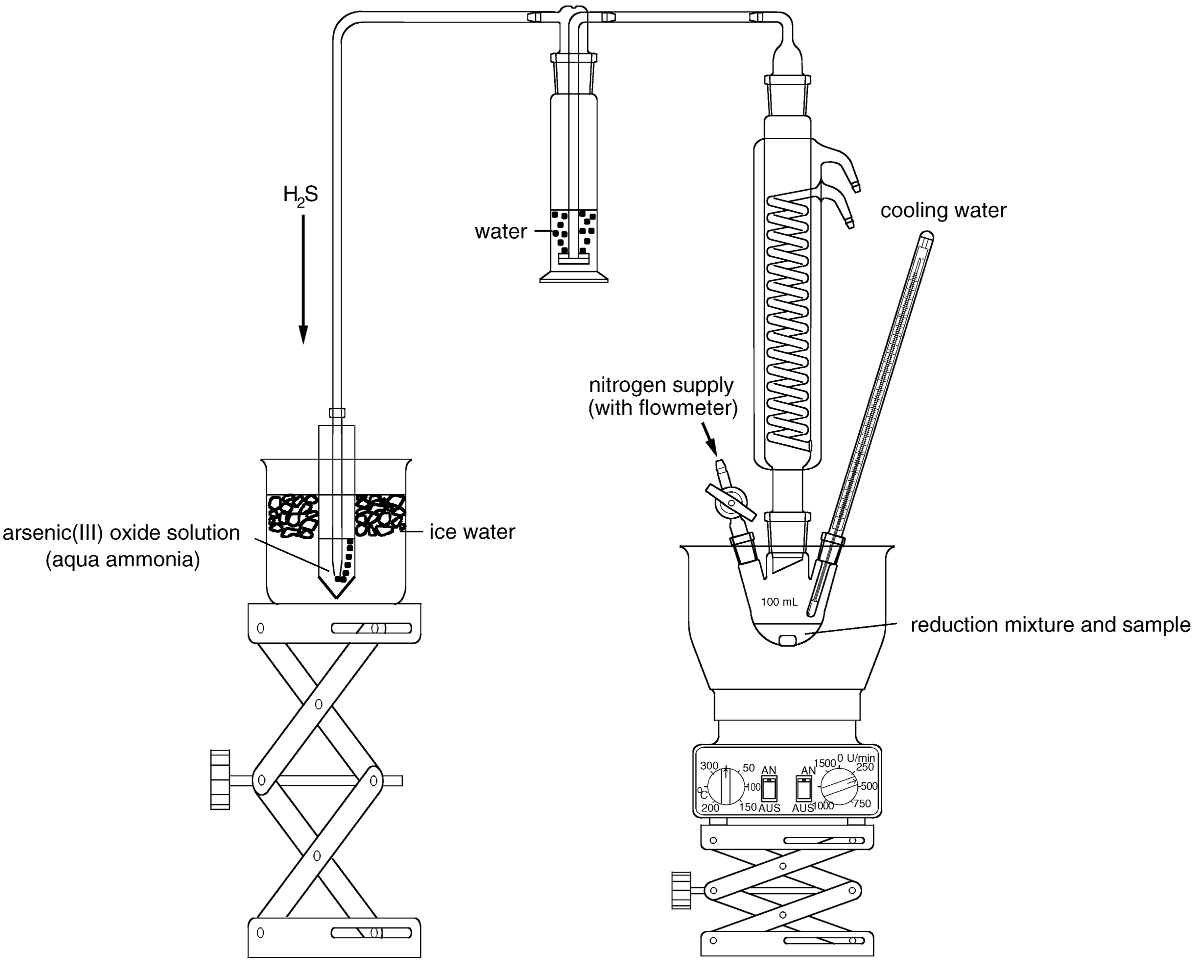

Fig. 2. Schematic view of the reduction apparatus.

Keeping the optimized parameters constant the reproducibility of the procedure could be improved and the spread of the procedural blanks could drastically be reduced. This resulted in a detection limit between 0.1 and 0.2 mg kg^{-1}, which depends on the quality of the acid batch used. The detection limit is calculated as the three-fold standard deviation of the blank, and is the lowest published detection limit for IDMS measurements of sulfur in fossil fuels (Fig. 2).

2.3. Mass spectrometry

All mass spectrometric measurements were performed using the multi-collector TIMS (MC-TIMS) instrument Sector54 (Micromass/GV Instruments), excepting the purity measurements of the deionised and ultra pure water.

Throughout the whole work only rhenium filaments were used. The filaments were degassed under vacuum to remove all impurities. Onto the clean filaments 1 μL sample solution, corresponding to 3 μg sulfur, and 1 μL silica-gel suspension (mixed from 0.95 g Aerosil 300, 1.35 mL H_3PO_4 (85%), 2.5 mL NH_3 (25%) and 50 mL H_2O) were loaded. The filament was heated by a current of 1.5 A to carefully evaporate the sample to dryness, while observing the process through a microscope. Regarding the loading procedure a speculation exists, that loading and heating of the sample at ambient air will lead to degradation of the As_2S_3 by oxidation. This was checked by loading two series, 27 samples each, one at ambient air and one under nitrogen atmosphere in a period of 3 days. The measured ion current ratios were statistically treated by Grubb's test, Bartlett test and a analysis of variance. Both series belonged to populations with the same mean value. The standard deviation of the preparation at ambient air was smaller than the standard deviation of the preparation under nitrogen atmosphere. This might derive from the more convenient working conditions at ambient air compared to conditions working in a glove box under nitrogen atmosphere. Subsequently all samples were loaded at ambient air.

Additionally differences in the filament form (band or boat) and in the loaded amount of sulfur (0.75, 1.5, 3 and 9 μg sulfur) and silica-gel suspension (1 and 3 μL) were tested. Statistical tests, however, could find no significant differences. Based on this filaments were prepared by loading

Table 5
Isotopic composition of NIST SRM-3154, SRM-1624d and BAM ^{34}S spike, measurement results with expanded uncertainties ($k = 2$)

	NIST SRM-3154	NIST SRM-1624d	BAM ^{34}S spike
Isotope abundance ratio			
$n(^{32}S)/n(^{34}S)$	22.555 (26)	22.428 (24)	0.002120 (56)
$n(^{33}S)/n(^{34}S)$	0.17779 (50)	0.17756 (44)	0.000253 (54)
$n(^{36}S)/n(^{34}S)$	0.00350 (42)	0.00444 (74)	0.000015 (15)
Molar mass of sulfur			
$g\,mol^{-1}$	32.06423 (12)	32.06487 (16)	33.96343 (13)

3 μg sulfur and 1 μL silica-gel suspension on rhenium single filaments in band form.

Measurements with silica-gel suspension only (without sample) were carried out to check for isobaric interferences on the masses 107 and 109 caused by ^{107}Ag and ^{109}Ag. Applying the same measurement conditions as for the samples no interferences could be observed with Faraday detectors.

The loaded filaments were mounted on a turret and were introduced into the TIMS ion source. The current of the rhenium filaments was chosen to yield an ion current of 9×10^{-12} A for $^{75}As^{32}S^{+}$ ions or $^{75}As^{34}S^{+}$ ions, respectively. For samples without spike showing natural-like isotopic compositions mass 107 was used as monitor mass and in terms of blends (isotope diluted samples) as well as spike samples mass 109 was used. During the measurement the filament current was kept. A complete measurement consisted of 200 measurement readings, each integrated over 5 s, which were recorded for all masses (107: $^{75}As^{32}S$, 108: $^{75}As^{33}S$, 109: $^{75}As^{34}S$, 111: $^{75}As^{36}S$) simultaneously. The whole measurement time from warm-up until the end takes 35 min. The values of the ion current ratios were calculated from the sum of all 200 single values. The basis b_i of each calculation was mass 109 (Eq. (1)). To control the evaporation and correct for mass fractionation five samples of the isotopic reference material have been measured per each turret (20 samples)

$$R_j = \frac{\sum_{i=1}^{200} a_{i,j}}{\sum_{i=1}^{200} b_i}. \qquad (1)$$

2.4. Spike characterization

For the characterization of the applied ^{34}S spike solution two back-spike solutions were used, which were produced by diluting the NIST reference material SRM-3154. This material is a solution of sulfuric acid, which was certified for its sulfur mass fraction ($C = 10.30$ (3) g kg^{-1}). The mass fractions of both back-spike solutions prepared from SRM-3154 are listed in Table 4.

By mixing spike and back-spike 10 blends were prepared, five for each back-spike solution. The spike and back-spike portions were adjusted to an exactly weighed mass (approximately 1 g), which yielded a blend isotope abundance ratio of $R(^{75}As^{32}S/^{75}As^{34}S) = 1$. Because SRM-3154 was certified only for the sulfur mass fraction, the sulfur isotopic composition has to be determined. The isotopic abundances and the molar mass were calculated from the observed isotope abundance ratios (Table 5). The mass fractionation was corrected by measuring a solution of IAEA-S-1 (Table 4), which is being sold as Ag_2S (solid). To dissolve the IAEA-S-1 material 104.7 mg Ag_2S (IAEA-S-1) were weighed in a quartz flask with a glass covered magnetic stirrer bar. The flask was filled with 18 mL HNO_3 and then approximately 0.2 mL bromine have been added drop wise (eight drops). The grey Ag_2S was dissolved, while yellow AgBr precipitated and the solution above changed colour to brownish orange. After 2 h continuous stirring the heating was turned on and the solution was heated to approximately 100 °C for another 2 h until the precipitate lumps. Then the solution was centrifuged, separated from the precipitate and diluted to a sulfur mass fraction of 138 mg kg^{-1}. The isotopic composition of the BAM ^{34}S spike is shown in Table 5, the determined ^{34}S mass fraction resulting from the spike characterization is displayed in Table 4.

3. Results and discussion

While developing the reference procedure for sulfur in fossil fuel, it has turned out, that inconsistent data for sulfur isotopic composition of reference samples were published in the literature. It is quite unclear to the reader, which data has to be used. Furthermore publications on IDMS measurements of sulfur have not paid much attention to isotopic abundance variations. Therefore this topic was investigated in detail. The IUPAC report [8] gives only isotopic abundances, although isotope abundance ratios would be mathematically more relevant for uncertainty calculations, because they are the primary data. In the case of sulfur the isotopic abundances in the category “best measurement” are given with the remark that they were taken from the original literature [9]. But this reference only offers isotope abundance ratios and no isotopic abundances. The way from isotope abundance ratios to isotopic abundances with special attention to uncertainty calculations was not given. In some cases it is quite useful to have access to isotope abundance ratios, the primary data, without further calculations. Moreover correlations could be considered and double counting of uncertainty contributions could be avoided. Therefore isotope abundance ratios should be displayed in the IUPAC tables together with the isotopic abundances, both accompanied by their combined uncertainty and the applied coverage factor. Table 6 summarizes the “representative value” or so called IUPAC value and the “best measurement” of the isotopic abundances of sulfur as stated

Table 6
Isotopic abundances of sulfur as stated by IUPAC and of IAEA-S-1

Isotope	IUPAC value[a]	Best measurement[b]	IAEA-S-1[c]	IAEA-S-1[d]
^{32}S	0.9499 (26)	0.9504074 (88)	0.9504074 (88)	0.9503957 (90)
^{33}S	0.0075 (2)	0.00748 (60)	0.00748 (55)	0.0074865 (12)
^{34}S	0.0425 (24)	0.0419599 (66)	0.0419599 (71)	0.0419719 (87)
^{36}S	0.0001 (1)	0.00014579 (89)	0.00014579 (89)	0.0001459 (21)

[a] Representative isotopic composition, column 9 of [8].

[b] Best measurement of a single terrestrial source, column 6 of [8], with two times standard deviation in parentheses from isotope abundance ratios of [9].

[c] Calculated from isotopic abundance ratios of [9], with expanded uncertainty ($k = 2$) in parentheses (this work).

[d] Calculated by Coplen et al. [6], from isotopic abundance ratios of [9].

by IUPAC, as well as the isotopic abundances for sulfur of IAEA-S-1. The IUPAC values (column 2 of Table 6) represent the isotopic composition of chemicals and/or natural materials that may be encountered in the laboratory. The uncertainties listed in parentheses cover the range of probable isotopic abundance variations among different materials as will as experimental errors [8]. The columns 3–5 list the isotopic abundances of IAEA-S-1 as stated by different authors citing the same reference. The original data for the isotope abundance ratios as given by Ding et al. [9] are as follows:

$$R\left(\frac{^{32}\mathrm{S}}{^{34}\mathrm{S}}\right) = 22.6504\,(20), \quad R\left(\frac{^{32}\mathrm{S}}{^{33}\mathrm{S}}\right) = 126.942\,(47),$$

$$R\left(\frac{^{36}\mathrm{S}}{^{34}\mathrm{S}}\right) = 6519\,(20).$$

The expanded uncertainties $U = ku_c$ are given in parentheses, with a coverage factor $k = 1$ and the combined standard uncertainty u_c. These data were also used to calculate the IUPAC molar mass of sulfur [8].

The values for the isotopic abundances in columns 3 and 4 (Table 6) agree with each other, but the uncertainty values for ^{33}S and ^{34}S do not. The data presented in column 4 were calculated on the basis of the data from Ref. [9] by using the software "GUM Workbench" [10]. The data in column 5 were calculated by Coplen et al. [6]. Both, the values of the isotopic abundance and the uncertainty values do significantly differ from the data shown in columns 3 and 4. Additionally it was not stated by Coplen et al. [6], which coverage factor was used for calculating the uncertainties given in column 5. This situation leaves the user slightly confused. The authors suggest to use the original literature [9] and calculate the isotopic abundances and molar mass on their own or to use the data from column 4 in Table 6, when working with IAEA-S-1. For all analyses and calculations without determination of the isotopic composition in the sample IUPAC values ([8] or column 2, Table 6) should be used.

In Table 7 the isotope abundance ratios calculated from IUPAC values as well as data from Ding et al. [9] are displayed. ^{34}S was used as reference isotope. The coverage factor for the uncertainties of IUPAC values was not stated. Therefore the uncertainties in columns 3 and 4, respectively were calculated on the assumption that the coverage factor is either 1 or 2. This is quite essential, as the uncertainty values are rather large and therefore have large influence on further calculations.

For covering the whole range of sulfur isotopic abundance variations with the IUPAC values a coverage factor $k = 1$ has to be assumed for the uncertainty of the isotopic abundances. From this the uncertainties of the isotope abundance ratios can be calculated applying a coverage factor $k = 2$. By this an isotope abundance ratio of $R(^{32}\mathrm{S}/^{34}\mathrm{S}) = 22.3506$ follows with $U = 2.6$, which in turn results in $\delta(^{34}\mathrm{S})$-values between −92 and 147‰. This covers the total range of the isotopic abundance variation of sulfur which is between $\delta(^{34}\mathrm{S}) = -55$‰ and $\delta(^{34}\mathrm{S}) = +135$‰ according to Ref. [5]. When the isotopic composition of the sample was not or could not be determined, the IUPAC values for the sulfur isotopic composition assuming a coverage factor of 1 has to be used, because it covers the maximum sulfur isotopic abundance variation.

The sulfur mass fractions obtained for the samples LGC-3021, LGC-3022, LGC-3023, SRM-2723a and CCQM-P26.1 are displayed in Table 8. The applied analytical procedure is described in detail in Section 2. For each sample six independent blends and five independent procedural blanks

Table 7
Isotopic abundance ratios of sulfur

	IUPAC value			IAEA-S-1[d]
	Ratio[a]	Uncertainty ($k = 1$)[b]	Uncertainty ($k = 1$)[c]	
$R(^{32}\mathrm{S}/^{34}\mathrm{S})$	22.3506	0.63	1.3	22.6504 (20)
$R(^{33}\mathrm{S}/^{34}\mathrm{S})$	0.176471	0.0055	0.011	0.178431 (68)
$R(^{36}\mathrm{S}/^{34}\mathrm{S})$	0.002353	0.0012	0.0024	0.0034745 (107)

[a] Isotope abundance ratios calculated with the isotopic abundance values of IUPAC [8].

[b] Assumption: uncertainties of the IUPAC isotopic abundance values have a coverage factor of $k = 2$.

[c] Assumption: uncertainties of the IUPAC isotopic abundance values have a coverage factor of $k = 1$.

[d] The isotope abundance ratios were calculated from [9]; expanded uncertainties are given in parentheses with $k = 1$.

Table 8
Sulfur mass fractions of reference materials together with their corresponding uncertainties, IUPAC values have been used for the sulfur isotopic composition of the sample

Sample	LGC-3021	LGC-3022	LGC-3023	SRM-2723a	CCQM-P26.1
Sulfur mass fraction in mg kg^{-1}					
Measured value	12.01	33.50	52.15	11.05	9.03
Uncertainty, $k=2$	0.59	0.25	0.30	0.29	0.30
Certified value	[c]	[c]	52.4	10.0	[c]
Uncertainty			1.3[a]	1.1[b]	
Sulfur mass of blank in μg					
Blank value	0.151	0.117	0.175	0.058	0.126
Uncertainty, $k=2$	0.047	0.036	0.029	0.028	0.045

[a] Expanded uncertainty with $k=4.3$.
[b] Expanded uncertainty with $k=2.2$.
[c] Reference material not yet certified (August 2004).

were prepared whereof each has been measured two times. All measured sulfur mass fractions in Table 8 were calculated by assuming IUPAC values for the isotopic composition of the sample. The total analyte mass of the blanks range between 0.06 and 0.18 μg sulfur and result in blank mass fractions between 0.2 and 0.6 mg kg^{-1}, when considering approximately 300 mg of sample weight. Below a sulfur level of 50 mg kg^{-1} the relatively high blank values and their uncertainties strongly contribute to the combined uncertainties of the sulfur mass fraction. This contribution is stronger the lower the sulfur mass fraction is. In the case of the samples LGC-3023 and CCQM-P26.1 this contribution makes up 36% or even 99% respectively of the total uncertainty. The calculated uncertainty budgets for all five samples reveal only four major contributing parameters: the blank value (36–99%), the isotopic abundance of ^{34}S (<1 to 34%) of the sample, the observed isotope abundance ratio ^{32}S/^{34}S of the blend (<1 to 3%) and the sulfur mass fraction of the spike (<1 to 16%). In the case of the samples LGC-3023 and SRM-2723a already certified values exist. The results obtained within this work agree well with these certified values within the stated uncertainties. Beyond this performance comparison against certified reference materials the validation consists of a thorough control of each single step of the procedure as well as a complete and detailed uncertainty budget. By this the developed ID-TIMS procedure was well validated for sulfur in fuel reference measurements.

The results for the sulfur analysis in the samples CCQM-K35 and SRM-1624d are summarized in Table 9. Different values for the sulfur isotopic composition in the sample were used for the calculations to demonstrate the influence on the mass fraction and the corresponding uncertainty. In columns 2 and 5 the measured isotopic composition of the sample was used, whereas in the columns 3, 4, 6 and 7

Table 9
Measured sulfur mass fractions of CCQM-K35 and SRM-1624d together with their corresponding uncertainties and the major contributions to it

Sample	CCQM-K35			SRM-1624d		
	[a]	[b]	[c]	[a]	[b]	[c]
Sulfur mass fraction in mg kg^{-1}						
Mean value	42.29	42.06	42.06	3896	3901	3901
Uncertainty, $k=2$	0.25	0.35	6.9	16	180	760
Sulfur mass of blank in μg						
Blank value	0.082	0.082	0.082	0.27	0.27	0.27
Uncertainty, $k=2$	0.031	0.031	0.031	0.12	0.12	0.12
Major contributions to the combined uncertainty in %						
$R_c(^{32}S/^{34}S)$	16.4	9.5	<0.1	33	0.6	<0.1
$R_x(^{32}S/^{34}S)$	1.9	Not used	Not used	7	Not used	Not used
$R_{xy}(^{32}S/^{34}S)$	7.8	4.2	<0.1	33	<0.1	<0.1
m_{Bl}	60.8	31.2	<0.1	<1	<0.1	<0.1
$C_y(^{34}S)$	12.2	6.2	<0.1	25	0.2	<0.1
$h_{IUPAC}(^{34}S)$	Not used	48.4	48.0	Not used	98.7	33.6
$R_{IUPAC}(^{32}S/^{34}S)$	Not used	Not used	51.6	Not used	Not used	66.1

[a] The sulfur mass fraction was calculated using the isotope abundance ratios of the sample.
[b] The sulfur mass fraction was calculated using the isotope abundance ratios of IUPAC [8].
[c] The explicit IUPAC values was used ($h_{IUPAC}(^{34}S)$, $R_{IUPAC}(^{32}S/^{34}S)$, M_{IUPAC}), explanation see text.

IUPAC values were used. For both samples good agreement within the stated uncertainties was observed between the values in columns 2–7. When using IUPAC values for the calculation the combined uncertainty increases according to the higher contribution of the IUPAC values and their uncertainties.

Here the major contribution to the combined uncertainty was made up by five parameters. These are the observed isotope abundance ratios of the sample $R_x(^{32}\mathrm{S}/^{34}\mathrm{S})$, of the blend $R_{xy}(^{32}\mathrm{S}/^{34}\mathrm{S})$ and of the isotopic reference material $R_\mathrm{c}(^{32}\mathrm{S}/^{34}\mathrm{S})$, as well as the procedure blank m_Bl and the sulfur mass fraction of the spike $C_y(^{34}\mathrm{S})$. Detailed numbers are given in Table 9. In the case of sample SRM-1624d, which shows the higher sulfur level, the contribution of the blank to the uncertainty proved negligible. In this case and generally at sulfur levels above 50 mg kg^{-1}, the use of IUPAC values lead to combined uncertainties for sulfur mass fractions which are ruled by the uncertainty of the IUPAC values (see columns 3 and 6, Table 9). Columns 4 and 7 in Table 9 shows the results when IUPAC tabulated values were used explicitly. This means the isotope abundance ratio was calculated separately from the IUPAC isotope abundance. The isotope abundance and the molar mass were taken from IUPAC tables, which is quite common. The uncertainty of the sulfur mass fraction was ruled by the uncertainty of the IUPAC values and dramatically increased from columns 3 and 6 to 4 and 7 in Table 9. In the case of sample SRM-1624d the expanded uncertainty rose from 16 to 760 mg kg^{-1}. In the latter case the uncertainty drastically was overestimated, because correlations between isotopic abundances, isotope abundance ratios and molar mass were not considered, which was caused by explicitly using IUPAC tabulated values. Therefore the primary data should be taken always, when using the IUPAC data for IDMS calculations.

4. Conclusion

An existing TIMS procedure for sulfur measurements was developed further. This includes the sample preparation as well as the TIMS measurements. The developed procedure was validated by two different certified reference materials. The obtained results agree well with the certified values within their uncertainties. With the presented procedure detection limits of approximately 0.2 mg kg^{-1} can be achieved. This are the lowest published detection limits for the total determination of sulfur in fossil fuels. The procedure already proved as reference procedure in two CCQM projects, which results will be published soon.

For reference measurements it is inevitable to determine the isotopic composition of sulfur in the sample for achieving lower combined uncertainties, which commonly is denoted as more accurate and precise results. Generally this is important at sulfur mass fraction levels above 50 mg kg^{-1}. Here the uncertainty contribution by the blank is low and the combined uncertainty is ruled by the IUPAC isotopic composition. In terms of low sulfur levels, below 50 mg kg^{-1}, the sulfur isotopic composition in the sample was more altered by the sulfur isotopic composition in the blank the lower the sulfur level in the sample is. In this case the original isotopic composition of the sample could not be measured accurately. Here it was better to use the IUPAC isotopic composition.

Calculations showed that the isotopic abundance variation of sulfur in fossil fuels is covered completely by the uncertainty of the IUPAC values. Sulfur mass fractions calculated by using the determined isotopic composition in the sample and by using IUPAC values do not significantly differ beyond calculated uncertainties.

An additional finding of this study was that even reference values for isotopic compositions differ in the literature, although the same source has been used. To avoid these differences the authors suggest for all future publications to publish isotopic abundance ratios, which are the primary data, as well as the calculated isotope abundances and the molar mass. All results should be accompanied by their combined uncertainties calculated according to ISO [11] and EURACHEM [12] guidelines.

Acknowledgement

The authors would like to thank Michael Czerwensky for performing the HR-ICPMS measurements.

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