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Absolute sulfur isotope amount ratios in two batches of high purity SO_2 gas: sulfur isotope reference materials IRMM-2012 and IRMM-2013

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Abstract

SI-traceable ("absolute") values have been obtained for sulfur isotope amount ratios $n(^{33}S)/n(^{32}S)$ and $n(^{34}S)/n(^{32}S)$, in two batches of high purity SO_2 gas (IRMM-2012 and IRMM-2013). The SO_2 gas was converted at IMR-Beijing to Ag_2S, then fluorinated to SF_6 gas both at IMR-Beijing and at IRMM-Geel. Yields of different conversion methods exceeded 99%. The sulfur amount-of-substance measurements were performed by gas mass spectrometry on SF_5^+ ions using "IRMM's amount comparator II". These isotope amount ratios were calibrated by means of gravimetrically prepared synthetic mixtures of highly enriched sulfur isotopes (^{32}S, ^{33}S and ^{34}S) in Ag_2S form. The ratio values in the SO_2 Secondary Measurement Standard are traceable to the SI system. They can be used in the calibration of field sulfur isotope measurements thus making these metrologically traceable to the SI.

Keywords: Sulfur; Absolute amount ratio; Isotope mass-spectrometry; Isotopic reference materials

1. Introduction

During last years, much instrumental progress has been made in (sulfur) isotope ratio measurements performed on ICP-MS. One of the most important improvements made was the application of a multiple ion collector device (MC–ICP-MS), which is able to obtain precisions on isotope ratio measurements down to 0.002% (R.S.D.) [1]. To achieve comparability, however, of such sulfur isotope data as well as for the determination of their degree-of-equivalence, measurement standards are further needed.

For the calibration of the earliest sulfur isotope ratio measurements, materials such as Park City pyrite (USA) and elemental sulfur from Merck were used [2]. However, by 1950, meteorite samples had been adopted both in the USSR and USA as primary standards and were thought to be isotopically homogeneous with $n(^{32}S)/n(^{34}S) = R_{32/34} = 22.22 \pm 0.01$. The isotopic composition was representative for terrestrial material [3,4].

By 1960, the troilite (FeS), a meteorite collected from the Canyon Diablo, Arizona (CDT) was designated to be a "primary" measurement standard for sulfur isotope measurements. In Russia, however, the use of the Shikote Alin meteorite [4] was continued. An additional problem was that different chemical preparations of CDT meteorite samples for measurement yielded different $\delta^{34}S$ values. Furthermore, the assigned value of 22.22 for $R_{32/34}$ of CDT was chosen rather arbitrarily. Since 1960, other reference samples have been established at IAEA, such as Ag_2S, $BaSO_4$ and elemental sulfur with isotope amount ratios that cover the range of natural sulfur.

In 1983, IAEA rejected CDT as reference material, due to its poor isotopic homogeneity, non-stoichiometry and the presence of Co/Ni sulfides and carbides [4]. So far, variations of the $\delta^{34}S$ value up to 0.4‰ were observed and more

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samples of different troilite inclusions from the CDT meteorite need to be measured to get a better idea of the extent of the isotopic inhomogeneity. Currently, CDT is not a CRM and should not be used for calibration of sulfur measurements. At the same time, new reference samples (IAEA-S1 and IAEA-S2) were developed at New Zealand and in Lublin (Poland) [5]. In 1993, IAEA recommended the use of a so-called virtual "Vienna-CDT or VCDT" as 'International Recognized Reference for Sulfur isotopes'. The connection of the new scale to the previous scale was defined by putting $\delta^{34}S_{IAEA\text{-}S1/VCDT} = -0.3‰$ through a consensus decision.

At the IAEA working group for sulfur isotope measurements (Vienna, September 2000 [6]), it had been decided to anchor the sulfur δ-scale to the calibrated isotope amount ratio measurements at IRMM-Geel and IMR-Beijing. Further recommendations were made to assign $\delta^{34}S$ values versus VCDT for IAEA-S2 and IAEA-S3 as 22.66 and −32.30‰, respectively. These "connections" are based on the "absolute" isotope amount ratio measurements at IRMM and IMR [7,8,11] for these materials. Though sulfur isotope amount ratio measurements made on SF_6 gas [7] were found to be very consistent, they differ from ratios measured on corresponding SO_2. Thus, a correlation between results of the two measurement procedures was established. Again, an IAEA-working group meeting (Vienna, 2000) decided to use Eq. (1) [6]:

$$\delta^{34}S_{SF_6} = 1.0339\delta^{34}S_{SO_2} - 0.34 \quad (1)$$

Direct sulfur isotope ratio measurements on SO_2 are difficult because of the adsorption in the spectrometer, especially in the inlet line and the expansion vessel, so hard to remove even by flushing. The second difficulty is due to the presence of ^{17}O and ^{18}O in the SO_2 spectrum. Several correction-algorithms have been developed but they all have their own uncertainty resulting in enlarging the combined uncertainty. Therefore, the decision was made at IRMM to convert a high purity SO_2 gas (Messer, D) into Ag_2S (IMR, Beijing) and fluorinate it to SF_6 (at IMR, Beijing by BrF_5 and at IRMM-Geel by F_2). To obtain absolute sulfur isotope amount ratios on the prepared SF_6 gas, a calibration was made against synthetically prepared mixtures of enriched sulfur isotopes [7]. Such values are traceable to the SI along the shortest possible route: they come from direct measurements of ion current ratios calibrated by synthetic isotope mixtures. Both ion current ratios (in the measurements and amount-of-substance in the mixtures) are ratios of numbers of well-defined entities. In this paper, the "absolute" or SI-traceable measurement results of S isotope amount ratios are presented.

2. Preparing samples for measurement: the conversion of SO_2 to SF_6

SO_2 gas was converted to SF_6 gas because the latter is well suited for mass spectrometry. It is chemically inert and is not sensitive to moisture, nor adsorbs to the walls of a vacuum system. In addition, fluorine has only one stable isotope, hence no corrections are needed for $R_{34/32}$ as in the case of SO_2 where the main uncertainty contribution in a measured ratio is attributed to the oxygen correction because "assigned" values (IUPAC values) for oxygen must be applied [9]. In the mass spectrometer, SF_6 displays a fairly simple mass spectrum upon electron impact and the major abundant ion SF_5^+ occurs in a mass region with low background [10]. However, it is impossible to covert SO_2 to SF_6 directly by reacting with fluorinating agents: BrF_5 or F_2. Thus, we used the chemical conversion route of SO_2 to Ag_2S and further to SF_6.

2.1. Preparation of Ag_2S from SO_2

First SO_2 was converted to $BaSO_4$: about 2 mmol of SO_2 gas (contained in a stainless steel bottle) was introduced (carried by an Ar flow) into a glass bottle which contained 500 mL mixture of I_2 (0.1 mol/L), KI (0.1 mol/L) and $BaCl_2$ (5 mmol/L). In this bottle, SO_2 reacted with I_2 and $BaCl_2$ under formation of $BaSO_4$:

$$SO_2 + I_2 + 2H_2O \rightarrow 4H^+ + {SO_4}^{2-} + 2I^- \quad (2)$$

$${SO_4}^{2-} + Ba^{2+} \rightarrow BaSO_4 \quad (3)$$

The $BaSO_4$ produced in this way was further reacted with the so called "Thode reagent", which is a mixture of HI, H_3PO_2 and HCl, in order to produce H_2S. The H_2S formed was trapped immediately in a cadmium acetate solution [11].

$$BaSO_4 + HI + 3H_3PO_2 + HCl + 2H_2O \rightarrow 2H_2S + Ba^{2+} + HI + 3H_3PO_4 + HCl \quad (4)$$

$$H_2S + CdAc_2 \rightarrow CdS + 2HAc \quad (5)$$

By adding $AgNO_3$ to this solution, CdS is transformed into Ag_2S:

$$CdS + 2Ag^+ + 2NO_3^- \rightarrow Ag_2S\downarrow + Cd^{2+} + 2NO_3^- \quad (6)$$

The Ag_2S is filtered and dried and is ready to be converted to the SF_6 gas needed for the isotope amount ratio measurements. The conversion from SO_2 to $BaSO_4$ has a yield of over 98%, whilst the step from $BaSO_4$ to Ag_2S had a conversion yield of more than 99%.

2.2. Conversion of Ag_2S to SF_6

At IMR-Beijing [11], BrF_5 has been used for decades to fluorinate different compounds such as Si, SiO_2, Ag_2S and others, while at IRMM-Geel [11] elemental fluorine has been used for years to fluorinate compounds such as $BaCO_3$, organic compounds (sugars, oils, polyethylene foils and others) and graphite [12,13].

2.2.1. Conversion of Ag_2S to SF_6 using BrF_5 (at IMR Beijing)

BrF_5 is convenient to handle in a vacuum system, more than either fluorine or BrF_3. Such a BrF_5 vacuum system and all details about the fluorinating unit are described by Ding et al. [8,11]. Small samples of Ag_2S (20–30 μmol), weighed in a small box made of Al foil, are reacted with an approximately five-fold excess of BrF_5 for about 14 h at 320 ± 20 °C:

$$Ag_2S + 4BrF_5 \rightarrow 2AgF + 4BrF_3 + SF_6\uparrow \quad (7)$$

After completion of the reaction, the SF_6 is purified by a two-fold fractional distillation (liquid nitrogen and dry ice/acetone), followed by a purification via gas chromatography [14]. The gas chromatograph (HP series 300) uses He carrier gas and a coiled 2 m length column of 0.25 in. o.d. stainless steel, packed with molecular sieve of 5A. The column is heated and may be baked to purge it of retained contaminants; separation is done at room temperature. A thermal conductivity detector at the GC monitors the eluted SF_6 gas mixed in the He flow. Both gases are diverted through a spiral trap at −196 °C (liquid nitrogen), where the He is slowly pumped off. The liquid nitrogen trap is then allowed to warm up to room temperature. The SF_6 gas is transferred to a glass tube and used for differential isotope measurements performed on a delta instrument at IMR or sent to IRMM for calibrated sulfur isotope amount ratio measurements [7,10].

2.2.2. Conversion of Ag_2S to SF_6 using F_2 (at IRMM-Geel)

Ag_2S samples prepared from two SO_2 bottles, were converted to SF_6 gas by fluorination with elemental fluorine. The conversion procedure has been described in detail in [12]. For each fluorination, a sample containing ∼100 μmol of sulfur was weighed into a nickel crucible, placed in a nickel reactor and converted in a fourfold molar excess of high purity fluorine, after having evacuated air from the reactor. The fluorination was performed at 520 °C for about 15 min and SF_6 was separated from the excess of fluorine by distillation at −196 °C by means of liquid nitrogen. The reaction products were checked for the absence of by-products as S_xF_y and $S_xF_yO_z$ and when necessary, SF_6 was purified using a CE-Instruments gas chromatograph type CE-8000^{top}, with a 2.5 m long and 0.25 in. diameter column packed with silica gel 50/80 mesh size.

3. Isotope amount ratio measurements on SF_6

3.1. The "delta" approach

Sulfur isotope measurements are routinely made on SO_2 by making a comparison of an isotope ratio, e.g., $(R_{32/34})_{sample}$ in the sample with that ratio $(R_{32/34})_{standard}$ in a reference sample. The measured delta value is (Eq. (8)):

$$\delta^{34}S = \left[\frac{(R_{34/32})_{sample}}{(R_{34/32})_{standard}} - 1\right] \times 1000 \quad (8)$$

The standard sample is said to carry the value $\delta^{34}S_{reference} = 0$ by definition. This measurement procedure enables laboratories, only interested in differential measurements, to compare their data with those of other laboratories.

At first sight, it does not seem to be extremely important to know the absolute value $(R_{32/34})_{standard}$. However, an assigned (consensus) value is usually entrusted to such a reference value. This approach is very practical and straightforward and helps the use of (differential) isotope measurements to a great extent. For sulfur, the standard sample CDT has been construed according to this principle. The material is regularly called a 'primary' material by practicing isotope scientists, and in a certain sense that is correct because a Primary Measurement Standard is one which is linked to the definition of a unit by a primary measurement procedure. The problem, however, is the (in)stability of the quantity value in this Primary Measurement Standard.

For the sulfur delta scale, the material IAEA-S1 has been assigned a $\delta^{34}S$ value of −0.3‰ on the new scale tied to VCDT [6]. Note that a VCDT material with delta value equal to zero does not exist, i.e., the zero point of the VCDT scale refers to a value carried by a 'virtual' material. This has been done to establish connection with the VCDT scale, but a "virtual" value clearly demonstrates the weakness of a traceability scheme which only relies on artifacts and non-traceable values for $(R_{32/34})_{standard}$.

As part of this work, measurements have been carried out with results traceable to the VCDT scale. $\delta^{34}S$ and $\delta^{33}S$ were measured as the $(^iSF_5)^+$ ion beams by means of a MAT 251 "delta" mass spectrometer. In the multiple collector system, four of the eight collectors are arranged for the mass positions m/e = 127, 128, 129 and 131, in order to measure $I(^{32}SF_5)^+$ to $I(^{36}SF_5)^+$.

From each of the two SO_2 gas bottles, filled with gases from a similar production unit (Messer, Germany) and assumed to have a similar sulfur isotopic composition, four gas samples of each bottle were converted to Ag_2S (IMR Beijing) and fluorinated by means of BrF_5 to SF_6 (IMR Beijing).

All eight gas samples (Tables 1 and 2) were measured on a MAT 251 at IMR Beijing against IAEA-S1 and a connection is made to the VCDT scale (Tables 1 and 2).

From Tables 1 and 2, it can be seen that the mean $\delta^{33}S$ and $\delta^{34}S$ values in bottle 1 (Table 1) are slightly lower than the ones obtained for bottle 2 (Table 2). The differences are small but with the indicated 1s repeatabilities of 0.1 δ‰ for $\delta^{33}S$ and the 0.25‰ for $\delta^{34}S$, they are significant. At the same time, these repeatabilities clearly indicate that the relatively complex chemistry (because of the different steps involved) is under control and that any small isotope fractionation effect during the sample preparation (SO_2 to SF_6 gas), has been highly reproducible and will cancel out dur-

Table 1
Four conversions of SO_2 gas from bottle 1 (code 84134) to Ag_2S with further fluorination to SF_6 gas by means of BrF_5 (conversions 1–4)

SO_2 bottle 1 (code 84134)	$\delta^{34}S_{VCDT}$ (‰)	$\delta^{33}S_{VCDT}$ (‰)
Conversion 1	−2.11	−1.16
Conversion 2	−1.91	−0.94
Conversion 3	−1.80	−1.01
Conversion 4	−2.11	−1.09
Mean	−1.98 (15)	−1.05 (10)

For each gas sample as well as for IAEA-S1, the ion current ratios $J_{129/127}$ and $J_{128/127}$ are measured at IMR-Beijing; $\delta(^{34}S_{VCDT})$ and $\delta(^{33}S_{VCDT})$ are calculated; the repeatability is expressed as 1s standard deviation.

ing the "delta measurement" within the measurement uncertainty.

3.2. The route to SI-traceable ("absolute) sulfur ratios $R_{33/32}$ and $R_{34/32}$

Differential measurements are an excellent tool for studying "differences". However, the long-term comparability of the sulfur isotope amount ratio measurements cannot be guaranteed because (reference) materials are never stable in the long range (sooner or later they must be replaced). Values which are traceable to SI units (such as the mole) are more stable than values defined by materials.

The strategy at IRMM-Geel when performing calibrated sulfur isotope amount measurements is based on calibrating the ion current measurement results, achieved by a transparent and highly reproducible isotope mass spectrometric procedure, by means of synthesized sulfur isotope amount ratio values realized in synthetic isotope mixtures of highly enriched sulfur isotopes. Synthetic sulfur isotope mixtures were, therefore, gravimetrically prepared with small uncertainties [6]. Typically, combined uncertainties of 0.005% could be obtained for the $R_{34/32}$ and $R_{33/32}$ ratios, and close to 0.1% for the $R_{36/32}$ ratio. The uncertainty sources need to be meticulously identified along the whole traceability chain of the calibrated quantity values.

An excellent tool for sulfur isotope amount ratio measurements is gas source electron impact mass spectrometry on SF_6 because it produces near-monoenergetic ions. With fluorine being mono-nuclidic, the mass spectrum is simple.

Table 2
Four conversions of SO_2 gas from bottle 2 (code 84863) to Ag_2S with further fluorination to SF_6 gas by means of BrF_5 (conversions 1–4)

SO_2 bottle 2 (code 84863)	$\delta^{34}S_{VCDT}$ (‰)	$\delta^{33}S_{VCDT}$ (‰)
Conversion 1	−2.34	−1.33
Conversion 2	−2.55	−1.27
Conversion 3	−2.56	−1.27
Conversion 4	−2.64	−1.10
Mean	−2.52 (13)	−1.32 (06)

For each gas sample as well as for IAEA-S1, the ion current ratios $J_{129/127}$ and $J_{128/127}$ are measured at IMR-Beijing; $\delta(^{34}S_{VCDT})$ and $\delta(^{33}S_{VCDT})$ are calculated; the repeatability is expressed as 1s standard deviation.

The sulfur electric current measurements must be converted to amount-of-substance measurements.

The sulfur amount-of-substance measurements on the SF_6 gas prepared from SO_2 were made on the Finnigan MAT 271 mass spectrometer as modified to IRMM requirements and now called "IRMM's amount comparator II" [10]. It is a special MAT-271 mass spectrometer with a molecular flow inlet system and single collector, operating with IRMM software. Over the years, this instrument led to highly improved measurements of SI-traceable isotope amount ratios and molar masses with associated measurement uncertainties of several elements (Si, Xe, Kr, C) [7,8,10,12,13].

The ion currents of $(^{32}SF_5)^+$, $(^{33}SF_5)^+$ and $(^{34}SF_5)^+$ at m/e positions = 127 to 129 in the mass spectrum and originating from the SF_6, are measured on a single Faraday collector. In gas mass spectrometry, the measured ion current ratios $I(^iSF_5)^+/I(^{32}SiF_5)^+$ are proportional to the corresponding amount-of-substance ratios $n(^iS)/n(^{32}S)$ in the sample, but not exactly equal to them: $n(^iS)/n(^{32}S) = K_{i/32}[I(^iSF_5)^+/I(^{32}SF_5)^+]$ with $i = 33$ or 34.

This conversion of the measured sulfur ion current ratios into sulfur amount-of-substance ratios (Table 3) is dominated by isotope fractionation during generation and transport of the ions. Mixtures of chemically pure and highly enriched sulfur isotopes [7–9] are used to determine the "overall" conversion factor K_{res} for the measured ion current ratios with a very small combined uncertainty (Table 3). Such isotope measurements result in the smallest combined uncertainty achievable, which give the measurements a "primary" character. Such measurement results establish "absolute", i.e., SI-traceable, amount ratios for sulfur and will turn the materials (SO_2 in this case) into an Isotope Reference Material needed for high-accuracy sulfur isotope abundance or sulfur isotope amount ratio measurements.

One portion of each of the two SO_2 gases (SO_2 from gas bottle 1 with code 84134 and SO_2 gas from gas bottle 2 with code 84863) was converted to Ag_2S as described in Section 2.1 of this paper.

From both Ag_2S portions, about 20 mg each, SF_6 gas was produced by conversion using BrF_5 (at IMR-Beijing). Four SF_6 gas samples obtained in this way were sent to IRMM-Geel in 0.25 in. glass ampoules for their measurements.

Via an in-house developed tube cracking system [14], the SF_6 gases were released in evacuated monel 400 ampoules, and connected to the mass spectrometer ("IRMM's amount comparator II") for measurement.

Table 3
Observed ion current ratios on prepared isotope amount ratios $R_{33/32}$ and $R_{34/32}$ for synthetic isotope mixture 1 (for details, see [7])

	$R_{33/32}$	$R_{34/32}$
Measured $I(^iSF_5)^+/I(^{32}SF_5)^+$	0.0078641 (12)	0.0441830 (10)
Prepared $n(^iS)/n(^{32}S)$	0.0078628 (44)	0.0441632 (18)
$K_{res} = [n(^iS)/n(^{32}S)]/[I(^iSF_5)^+/I(^{32}SF_5)^+]$	0.99983 (58)	0.999552 (47)

The resulting conversion factor K is given with combined uncertainties; they apply to the last two digits; $U = ku_c$ ($k = 1$).

Table 4
SO_2 from 'gas bottle 1' with code 84134 and SO_2 gas from 'gas bottle 2' with code 84863, converted to Ag_2S and further with BrF_5 to SF_6 gas (IMR-Beijing)

Ag_2S to SF_6 via the BrF_5 route	$I(^{33}SF_5)^+/I(^{32}SF_5)^+$	$I(^{34}SF_5)^+/I(^{32}SF_5)^+$
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 1 (code 84134)	0.0078869 (10)	0.0442791 (10)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 1 (code 84134)	0.0078859 (10)	0.0442784 (11)
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 2 (code 84863)	0.0078891 (11)	0.0442877 (11)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 2 (code 84863)	0.0078885 (10)	0.0442858 (10)

On the four SF_6 samples, the ion current ratios $I(^{33}SF_5)^+/I(^{32}SiF_5)^+$ and $I(^{34}SF_5)^+/I(^{32}SiF_5)^+$ were measured six times. The repeatability is indicated as 1s standard deviation and apply to the last two digits.

Table 5
Absolute isotope amount ratios (IRMM-Geel) for both SO_2 gas bottles ('bottle 1' with code 84134 and 'bottle 2' with code 84863), resulting from the products of the residual correction factors (Table 3) and the mean observed ion current ratios $I(^{33}SF_5)^+/I(^{32}SiF_5)^+$ and $I(^{34}SF_5)^+/I(^{32}SiF_5)^+$ measured on SF_6 gases obtained (Table 4) via the BrF_5 route (IMR-Beijing)

Ag_2S to SF_6 via the BrF_5 route	$n(^{33}S)/n(^{32}S)$	$n(^{34}S)/n(^{32}S)$
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 1 (code 84134)	0.0078856 (43)	0.0442593 (23)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 1 (code 84134)	0.0078846 (43)	0.0442586 (24)
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 2 (code 84863)	0.0078878 (43)	0.0442679 (24)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 2 (code 84863)	0.0078872 (43)	0.0442659 (23)

The combined uncertainties are given in brackets and apply to the last two digits; $U = ku_c$ ($k = 1$).

Table 6
SO_2 from 'gas bottle 1' with code 84134 and SO_2 gas from 'gas bottle 2' with code 84863, converted to Ag_2S (IMR-Beijing) and further converted with F_2 to SF_6 gas (IRMM-Geel)

Ag_2S to SF_6 via the F_2 route	$I(^{33}SF_5)^+/I(^{32}SF_5)^+$	$I(^{34}SF_5)^+/I(^{32}SF_5)^+$
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 1 (code 84134)	0.0078851 (11)	0.0442784 (10)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 1 (code 84134)	0.0078844 (12)	0.0442780 (08)
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 2 (code 84863)	0.0078880 (10)	0.0442862 (11)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 2 (code 84863)	0.0078874 (11)	0.0442869 (10)

On the four SF_6 gases the ion current ratios $I(^{33}SF_5)^+/I(^{32}SiF_5)^+$ and $I(^{34}SF_5)^+/I(^{32}SiF_5)^+$ are measured six times. The repeatability is indicated as 1s standard deviation and apply to the last two digits.

On all four SF_6 gas samples produced, the sulfur ion current ratios, $I(^{33}SF_5)^+/I(^{32}SiF_5)^+$ and $I(^{34}SF_5)^+/I(^{32}SiF_5)^+$ were measured (Table 4) as described in this paper and in references [7,8,10].

When applying the correction factors for residual errors from Table 3 to the observed ion current ratios in Table 4, SI-traceable sulfur isotope amount ratios for both SO_2 gases (bottles) can be obtained (Table 5): $n(^iS)/n(^{32}S) = K_{i/32}[I(^iSF_5)^+/I(^{32}SF_5)^+]$ with $i = 33$ or 34.

At IRMM-Geel, two samples of Ag_2S from each bottle were fluorinated to SF_6 gas by means of F_2 [12]. Each of the four obtained SF_6 gas samples was condensed into a monel 400 ampoule and connected to "IRMM's amount comparator II" for measurements of the sulfur ion current ratios, $I(^{33}SF_5)^+/I(^{32}SiF_5)^+$ and $I(^{34}SF_5)^+/I(^{32}SiF_5)^+$. On each of the four produced SF_6 gases, again six times the sulfur ion current ratios were measured (Table 6).

Within the combined uncertainties, $U = ku_c$ ($k = 1$), the different chemical conversions SO_2 to SF_6 gas, via the BrF_5 route or via the F_2, the sulfur isotope amount ratios $n(^{33}S)/n(^{32}S)$ and $n(^{34}S)/n(^{32}S)$ agree within measurement uncertainty for each of the two bottles (Tables 5 and 7). But in bottle 1, the sulfur amount ratios are slightly lower than the ones in bottle 2 (Tables 5, 7 and 9). This was also confirmed by the delta measurements (Tables 1 and 2), however, both gases are coming from the same production process.

The absolute sulfur amount ratios for bottles 1 and 2 were calculated from the respective results obtained via fluorination with BrF_5 and F_2 as given in Tables 5 and 7. The results are given in Table 8.

Table 7
Absolute isotope amount ratios (IRMM-Geel) for both SO_2 gas bottles ('bottle 1' with code 84134 and 'bottle 2' with code 84863), resulting from the products of residual correction factors (Table 3) and the mean observed ion current ratios $I(^{33}SF_5)^+/I(^{32}SiF_5)^+$ and $I(^{34}SF_5)^+/I(^{32}SiF_5)^+$ measured on SF_6 gases obtained (Table 6) now via the F_2 route (IRMM-Geel)

Ag_2S to SF_6 via the F_2 route	$n(^{33}S)/n(^{32}S)$	$n(^{34}S)/n(^{32}S)$
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 1 (code 84134)	0.0078838 (43)	0.0442586 (23)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 1 (code 84134)	0.0078831 (43)	0.0442582 (24)
Ag_2S to SF_6 (conversion 1) from SO_2 bottle 2 (code 84863)	0.0078867 (43)	0.0442664 (24)
Ag_2S to SF_6 (conversion 2) from SO_2 bottle 2 (code 84863)	0.0078861 (43)	0.0442671 (23)

The combined uncertainties are given in brackets and apply to the last two digits; $U = ku_c$ ($k = 1$).

Table 8
Absolute isotope amount ratios $n(^{33}S)/n(^{32}S)$ and $n(^{34}S)/n(^{32}S)$ for both SO_2 gas bottles ('bottle 1' with code 84134 and 'bottle 2' with code 84863)

Ag_2S to SF_6	$n(^{33}S)/n(^{32}S)$	$n(^{34}S)/n(^{32}S)$
SO_2 bottle 1 (code 84134)	0.0078843 (11)	0.0442587 (05)
SO_2 bottle 2 (code 84863)	0.0078873 (12)	0.0442668 (09)

The combined uncertainties are given in brackets and apply to the last two digits; $U = ku_c$ ($k = 1$).

Table 9
Absolute isotope amount-of-substance fractions $f(^iS)/f(S)$ and sulfur molar mass for both SO_2 gas bottles ('bottle 1' with code 84134 and 'bottle 2' with code 84863)

	SO_2 bottle 1 (code 84134)	SO_2 bottle 2 (code 84863)
$f(^{32}S)/f(S)$	0.9503056 (53)	0.9502956 (53)
$f(^{33}S)/f(S)$	0.00749250 (66)	0.00749527 (66)
$f(^{34}S)/f(S)$	0.04205929 (53)	0.04206655 (53)
$f(^{36}S)/f(S)$	0.0001426 (55)	0.0001425 (55)
$M(S)$ (g mol^{-1})	32.064070 (21)	32.064087 (21)

The combined uncertainties are given in brackets and apply to the last two digits; $U = ku_c$ ($k = 1$).

From Table 8 and applying the ISO/GUM [14,15] software, the sulfur amount fractions and their sulfur molar mass [16] can be calculated for both bottles 1 and 2 (Table 9).

4. Conclusion

Measuring SI-traceable ("absolute") isotope amount ratios is a measurement capability which exists at very few places world-wide. This work presents such measurements of the sulfur isotope amount ratios $n(^{33}S)/n(^{32}S)$ and $n(^{34}S)/n(^{32}S)$ in two SO_2 gases. These sulfur isotope amount ratios and the sulfur amount fractions, are SI-traceable because they are calibrated by Primary Measurement Standards consisting of synthetic isotope mixtures. They turn the SO_2 gases in Secondary Measurement Standards with values independent of human arbitrariness or consensus decisions. They can help to make the values of sulfur isotope measurement results traceable to the SI, thus offering the basis for a truly international sulfur measurement system.

Both SO_2 materials can now be used to anchor sulfur delta isotopic measurement scales to the international system of units SI. Further, both materials can serve as "anchors" to connect the VCDT relative δ-scale to a fixed absolute sulfur isotope amount scale. Differential sulfur isotope measurements on δ-scale can be performed easily with a precision of 0.1‰, but they can now be connected to an "absolute" sulfur isotope amount ratio scale.

These new Measurement Standards (previously called 'Isotope Reference Materials') enable to achieve comparability of sulfur isotope data and determination of their degree-of-equivalence.

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