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A primary isotopic gas standard for sulfur in the form of SF_6 with Système International d'Unités traceable values for isotopic composition and molar mass

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Abstract

A batch of SF_6 gas prepared by Messer (Germany) was metrologically certified for absolute isotope abundance ratios and molar mass (atomic weight) of sulfur following the ISO/BIPM Guide to the expression of uncertainties in measurements. The certification is based on the "Avogadro II Measurement Procedure" using the "Avogadro II amount comparator," which was developed in the framework of the redetermination of the Avogadro constant. For the correction of small remaining systematic effects of unknown nature, synthetic isotope mixtures of Ag_2S converted to SF_6 were used in order to obtain "calibrated" or "absolute" values with small combined uncertainty. The values for this sulfur primary isotopic gas standard (PIGS) are traceable to the Système International d'Unités (SI) in the shortest possible way and can therefore serve as a link to SI when used in differential measurements. The PIGS is now commercially available. (Int J Mass Spectrom 193 (1999) 1–8) © 1999 Elsevier Science B.V.

Keywords: Primary isotopic gas standard; Molar mass; Synthetic isotope mixtures; Isotopic composition; Gas isotope mass spectrometry; Isotope abundance ratio; Traceability; SI; Sulfur

1. Introduction

Variations of the sulfur isotopic composition in nature are well known and are related to the biological cycle, S-bearing gases of volcanoes, (present day and ancient) oceans, (recent and ancient) sediments, fuel mineral deposits, etc. [1]. For many applications in research or investigations of practical interest, the measurements of the absolute isotopic composition is not necessary: it is often sufficient to measure the relative differences in the isotope abundance ratio compared to a reference, e.g. the average isotopic composition. The δ (‰) notation is commonly used: it is the relative difference between an isotope abundance ratio in a sample material with respect to that in a reference material. It is calculated by δ (‰) $= [(R_{\text{sample}}/R_{\text{ref}}) - 1] \times 1000$, where R stands for the isotope abundance ratio concerned: e.g. $R = f(^{34}\text{S})/f(^{32}\text{S})$, where f is the isotope abundance.

In order to establish international comparability the measurement community agreed in 1962 on Canyon Diablo Troilite (CDT) as international reference material for the sulfur isotopic composition. However,

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after more than 30 years the CDT material was proven to be slightly inhomogeneous in the sulfur isotopic composition [2,3] and its availability became limited. This caused two problems with the consequence that the comparability of sulfur isotopic data generated by different laboratories was in danger. (1) The inhomogeneity limits the internal comparability of delta measurements of sulfur against CDT. (2) The comparability of measurement results in time is in danger because CDT serves as an artefact with limited availability and its absolute isotopic composition ($R_{34/32}$) is only based on a consensus—thus not a Système International d'Unités (SI) traceable—value. Whereas the first problem can not be solved anymore, it was proposed to overcome the second problem by establishing the link between CDT and a new reference material. The IAEA Advisory Group on Reference Materials proposed in 1993 to introduce a new V-CDT scale [4,5] fixed to a new reference material (IAEA-S-1) in form of Ag_2S distributed by the IAEA (Vienna). The proposal was accepted by CAWIA in 1995 [6]. Based on the mean of mass spectrometric measurements reported by 15 laboratories, the link between V-CDT and IAEA-S-1 was established by $^{34}\delta_{(\text{IAEA-S-1})} = -0.3‰$ versus CDT with an uncertainty of zero. Only 3 laboratories used the SF_6 route for their measurements [5], others measured on SO_2, a method which suffers more from adsorption and more critically where the variability of the oxygen isotopes needs to be taken into account.

2. Need for making a primary isotopic gas standard for sulfur

As long as the agreed reference material is stable, homogeneous and available, there is no need for absolute measurements in many applications. However, values for the isotope abundance ratios of the reference samples are not always stable in time and may be subject to new "consensus" agreements by the measurement community. Moreover, to establish comparability in time and space and independent of the actual agreed reference samples, the knowledge of the SI traceable absolute isotopic composition of a reference material for delta measurements is required. And finally without SI traceable absolute values the measurement community will be faced again with the second problem mentioned above when on one day IAEA-S-1 is exhausted.

With this in mind, IRMM decided not only to measure SI traceable values for the isotopic composition of IAEA-S-1, IAEA-S-2, IAEA-S-3 reference materials, two Chinese standards and to reassess the absolute values of V-CDT [7], but also to develop and metrological certify a Primary Isotopic Gas Standard (PIGS) for sulfur in the form of SF_6 with very small combined uncertainties on the absolute sulfur isotope abundance ratios ($R_{34/32}$ and for the very first time $R_{33/32}$), and to make this widely available for sulfur isotopic measurements as supplement to the existing solid (mainly Ag_2S) standards. Bottling of the PIGS was done by and at Messer (Duisburg, Germany) who ensures the distribution. SF_6 was chosen because already in 1978 by Rees as summarized in [1] pointed out that measurements on this gas are more precise and, more importantly, have the potential for smaller combined uncertainties than those obtained using SO_2, because its adsorption is much lower, its interaction with water is much smaller and fluorine is monoisotopic. It is likely that the significant differences between results reported for IAEA-S-1 by different laboratories are due to the CDT inhomogeneity and/or the use of different instruments and chemical procedures. As indicated previously, SF_6 is not in widespread use in the measurement community due to the potentially dangerous preparation methods. SO_2 is certainly an interesting PIGS candidate, bit starting with SO_2 would have meant to start with a more complicated system due to the variability of the oxygen isotopes. However, IRMM recently started the work on SO_2.

The approach of delta measurements to directly measure differences versus a reference sample by using a double inlet system (viscous leak) and double or multiple collectors is not applicable for absolute measurements as it relies on "reference samples" close to the isotopic composition under investigation—a visious circle. A basically different measurement procedure must be used. We chose the measure-

Table 1
Experimental and theoretical values for the "square-root-of-mass ratio"; combined uncertainties u_c are given in parentheses and apply to the last digit(s) of the values

	$({}^iM/{}^lM)^{1/2}$ as predicted by the kinetic gas theory	$({}^iM/{}^lM)^{\Phi}$ experimentally observed
$M({}^{33}SF_6)/M({}^{32}SF_6)$	1.003 42	1.003 47(89)
$M({}^{34}SF_6)/M({}^{32}SF_6)$	1.006 83	1.006 86(13)

ment procedure and instrument used in the framework of the redetermination of the Avogadro constant. It implies a single collector magnetic scanning approach and a molecular leak as described in [8–11]. Absolute isotope amount ratios of different elements have been measured at IRMM with small combined uncertainty [12–15]. For the metrological certification of the PIGS the measurement approach applying the Avogadro measurement procedure was verified with drastically reduced uncertainty by using two synthetic isotope mixtures of Ag_2S prepared and converted to SF_6 at IRMM [15]. The composition of the mixtures was close to the average of the natural sulfur isotopic composition.

The ISO/BIPM Guide on the expression of uncertainty in measurements [16] was followed in the metrological certification of the PIGS. The combined uncertainty on the measurement results for PIGS certification is very small, i.e. smaller or at least comparable to the precision of "differential" measurements.

3. Description of the primary isotopic gas standard for sulfur as SF_6, IRMM-PIGS-2010

The material for the primary isotopic gas standard is a SF_6 gas with a chemical purity of $x(SF_6) = n(SF_6)/n(\text{gas}) = 0.999\,999 \pm 0.000\,001$ from one homogenized batch supplied by Messer, Duisburg* (Germany). It is bottled in 1 L aluminum cans at a pressure of 1.2×10^6 Pa. Messer developed technological procedures to ensure minimum interaction between gas and inner walls of the containers. In order to avoid possible mass fractionation effects during sampling gas from the can, the latter is equipped with a specially developed (to prevent mass fractionation during sampling) valve (Messer article no. 795.08312).

4. Measurements of the sulfur isotope abundance ratios: the instrument used

The re-determination of the Avogadro constant [8–10] required high accurate silicon isotope abundance ratio measurements. The Si was converted into SiF_4 as gas source isotope mass spectrometry is highly developed. These measurements were performed using a Finnigan MAT 271 mass spectrometer modified at IRMM [8], and now customarily called the IRMM/MAT 271 mass spectrometer or "Avogadro II amount comparator." Its use has led to significantly improved measurements of isotope abundance ratios and molar masses of several elements (e.g. Si, Pt, Kr, and Xe).

In this instrument, as in any other gas mass spectrometer, adsorption is responsible for memory effects, which is particularly important when samples with very different isotopic composition are measured sequentially. Adsorption models for this particular instrument [17–19] have been recently developed. They allow to monitor and to predict adsorption and desorption coefficients as well as the associated isotope fractionation effects for flow rates through the molecular leak at the inlet of the spectrometer. These models have also been applied successfully to reduce the combined uncertainty of the "calibrated" measurement of the sulfur isotope abundance ratios of the PIGS by decreasing the uncertainty of the isotopic measurements of the highly enriched starting materials for the synthetic isotope mixtures (Table 2). It is important to note that sample cross contamination due to memory effects is an often underestimated source of uncertainty when measurements on highly enriched materials are performed alternately. Memory effects can persist for a (very) long time in a mass spectrom-

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eter, especially if resulting from isotopically different species of the same gas [19].

5. Measurements of the sulfur isotope abundance ratios: the measurement technique used

The ion currents from the isotopically distinct molecules of ${}^{i}SF_6$ were measured by magnetic-field scans directing the ion beam over a single Faraday cup. Then the mean ratios of the recorded ion currents at *m/z* 127 (${}^{32}SF_5^+$) to 131 (${}^{36}SF_5^+$) were calculated.

During the measurement, the sample in the expansion vessel of the spectrometer changes in its isotopic composition as a function of time because the effusion rate from the expansion vessel through the leak in the gold foil at the inlet of the spectrometer [17] is mass dependent. The gas effusion through the gold foil holes is very close to ideal molecular flow, as the pressure in the inlet system is about 0.55 Pa at a working temperature of 75 °C. The corresponding mean free path of molecules is about 0.01 m compared to the hole dimensions of 20 μm. The SF_6 gas flowing into the ion source has isotope abundance ratios $R_{i/32}$(flow) which is related to those of the gas in the inlet system $R_{i/32}$(inlet) through the well known relationship $R_{i/32}(\text{flow}) = R_{i/32}(\text{inlet}) \times ({}^{i}M/{}^{32}M)^{-1/2}$ where $R_{i/32} = n({}^{i}SF_6)/n({}^{32}SF_6)$ is the amount (abundance) ratio of the isotopic molecules with mass $M({}^{i}SF_6)$ and the isotopic molecules with mass $M({}^{32}SF_6)$. The superscript 32 is used for the molecule yielding the most abundant ion species in the mass spectrum, i.e. the one carrying the isotope ${}^{32}S$ ($M =$ 146 for ${}^{32}SF_6$, 147 for ${}^{33}SF_6$, 148 for ${}^{34}SF_6$, and 150 for ${}^{36}SF_6$).

Table 2
Measured isotope abundance fractions *f* of the isotopically enriched sulfur materials used for the preparation of synthetic isotope mixtures; combined uncertainties u_c are given in parentheses and apply to the last digit(s) of the values

	Enriched ${}^{32}S$	Enriched ${}^{33}S$	Enriched ${}^{34}S$
$f({}^{32}S)$	0.999 105 0(17)	0.046 495 1(18)	0.036 883 7(15)
$f({}^{33}S)$	0.000 481 6(14)	0.949 360 0(22)	0.000 453 3(4)
$f({}^{34}S)$	0.000 409 5(14)	0.004 134 8(11)	0.962 645 6(23)
$f({}^{36}S)$	0.000 003 9(7)	0.000 010 1(3)	0.000 017 4(18)

As the molecules containing the lighter isotope effuse at a higher rate through the molecular leak than those containing the heavier isotope, the gas remaining in the inlet system becomes progressively enriched in the heavier isotope. Thus, the desired initial isotope amount ratio in the gas sample is obtained by extrapolation of the logarithm of the measured isotopic ion current ratio values (between 5 min and 2 h) to time $t = 0$, i.e. to the time when the gas starts to flow into the ion source. The gas effusion can be represented as a first order reaction, where k_{Li} is the effusion kinetic constant of the molecular species containing the isotope *i* through the inlet system leak:

$$dn_i/dt = -k_{Li}n_i \tag{1}$$

hence

$$dn_i/n_i = -k_{Li}dt$$

thus

$$\ln(n_i/n_i^0) = \ln\,(I_i/I_i^0) = -k_{Li}dt \tag{2}$$

Eq. (2) can also be written for the most abundant isotope ${}^{32}S$:

$$\ln\,(n_{32}/n_{32}^0) = \ln\,(I_{32}/I_{32}^0) = -k_{L32}dt \tag{3}$$

By combining Eqs. (2) and (3), the relationship of the isotope amount ratio versus time is derived to be

$$\ln R_{i/32} = \ln R_{i/32}^0 + (k_{L32} - k_{Li})t \tag{4}$$

Eq. (4) provides the basis for obtaining the initial isotope amount ratio by linear extrapolation of ln $R_{i/32}$ to time $t = 0$.

Remembering Eq. (3), it can also be transformed into:

$$\begin{aligned}&[(\ln R_{i/32}/\ln R_{i/32}^0)/\ln\,(I_{32}/I_{32}^0)]\\&\quad = [(k_{Li} - k_{L32})/k_{L32}]\\&\quad = a_{i/32}^L - 1 = ({}^{32}M/{}^{i}M)^{1/2} - 1\end{aligned} \tag{5}$$

where $a_{i/32}^L = k_{Li}/k_{L32}$ is the isotope fractionation factor for effusion through the pinhole leak equal to $({}^{32}M/{}^{i}M)^{-\Phi}$.

Φ takes the value 1/2 if the gas flow through the

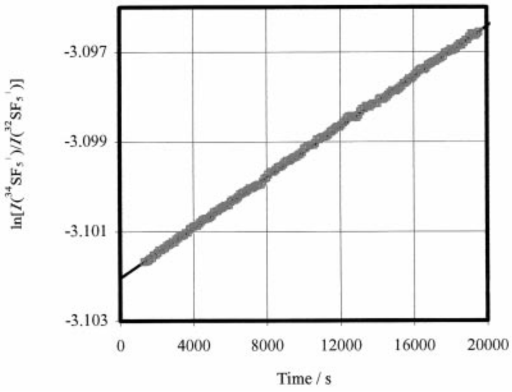

Fig. 1. By plotting $\ln(R_{i/1})$ vs. t [Eq. (4)] or $\ln(I_{32}/I_{32}^0)$ [Eq. (3)] a linear relationship is obtained, the slope of which yields an experimental value for the square root of the isotope mass ratio. Theoretical and experimental values are given in Table 1.

leak behaves strictly according to kinetic gas theory thus without any adsorption or other effects in the inlet system. These ideal conditions are well approached in the IRMM Avogadro II amount comparator [18]: plotting $\ln R_{i/32}$ versus t [Eq. (4)]. Applying Eq. (5) permits the calculation of $R_{i/32}$, and a linear relationship is obtained, the slope of which gives an experimental value for the a^L. As displayed in Fig. 1 and Table 1, the investigated SF_6 behaves as an ideal gas within the experimental uncertainty. It is important to note that this is monitored during the isotope abundance ratio measurement.

6. Verification of the measurement procedure with reduced uncertainty by measurements of synthetic mixtures of enriched sulfur isotopes

The Avogadro procedure is a measurement procedure, known to yield isotopic measurement results of high metrological quality [8–14]. Nevertheless, small residual systematic effects of unknown nature must be quantified. The introduction of a residual correction factor K_{res}(K_{res} = prepared amount ratio/observed amount ratio), needed to convert observed ratios into corrected ratios, enables to account for that. As a first approximation K_{res} and its uncertainty can be estimated on the basis of K factors measured earlier for other gases. However, this would be associated with a large uncertainty and is therefore not applicable for the certification of primary standards. Instead it was chosen to apply the Avogadro measurement procedure to synthetic isotope mixtures of Ag_2S, which were converted to SF_6, in order to verify and quantify the degree of understanding of the measurement process against the known values of the mixtures (based on gravimetric preparation), reaching a much reduced uncertainty. Moreover, this approach enables to investigate the dependence of K on the isotopes as well as on the size of the amount ratio concerned.

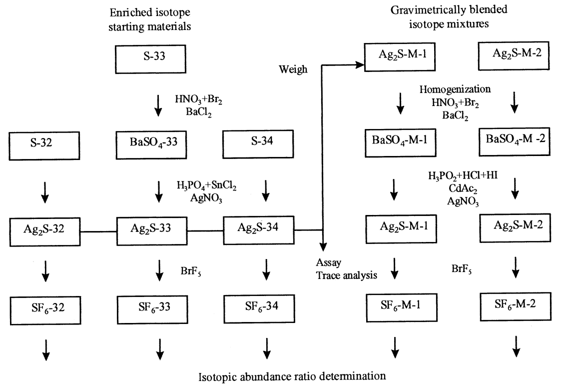

Fig. 2. Flow scheme for the preparation of synthetic sulfur isotope mixtures.

The preparation of the synthetic isotope mixtures and the conversion to SF_6 is described in detail elsewhere [15] and summarised as follows: A set of synthetic isotope mixtures for the calibration of measurements of sulfur isotope amount ratios and molar mass was gravimetrically prepared from high purity Ag_2S materials enriched in ^{32}S, ^{33}S, and ^{34}S. The mixtures had an isotopic composition such as to closely resemble the (natural) isotopic compositions of the materials to be measured. In order to meet both metrological and cost boundary conditions, the isotopically highly enriched starting materials (Table 2) have been chosen carefully. On the one hand, there is the need to prepare more than one mixture, using the three materials enriched in ^{32}S, ^{33}S, and ^{34}S. On the other hand, only small amounts can be prepared within the limitations of the availability of the materials. It was decided to prepare one mixture close to

Table 3
Uncertainty contributions on the isotope abundance fractions f for synthetic sulfur isotope mixture 1; combined uncertainties u_c are given in parentheses and apply to the last digit(s) of the values

Isotope abundances as calculated from mixing process		Uncertainty contribution in the seventh decimal from				
		Abundances of mixture components	Chemical purity	Stoichiometry	Weighing	Atomic masses
$f(^{32}S)$	0.950 546 8(23)	15	9.7	<0.01	14	0.98
$f(^{33}S)$	0.007 474 0(14)	13	1.5	<0.01	3.2	0.95
$f(^{34}S)$	0.041 949 1(16)	7.3	8.9	<0.01	11	0.90

natural sulfur isotopic composition where as in the second mixture the ratio of $n(^{33}S)/n(^{32}S)$ was lower. The scheme illustrated in Fig. 2 was followed.

A careful study [15,21] had shown that Ag_2S perfectly fulfills all the necessary requirements of a precursor material for the preparation of the synthetic sulfur isotope mixtures. It is stable, stoichiometric, and nonhygroscopic and can be weighed to determine the S content with high accuracy. It can be well characterised for impurities and the conversion to SF_6 can be performed quantitatively. The mass ratios of the precursor compounds (Ag_2S) are an excellent pathway to the isotope amount ratios, the quantity that is measured by gas isotope mass spectrometry. Gravimetry is a primary method of measurement that can yield results reliable to 10^{-4} relative [11,23]. The isotope amount ratios of the synthetic mixtures and their uncertainties were calculated using the IRMM Isotope Mixture Program SPIRIT, an algorithm based on the principle of calculating isotope amount ratios for a mixture from 2 or 3 isotopically enriched starting materials [20]. The required input data in the case of sulfur were the isotopic composition of the starting materials (Ag_2S), the masses of the mixture and the impurities of the starting materials and the associated uncertainties. Table 3 summarises for example the individual uncertainty contributions for one synthetic isotope mixtures, thus establishing a complete and conservative uncertainty budget. The values from Table 4 indicate, that the residual correction factor K_{res} for isotope amount ratio measurements of SF_6 is very close to unity within uncertainties of $u_c(K_{\text{res}}) = 0.000\,049$ for $n(^{34}S)/n(^{32}S)$ and $u_c(K_{\text{res}}) = 0.000\,24$ for $n(^{33}S)/n(^{32}S)$. This observation is consistent with the fact that SF_6 is a very inert gas having close to ideal gas behaviour. Moreover, the closeness of the values of K_{res} to unity indicates not only, that the measurement procedure is well understood, but in fact can be seen as measure for the "degree of imperfection" of the measurement. In addition, comparing values obtained using the Avogadro II measurement procedure including K_{res} as explained above with earlier (independent) work of one of the authors [21] show consistent results.

7. Primary isotopic gas standard IRMM-PIGS 2010: Measurement of the individual bottles

For studying the homogeneity, the mean ratio observed for each bottle ($n = 4$) was normalised to

Table 4
(a) Isotope amount ratios for mixture 1 as calculated from gravimetric preparation, (b) observed on the Avogadro II amount comparator, and (c) calculated correction factors $K_{\text{res}} = R_{\text{prep}}/R_{\text{obs}}$; Combined uncertainties u_c are given in parentheses and apply to the last digit(s) of the values

	(a) Isotope amount ratios as derived from the gravimetric preparation R_{prep}	(b) Observed amount ratios as measured by means of the Avogadro II amount comparator, R_{obs}	(c) Correction factor for residual systematic effects $K_{\text{res}} = R_{\text{prep}}/R_{\text{obs}}$
$n(^{33}S)/n(^{32}S)$	0.007 862 9(15)	0.007 862 5(12)	1.000 05(24)
$n(^{34}S)/n(^{32}S)$	0.044 163 2(18)	0.044 172 6(10)	0.999 786(49)

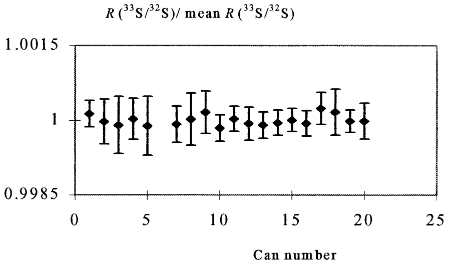

Fig. 3. Mean observed isotope amount ratios $R(^{33}S/^{32}S)$ for each can ($n = 4$) normalised to the mean isotope amount ratios observed for all cans ($n = 76$) with combined uncertainties ($U = ku_c$ with $k = 2$). The mean ratio for all cans was 1.000 00 ± 0.000 10. All cans and synthetic isotope mixtures were measured in the same series of tightly controlled measurements in a period of 11 days.

the mean ratio for all bottles and displayed in Figs. 3 and 4 for the ratios $n(^{33}S)/n(^{32}S)$ and $n(^{34}S)/n(^{32}S)$. The uncertainty $U = ku_c$ (with $k = 2$) indicated by the uncertainty bars are overlapping for the different bottles, thus no significant difference in the isotopic composition of the bottles could be found. Can 6 was found to be considerably contaminated with air. Since this affects the measurement precision can 6 was excluded.

From the observed ratios (Table 5) and the measured K_{res} factors (Table 4) the absolute isotope abundance ratios of the PIGS can be calculated and compared to the IUPAC selected best measurement [6] (Table 6). From the isotope abundance fractions, and using the tabulated atomic masses [22] the absolute isotopic composition and molar mass of sulfur in the PIGS was calculated (Table 7).

Table 5
Observed isotope abundance ratios for IRMM-PIGS-2010; combined uncertainties $U = ku_c$ (with $k = 1$) are given next to the digits where they apply; all bottles were measured four times, bottle 6 excluded as described in the text, $n = 76$

	Observed sulfur isotope abundance ratios for IRMM-PIGS-2010 using the Avogadro measurement procedure
$n(^{33}S)/n(^{32}S)$	0.007 945 31(90)
$n(^{34}S)/n(^{32}S)$	0.044 928 6(44)
$n(^{36}S)/n(^{32}S)$	0.000 157 0(50)

Table 6
Absolute sulfur isotope abundance ratios for IRMM-PIGS-2010 as obtained after applying K_{res} (from Table 4) determined by means of isotope sulfur synthetic mixture 1; uncertainties indicated for the PIGS are expanded uncertainties $U = ku_c$, where u_c is the combined uncertainty, with coverage factor $k = 3$ following the ISO/BIPM Guide to the expression of uncertainties in measurements [16]; the PIGS values are compared to the IUPAC selected "best measurement" of sulfur [6], $U = ku_c$ with $k = 2$

	Absolute isotope abundance ratios of IRMM-PIGS-2010 ($U = 3\ u_c$)	Isotope abundance ratio of the IUPAC selected best measurement of sulfur [6] ($U = 2\ u_c$)
$n(^{33}S)/n(^{32}S)$	0.007 945 7(63)	0.007 893(74)
$n(^{34}S)/n(^{32}S)$	0.044 928(17)	0.044 360(42)
$n(^{36}S)/n(^{32}S)$	0.000 15(2)	0.000 178(21)

8. Conclusions

A primary isotopic gas standard (IRMM-2010) for sulfur in the form of SF_6 was developed and metrological certified for absolute sulfur isotope abundance ratios with very small uncertainty. The measurement uncertainty was evaluated following the ISO/BIPM Guide on the expression of uncertainty in measurements. The existing Avogadro II measurement procedure was verified for SF_6 by using two gravimetrically prepared isotope mixtures of Ag_2S (with an isotopic composition close to the composition of the PIGS), which were converted to SF_6. This results in a drastically reduced uncertainty statement for the PIGS. The PIGS values are traceable to the SI along the shortest possible way and can serve as "primary standard" [23] as a link

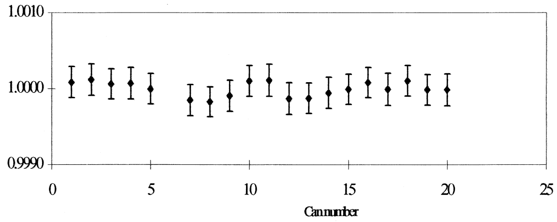

Fig. 4. Mean observed isotope amount ratios $R(^{34}S/^{32}S)$ for each can ($n = 4$) normalized to the mean isotope amount ratios $R(^{34}S/^{32}S)$ observed for all cans ($n = 76$) with combined uncertainty $U = ku_c$ (with $k = 2$). The mean ratio for all bottles was 0.999 99 ± 0.000 20.

Table 7
Absolute isotopic composition and molar mass M(S) (numerically equal to the atomic weight) of the sulfur in the primary isotopic gas standard IRMM-PIGS-2010; all uncertainties indicated are expanded uncertainties $U = ku_c$, where u_c is the combined uncertainty with a coverage factor $k = 3$; the sulfur atomic masses used in the calculation for the molar mass are taken from [22]

Isotope	Amount fraction	Mass fraction	Uncertainty
^{32}S	0.949 646	0.946 884	0.000 027
^{33}S	0.007 546	0.007 759	0.000 010
^{34}S	0.042 666	0.045 197	0.000 015
^{36}S	0.000 142	0.000 160	0.000 014
molar mass of 32.065 333 80			

to SI for differential isotope abundance ratio measurements of sulfur in e.g. geological, atmospheric and other samples. It was decided to make this Primary Isotopic Gas Standard commercially available as IRMM-PIGS-2010 via Messer. It is available in 1 L cans under a pressure of 1.2×10^6 Pa. IRMM-PIGS-2010 continues the existing PIGS series of Xe and Kr with a third element: sulfur as SF_6 [24].

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References

[1] H.R. Krouse, V.A. Grinenko, Stable Isotopes: Natural and Anthropogenic Sulfur in the Environment, Wiley, New York, 1991.
[2] M.L. Jensen, N. Nakai, NSF Symposium, 1962, pp. 30–35.
[3] G. Beaudoin, D. Taylor, D. Rumble, M. Thiemens, Proceedings of a Consultants Meeting, Vienna (A) 1–3 December, 1993, pp. 47 and 48.
[4] R. Gonfiantini, W. Stichler, K. Rozanski, Proceedings of a Consultants Meeting, Vienna (A) 1–3 December, 1993, pp. 13–30.
[5] B.W. Robinson, Proceedings of a Consultants Meeting, Vienna (A) 1–3 December, 1993, pp. 39–46.
[6] K.J.R. Rosman, P.D.P. Taylor, IUPAC–CAWIA, Isotopic Compositions of the Elements 1997, Pure Appl. Chem. 70 (1998) 217–235.
[7] T. Ding, S. Valkiers, H. Kipphardt, P.D.P. Taylor, P. De Bièvre, R. Gonfiantini, R. Krouse, unpublished.
[8] P. De Bièvre, S. Valkiers, Metrologia 31 (1994) 245–249.
[9] P. De Bièvre, S. Valkiers, F. Schaefer, H.S. Peiser, P. Seyfried, PTB Mitteil. 104 (1994) 225–236.
[10] P. De Bièvre, S. Valkiers, H.S. Peiser, P. Becker, F. Lüdicke, F. Spieweck, J. Stümpel, IEEE Trans. Instrum. Meas. 44 (1995) 530–532.
[11] P. De Bièvre, G. Lenaers, T.J. Murphy, H.S. Peiser, S. Valkiers, Metrologia 32 (1995) 103–110.
[12] Y. Aregbe, S. Valkiers, K. Mayer, P. De Bièvre, R.M. Wessel, A. Alink, Metrologia 35 (1998) 7–16.
[13] P. De Bièvre, S. Valkiers, H.S. Peiser, P. Hansen, P.D.P. Taylor, Metrologia 33 (1996) 447–455.
[14] S. Valkiers, Y. Aregbe, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. 173 (1998) 55–63.
[15] T. Ding, S. Valkiers, H. Kipphardt, P.D.P. Taylor, P. De Bièvre, unpublished.
[16] ISO, IEC, OIML, BIPM, Guide to the expression of uncertainty in measurement ISO Genève, 1992.
[17] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. Ion Processes 161 (1997) 15–26.
[18] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. Ion Processes 163 (1997) 207–219.
[19] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. Ion Processes 171 (1997) 231–242.
[20] F. Schaefer, Int. J. Mass Spectrom. Ion Processes 133 (1994) 65–71.
[21] T. Ding, R. Bai, Y. Li, D. Wang, X. Zou, Q. Zhang, Sci. China 42 (1999) 1.
[22] A.H. Wapstra, G. Audi, Nucl. Phys. A 565 (1993) 1.
[23] T.J. Quinn, Metrologia 37 (1997) 61–65.
[24] S. Valkiers, H. Kipphardt, R. Damen, P. De Bièvre, and P.D.P. Taylor. Poster presented at Conference of Spectroscopy in Theory and Practice, Bled, Slov., 11–15 April 1999.