International Journal of Mass Spectrometry 197 (2000) 131–137

Preparation of two synthetic isotope mixtures for the calibration of isotope amount ratio measurements of sulfur

T. Ding[a], S. Valkiers[b,*], H. Kipphardt[b], C. Quetel[b], P. De Bièvre[b], P.D.P. Taylor[b], R. Gonfiantini[c]

[a]*Institute of Mineral Deposits, CAGS, Beijing 100037, People's Republic of China*
[b]*Institute for Reference Materials and Measurements, EC-JRC, B-2440 Geel, Belgium*
[c]*Istituto di Geocronologia e Geochimica Isotopica del CNR, I-56127 Ghezzano, Pisa, Italy*

Received 27 July 1999; accepted 28 September 1999

Abstract

Two synthetic isotope mixtures for the calibration of sulfur isotope amount ratio measurements were gravimetrically prepared from high purity Ag_2S materials enriched in ^{32}S, ^{33}S, and ^{34}S. The mixtures were made so as to closely resemble the (natural) isotopic composition of the materials to be "calibrated". This allowed a totally independent evaluation, on the same samples, of the relative combined uncertainty of: (a) the procedure to perform direct measurements of the amount of substance ratios of gas isotopes in the redetermination of the Avogadro constant and (b) the gravimetric preparation procedure. The result of both procedures, mass spectrometry and gravimetry, agree to a relative uncertainty of 3×10^{-4} for sulfur amount ratio measurements of the major abundant isotopes. Thus it seems that a direct measurement of isotopic gas mixtures (e.g. of natural isotopic composition) is now possible for sulfur—and probably also for other gaseous isotopes—without necessarily having to rely on "calibration" by means of values provided by measurements of gravimetrically prepared isotope mixtures. However, synthetic mixtures may be needed for validation and verification purposes, in particular for quality assurance. (Int J Mass Spectrom 197 (2000) 131–137) © 2000 Elsevier Science B.V.

Keywords: Sulfur; Absolute isotope amount ratio; Synthetic isotope mixtures; Sulfur hexafluoride; Mass spectrometry

---

1. Introduction

Sulfur isotope geochemistry has been a particularly rewarding field of investigation because of the relatively large percentage mass difference between the two principal isotopes, the variety of chemical forms of sulfur, and their widespread occurrences in earth's lithosphere, hydrosphere, and atmosphere. Sulfur isotope geochemistry studies began in the late 1940s [1,2].

Sulfur isotope ratio studies have been concerned with such problems as isotope fractionation [3] in the biological sulfur cycle, the sulfur-bearing gases of volcanoes, the isotopic composition of present-day and ancient oceans, isotope distribution patterns in recent and ancient sediments and in coal and petroleum, the evolution of early life, and modes of formation and depositional histories of sulfide minerals.

Mass spectrometric techniques used for sulfur isotope amount measurements make the determination of differences in $^{34}S/^{32}S$ ratio samples more

---

* Corresponding author. E-mail: staf.valkiers@ping.be

1387-3806/00/$20.00 © 2000 Elsevier Science B.V. All rights reserved
PII S1387-3806(99)00235-3

precise than the determination of the absolute values of the ratios for their sample [4]. Using approximately 1 mg of sulfur, as sulfur dioxide, it is possible to compare samples with a precision on the order of 0.1‰ [5,6]. By means of inductively coupled plasma double focusing sector field mass spectrometry (ICP-SMS) sulfur isotope ratios could be determined at concentration levels down to 1 ng g^{-1} with precisions better than 0.1% [7,8], where as with quadrupole ICP-MS sulfur isotope ratios are difficult to determine due to interfering O_2^+ and NO^- molecular ions of high signal intensity at isotopes ^{32}S and ^{34}S [9].

The use of troilite from the Canyon Diablo meteorite (CDT) as a standard makes interlaboratory comparison [10] of results much easier than if a number of personal standards are used. However, after more than 30 years, the CDT material is virtually exhausted and no longer available for distribution to laboratories. To establish continuity of sulfur isotope measurements, the advisory group of IAEA on reference materials for stable isotope measurements [11], proposed a V-CDT scale, defined by a new reference material IAEA-S-1. The link between IAEA-S-1 and V-CDT, $\delta(^{34}S) = -0.3 \pm 0‰$ was obtained by evaluating differential measurement results from 15 laboratories all over the world [11]. This proposal was accepted by CAWIA in 1995 [12]. From that point in time it is recommended that all δ measurements of sulfur isotopic composition be reported vs. V-CDT be reported, i.e. in conventional notation

$$\delta(^{i}S)_{\text{V-CDT}}(‰) = \{[n(^{i}S)/n(^{j}S)]_{\text{sample}}/[n(^{i}S)/n(^{j}S)]_{\text{V-CDT}} - 1\} \times 10^3 \text{ (where } i = 33, 34, \text{ and } 36, \text{ and } j = 32)$$

To be independent of the consensus values for the link between IAEA-S-1 and V-CDT, calibrated "absolute" measurements of the $n(^{33}S)/n(^{32}S)$ and $n(^{34}S)/n(^{32}S)$ ratios are needed. Those measurements are traditionally called "absolute", when a precise comparison is made with two or more gravimetrically prepared synthetic isotope mixtures (in modern CCQM language: using gravimetry as a "primary method of measurements"). Such values would also "anchor" the (floating) δ scale for sulfur isotopic measurements.

Preliminary work on the calibration of the $n(^{32}S)n(^{34}S)$ amount ratio of IAEA-S-1 and V-CDT was done previously by Ding et al. [13] using synthetic isotope mixtures. The absolute $n(^{32}S)/n(^{34}S)$ amount of V-CDT obtained in their study was 22.649 6(60), much higher than the assigned ratio of 22.22 for CDT [10]. Since this big change would influence the isotopic composition of the internationally agreed sulfur standard by relatively 2%, an independent measurement is needed for verification. Moreover, the $n(^{32}S)/n(^{33}S)$ isotope amount ratio for the new conventional reference sample IAEA-S-1 has not been calibrated and therefore does not have an absolute basis. New synthetic isotope mixtures were gravimetrically prepared from high purity Ag_2S materials enriched in ^{32}S, ^{33}S, and ^{34}S. The Ag_2S mixtures were converted into SF_6. Measurements of the isotope amount ratios of the synthetic mixtures using the "Avogadro measurement procedure" [14,15] yielded independent values.

2. Experimental

2.1. The sulfur synthetic isotope mixtures

Since elemental sulfur has four stable isotopes: ^{32}S (94.93%), ^{33}S (0.76%), ^{34}S (4.26%), and ^{36}S (<0.015% abundant), it is essential to have at least two materials enriched in different sulfur isotopes. However, we decided to make mixtures of three isotopes in order to reduce the uncertainty on the measurement results. ^{36}S was not added because it was too expensive. These materials are only available in rather small amounts in the form of elemental sulfur. The elemental sulfur was converted to Ag_2S and then measured for chemical purity.

2.2. The preparation of Ag_2S

The material enriched in ^{32}S and ^{34}S was converted via H_2S to Ag_2S [16] (Table 1). The reduction of S to H_2S was performed by means of the reagent "KIBA"

Table 1
Specific experimental conditions for the preparation of Ag_2S from the starting materials

	$m(Ag_2S)$/g	V_1/L	V_2/L	V_3/L	$m(SnCl_2)$/g	$V(H_3PO_4)$/L
^{32}S	7.59	4	2	2	300	2
^{34}S	0.952	2	1	1	200	1
^{33}S	0.324 (as $BaSO_4$)	0.25	0.5	0.5	34	0.15

Table 2
Impurities (by ICP-MS: type VG Elemental PQ2+, Cheshire, England) in the isotopically enriched Ag_2S materials used in the preparation of the mixtures. The uncertainties are given in brackets and apply to the last two digits. $U = ku_c(k = 2)$

Impurity (μg/g)	$Ag_2{}^{32}S$	$Ag_2{}^{33}S$	$Ag_2{}^{34}S$
Mg	2.9 (1.1)	2.6 (1.0)	2.4 (0.9)
Al	4.1 (2.1)	3.9 (2.0)	3.9 (2.0)
Ti	2.1 (0.8)	2.1 (0.8)	2.2 (0.8)
Cr	0.34 (13)	0.34 (13)	0.30 (12)
Ni	4.5 (1.8)	4.6 (1.9)	4.1 (1.7)
Cu	0.22 (08)	1.08 (40)	0.41 (10)
Zn	27 (10)	1.7 (0.7)	21.7 (8.6)
As	0.87 (35)	3.0 (1.2)	5.6 (2.2)
Zr	0.65 (26)	1.5 (0.6)	1.0 (0.4)
Ba	0.43 (17)	0.45 (19)	0.43 (19)
Ir	0.43 (17)	0.68 (21)	0.66 (22)
Hg	1.0 (0.4)	0.87 (40)	1.1 (0.4)

($SnCl_2 + H_3PO_4$) at boiling temperature in glassware (V_1). The H_2S produced was carried by argon (30 mL/min) through two washing bottles (V_2 and V_3) filled with de-ionized water, into a glass beaker containing a $AgNO_3$ solution (3% w/w) in order to precipitate Ag_2S. Due to sublimation some of the sulfur was not completely converted. After complete precipitation of Ag_2S, the supernatant liquid was decanted. Warm NH_4OH solution was added to dissolve AgCl. Hot sub-boiling distilled water was added, and the solution was shaken to resettle the Ag_2S precipitate. Then the solution was decanted. This procedure was repeated 12 times in order to remove as many Cl^- and NO_3^- ions as possible. Ag_2S was transferred to a 50 mL beaker and dried in a vacuum oven at 70 °C.

In order to reduce the loss of ^{33}S material due to sublimation, it was first converted to $BaSO_4$. Therefore 49 mg of ^{33}S was placed into a 400 mL beaker. A small amount of sub-boiling distilled water was added, followed by the addition of concentrated HNO_3. The beaker was heated gently on a water bath and Br_2 solution was added dropwise until all sulfur had disappeared. Heating was continued to remove the excess Br_2 and HNO_3. When the volume of solution was reduced so that mainly H_2SO_4 remained, 5 mL of HCl were added three times to remove traces of HNO_3. Sub-boiling distilled water was then added to bring the volume of the solution up to 50 mL, before it was filtered through filter paper No. 587, then washed with sub-boiling distilled water to bring the volume up to 300 mL. The pH of the solution was adjusted to 6, and the solution boiled in a glass beaker. A boiling solution of 10% $BaCl_2$ (30 mol% in excess as required by H_2SO_4 present) was added. Boiling was continued for 45 min. The solution was filtered through filter paper No. 587 and the precipitate washed ten times with sub-boiling distilled water. The filter paper with $BaSO_4$ was put into a platinum crucible and ashed in a Muffle furnace, where the temperature was raised to 800 °C to remove all organic material. The yield of $BaSO_4$ was 98 ± 1%.

The chemical impurities were measured for all three materials. Results are listed in Table 2. Nonmetals such as Cl, O, and N have not been analyzed. However, this is only of minor importance because the calculation of the isotope amount ratios of the synthetic mixtures are only affected by the ratio of the impurities of the different starting materials. Because all three materials are processed in the same way and have the same chemical history, which means that their impurities are correlated, the absolute chemical purity is not needed. However the uncertainty of the impurity statement has a small but significant influence on the mixing ratio.

2.3. *The preparation of synthetic sulfur isotope mixtures*

The sulfur isotopic composition (Table 3) calculated from the first measurements of the isotope amount ratios of the starting materials with larger uncertainty, enables us to estimate the mass ratios of the different Ag_2S precursor compounds required to

Table 3
The mass abundances g of $Ag_2{}^{32}S$, $Ag_2{}^{33}S$, $Ag_2{}^{34}S$, and $Ag_2{}^{36}S$ (in %) in the different Ag_2S starting materials. The combined uncertainties are given in brackets and apply to the last two digits

Material	$g(Ag_2{}^{32}S)$/%	$g(Ag_2{}^{33}S)$/%	$g(Ag_2{}^{34}S)$/%	$g(Ag_2{}^{36}S)$/%
$Ag_2{}^{32}S$	99.906 40 (18)	0.049 66 (14)	0.043 505 (81)	0.000 435 (79)
$Ag_2{}^{33}S$	4.514 36 (17)	95.058 01 (22)	0.426 52 (11)	0.001 105 (34)
$Ag_2{}^{34}S$	3.479 24 (14)	0.044 095 4 (70)	96.474 82 (23)	0.001 85 (19)

bracket the natural isotopic amount ratios. Two synthetic isotope mixtures, M-1 and M-2, were prepared by mixing $Ag_2{}^{32}S$, $Ag_2{}^{33}S$, and $Ag_2{}^{34}S$ (according to Tables 4 and 5). M-1 closely resembles the natural sulfur isotope ratios. Because insufficient ^{33}S was available, the ratio of $n(^{33}S)/n(^{32}S)$ in M-2 was much lower than in natural sulfur.

Prior to weighing the precursor compounds were heated 2 h at 70 °C in a vacuum oven, and then allowed to cool in a desiccator at room temperature. The weighings were done at the IRMM Mass Metrology Laboratory. A Mettler electronic single plate balance was used for weighing. Standard weights were used for checking the accuracy of the balance. Substitution weighing was used for measuring the mass of the samples. Immediately after the weighing, the enriched isotope samples were put together and the materials isotopically homogenized by converting them to $BaSO_4$ [13,17] and then back to Ag_2S [16].

2.4. The preparation of SF_6

Subsamples of all Ag_2S materials were converted to SF_6 by reacting them with BrF_5 in vacuum at 320 ± 20 °C which is described in detail in [17]:

$$Ag_2S + BrF_5 = 2\,AgF + 4\,BrF_3 + SF_6$$

Table 4
The masses m of different Ag_2S starting materials used for the preparation of the isotope mixtures. The combined uncertainties are given in brackets and apply to the last digit

	M-1 (m/mg)	M-2 (m/mg)
$Ag_2{}^{32}S$	17 374.7 (5)	18 635.9 (5)
$Ag_2{}^{33}S$	135.395 (5)	39.790 (5)
$Ag_2{}^{34}S$	796.16 (2)	797.94 (2)

The amount of Ag_2S used in each fluorination was 20 μmol. Ag_2S was weighed in a small box made from Al foil, then placed in a nickel reaction vessel and brought under vacuum. BrF_5 purified by a tenfold distillation was condensed into the reaction vessel by freezing with liquid nitrogen. Then the reaction vessel was heated to 320 ± 20 °C for about 14 h. After completion of the reaction, SF_6 gas produced was separated by twofold fractional distillation (liquid nitrogen and dry-ice/acetone), followed by fine purification using via gas chromatography. Based on the experience described in [13,17] a gas chromatograph from Interscience type 8000^{TOP} with a 2 m long and 6 mm diameter column packed with Poropack A (80–100 mesh) was used. No indication for cross-contamination was found if processing one sample just for conditioning. For every material 4 × 2 samples have been converted and no significant differences between the individual samples have been found.

2.5. The "Avogadro II measurement procedure"

All sulfur isotope amount ratio measurements were performed using the "Avogadro II amount comparator" and the "Avogadro II measurement procedure" [15,18,19]. The instrument was built by Finnigan MAT as "MAT 271" and further developed at IRMM for the purpose of making high accuracy isotope ratio measurements on SiF_4 in order to deliver improved values for the molar mass of silicon in the framework of the redetermination of the Avogadro constant [14]. Gravimetric mixtures of isotopically enriched silicon had been prepared to assess the performance of the measurement procedure and software, leading to ratio measurements with a combined uncertainty of 10^{-5}

Table 5
The amount abundances f of ^{32}S, ^{33}S, ^{34}S, ^{36}S in enriched Ag_2S materials enriched in ^{32}S, ^{33}S and ^{34}S. $U = ku_c$ with $k = 1$

Sample	$f(^{32}S)$/(%)	$f(^{332}S)$/(%)	$f(^{34}S)$/(%)	$f(^{36}S)$/(%)
$Ag_2{}^{32}S$	99.910 51 (17)	0.048 16 (14)	0.040 950 (76)	0.000 387 (70)
$Ag_2{}^{33}S$	4.649 50 (18)	94.936 01 (22)	0.413 48 (11)	0.001 012 (31)
$Ag_2{}^{34}S$	3.688 37 (15)	0.045 328 9 (72)	96.264 56 (23)	0.001 74 (18)

relative for $n(^{i}Si)/n(^{28}Si)$ ratios. The "Avogadro measurement procedure" led to a significant improvement of the absolute amount of ratio and molar mass values of silicon. Absolute ratio measurements of xenon [20] and krypton [18] have been made recently using the same procedure (inlet system control, software, mass spectrometric measurement, data acquisition, treatment, and synthetic isotope mixtures).

During the isotope amount ratio measurement "observed square-root-of-mass ratios" (Table 6) can be compared against theoretical values obtained from kinetic gas theory [14,15,18,20]. The experimental verification of any deviations (i.e., possible isobaric effects) from theoretical values of the effusion fractionation factor is a powerful tool to measure the "degree of imperfection" of the Avogadro measurement procedure.

The isotope amount ratio measurements of sulfur in SF_6 gas were carried out in a scheme applying symmetrical scanning to eliminate short time effects. Within one measurement cycle the magnetic field was varied from the lowest mass position ($^{32}SF_5^+$) to the highest position ($^{36}SF_5^+$) and vice versa. One measurement cycle consisted of 15 scans with an integration time of 8 s in the measurement of each ion current as well as a delay time of 8 s between measurements of the ion currents.

Usually a set of measurements on one sample consisted of six measurement cycles. In addition, long duration measurements of more than 20 h were performed to investigate specific measurement parameters in more detail. For every cycle the logarithmically extrapolated observed values of the mean ion-current ratios J and corresponding uncertainties were calculated and printed out as a function of time t. This enables us to calculate the mean ion-current ratio value at time $t = t_0$, the moment when the gas is allowed to enter the mass spectrometer, with its uncertainty. These values are listed for two synthetic mixtures in Table 7.

Table 6
Experimental versus theoretical values for the "square-root-of-mass-ratio" as predicted by KGT (kinetic gas theory). $U = ku_c(k = 1)$

Ratio	$\alpha = (^{i}M/^{j}M)^{1/2}$ as predicted from kinetic gas theory	α^L experimentally observed (from M-1 and M-2)
$^{33}SF_6/^{32}SF_6$	1.003 42	1.003 47 (89)
$^{34}SF_6/^{32}SF_6$	1.006 83	1.006 86 (13)

3. Results and discussion

The isotope amount ratios of the synthetic isotope mixtures and their uncertainties were calculated using the IRMM isotope mixture program SPIRIT [21]. This algorithm is based on the principle of calculating isotope amount ratios for a mixture from two or three isotopically enriched starting materials. The required input data in the case of sulfur were the isotopic composition of the starting materials (Ag_2S), the masses of the mixture components, and the impurities of the starting materials all with stated uncertainties and correlations.

Table 8 gives a summary of calculated isotope amount ratios with all uncertainty components

Table 7
The observed $J(^{33}S/^{32}S)$ and $J(^{34}S/^{32}S)$ ratios of M-1 and M-2. $U = ku_c(k = 1)$

Sample	$J(^{33}S/^{32}S)$	$J(^{34}S/^{32}S)$	Number of measurements
M-1	0.007 862 5 (12)	0.044 172 6 (10)	9
M-2	0.002 515 8 (6)	0.041 297 8 (11)	9

Table 8
Calculated isotope amount ratios of synthetic isotope mixtures of sulfur with uncertainty contribution. $U = ku_c$ with $k = 1$

Calculated isotope amount ratio		10^{-6} times uncertainty contribution				
		U	Due to isotope amount ratio measurement of mixture component	Due to measurement of the chemical purity	Due to weighing	Due to the atomic masses [25]
M-1	$n(^{33}S)/n(^{32}S)$ 0.007 862 9	1.5	1.4	0.16	0.34	0.01
	$n(^{34}S)/n(^{32}S)$ 0.044 163 2	1.8	0.80	0.98	1.30	0.01
M-2	$n(^{33}S)/n(^{32}S)$ 0.002 518 9	1.4	1.38	0.05	0.34	0.01
	$n(^{34}S)/n(^{32}S)$ 0.041 287 3	1.6	0.79	0.91	1.30	0.01

[21,23], thus establishing a complete and fully orthodox uncertainty budget.

The ion-current ratios of different Ag_2S starting materials used in the preparation of the isotope mixtures are listed in Table 9.

Although the direct measurement procedure used (“Avogadro procedure”) is capable of yielding isotope amount ratios of high metrological quality [15], small residual systematic effects of unknown origin need to be quantified. The conversion of the observed ion-current ratio into the isotope amount ratio R can be described by the following formalism:

$$
\begin{aligned}
R_{(ij)} &= n(^{i}E)/n(^{j}E) \\
&= [K_{\mathrm{mad}}(^{i}E)/K_{\mathrm{mad}}(^{j}E)] \times [K_{\mathrm{ion}}(^{i}E)/K_{\mathrm{ion}}(^{j}E)] \\
&\quad \times [\boldsymbol{K}_{\mathbf{res}}(^{\boldsymbol{i}}\boldsymbol{E})/\boldsymbol{K}_{\mathbf{res}}(^{\boldsymbol{j}}\boldsymbol{E})] \times [I(^{i}E)/I(^{j}E)]
\end{aligned}
$$

where

$K_{\mathrm{mad}}(^{i}E)/K_{\mathrm{mad}}(^{j}E)$ = accounting for mass fractionation at the inlet system (which can be derived from kinetic gas theory, effusion, and adsorption/desorption effects,

$K_{\mathrm{ion}}(^{i}E)/K_{\mathrm{ion}}(^{j}E)$ = accounting for different ionisation probabilities of different isotopic species (assumed equal to unity with 10^{-6} rel. uncertainty)

$\boldsymbol{K}_{\mathbf{res}}(^{\boldsymbol{i}}\boldsymbol{E})/\boldsymbol{K}_{\mathbf{res}}(^{\boldsymbol{j}}\boldsymbol{E})$ + residual conversion factor obtained from the synthetic isotope mixtures (i.e. comparing observed ion-current ratio and prepared isotope amount ratio values).

Values for $\mathbf{K}_{\mathbf{res}}$ are summarized in Table 10. They are very close to unity.

4. Conclusion

Two synthetic isotope mixtures for the calibration of measurements of sulfur isotope amount ratios and molar mass were gravimetrically prepared from high purity Ag_2S materials enriched in ^{32}S, ^{33}S, and ^{34}S.

The isotopic compositions of mixtures were made to closely resemble that of “natural” material. The combined uncertainties were estimated according to the ISO/BIPM Guide on Expression of Uncertainty in Measurement [22].

Table 9
The observed $I(^{33}S)/I(^{32}S)$, $I(^{34}S)/I(^{32}S)$, $I(^{36}S)/I(^{32}S)$ ratios in enriched Ag_2S materials ^{32}S, ^{33}S, and ^{34}S. $U = ku_c$ with $k = 1$

Sample	$I(^{33}S)/I(^{32}S)$	$I(^{34}S)/I(^{32}S)$	$I(^{36}S)/I(^{32}S)$
$Ag_2{}^{32}S$	0.000 482 0 (14)	0.000 409 87 (46)	0.000 003 87 (70)
$Ag_2{}^{33}S$	20.418 54 (82)	0.088 930 (23)	0.000 217 6 (66)
$Ag_2{}^{34}S$	0.012 289 7 (19)	26.099 5 (11)	0.000 472 (48)

Table 10
Residual correction factor obtained from the mixture (i.e. comparing observed ion current ratios and prepared isotope amount ratios). $U = k.\ u_c(k = 1)$

Ratio	Correction factor K_{res} = prepared amount ratio/measured amount ratio	
	M-1	M-2
$n(^{33}S)/n(^{32}S)$	1.000 04 (24)	1.000 91 (62)
$n(^{34}S)/n(^{32}S)$	0.999 782 (46)	0.999 745 (48)

The conversion for residual systematic effects of unknown origin in the SF_6 measurements are very close to unity within a stated uncertainty of ±0.000 048 for $n(^{34}S)/n(^{32}S)$ and ±0.000 62 for $n(^{33}S)/n(^{32}S)$. This observation is consistent with the fact that SF_6 has close to ideal gas behavior. On that basis a primary isotopic gas standard [21,23] has been certified and “calibrated” measurements performed on the IAEA sulfur isotope reference materials as well as the two Chinese National Standards [24].

Acknowledgements

We wish to thank the International Atomic Energy Agency (IAEA) for providing Tiping Ding with an IAEA fellowship during the period of this study at IRMM. We would also like to thank F. Hendrickx from mass metrology for his help in weighing the starting materials when making synthetic mixtures. The kind help from Paul Vercammen (Belgian Valve and Fittings, Zaventem), D. Vendelbo, P. Hansen, R. Damen, and G. Van Baelen in construction of sample preparation line and maintenance of the amount comparator is warmly acknowledged.

References

[1] H.G. Thode, J. McNamara, C.B. Collins, Can. J. Res. B27 (1949) 361.
[2] A. Trofimov, Dokl. Akad. Nauk. SSSR 66 (1949) 181.
[3] H.R. Krouse, V.A. Grinenko, Stable Isotopes: Natural and Anthropogenic Sulfur in the Environment, Wiley, New York (1991).
[4] J. McNamara, H.G. Thode, Phys. Rev. 78 (1950) 307.
[5] C.E. Rees, Geochim. Cosmochim. Acta 42 (1978) 383.
[6] C.R. McKinney, J.M. McCrea, S. Epstein, H.A. Allen, H.C. Urey, Rev. Sci. Instrum. 21 (1950) 724.
[7] T. Prohaska, C. Latkoczy, G. Stingeder, J. Anal. At. Spectrom. 14 (1999) 1501.
[8] F. Vanhaecke, L. Moens, R. Dams, Anal. Chem. 68 (1996) 567.
[9] P. Mason, K. Kaspers, M. Van Bergen, J. Anal. At. Spectrom. 14 (1999) 1067.
[10] M.L. Jensen, N. Nakai, Sulfur isotope meteorite standards, results and recommendations. Biogeochemistry of Sulfur Isotopes, NSF Symp. (1962) 30.
[11] B.W. Robinson, Sulfur isotope standards. Reference and intercomparison materials for stable isotopes of light elements; as cited in R. Gonfiantini, W. Stichler, K. Rozanski, Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements. Reference and intercomparison materials for stable isotopes of light elements. Proceedings of a consultants meeting held in Vienna, 1–3 December (1993) 13–30.
[12] Commission on Atomic Weights and Isotopic Abundances, Pure Appl. Chem. 70 (1998) 217.
[13] T. Ding, R. Bai, Y. Li, D. Wan, X. Zou, Q. Zhang, Sci. China D.42 (1999) 45.
[14] P. De Bievre, S. Valkiers, F. Schaefer, H.S. Peiser, P. Seyfried, PTB Mitteil. 104 (1994) 225.
[15] P. De Bievre, S. Valkiers, H.S. Peiser, P. Hansen, P.D.P. Taylor, Metrologia 33 (1996) 447.
[16] S. Valkiers, H. Kipphardt, T. Ding, R. Damen, P.D.P. Taylor, P. De Bievre, Int. J. Mass Spectrom 193 (1999) 1.
[17] T. Ding, H. Li, G. Zhang, Y. Li, J. Li, A study on determining $^{33}S/^{32}S$, $^{34}S/^{32}S$ and $^{36}S/^{32}S$ ratios by using SF_6 method. In Certified Reference Materials, Proceedings of ISCRM’89, International Academic, 1989, pp. 292–297.
[18] S. Valkiers, Y. Aregbe, H. Kipphardt, P.D.P. Taylor, P. De Bievre, unpublished.
[19] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. De Bievre, Int. J. Mass Spectrom. 171 (1997) 231.
[20] S. Valkiers, Y. Aregbe, P.D.P. Taylor, P. De Bievre, Int. J. Mass Spectrom. Ion Processes 173 (1998) 55.
[21] F. Schaefer, Int. J. Mass Spectrom. Ion Processes 161 (1997) 15.
[22] ISO, IEC, OIML, BIPM, Guide to the Expression of Uncertainty in Measurement, ISO, Geneva 1992.
[23] S. Valkiers, H. Kipphardt, P.D.P. Taylor, P. De Bievre, A primary isotopic gas standard (PIGS) for sulfur, 5th Symposium on Food Authenticity, La Baule, France, June 9–11, 1999.
[24] T. Ding, S. Valkiers, H. Kipphardt, P.D.P. Taylor, P. De Bievre, R. Gonfiantini, R. Krouse, unpublished.
[25] G. Audi, A.H. Wapstra, Nucl. Phys. A 565 (1993) 1.