Stable isotope primary reference gas mixtures for determination of SI traceable isotope ratio of international reference materials

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GAWG/IRWG Workshop: Developments in Isotope Ratio Measurements METAS, Berne, Switzerland October 10, 2019



SI traceable standard gas mixtures for isotope ratio measurements

Necessity of absolute isotope ratio measurements

- Delta value isotope ratio measurements
 - cannot presently be made traceable to the SI
 - should be made traceable to materials recognized as international standards
- These materials are not listed in the Appendix C of the BIPM database
 - since at present, the values assigned to these reference materials are based on consensus values
- The CIPM encourages
 - the continuation of programmes within the NMIs to develop absolute isotope ratio measurement values for such Reference Materials
 - active engagement with the IUPAC community



SI traceable standard gas mixtures for isotope ratio measurements

Absolute isotope ratio measurements in KRISS

- Atmospheric Ar
 - Redetermination of isotopic abundance of atmospheric Ar
 - : Lee et al, GCA, 70 (2006) 4507, adopted by IUPAC 2009
 - Contribution to acoustic determination of $k_{\rm B}$
 - : Yang et al, Metrologia, 52 (2015) S394
- Atmospheric N₂
 - Redetermination of atomic weight of atmospheric N_2
 - : Yang et al, under preparation to publish
- Pure Ne
 - Measurements of isotopic compositions of 3 pure Ne
 - : Yang et al, Int. J. Thermophys., 36 (2015) 2072, contributed to ITS-90
 - Measurements of atomic weights of 7 pure Ne by gas chromatograph
 - : Kim et al, under preparation to publish



Isotopic abundance and molar mass of Ar



Available online at www.sciencedirect.com

Geochimica

Geochimica et Cosmochimica Acta 70 (2006) 4507-4512

www.elsevier.com/locate/gca

A redetermination of the isotopic abundances of atmospheric Ar

ScienceDirect

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Received 10 October 2005; accepted in revised form 29 June 2006

Abstract

Atmospheric argon measured on a dynamically operated mass spectrometer with an ion source magnet, indicated systematically larger $^{+0}Mr^{10}Ar$ ratios compared to the generally accepted value of Nico N. A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium. *Phys. Rev.* **77**, 789–7931 295 5 \pm 05, which has served as the standard for all isotopic measurements in geochemistry and cosmochemistry. Gravimetrically larger of highly enriced ^{+0}Ar and ^{+0}Ar were utilized to redetermine the isotopic abundances of atmospheric Ar, using a dynamically operated isotope ratio mass spectrometer with minor modifications and special gas handling techniques to avoid fractionation. A new ratio $^{+0}Ar/r^{0}Ar$ and ^{-0}Ar (^{+0}Ar) and ^{-0}Ar is precision of 0.1%, approximately 1% higher than the previously accepted value. Combined with the $^{+0}Ar/r^{0}Ar$ (^{+0}Ar) ^{-0}Ar (^{-0}Ar) determined with a VG5400 noble gas mass spectrometer in static operation, the prevent abundances of ^{+0}Ar , ^{+0}Ar , ^{-0}Ar (^{-0}Ar) ^{-0}Ar = 0.5336 ± 0.0004, 0.0529 ± 0.0004, respectively. We calculate an atomic mass of Ar of 39.478 ± 0.0002. Accurate Ar isotopic abundances are relevant in numerous applications, as the calibration of the mass spectrometer instance of the mass spectrometer instance of the spectral determined to be applications are relevant in numerous applications, as the calibration of the mass spectrometer instance of the spectral determined to be applications are relevant in numerous applications, as the calibration of the mass spectrometer instance of the spectral determined to be applications of the mass spectrometer instance of the spectral determined to be applications of the mass spectrometer instance of the spectral determined to be applied to the spectral determin

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IOP Publishing | Bureau International des Poids et Mesures

Metrologia 52 (2015) S394-S409

doi:10.1088/0026-1394/52/5/S394

Matrologia

Improving acoustic determinations of the Boltzmann constant with mass spectrometer measurements of the molar mass of argon

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Received 20 April 2015, revised 24 July 2015 Accepted for publication 14 August 2015 Published 30 September 2015



Abstract

We determined accurate values of ratios among the average molar masses MAr of 9 argon samples using two completely-independent techniques: (1) mass spectrometry and (2) measured ratios of acoustic resonance frequencies. The two techniques yielded mutually consistent ratios (RMS deviation of $0.16 \times 10^{-6} M_{At}$ from the expected correlation) for the 9 samples of highly-purified, commercially-purchased argon with values of $M_{\rm Ar}$ spanning a range of 2 \times 10⁻⁶ M_{Ar}. Among the 9 argon samples, two were traceable to recent, accurate, argon-based measurements of the Boltzmann constant k_R using primary acoustic gas thermometers (AGT). Additionally we determined our absolute values of M_{Ar} traceable to two, completely-independent, isotopic-reference standards; one standard was prepared gravimetrically at KRISS in 2006; the other standard was isotopically-enriched 40Ar that was used during NIST's 1988 measurement of k_B and was sent to NIM for this research. The absolute values of MAI determined using the KRISS standard have the relative standard uncertainty $u_t(M_{Ax}) = 0.70 \times 10^{-6}$ (Uncertainties here are one standard uncertainty.); they agree with values of $M_{A_{A}}$ determined at NIM using an AGT within the uncertainty of the comparison $u_t(M_{At}) = 0.93 \times 10^{-6}$. If our measurements of M_{At} are accepted, the difference between two, recent, argon-based, AGT measurements of k_B decreases from $(2.77 \pm 1.43) \times 10^{-6} k_B$ to $(0.16 \pm 1.28) \times 10^{-6} k_B$. This decrease enables the calculation of a meaningful, weighted average value of $k_{\rm B}$ with a uncertainty $u_{\rm r}(k_{\rm B}) \approx 0.6 \times 10^{-6}$.



Isotopic abundance of atmospheric Ar

Isotope ratio of atmospheric Ar

Isotope ratio	A. O. Nier (1950)	Lee <i>et al</i> (2006)
⁴⁰ Ar/ ³⁶ Ar	295.5 ± 0.5	298.56 ± 0.31
³⁸ Ar/ ³⁶ Ar	0.1880 ± 0.0003	0.1885 ± 0.0003

Gravimetric method: preparation of Ar isotopic mixtures according to ISO 6142 (2001) Automatic weighing system: electronic mass-comparators

Mettler Toledo AX1005

- 1.1 kg capacity
- 0.01 mg resolution





Mettler Toledo XP10003S - 10.1 kg capacity

- 1 mg resolution

Lee et al, Geochim. Cosmochimica Acta, 70 (2006) 4507



Isotopic abundance of atmospheric Ar

Mass spectrometer in KRISS



- Finnigan MAT 271 mass spectrometer
- Works for all mass/charge ratio
- Good linearity (works for dynamic range of 5.5 decade)
- Moderate repeatability

"Partial pressure" machine



Acoustic determination of $k_{\rm B}$ and molar mass of Ar



Measured k is proportional to M, molar mass of thermometric gas. Thus, u(M) directly adds into $u(k_B)$



The u(k)'s in argon-based measurements, except for NIST-88, are based on uncertainty assigned at KRISS, $u_r(M) =$ 0.7×10^{-6}

Note:
$$u_r(k_{CODATA-2014}) = 0.57 \times 10^{-6}$$

Yang et al, Metrologia, 52 (2015) S394



Absolute isotope ratio measurement – N₂

Atomic weight of atmospheric N₂

Atomic weight of the elements [IUPAC report]





Mass discrimination factor

- Mass discrimination factor, f_{MD}
 - Conversion of isotopic signal ratio to true isotope ratio in mass spectrometry
 - Mass dependent property from various origins [Wood et al., 1978; De Laeter, 2001]
 - : Inlet system, ionization source, ion beam filter, detector, and so on
 - Calculation of f_{MD} using isotope reference mixture

 $f_{\rm MD} = \left[\frac{\mathsf{R}(i/j)_{\rm ref}}{\mathsf{r}(i/j)_{\rm ref}} - 1\right] \div \Delta m \times 100 \qquad \begin{bmatrix}\mathsf{R}(i/j)_{\rm ref} : \text{Real isotope ratio of reference mixture}\\ r(i/j)_{\rm ref} : \text{Isotope signal ratio of reference mixture}\\ \Delta m : \text{Mass difference between two isotopes, } i \text{ and } j (i>j) \end{bmatrix}$

> Δm : Reflection of mass dependent property of f_{MD}



Calculation of true isotope ratio of sample

$$\mathsf{R}(i/j)_{\mathsf{sample}} = \left[\frac{f_{\mathsf{MD}}}{100} \times \Delta m + 1\right] \times \mathsf{r}(i/j)_{\mathsf{sample}} \quad \left[\begin{array}{c} \mathsf{R}(i/j)_{\mathsf{ref}} : \mathsf{Real isotope ratio of sample} \\ \mathsf{r}(i/j)_{\mathsf{ref}} : \mathsf{Isotope signal ratio of sample} \end{array} \right]$$

- N₂ isotope reference mixtures
- Preparation of artificial isotope reference mixtures
 - Gravimetry : Primary method for preparation of gas mixtures [ISO-6142, 2001]
 - Calibration of f_{MD} for absolute isotope ratio measurement





Preparation of air samples

Collection of dry air samples

- Different locations, free of local pollution sources (WMO GAW network)
 - > Niwot Ridge (USA), 2001 (by NOAA)
 - > Jeju Island (Korea), 2007 & 2014
 - Anmyeon Island (Korea), 2011



Elimination of interfering gas species in air samples

- Interference components on nitrogen isotope ratio (m/z 28, 29, and 30)
 - > O₂ : 2nd abundant constituent of air, produce of CO and NO at EI source
 - > CO₂ : Constituent of air, which produce CO by fragmentation at EI source
 - Hydrocarbons : Contaminant by local sources or oil pumps of mass spectrometer



Purification of air samples





Isotope ratio of atmospheric N₂





Isotopic composition of pure Ne

Int J Thermophys (2015) 36:2072–2084 DOI 10.1007/s10765-015-1883-6



Triple-Point Temperature and the Isotopic Composition of Three Commercial Neon Gases

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Received: 10 October 2013 / Accepted: 8 April 2015 / Published online: 30 April 2015 © Springer Science+Business Media New York 2015

Abstract The triple-point temperature of neon, T_{tp-Ne} , is known to have dependence on the isotopic composition. Recently, the Technical Annex for the International Temperature Scale of 1990 was updated to specify the method of correction for the isotopic reference ratio of neon. In this study, to confirm this correction in the Technical Annex independently, the effects of the isotopic composition of neon on T_{tp-Ne} for three commercial neon gas sources were studied. For the measurement of the isotopic composition, a gas mass spectrometer was used to compare the sample gases with a reference neon gas whose isotopic composition was known with high precision by a gravimetric method. For the measurement of T_{tp-Ne} , an open-cell type cryostat for the realization of low-temperature fixed points was used. The physical cell and the thermal environment around it remained very similar for all Ttp-Ne measurements with the neon gases due to the nature of the open-cell type system. Therefore, the difference in $T_{\rm tp-Ne}$ among different samples could be measured with a relatively low uncertainty, canceling many systematic effects that are common to all measurements. Our result was consistent with the correction in the Technical Annex. Furthermore, because one of the commercial neon gases was the bottle that was used for KRISS measurements in the international comparison CCT-K2, it is now possible to correct the measurement for the reference isotopic ratio and compare it with other measurements for which isotopic composition data are available.



Triple point of Ne for ITS-90 (CCT)

- Triple point of Ne: define fixed point in the International Temperature Scale in 1990 (ITS-90) at T = 24.5516 K
- Variety in "isotopic abundance of Ne": ²²x from 0.0925 % to 0.0945 %





Isotopic composition of pure Ne

- Certified isotope reference mixtures of Ne
 - 3 different isotope ratios were prepared by gravimetric method
- Isotopic abundance of Ne samples

Gas manufacturer	Nominal chemical purity	21 _x	22 _x	Atomic weight
Linde industrial gases	99.999%	0.002 657(11)	0.092 16(11)	20.1793(2)
Messer	99.999%	0.002 675(11)	0.093 98(11)	20.1830(2)
Matheson gas products	99.994 %	0.002 656(11)	0.092 30(11)	20.1796(2)
IUPAC standard value	_	0.0027	0.0925	20.1797

• CCT can determine the T_{90} (Ne TP) using following correction equation; $T_{meas} = T_{90}$ (Ne TP) + $k_0 + k_1({}^{22}x + {}^{21}x/2) + k_2({}^{22}x + {}^{21}x/2)^2$ with determined coefficient k_0 , k_1 , and k_2 from measured isotope compositions of Ne samples



Atomic weights of pure Ne samples: GC-TCD

- GC-TCD response is inversely proportional to square of atomic weight of sample
- Natural isotope abundance of Ne: ²²x from 0.0925 % to 0.0945 %
 → we can see chromatogram with Ne sample and Ne carrier gases





Isotope abundances of pure Ne samples: Mass spectrometry

• Verification of isotope ratios by mass spectrometer





Isotope abundances of pure Ne samples: Mass spectrometry

		Atomic weight	Atomic weight	Atomic weight
Gas Manufacturer	Area	from literature	from GC-TCD	from MS
		(g mol ⁻¹) ^{a)}	(g mol⁻¹)	(g mol⁻¹)
Linde industrial gases	1.1	20.1793(4)		20.17
Messer	40.	20.1830(4)		20.18
Matheson gas products	4.3	20.1796(4)		20.17
Sample #1	-1.6		20.17	20.17
Sample #2	11.		20.18	20.18
Sample #3	41.		20.18	20.18
Carrier gas			20.17	20.17
IUPAC standard value		20.1797(6)		

*The uncertainties with the coverage factor of k = 2 are shown in parentheses.

a) Values of the neon standards atomic weight are reported in Int J Thermophys (2015) 36:2072-2084.



SI traceable standard gas mixtures for isotope ratio measurements

What are needed to measure absolute isotope ratio

- Purity analysis
 - Isotope-enriched source gases and isotopic reference materials
- Isotopic equilibrium (in case of CO₂)
- Gravimetrically prepared isotope gas mixtures
 - At least 3 different isotopic ratios
 - One should have very closed isotope ratio with reference material
- Air sampling system (noble gases: Ne, Kr, and Xe)
 - No mass fractionation
 - Separation techniques
- Instrument for measuring absolute isotope ratios
 - Finnigan MAT 271 mass spectrometer



Next 5 years plans for absolute isotope ratio in KRISS (Gas group)

Next plans for measuring absolute isotope ratio in KRISS

- Atomic weight and Isotope abundances
 - Noble gases: Ne, Kr and Xe
 - Gravimetrically prepared isotope standard gas mixtures
 - Atmospheric gases separated from air
- Absolute isotope ratio of carbon
 - Isotopic equilibrium: source gases and final mixtures
 - Gravimetrically prepared CO₂ mixtures
 - CO₂ from phosphoric acid reaction with VPDB



SI traceable standard gas mixtures for isotope ratio measurements

Summary

- In KRISS, we have investigated the absolute isotope ratio measurements for atmospheric Ar and N₂, and commercial Ne
 - New value of isotopic abundance of atmospheric Ar
 - Gravimetrically prepared Ar reference gas mixtures have contributed to determine the Boltzmann constant $(k_{\rm B})$
 - New value of atomic weight and isotopic abundance of atmospheric $\rm N_2$ will be published
 - Atomic weights of several Ne samples result from gas chromatograph will be published
- Absolute isotope ratio measurements for Noble gases (Ne, Kr, and Xe) and carbon in CO₂ during next 5 years
 - Gravimetrically preparation of SI traceable isotope reference gas mixtures
 - Determination of isotopic abundance of international reference materials to make a linkage with the SI



Thank you for your attention!



