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A primary isotopic gas standard for krypton with values for isotopic composition and molar mass traceable to the Système International d'Unités

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Abstract

Isotope amount ratios of krypton were measured on subsamples from one large batch of high purity krypton separated from the atmosphere. Synthetic mixtures of enriched krypton isotopes were used to "calibrate" the measurements with small uncertainties. The result is a primary isotopic gas standard (PIGS) IRMM-2030 with certified values for isotope ratios, isotopic composition, and molar mass of krypton with small combined uncertainties u_c, evaluated according to the ISO/BIPM Guide (GUM). It is commercially available from IRMM-Geel or from MESSER (Duisburg, D). The certified krypton isotope amount ratios in the PIGS IRMM-2030 are as follows: $n(^{78}\text{Kr})/n(^{84}\text{Kr})=0.006\ 232\ 5(55)$, $n(^{80}\text{Kr})/n(^{84}\text{Kr})=0.040\ 107(17)$, $n(^{82}\text{Kr})/n(^{84}\text{Kr})=0.203\ 43(12)$, $n(^{83}\text{Kr})/n(^{84}\text{Kr})=0.201\ 79(11)$, and $n(^{86}\text{Kr})/n(^{84}\text{Kr})=0.303\ 205(59)$ with expanded uncertainty $U=ku_c$ and coverage factor $k=2$. The molar mass of Kr in this sample is $M(\text{Kr})=83.798\ 02(16)$ g/mol. These values are in good agreement with published measurements of atmospheric krypton but have smaller combined uncertainties and are "calibrated" by means of synthetic isotope mixtures. The values of the PIGS are traceable to the SI. Measurements of isotope amount ratios of krypton in other samples can be linked to SI using this PIGS. (Int J Mass Spectrom 206 (2001) 129–136) © 2001 Elsevier Science B.V.

Keywords: Primary isotopic gas standard; Molar mass; Isotopic composition; Gas isotope mass spectrometry; Isotope amount ratio; Traceability; SI; Krypton

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1. Introduction

Measurements of isotopic variations of krypton in nature reveal knowledge about our past, present, and future. In 1950 A.O. Nier published his work on highly precise measurements of the isotope abundance of krypton [1], to be accepted as the best measurements of krypton in air for the next decades. Since then mass spectrometric methods have evolved and measurements have been performed on this noble gas applying various measurement techniques such as sector field, quadrupole, isotope dilution, plasma source ion trap mass spectrometry, and others [2–4]. There is a wide variety of applications in cosmochemistry, geochemistry and environmental sciences for isotope amount ratio measurements of krypton.

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Isotopic variations in extraterrestrial materials are caused by mass fractionation, nuclear reactions, radioactive decay, cosmic rays and other processes [5]. Measuring the variations of isotopic krypton composition in meteorites and lunar soils compared to terrestrial krypton allows one to investigate the origin of isotopic anomalies. In astrophysics isotope abundance measurements of krypton are used to underpin theories about the origin of the chemical elements. The isotopic composition of krypton trapped in grains of meteorites provide a record of stellar nucleosynthesis, the theory that the abundance of medium-heavy and heavy nuclides is due to capture by lighter nuclides of free neutrons on either a slow time scale (s-process) or rapid time scale (r-process) [6,7]. Determination of paleotemperatures derived from krypton and other noble gases dissolved in groundwater enables the change and temperature fluctuations with time to be observed [8].

Another important aspect is that not only radioactive [9] but also stable krypton isotopes are used for environmental monitoring. One particular application for stable noble gas monitoring is in view of nuclear safeguard's purposes as a method to identify reprocessing activities. By analyzing fissiogenic krypton that is released during the reprocessing of spent nuclear fuel conclusions on the reactor operating scenario and thus on possible clandestine Pu production can be drawn [10,11]. For this specific application stack noble gas samples are measured for their alteration of isotopic composition in air on a microwave plasma ion source mass spectrometer [12].

In general it can be said that for all applications characteristic krypton isotopic signatures have to be read in comparison to atmospheric krypton despite interfering background signals [13]. To accomplish this task, reliable and comparable measurements of high metrological care are required. The best way to realize comparability of results from different laboratories in space and time, is to use SI units for reporting measurement results (and their uncertainties). This should also be applied for isotopic measurements. Measured values should be expressed in SI units which anchor in "absolute" measurement scales (mol/mol). Thus, IRMM decided to certify primary isotopic gas standards (PIGS). These PIGS do not only have the same features as conventional isotopic reference materials (such as sample homogeneity, stability and availability), but their certified values have been obtained by measurements calibrated by means of synthetically prepared mixtures of enriched isotopes. In this way small residual systematic effects could be accounted for, if present. A fully documented and transparent uncertainty budget was established according to the GUM [14].

A PIGS needs to fulfill the following criteria:

(1) Certified isotopic composition in terms of isotope amount ratios (measured in mol/mol). (2) Fully documented, transparent, and reliable uncertainty budget evaluated according to the ISO/BIPM Guide (GUM) [14]. This budget includes homogeneity and intrinsic, long-term stability of the quantity certified (i.e. the amount ratios) within the certified range. (3) Wide and open availability of the samples in adequate amounts so that different laboratories can use them over long periods of time. (4) SI traceability of the values certified, i.e. independent on artifacts. (5) Small combined uncertainties on the certified values.

2. Direct measurement of krypton using the "Avogadro II amount comparator method"

Direct isotope amount ratio measurements (not using synthetic mixtures of enriched isotopes to correct for possible small remaining systematic effects of unknown origin) were performed on the "IRMM Avogadro II amount comparator," an IRMM-modified Finnigan-MAT 271 mass spectrometer. The measurement procedure was developed for high accuracy measurements of the molar mass of silicon in the framework of the redetermination of the Avogadro constant [15]. The measurement protocol and the software enabled isotope amount ratio measurements to a relative (combined) uncertainty on $[n(^{i}\mathrm{Si})/n(^{28}\mathrm{Si})]$ of 1×10^{-5} [16].

The krypton ion currents were measured in symmetrical sequences, from $m/z = 78$ to 86 and back. Subsequently the values of the krypton ion current

Tabel 1
Theoretical vs. experimental values for $[m(^{i}\mathrm{Kr})/m(^{84}\mathrm{Kr})]^{-\phi}$ with combined uncertainties u_c (applying to the last two digits)

mass ratio $m(^{i}\mathrm{Kr})/m(^{84}\mathrm{Kr})$	$[m(^{i}\mathrm{Kr})/m(^{84}\mathrm{Kr})]^{-\phi}$ theoretical	experimental $^{\mathrm{nat}}\mathrm{Kr}$	experimental synthetic mixture F1
$m(^{78}\mathrm{Kr}\}/m(^{84}\mathrm{Kr})$	0.963 62	0.969 0 (14)	0.968 8 (23)
$m(^{80}\mathrm{Kr})/m(^{84}\mathrm{Kr})$	0.975 90	0.977 31 (41)	0.976 96 (23)
$m(^{82}\mathrm{Kr})/m(^{84}\mathrm{Kr})$	0.988 02	0.988 74 (36)	0.988 495 8 (84)
$m(^{83}\mathrm{Kr})/m(^{84}\mathrm{Kr})$	0.994 03	0.994 76 (19)	0.994 495 (74)
$m(^{86}\mathrm{Kr})/m(^{84}\mathrm{Kr})$	1.011 83	1.014 0 (16)	1.012 13 (92)

ratios $J = I(^{i}\mathrm{Kr})/I(^{j}\mathrm{Kr})$ with their standard uncertainties calculated from the mean ion currents were extrapolated to time zero $J_0 = I_0(^{i}\mathrm{Kr})/I_0(^{j}\mathrm{Kr})$, the time the valve from the expansion vessel to the ion source was opened and the gas started to flow ("effuse") into the spectrometer. For ideal gas behaviour the effusion fractionation factor $K_{\mathrm{mad}}(^{i}\mathrm{Kr})/K_{\mathrm{mad}}(^{j}\mathrm{Kr})$ is inversely proportional to the square root of masses of the measured isotopes [17]. Applying the following equation the effusion fractionation factor was monitored during the measurement and thus the actual diffusion behaviour of the gas leaking into the ion source could be verified for its closeness to ideal gas behaviour:

$$\frac{K_{\mathrm{mad}}(^{i}\mathrm{Kr})}{K_{\mathrm{mad}}(^{j}\mathrm{Kr})} = \frac{k_{^{i}Kr}}{k_{^{j}Kr}} = \left(\frac{m(^{i}\mathrm{Kr})}{m(^{j}\mathrm{Kr})}\right)^{-\phi}$$

where

$$k_{^{i}\mathrm{Kr}} = \frac{\ln\left(\frac{I(^{i}\mathrm{Kr})}{I_0(^{i}\mathrm{Kr})}\right)}{t}$$

and $\phi = ½$ for ideal gas behaviour.

Experimental $[m(^{i}\mathrm{Kr})/m(^{j}\mathrm{Kr})]^{-\phi}$ for krypton are given in Table 1. They were found to be very close to values for ideal gas behaviour, resulting in relative differences for the extrapolated isotope amount ratios on the 4×10^{-5} level only. Moreover, applying model equations for adsorption and desorption the measured ratios were investigated for possible fractionation effects in the inlet system [18,19].

The extrapolated ion current ratios $J^{0}_{i/j}$ were related to the isotope amount ratio $R^{0}_{i/j}$ by

$$R^{0}_{i/j} = K_{\mathrm{conv}}\, J^{0}_{i/j}.$$

with

$$R^{0}_{i/j} = n(^{i}\mathrm{Kr})/n(^{j}\mathrm{Kr})$$

where $i = 78, 80, 82, 83, 86$ and $j = 84$. K_{conv} (conversion factor) converts ion current ratios into isotope amount ratios

From our experience with other gases, K_c is at least equal to unity $\pm5\times10^{-3}$. However for the certification of the PIGS smaller uncertainties are required. Therefore K_c has to be determined experimentally using synthetic isotope mixtures of enriched Kr isotopes. From the observed ion current ratios and from the known isotope amount ratio of the prepared mixtures, K_c could be derived within small uncertainty.

3. Synthetic Kr isotope mixture

Synthetic mixtures of krypton have been prepared in order to perform an independent confirmation that K_c is close to unity with small combined uncertainty applying the Avogadro II amount comparator method for krypton isotope ratio measurements. To date this has been confirmed for Si, Xe, and S [15,20,21]. At the same time the synthetic Kr isotope mixtures enabled to "calibrate" the measurements with small combined uncertainty.

3.1. Preparation

Synthetic mixtures of krypton have been prepared volumetrically [18] in co-operation with Los Alamos

Table 2
Isotopic composition of the starting materials (in amount fraction ×100) with combined uncertainties u_c (applying to the last two digits)

isotope	enriched ^{86}Kr amount fractions × 100	natural Kr amount fractions × 100
^{78}Kr	0.000 581 (37)	0.354 315 (26)
^{80}Kr	0.000 152 5 (97)	2.281 75 (18)
^{82}Kr	0.000 884 (81)	11.584 77 (61)
^{83}Kr	0.002 774 (43)	11.497 59 (40)
^{84}Kr	0.811 361 (46)	56.988 96 (58)
^{86}Kr	99.184 25 (11)	17.292 62 (49)

National Laboratory (LANL) in New Mexico, USA. Krypton of natural isotopic composition and 99% enriched ^{86}Kr were used as starting materials for blending (Table 2). In a volumetric procedure, the value of a synthetically prepared amount ratio can be achieved quite accurately using only a very small amount of enriched ^{86}Kr. Gravimetry [22] would have required typically a minimum mass of about 1 g of each of the isotopically enriched gaseous starting materials to achieve the envisaged uncertainty.

Table 3
Blanding ratios of enriched and natural krypton in mass ratios × 100 with combined uncertainties u_c

mixture label	Blending ration $\epsilon = [m(^{\text{enr}86}\text{Kr})/m(^{\text{nat}}\text{Kr}) \times 100]$	u_c	u_c/ϵ, (in %)
B1	0.021 04	0.000 31	1.5
C1	0.025 61	0.000 37	1.4
D1	0.030 57	0.000 44	1.4
E1	0.088 5	0.001 3	1.5
F1	1.014	0.015	1.4

A total of five krypton mixtures were prepared. Table 3 gives a summary of the prepared blending ratios ϵ in $[m(^{\text{enr}86}\text{Kr})/m(^{\text{nat}}\text{Kr})\times 100]$ with combined uncertainties u_c.

3.2. Calculated isotope amount ratios, R_{prep}, for the Kr synthetic mixtures

From the measurements of the enrichment and the purity of the starting materials, the “prepared” isotope amount ratios of the synthetic mixtures and their uncertainties were calculated for the blending ratios (Tables 2 and 3), using the isotope mixture programme SPIRIT [23]. An example for a complete uncertainty budget is given in Table 4, as established for mixture E1.

3.3. Measurement of conversion factor K_{conv}

To convert ion current ratios into isotope amount ratios the observed values for the ion current ratios J of the synthetic mixtures are compared to the prepared isotope amount ratio values R. This comparison determines the conversion factor K_{conv} for small residual systematic effects of unknown origin.

Note that K_{conv} has to be applied to the values of the observed isotopic composition of the starting materials (Table 2) and then to be iterated. However, since the values of K_{conv} are very close to unity, the iterated values do not change significantly [18].

Table 4
Uncertainty budget of krypton synthetic mixture E1 with combined uncertainty u_c

		combined uncertainty (×10^5) originating from the starting materials for the knowledge of their				
Prepared isotope amount ratio R mixture E1		u_c	amount ratios of mixt. comp.	Chemical purity	weighing	atomic massess[a]
$n(^{78}\text{Kr})/n(^{84}\text{Kr})$	0.006 217 24	0.045	0.045	0.000 000 15	0.000 99	<0.000 008
$n(^{80}\text{Kr})/n(^{84}\text{Kr})$	0.040 038 2	0.42	0.42	0.000 001 1	0.000 72	<0.000 008
$n(^{82}\text{Kr})/n(^{84}\text{Kr})$	0.203 280	1.2	1.2	0.000 005 6	0.003 6	<0.000 008
$n(^{83}\text{Kr})/n(^{84}\text{Kr})$	0.201 750 4	0.76	0.76	0.000 005 4	0.003 6	<0.000 008
$n(^{86}\text{Kr})/n(^{84}\text{Kr})$	0.303 956	2.4	1	0.003 4	2.2	<0.000 008

[a] See [29].

Table 5
Conversion factors accounting for small residual systematic effects as determined by means of the volumetrically prepared synthetic krypton isotope mixture “E1” with combined uncertainties u_c (applying to the last two digits)

conversion factor K_{conv} = prepared isotope amount ratio/observed ion current ratio	
$n(^{78}\text{Kr})/n(^{84}\text{Kr})$	1.001 44 (35)
$n(^{80}\text{Kr})/n(^{84}\text{Kr})$	1.000 39 (19)
$n(^{82}\text{Kr})/n(^{84}\text{Kr})$	1.000 07 (29)
$n(^{83}\text{Kr})/n(^{84}\text{Kr})$	1.000 01 (27)
$n(^{86}\text{Kr})/n(^{84}\text{Kr})$	0.999 961 (81)
mean K_{conv} factor (all ratios)	1.000 37 (73)
mean K_{conv} factor (for major abundance ratios)	1.000 01 (41)

All values calculated for K_{conv} (from all five mixtures) were equal to unity within measurement uncertainty (Table 5, Fig. 1), except for the two minor abundant isotopes ^{78}Kr and ^{80}Kr (small ion currents).

4. Kr PIGS IRMM-2030

4.1. Homogeneity measurements

The homogeneity measurements on the PIGS were of the “direct type” applying Avogadro measurement procedure on the Avogadro II amount comparator without using synthetic isotope mixtures. To determine the homogeneity of the batch, measurements were performed on 24 bottles, measuring one of them six times and the others twice each. All PIGS bottles were measured in a tightly controlled series. Then the isotope amount ratios of each bottle were compared to the mean value of the isotope amount ratios of all bottles. An example for the ratio $R_{83/84}$ is given in Fig. 2. On the basis of the measurements results obtained on the major abundance ratios, the homogeneity can be expressed as $K_H=1.0000\pm0.0001$.

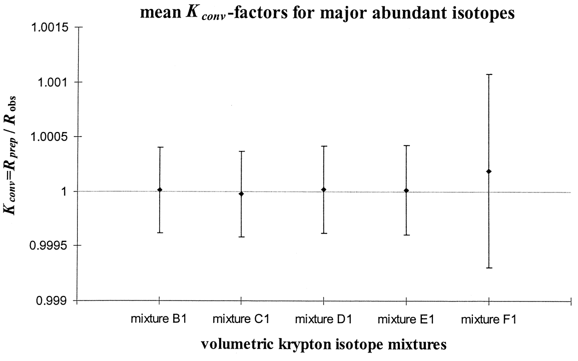

Fig. 1. Mean conversion factors for the volumetrically prepared synthetic krypton isotope mixtures: $U=ku_c$ ($k=1$).

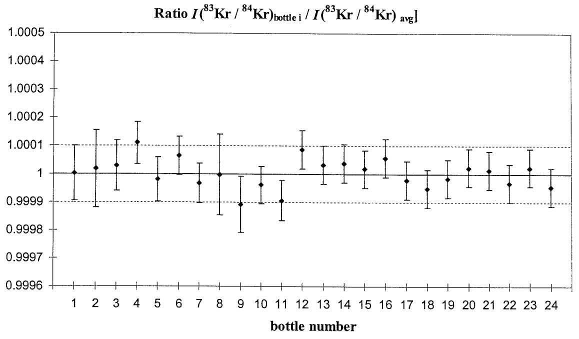

Fig. 2. Isotopic homogeneity of the krypton subsamples. $U=ku_c$ ($k=1$), as measured for the ratio ^{83}Kr/^{84}Kr.

4.2. Isotope amount ratio values for the PIGS(IRMM-2030) from the direct measurement using the Avogadro procedure

The Avogadro II amount comparator method is a rather sophisticated measurement procedure, but increasingly known to yield measurement results of high metrological quality. It converts the measured ion current ratios into observed isotope amount ratios. The directly observed ion current ratio measurements (Table 6), which are using this procedure is a very

Table 6
Observed ion current ratios of the Primary Isotope Gas Standard (IRMM-2030) with combined uncertainty u_c (applying to the last two digits)

Observed ion current ratios J of the Primary Isotopic Gas Standard (IRMM-2030) from the direct measurement procedure using the “Avogadro procedure”	
$I(^{78}\text{Kr}^+)/I(^{84}\text{Kr}^+)$	0.006 223 5 (17)
$I(^{80}\text{Kr}^+)/I(^{84}\text{Kr}^+)$	0.040 091 2 (34)
$I(^{82}\text{Kr}^+)/I(^{84}\text{Kr}^+)$	0.203 415 (16)
$I(^{83}\text{Kr}^+)/I(^{84}\text{Kr}^+)$	0.201 788 (14)
$I(^{86}\text{Kr}^+)/I(^{84}\text{Kr}^+)$	0.303 217 (16)

Table 7
Certified isotope amount ratios of the Primary Isotope Gas Standard IRMM-2030 compared to the IUPAC selected best measurements; $U = ku_c$ ($k = 2$) (U applies to the last two digits)

	Certified amount ratios of the Primary Isotopic Gas Standard (IRMM-2030)	Amount ratios from the IUPAC selected "best measurement" of krypton[a]
$n(^{78}\mathrm{Kr})/n(^{84}\mathrm{Kr})$	0.006 232 5 (55)	0.006 320 (47)
$n(^{80}\mathrm{Kr})/n(^{84}\mathrm{Kr})$	0.040 107 (17)	0.039 975 (71)
$n(^{82}\mathrm{Kr})/n(^{84}\mathrm{Kr})$	0.203 43 (12)	0.203 30 (47)
$n(^{83}\mathrm{Kr})/n(^{84}\mathrm{Kr})$	0.201 79 (11)	0.202 25 (12)
$n(^{86}\mathrm{Kr})/n(^{84}\mathrm{Kr})$	0.303 205 (59)	0.303 72 (12)

[a] See [26].

good approximation for the isotope amount ratios. It is based on rather simple physical principles (gas kinetics) [18] enabling the ideal gas behaviour of the krypton during the measurement to be verified in terms of quantitative compliance with kinetic gas theory values within stated uncertainty.

4.3. Isotope amount ratio values for the PIGS(IRMM-2030) from measurements calibrated by means of synthetic mixtures

Determination of the conversion factor K_{conv}, by means of synthetic mixtures. accounts for possible small residual systematic effects of unknown origin. K_{conv} multiplied with the observed isotope amount ratios from the direct measurement using the "Avogadro procedure" yields, thus, in certified isotope amount ratios (Tables 7 and 8). Since the correction factors were not significantly different from unity the values from the measurements using the Avogadro procedure did not change significantly. Their uncertainty however increased slightly. The observed and the certified isotope amount ratios for the major abundant isotopes of the Kr-PIGS IRMM-2030 agreed within the stated uncertainty of $<5\times10^{-4}$ relative, which is a further confirmation of the metrological quality of the Avogadro II amount comparator method [15,16,18].

5. Conclusion

A PIGS was prepared for krypton, starting from a homogenized batch of krypton separated cryogenically from air. The PIGS is made available in 1 L aluminum cans at a pressure of 1.2×10^6 Pa with a special valve (Messer 795.08312) to avoid possible mass fraction effects while sampling.

Applying the IRMM Avogadro II amount comparator method the krypton isotope amount ratios were measured verifying the closeness to ideal gas behavior of the krypton during the measurement. The measurement procedure was verified by means of synthetic krypton mixtures yielding in certified krypton isotope amount ratios with a relative combined uncertainty $u_c<5\times10^{-4}$. The deduced conversion factor for the major abundant krypton isotopes, comparing synthetically prepared with measured isotope amount ratios of krypton, was equal to unity within a combined uncertainty of $u_c<8\times10^{-5}$. All the measurement uncertainties were evaluated following the ISO/BIPM Guide on the expression of uncertainty in measurements. This is a further confirmation that the applied IRMM Avogadro II amount comparator method for measuring isotope amount ratios is well understood, yielding results of the highest metrological quality. Hence measurements of isotope ratios of krypton "calibrated" against PIGS IRMM-2030 are traceable to the SI. The PIGS IRMM-2030 is a krypton standard for calibration purposes of instrument setups where reliable and comparable isotope amount ratio measurements of krypton are indispensable.

The PIGS (IRMM-2030) is the first isotopic reference material ever prepared for krypton. The certified isotope amount ratios obtained on PIGS

Table 8
Measured and certified isotopic composition and molar mass M(Kr) (numerically equal to atomic weight) of the Primary Isotopic Gas Standard IRMM-2030; $U = ku_c$ ($k = 2$)

Isotope	Amount fraction × 100	mass fraction × 100	uncertainty
^{78}Kr	0.355 18	0.330 26	±0.000 32
^{80}Kr	2.285 60	2.179 72	±0.000 96
^{82}Kr	11.593 0	11.332 3	±0.006 2
^{83}Kr	11.499 6	11.378 3	±0.005 8
^{84}Kr	56.987 7	57.064 9	±0.005 8
^{86}Kr	17.279 0	17.714 6	±0.003 2
molar mass of krypton M(Kr) = (83.798 02 ± 0.000 16) g mol^{-1}			

The krypton atomic masses used in the calculations were taken from [29].

IRMM-2030 are compared in Figs. 3–5 with previous measurement results on atmospheric krypton [1,2,24–27]. They were found to be in good agreement but now have considerably smaller, yet expanded uncertainties.

As a spin-off of this work the International Union of Pure and Applied Chemistry (IUPAC) accepted the measurements of the isotope abundance and molar mass of krypton performed by Valkiers et al. [24], applying the IRMM Avogadro II amount comparator method, as "best measurement from a single terrestrial source" [28].

So far PIGS for Xe [20] and SF_6 [21] have been characterized. The preparation of the PIGS IRMM-2030 continues this series, confirming once more the high metrological potential of the IRMM Avogadro II amount comparator method.

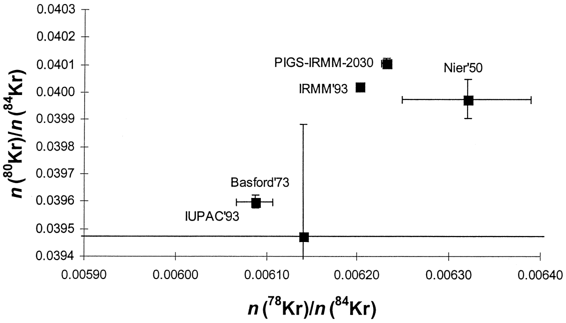

Fig. 3. Three-isotope plot for $n(^{80}\mathrm{Kr})/n(^{84}\mathrm{Kr})$ to $n(^{78}\mathrm{Kr})/n(^{84}\mathrm{Kr})$: published values compared to this work. $U=ku_c$ ($k=2$).

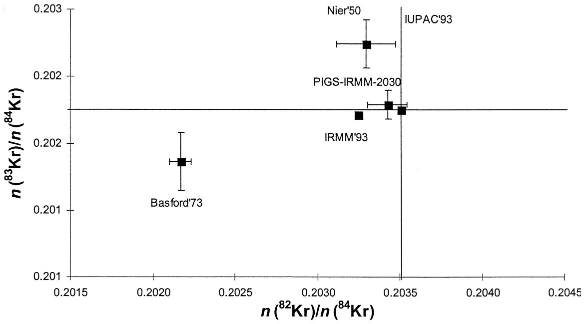

Fig. 4. Three-isotope plot for $n(^{83}\mathrm{Kr})/n(^{84}\mathrm{Kr})$ to $n(^{82}\mathrm{Kr})/n(^{84}\mathrm{Kr})$: published values compared to this work. $U=ku_c$ ($k=2$).

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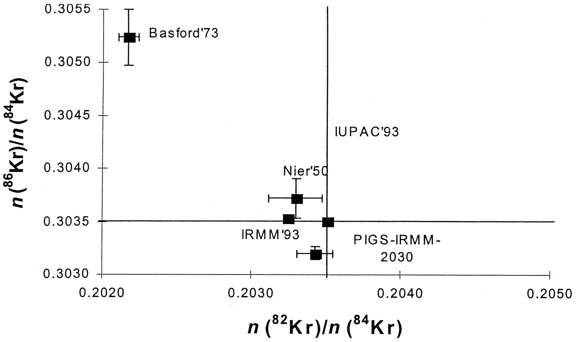

Fig. 5. Three-isotope plot for $n(^{86}\mathrm{Kr})/n(^{84}\mathrm{Kr})$ to $n(^{82}\mathrm{Kr})/n(^{84}\mathrm{Kr})$: published values as compared to this work. $U=ku_c$ ($k=2$).

References

[1] A.O. Nier, Phys. Rev. 79 (1950) 450.
[2] Y. Sano, T. Tominaga, H. Wakita, Geochem. J. 16 (1982) 279.
[3] M.E. Cisper, A.W. Garrett, Y.X. Duan, J.A. Olivares, P.H. Hemberger, Int. J. Mass Spectrom. 178 (1998) 121.
[4] J.R. Walton, A.E. Cameron, R.L. Walker, T.L. Hebble, Int. J. Mass Spectrom. Ion. Phys.12 (1973) 439.
[5] M. Shima, Geochim. Cosmochim. Acta 50 (1986) 577.
[6] U. Ott, F. Bergmann, J. Yang, S. Epstein, Nature 332 (1988) 700.
[7] U. Ott, Nature 364 (1993) 25.
[8] M. Stute, P. Schlosser, J.F. Clark, W.S. Broecker, Science 256 (1992) 1000.
[9] W. Weiss, H. Sartorius, H. Stockburger, Proceedings of a Consultant Meeting on Isotopes of Noble Gases as Tracers in Environmental Studies, IAEA, Vienna, Austria, 1989.
[10] C.W. Nakleh, R.T. Perry Jr., J. Poths, W.D. Stanbro, W.B. Wilson, B.L. Feary, Proceedings on the International Workshop on the Status of Measurement Techniques for the Identification of Nuclear Signatures, IRMM, Geel, Belgium, 1997, pp. 159–174.
[11] B. Hudson, Lawrence Livermore National Laboratory, IAEA task 90/OA211 Interim report.
[12] J. Poths, E.P. Chamberlin, Int. J. Mass Spectrom.146/147 (1995) 47.
[13] T. Florkowski, K. Rózanski, Handbook of Environmental Isotope Geochemistry, Vol. 2, The Terrestrial Environment, Elsevier, New York, 1986.
[14] Guide to the expression of uncertainty in measurements (GUM), first edition 1993, corrected and reprinted 1995, International Organization for Standardization, Genève.
[15] P. De Bièvre, S. Valkiers, Metrologia 31 (1994) 245.
[16] R. Gonfiantini, P. De Bièvre, S. Valkiers, P.D.P. Taylor, Proc. Conf. Electrom. Meas. 46 (1997) 2.
[17] R.D. Present, Kinetic Theory of Gases, McGraw-Hill, New York, 1958.
[18] Y. Aregbe, Dissertation, University of Technology Vienna, April 1998.
[19] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom 163 (1997) 207.
[20] S. Valkiers, Y. Aregbe, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. 173 (1998) 55.
[21] S. Valkiers, H. Kipphardt, T. Ding, R. Damen, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. 193 (1999) 1.
[22] Y. Aregbe, S. Valkiers, K. Mayer, P. De Bièvre, Metrologia 31 (1994) 245.
[23] F. Schaefer, S. Valkiers, P.D.P. Taylor, P. De Bièvre. Int. J. Mass Spectrom. 133 (1994) 65.
[24] S. Valkiers, F. Schaefer, P. De Bièvre, Separation Technology, E.F.Vansant (Ed.), Elsevier, New York, 1993, pp. 965–968.
[25] Y. Aregbe, S. Valkiers, K. Mayer, P. De Bièvre, Int. J. Mass Spectrom. 153 (1996) L1.
[26] IUPAC-CAWIA, Atomic Weights of the Elements 1993, Pure Appl. Chem. 66 (1994) 423.
[27] J.R. Bashford, J.C. Dragon, R.O. Pepin, M.R. Coscio, R. Murthy, Geochim. Cosmochim. Acta Suppl. 4 II (1973) 1915.
[28] IUPAC, Pure Appl. Chem. 70 (1998) 217.
[29] A.H. Wapstra, G. Audi, Nucl. Phys.A 565 (1993) 1.