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Preparation of argon Primary Measurement Standards for the calibration of ion current ratios measured in argon

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ABSTRACT

In this work a procedure is described to prepare SI-traceable argon isotope amount ratios in high purity argon. Following a gravimetric approach, a total of three synthetic isotope mixtures have been prepared, from argon gases enriched in ^{36}Ar, ^{38}Ar and ^{40}Ar, close to the natural isotopic composition of argon. These synthetic mixtures serve as reference gases to calibrate ion current ratio measurements in argon. In this way SI-traceable measurements of argon isotope amount ratios can be performed without any assumptive correction. On a high purity argon gas separated from air the absolute argon isotope amount ratios $R_{36/40}$ = 0.00334774 (93) and $R_{38/40}$ = 0.00063529 (57) were measured. From these ratios, the average molar mass of argon gas can be determined with a total relative combined uncertainty of 0.09×10^{-6}.

1. Introduction

For the redetermination of the molar gas constant [1] the speed of sound was measured in argon close to the triple point of water T_{TPW}. One of the most significant challenges faced by Moldover [1] was the determination of the molar mass, M(Ar), of the argon actually used in his experiment. Moldover finally achieved an uncertainty of 0.7 parts in 10^6 (0.7 ppm) in M(Ar) using a complicated comparison between his unknown argon sample and a sample of nearly monoisotopic ^{40}Ar. This procedure was required because, as Moldover notes, commercial processing of argon derived from liquid air produces a variability in isotope ratios of around 1%.

The value of the molar gas constant R recommended by the Committee on Data for Science and Technology (CODATA) in 2006 [2] is essentially the weighted mean of only two independent results for the speed of sound in argon obtained at a temperature close to, and known in terms of, the triple point of water T_{TPW}. One result is from the National Institute of Standards and Technology (NIST), USA, with a relative uncertainty $u_r = 1.7 \times 10^{-6}$, and the other from the National Physical Laboratory (NPL), UK, with $u_r = 8.4 \times 10^{-6}$. Although the two results of acoustic gas thermometry are consistent, because of the large difference in their uncertainties, the 2002 recommended value of R, and hence the 2002 recommended value of the Boltzmann constant k with $u_r(k) = 1.8 \times 10^{-6}$, is to a very large extent determined only by the NIST result. Therefore, it is presently unwise to fix the value of the Boltzmann constant due to severe lack of independent data.

Recently (2008) a Joint Research Programme-implementing the Metrology European Research Area (JRP-iMERA) project was started to measure the Boltzmann constant k fully independently. The new measurement of k will be used in a redefinition of the *kelvin*, which leads to an improved International System of Units (SI). Methods to determine k with the required uncertainty are summarised by [3] together with an assessment of the likely achievable uncertainty. The technique expected to achieve the lowest uncertainty (of the order one part in 10^6) is a development of Moldover's 1988 [1] experiment measuring the speed of sound of a dilute gas in an acoustic resonator. However this experiment faces exactly the same problem of determining the molar mass of the gas used in the experiment. One solution would be to use helium which is naturally nearly monoistopic, and there are considerable advantages to this approach: most notably the ability to calculate transport properties of the gas with very low uncertainty. However, the low density of helium results in low signal levels, and the high speed of sound results in acoustic resonances which extend well into the region of interaction with shell resonances in the resonator wall. Using argon, has many experimental advantages, but requires a determination of the isotopic mass of *the actual gas used in the experiment*.

Therefore the recommended Commission on Isotopic Abundances and Atomic Weights (CIAAW) value [4] for the argon isotopic composition with respect to the range of observed compositions, cannot be used as the value of M(Ar). For a total uncertainty

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below 1×10^{-6} on k, molar mass with total combined uncertainties of 3×10^{-7} is required. Meeting these requirements, and at the same time guaranteeing long term metrological comparability of measured M(Ar) values, can only be achieved through calibrated molar mass measurements using Primary Measurement Standards (PMSs). Such PMS are 'realizations' of the SI units involved (in this specific case of the derived unit mol/mol) in the form of 'synthesized' isotope amount ratios with small full measurement uncertainties, which is done at IRMM-Geel (Belgium). Using these techniques we can determine the molar mass of the actual gas used in a resonator with an uncertainty in M(Ar) of the order 0.16×10^{-6}.

In this work we undertake a redetermination of the absolute isotope abundances of Ar because the existing values, determined in 1950 by Nier [6], are subject to a number discussions. In fact, Nier's work on Ar, although outstanding in 1950, could be improved with modern mass spectrometry and the experience gained during the last years [5].

A critical review of Nier's [6] paper reveals the following imperfections:

1. Two mass spectrometers, MS1 and MS2, were used where MS1 was assumed to have a pure viscous flow whereas the MS2 had a molecular leak. The data from MS1 were therefore corrected using a square root of mass correction. However, MS2 had a residual impurity at the peak $u/e = 38$ (where u is the atomic mass unit and e the electronic charge) and therefore was discarded.
2. The method of measuring gas volumes was by use of taps and flasks.
3. The isotopic composition of the enriched starting materials ^{36}Ar and ^{40}Ar were not measured accurately: the isotopic composition of ^{40}Ar was stated to be 0% ^{36}Ar, 0% ^{38}Ar and 99.32% ^{40}Ar, with impurity levels of 0.68%.
4. The mass spectrometer was calibrated with four mixtures of two enriched isotopes. The correction factors K were 0.9983, 0.9882, 0.9949 and 0.9932 respectively to give an average value of 0.9937 ± 0.0013. This represents the mass fractionation correction factor. One would like to know the reason for the low 0.9882 value. Presumably the viscous leak correction factor has been included in the calculations.
5. All errors indicated are type A uncertainties (called 'probable errors').

In a subsequent paper Nier [7] used the calibrated mass spectrometer to measure the isotopic composition and atomic weight of Ne, Kr, Rb, Xe and Hg. In this article he points that there is a residual peak caused by water vapor. Thus, in determination the ion current ratio $^{36}Ar^{++}/^{40}Ar^{++}$, the $u/e = 18$ peak and, then, the ratio as well was too high. It is unclear what the effect is on the original Ar measurements, but it does leave a question mark about the quality of the original argon measurements.

2. Mixtures with gravimetrically prepared Ar isotope amount ratios

To be independent of consensus values, calibrated "absolute" isotope argon amount ratio measurements (Primary Measurement Standards) are needed. Their ratio values are fully independent of unstable consensus values. Consequently they must be realized by another approach: synthesizing them with sufficiently small uncertainties. When measuring "unknown" Ar samples, their ion current ratios can then be converted into isotope amount ratios by use of a correction factor:

$$K_{i/40} = \frac{R_{i/40\ \mathrm{true}}}{r_{i/40\ \mathrm{measured}}} \quad (i = 36 \text{ and } 38) \tag{1}$$

which is defined (via synthetic isotope mixtures) to be the ratio of the "true" isotope amount ratio $R_{i/40\,\mathrm{true}}$ to $r_{i/40}$. The observed ion current ratio. $R_{i/40\,\mathrm{true}}$ is derived from the preparation of the synthetic isotope mixtures, and the ion current ratio $r_{i/40}$ is derived from the measurement of the mixtures. This approach is chosen in this work [8,9].

2.1. General considerations

When high purity Ar is weighed on a balance, the chemical amount n_{Ar} is given by

$$n_{\mathrm{Ar}} = \frac{m_{\mathrm{Ar}}(1 - \varepsilon_{imp})}{M_{\mathrm{Ar}}} \tag{2}$$

where ε_{imp} is a small correction term for the (mass of) chemical impurities in the Ar (Eq. (2)). A stoichiometry term for gases (in contrary to solids) can be neglected. As n_{Ar} is not a function of other amounts (but only a function of molar mass M_{Ar} and mass m_{Ar}), this procedure is called a '*primary measurement procedure*', as the result is obtained by *other* means than the measurements for which it is intended as a calibrator. These methods have two important features which make them metrologically superior: the metrological traceability is easy to understand and they yield values with small total combined uncertainties.

'Gravimetry' and the ensuring mass ratio are mostly used to produce mixtures of isotopes with isotope amount ratios having small total combined uncertainties [8,9]. For this purpose, materials of high isotope enrichment are used and their isotope ratio in a mixture X of such materials (A and B) is given by (3):

$$\frac{n(^iE, X)}{n(^jE, X)} = \frac{n(^iE, A) + n(^iE, B)}{n(^jE, A) + n(^jE, B)} = \frac{f_{i,A}n(E, A) + f_{i,B}n(E, B)}{f_{j,A}n(E, A) + f_{j,B}n(E, B)} \tag{3}$$

where f denotes the isotope abundance, for isotope ^iE, ^jE in sample A, e.g., $f_{i,A} = R_{i,A}/\Sigma R_{i,A}$. The amounts n can be expressed using (3). The starting materials A and B must be of high chemical purity, and the order of magnitude of the impurities known (as ε_{imp}).

For Ar mixtures, the imperfection prior to mixing is then carefully assessed: the purity of the gas and the isotope enrichment. The systematic effects are measured, their uncertainties evaluated, and then combined with the uncertainty of the mass measurements (weighings). Depending on the target measurement uncertainty and on the amounts of the materials available, mixtures can be prepared to various final measurement uncertainties from various starting materials.

2.2. Theoretical reflections on the preparation of mixtures

When targeting small total combined uncertainties by working at atmospheric pressure, volumetric mixing can be performed based on measurements of the pressure and of the volume of the parent gases for the mixture preparation. In volumetric mixing procedures, the amount of gas n is related to the volume V of the mixing vessel, the pressure p and the temperature T in the vessel following the equation $pV = nRT$, with R being the molar gas constant. The behaviour of real gases however is better described by the empirical [14] 'van der Waals'-equation (4):

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{4}$$

The an^2/V^2 term accounts for the attractive forces of the molecules and are responsible for a pressure increase, while the b-term accounts for repulsive forces which in turn decreases the volume available for the molecules [10]. At the critical point of Ar ($T_c = 150.86$ K) the terms a and b are related to the critical volume V_c ($0.07459\ \mathrm{m^3\ kmol^{-1}}$) and pressure p_c (4.898 MPa)

Table 1
The Ar gases with their amount ratios used for the preparation of the three synthetic mixtures. The stated uncertainties are total combined standard deviations calculated according to [15].

	Material 1: ^{40}Ar Isotec 601799	Material 2: ^{36}Ar Isotec 601772	Material 3: ^{38}Ar Russia St. Petersburg, KPR210556
$r_{36/40}$	0.00049101 (46)	2200.01 (94)	1.213021 (58)
$r_{38/40}$	0.00041028 (35)	8.97004 (29)	1.131012 (49)
Enrichment (amount %)	99.909952 (33) ^{40}Ar	99.54886 (11) ^{36}Ar	33.82179 (65) ^{38}Ar

Table 2
The masses in mg of the different starting materials used for preparing the mixtures. The stated uncertainties are total combined standard deviations calculated according to [15].

Isotope	IRMM-Ar-Mix1	IRMM-Ar-Mix2	IRMM-Ar-Mix3
99.909952 (33) % ^{40}Ar	9720.0012 (90)	9753.2251 (90)	9992.3521 (90)
99.54886 (11) % ^{36}Ar	23.0462 (90)	22.8512 (90)	23.7828 (90)
33.82179 (65) % ^{38}Ar	5.7822 (90)	5.5955 (90)	5.9985 (90)

as follows [10]: $V_c = 3b$ and $p_c = a/27b^2$. This results in a value for $a_{Ar} = 0.0817\ Pa\ m^6\ mol^{-2}$ and for $b_{Ar} = (2.486) \times 10^{-5}\ m^3\ mol^{-1}$. When mixing gases at a pressure of 10^6 Pa (10 bar), this would result in a correction of 1.37×10^4 Pa (or 1.3% relative) of the pressure compared to the calculation via the ideal gas law ($(an^2/V^2) = nb = 0$) or the 'van der Waals' law reduced to the ideal gas law.

3. Preparation of the synthetic isotope mixtures

3.1. The starting materials

The starting materials used for the preparation of the mixtures are enriched ^{40}Ar, ^{36}Ar and ^{38}Ar. The enriched ^{40}Ar and ^{36}Ar gas was supplied by ISOTEC (Sigma–Aldrich) with specifications as follows: ^{40}Ar (Lot no.: 601799, 40 g) min 99.9% ^{40}Ar, and ^{36}Ar (Lot no.: 601772, 300 mg) min 99.4% ^{36}Ar. The smaller amount of ^{38}Ar (Russia, St. Petersburg, Lot no.: KPR210556, 90 mg) had an isotope enrichment of 33.82% ^{38}Ar (Table 1).

An impurity check on all these starting materials was performed before starting the experimental work (by means of the IRMM-MAT 271 gas mass spectrometer). When the impurities are added together, their amount content was below 0.0001% (g/g) for all parent gases, which makes their impact on the mixture calculations extremely small, but the effect anyhow, was taken into account (Table 7).

3.2. Isotope mixing procedure

For the calibration of the measured Ar isotope amount ratios $r_{i/40}$, three different synthetic isotope mixtures (IRMM-Ar-Mix1, 2 and 3) close to natural Ar isotopic composition are prepared by mixing argon gases differently enriched in ^{36}Ar, ^{40}Ar and ^{38}Ar isotopic composition (Table 1). The mixtures will act as Primary Metrological Standards for the argon isotope amount ratio measurements on high purity natural Ar. They will help to anchor Ar isotope measurements on different Ar samples and therefore offer the basis for comparability of the measurement results, without any assumptive correction.

The preparation of synthetic isotope mixtures in gaseous form, however, is more difficult to achieve than by mixing solids. The full uncertainty is very much limited (Tables 2 and 7) by the typically high tare mass of the gas ampoule (~180 g) relative to the mass of gas (few about 9 g for ^{40}Ar, but only a few mg for ^{38}Ar). To decrease the measurement uncertainty of the gas amount, the amount of gas needs to be increased as far as possible without crossing the borders of the pressure safety in the ampoules. High pressure however could from the other side enlarge the measurement uncertainties due to very small leaks, so a careful testing of the leaks is absolutely required. Furthermore, large amounts of isotopically enriched gases (especially ^{36}Ar and ^{38}Ar) are expensive. Therefore, the tare mass of the ampoules should be reduced as much as possible to finally reach the 0.01 mg total uncertainty on all weighings.

To meet those requirements a mixing preparation system (Fig. 1) has been recently built based on gas flow rates which are controlled by a Multichannel flow controller which is computer controlled [11]. Each gas component quantity (^{36}Ar, ^{38}Ar and ^{40}Ar) is introduced sequentially into their respective ampoule (container C1 for ^{40}Ar, C2 for ^{38}Ar and C3 for ^{36}Ar) using a mass flow controller during a well defined time where from the pressure measured (Pfeiffer CMR271) the amount of gas in each container can be calculated and the amount of each component gravimetrically determined (Fig. 1). After connecting the ampoules (C1, C2 and C3) again to the system, A NI-Virtual Lab View software application has been elaborated to further monitor and control the mixing process of the three gases by successive trapping into liquid He. In this way three different Ar mixtures with an isotopic composition close to natural Ar were made (Table 3).

Three identical C1, C2, C3 stainless steel cylinders (modified SS-4CS-SWA4T49-2-100 Swagelok®) with appropriate valves (SS-42S4 Swagelok®) were used for the mixing and attached to the ¼ inch. stainless steel vacuum line, which was connected to a two-stage rotary fore-pump (pressure < 1 Pa) and a turbo-molecular pump with a liquid N_2 cryogenic trap (<10^{-6} Pa).

Prior to the preparation of the three IRMM-Ar-mixtures, the whole line was first evacuated to a pressure of <10^{-6} Pa and carefully checked for complete leak-tightness, by measuring the ion current ratio $I[^{28}(N_2)^+]/I[^{28}(N_2)_{baseline}{}^+]$. A steady ratio indicates the absence of leaks (or other effects such as adsorption and desorption) which would bias the results. The evacuated ampoules C1, C2, C3 were disconnected from the system and weighed.

All weighings were performed on a Mettler Toledo AX205 balance. It is specified to have a maximum load of 200 g, readability and repeatabilities below 0.01 mg respectively, and a linearity of ±0.005 mg. The gas cylinders (100 mL) used for the preparation of

Table 3
The measured ion current ratios $r_{i/40} = I[^iAr^+]/I[^{40}Ar^+]$ with $i = 36$ and 38 of the 3 different mixtures (IRMM-Ar-Mix1, 2 and 3), with their discrepancy from natural Ar. The stated uncertainties are total combined standard deviations calculated according to [15].

			$\delta = ((r_{i/40})_{mixture}/(r_{i/40})_{air} - 1) \times 10^3$
IRMM-Ar-Mix1	$r_{36/40}$	0.0033417 (25)	−10.74
	$r_{38/40}$	0.00063342 (12)	−4.05
IRMM-Ar-Mix2	$r_{36/40}$	0.0033017 (16)	−22.58
	$r_{38/40}$	0.00062557 (16)	−16.40
IRMM-Ar-Mix3	$r_{36/40}$	0.0033536 (11)	−7.22
	$r_{38/40}$	0.00063533 (12)	−1.05

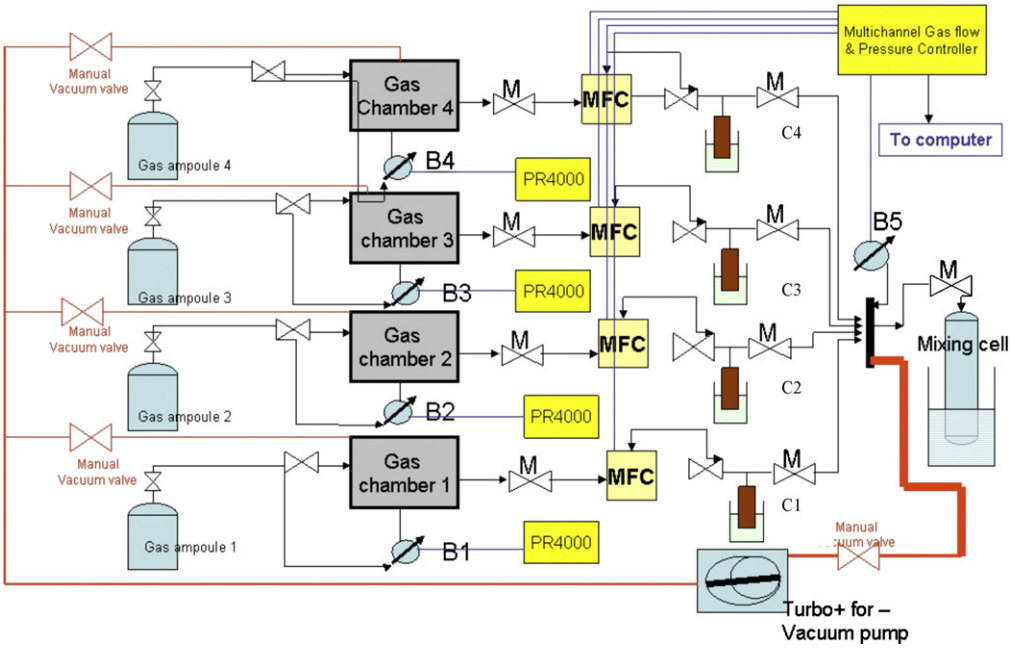

Fig. 1. Schematic presentation of the gas mixing line.

these mixtures weighed approximately 175 g including the valve, whereas the mass of the gases varied from 5.5 mg ^{38}Ar to about 10 g ^{40}Ar (Table 2). The high tare of the gas ampoule thus limited the uncertainty of the weighings of the gases. Particularly with regard to moisture adsorbed on the outer ampoule surface, good repeatability conditions can only be achieved under optimal temperature and humidity conditions in the weighing room (temperature 22.00 ± 0.05 °C, and humidity 50 ± 3%). To minimise weighing errors, all weighings were performed relative to a reference container with similar shape and surface as the sample container. Both containers were exposed to exactly the same conditions prior to weighing, i.e., after cleaning the outer surface with ethanol (to remove any contamination, e.g., fingerprints) the containers were dried at 350 K for about 12 h and then placed next to the balance to equilibrate with ambient conditions. Already after about 3 h of conditioning in the weighing room, the mass of the container and reference container was constant within the readability of the balance (0.01 mg), whereas the repeatability of weighings of a single ampoule was of the same order.

The handling of the ampoule (e.g., connecting and disconnecting from the mass spectrometer) could influence its tare weight. No small weight loss of the container however could be observed (abrasion of small metal pieces during screwing were an inherent possibility). To be on the safe side however, the uncertainty on the ampoule tare weight was conservatively increased to 0.01 mg.

The ampoules (C1, C2 and C3) were connected again to the system and the whole line evacuated again (Fig. 1). The mixtures were prepared by trapping the 3 enriched isotopes into the mixing cell. Mixtures IRMM-Ar-Mix1, 2 and 3 (Table 2, Fig. 2) were prepared closely approaching the natural argon isotopic composition from air [4], with IRMM-Ar-Mix 2 most depleted (Tables 2 and 3).

3.3. The procedure for measuring the mixtures and the parent gases

When aiming at highest metrological quality, gas source mass spectrometry is highly desirable because of its very good repeatability of the results. Additionally, the use of molecular flow sample gas inlet will result in a predictable mass discrimination, at the point of effusion of the gas in the spectrometer source, a property which has been exploited to the maximum in the redetermination of the Avogadro constant [8,9]. Applying this procedure, it is possible to identify and to quantify the known systematic effects and just leaving small 'residual' factor K which can be determined by means of the prepared synthetic isotope mixtures.

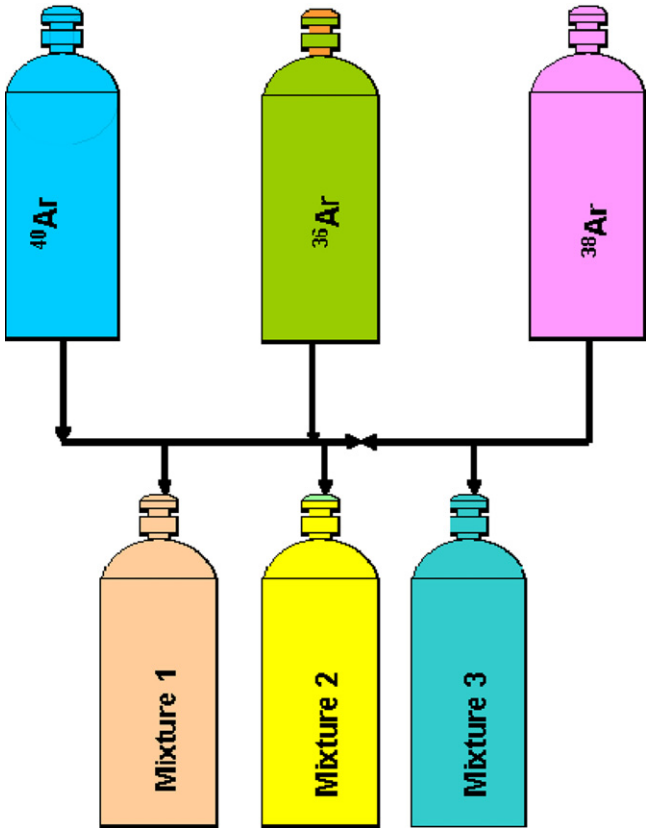

Fig. 2. Gravimetrical argon isotope mixture (IRMM-Ar-Mix1, 2 and 3) prepared by mixing 99.90 atm% ^{40}Ar, 99.54% ^{36}Ar and ^{38}Ar and 33.82% ^{38}Ar (Table 1) to mixtures with an Ar isotopic composition close to natural argon.

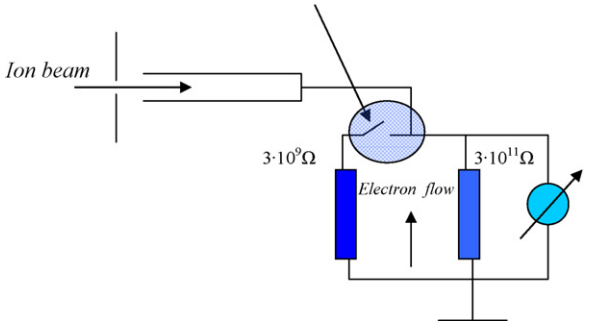

Fig. 3. Schematic presentation of the Faraday cup configuration on the MAT 271 with two amplification channels as used for measuring the enriched Ar isotopes (Table 1).

The isotope amount ratio measurements were carried out by means of IRMM's MAT271 gas mass spectrometer [12,13] by measuring the ion current ratios $r_{i/40} = I[^{i}Ar^{+}]/I[^{40}Ar^{+}]$ with $i = 36$ and 38. For the Ar mixtures and natural Ar samples the ion current ratio measurements were monitored by using a single Faraday cup (positioned at 36, 38 and 40u/e), with its signal amplified by a 3×10^9 Ω resistor. Short-term fluctuations are eliminated by symmetrically scanning the peaks 36–40u/e). Each ion current ratio measurement takes about 2 h, and mean ion current ratios of at least 5 successive measurements are obtained, with associated standard deviations (Table 3).

For the highly enriched Ar gases the entire measurement procedure had to be further developed in order to be able to measure extremely small ion currents (down to 1 fA). Such ion current ratio measurements were monitored sequentially using one Faraday cup with signals amplified over two high Ohmic resistors; 3×10^9 Ω for $I[^{40}Ar^{+}]$ and I $[^{36}Ar^{+}]$, and 3×10^{11} Ω for $I[^{36}Ar^{+}]$ and $I[^{38}Ar^{+}]$ with $I(^{36}Ar)^{+}$as a link between the two amplifications (Fig. 3).

Different sources of measurement uncertainties (Table 7) can be easily identified and as a result, isotope amount ratios with small combined uncertainties can be obtained. In the ideal case the measured ion current ratios $r_{i/40}$ could be directly converted into isotope amount ratios R_{true}. The correction factors $K = (R_{i/40}/r_{i/40})$, defined to be with $R_{i/40}$ derived from preparation of the synthetic mixture, would then be expected to be close to unity.

4. Results and discussion

4.1. Determination of the residual correction factors $K_{i/40}$ for conversion of $r_{i/40}$ to $R_{i/40}$ in Ar isotopic measurements.

In order to determine the absolute isotope amount ratios $R_{i/40} = r_{i/40}K_{i/44}$ (with $i = 36$ and 38) of the three isotope mixtures prepared (Tables 3 and 4), the absolute argon isotope amount ratios $R_{36/40}$ and $R_{38/40}$ of all starting materials (parent gases) need to be known. They are calculated from the measured ion current ratios $r_{i/40}$ on the parent gases (Table 1). However to obtain the absolute values of the starting materials, the residual correction factors $K_{i/40}$, which are intended to be determined via the synthetic isotope mixtures, already need to be known. To achieve this, an iterative procedure is chosen (Fig. 4).

For the initial step in the iterative process, the correction factors $K_{i/40}$ were assumed to be one. Then, by comparing the measured ratios $r_{i/40}$ of the mixtures to the calculated ones, first estimates of $K_{i/40}$ were obtained. These preliminary correction factors were, in turn, used to calculate the amount ratios $R_{i/40}$ of the starting materials from the measured ion current ratios $r_{i/40}$ (Table 1). A new (slightly modified) set of conversion factors was thus obtained. This iteration process was continued until no change in $K_{i/40}$ could

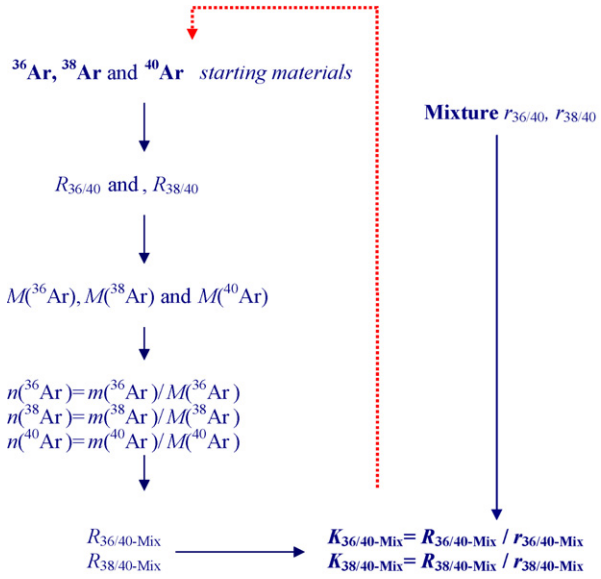

Fig. 4. The iterative procedure used to determine the absolute isotope amount ratios $R_{i/40}$ of the synthetically prepared isotope mixtures (Tables 3 and 4).

Table 4
Prepared isotope amount ratios $R_{i/40}$, measured ion current ratios $r_{i/40}$ and resulting correction factors $K_{36/40} = R_{36/40}/r_{36/40}$ and $K_{38/40} = R_{38/40}/r_{38/40}$ for the three synthetic mixtures. The stated uncertainties are total combined standard deviations calculated according to [15].

	IRMM-Ar-Mix1	IRMM-Ar-Mix2	IRMM-Ar-Mix3
$[r_{36/40}]$meas	0.0033417 (25)	0.0033017 (16)	0.0033536 (11)
$[r_{38/40}]$meas	0.00063342 (12)	0.00062557 (16)	0.00063533 (12)
$[R_{36/40}]$abs	0.0033425 (12)	0.0033035 (11)	0.0033546 (10)
$[R_{38/40}]$abs	0.0006338 (17)	0.0006265 (17)	0.0006359 (16)
$K_{36/40}$	1.00024 (98)	1.00054 (68)	1.00032 (50)
$K_{38/40}$	1.0006 (27)	1.0015 (28)	1.0010 (26)

be observed anymore. The iteration converged quickly and already after the fifth step the conversion factors stay constant (the variations on $K_{i/40}$ were below 0.01‰), and the iterative process could be stopped. The final correction factors $K_{i/40}$ obtained from the various mixtures are given in Table 4 and visualised in Figs. 5 and 6. The weighted mean conversion factors for the 3 prepared mixtures are close to unity: $K_{36/40} = 1.0037\,(38)$ and $K_{38/40} = 1.0010\,(15)$ (Table 7).

4.2. Absolute $R_{36/40}$ and $R_{38/40}$ values for Alphagaz 304033

Via the correction factors $K_{i/40}$ (Tables 4 and 5), the ion current ratios $r_{i/40}$ ($i = 36$ and 38) measured on high purity Ar (N6.0, Lot no.: 304033) separated from air, could be converted into absolute isotope amount ratios $R_{36/40}$ and $R_{38/40}$, respectively. The results are presented in Table 6. In Table 8 both $R_{36/40}$ and $R_{38/40}$ values are compared to the values obtained by Nier [6] and Lee et al. [5] (Table 7).

In general it can be said that the Lee [5] and IRMM values (Table 8) are in good agreement, while the $R_{36/40}$ obtained by Nier [6] is significant higher. Of course the variability of the isotopic com-

Table 5
Weighted means of the correction factors for the three prepared mixtures: IRMM-Ar-Mix1, 2 and 3. The stated uncertainties are total combined standard deviations calculated according to [15].

Weighted mean $K_{36/40}$	1.00037 (38)
Weighted mean $K_{38/40}$	1.0010 (15)

Table 6
Ion current ratios $r_{i/40}$ of the Ar gas obtained from the Alphagaz sample (Lot 3040330 cryogenic separation from air) and the relevant amount ratios calibrated via the synthetic isotope mixtures (Tables 4 and 5). The stated uncertainties are total combined standard deviations calculated according to [15].

	Alphagaz Lot 304033
Measured ion current ratio	
$r_{36/40}$	0.0033465 (10)
$r_{38/40}$	0.00063466 (28)
Absolute amount ratio $R_{i/40} = Kr_{i/40}$	
$R_{36/40}$	0.00334774 (93)
$R_{38/40}$	0.00063529 (57)

position of Ar in nature and the commercial process for extracting Ar from liquid air indeed changes slightly the Ar isotopic abundances. With respect to the possible variation of Ar in nature it is of interest to note that the radioactive decay of the minor isotope of potassium (^{40}K) to ^{40}Ar (and also to ^{40}Ca) gives rise in some argon samples to an anomalous Ar isotopic composition. In addition, owing the wide distribution of potassium, even major sources of argon are slightly variable. Therefore a more precise comparison cannot be given (Table 8).

Using the results in Table 6 the average molar mass of argon gas derived from liquid air is found to be $M(\mathrm{Ar}) = 39.9477969\,(37)$, with a total relative combined uncertainty of 0.09×10^{-6}. Techniques with this level of uncertainty will be sufficient to determine the molar mass of argon gas samples from teams working to redetermine the Boltzmann constant with an uncertainty easily sufficient to achieve a fractional uncertainty on k of less than 1×10^{-6}.

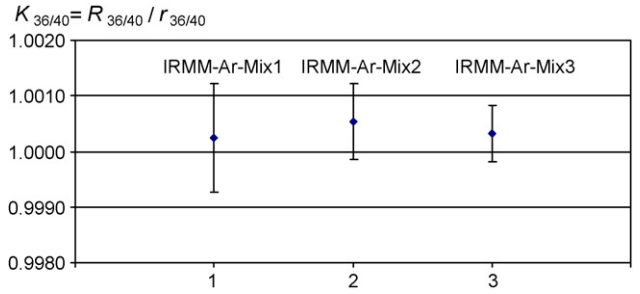

Fig. 5. The resulting conversion factors $K_{36/40} = R_{36/40}/r_{36/40}$ for the three gravimetrically prepared isotope mixtures as calculated from the prepared isotope amount ratios $R_{36/40}$ and the measured ion current ratios $r_{36/40}$ (the error bars indicate the standard uncertainty).

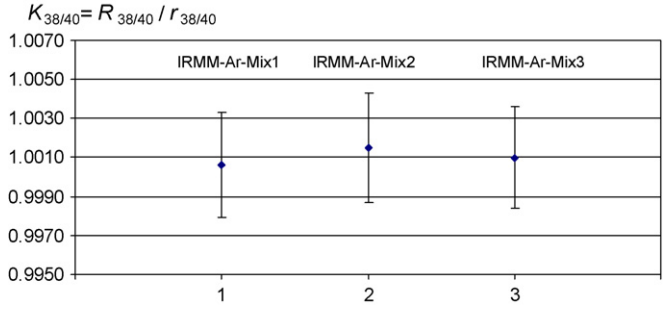

Fig. 6. The resulting conversion factors $K_{38/40} = R_{38/40}/r_{38/40}$ for the three gravimetrically prepared isotope mixtures as calculated from the prepared isotope amount ratios $R_{38/40}$ and the measured ion current ratios $r_{38/40}$ (the error bars indicate the standard uncertainty).

Table 7
Uncertainty contribution expressed in % to the different correction factors (exemplified for IRMM-Ar-Mix1). The stated uncertainties are total combined standard deviations calculated according to [15].

IRMM-Ar-Mixture 1	$K_{36/40} = 1.00024\,(98)$ $uK_{36/40}$ (in %)	$K_{38/40} = 1.0006\,(27)$ $uK_{38/40}$ (in %)
$r_{36/40}$ measured on 40Ar Isotec 601799	0.2	0.2
$r_{38/40}$ measured on 40Ar Isotec 601799	66.3	68.3
$r_{36/40}$ measured on IRMM-Ar-Mixture 1	7.4	4.5
$r_{38/40}$ measured on IRMM-Ar-Mixture 1	7.8	8.0
Mass Material 2: 36Ar Isotec 601772	0.3	0.2
Mass Material 3: 38Ar St. Petersburg, KPR210556	17.8	18.8
Impurities	<0.01	<0.01
Nuclidic masses	<0.01	<0.01

Table 8
Comparison between the measured results of the isotope amount ratios $R_{i/40}$ of Ar gas separated from air (by Alphagaz, Lot 3040330, cryogenic separation), Nier [6] and Lee et al. [5]. The stated uncertainties are total combined standard deviations calculated according to [15].

	Nier 1950	Lee 2006	IRMM this work
$R_{40/36}$	296.0 (5)	298.56 (31)	298.709 (96)
$R_{38/36}$	0.1880 (3)	0.1885 (3)	0.18977 (10)
$R_{36/40}$	0.003378 (6)	0.0033491 (35)	0.00334774 (93)
$R_{38/40}$	0.00063513 (85)	0.00063136 (69)	0.00063529 (57)

4.3. *Variability of $R_{36/40}$ and $R_{38/40}$ values in commercial Argon*

In the course of collaborative work (EMRP–European Metrology Research Programme: Project T1.J1.4) argon samples from laboratories across Europe were measured in order to determine the molar mass of argon used in acoustic resonator determinations of the Boltzmann constant. The results are summarised in Table 9 and Figs. 7 and 8. In addition to the measurements made in 2009, these tables also include some historical data (Samples 4 and 5) from INRIM.

The results indicate that, as noted by Moldover [1], the ratios $R_{36/40}$ and $R_{38/40}$ vary depending on details of the procedures used for the separation and purification of the argon. Additionally several samples were re-measured after a period of several months. Measurements 6, 7 and 9 were re-measurements of the gas samples used for measurements 1, 2 and 8, respectively. The variability between re-measured samples is less than the variability between

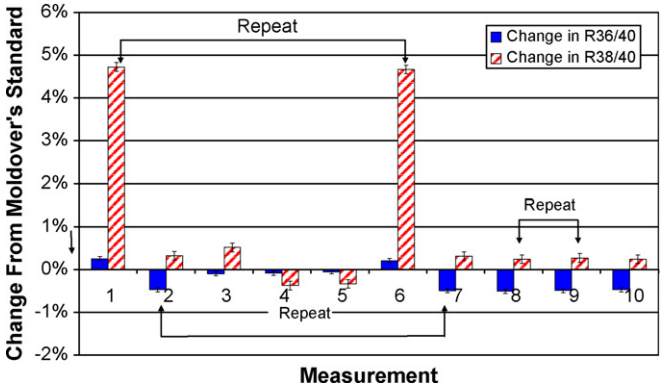

Fig. 7. The variability of $R_{36/40}$ and $R_{38/40}$ for 10 measurements on 7 samples. The figure shows the deviations of the ratios from those estimated by Moldover [1]: $R_{36/40} = 0.00334928$ and $R_{38/40} = 0.000631504$. Measurements 6, 7 and 9 are repeats of measurements 1, 2 and 8.

Table 9
Variability of the results of the measurements of $R_{36/40}$ and $R_{38/40}$ and molar mass (10 measurements, 7 samples). The same data are shown in Fig. 7.

Measurement	Gas	Comment	$R_{36/40}$	$R_{38/40}$	M(Ar)
1	Air Products BIP+	NPL Sample 1	0.003357700	0.000661330	39.94770621
2	Air Products BIP	NPL Sample 2	0.003333500	0.000633540	39.94785710
3		LNE Sample 1	0.00334600	0.00063477	39.94780511
4		INRIM Sample A	0.00334633	0.00062914	39.94781493
5		INRIM Sample B	0.00334745	0.00062939	39.94781000
6	Air Products BIP+	NPL Sample 1 re-measured	0.003356200	0.000660940	39.94771293
7	Air Products BIP	NPL Sample 2 re-measured	0.003332800	0.000633480	39.94785999
8	Air Products BIP	NPL Sample 3	0.003332300	0.000633040	39.94786284
9	Air Products BIP	NPL Sample 3 re-measured	0.003332900	0.000633220	39.94786011
10	Air Products BIP	NPL Sample 4	0.003333500	0.000633010	39.94785814

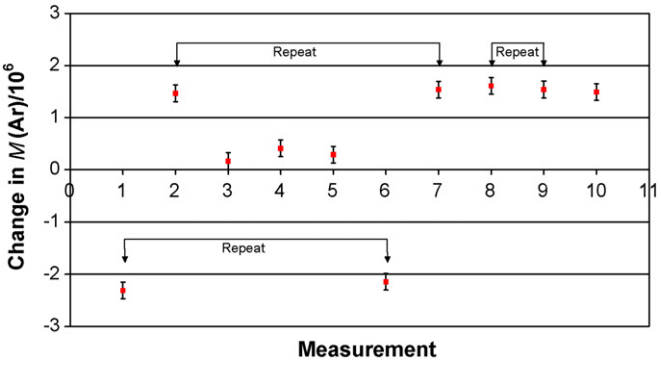

Fig. 8. Variability of the Ar molar mass (10 measurements, 7 samples) shown as deviations from 39.9477986 g mol^{-1}. Measurements 6, 7 and 9 are repeats of measurements 1, 2 and 8. The reproducibility of the measurements is better than 1 part in 10^6 but the variability between samples of different sources amounts to more than 3 parts in 10^6.

different samples, although there is consistency with gases from the same source. All the repeated data agree with each other within their combined standard uncertainties.

Most striking is the result from a sample of 'BIP+' argon which has an anomalously high value of $R_{38/40}$. The gas was sampled in the same way as the other NPL samples, in similar bottles, and there was no reason to assume any chemical interference since the gas is nominally the purest available. The sampling was made after the gas had passed through a heated getter. The repeated measurement made several months later agreed with the first within their combined standard uncertainties We are carrying out further trials on BIP+ gas to identify the source of this anomaly.

5. Conclusions

Three gaseous mixtures were prepared from isotopically enriched ^{36}Ar, ^{38}Ar and ^{40}Ar close to the natural isotopic composition of Ar. The ratio values were 'synthesized' by preparing gravimetric gas mixtures and measuring them by a gas mass spectrometer of proven linearity. These mixtures are realizations of the unit mol/mol and are therefore Primary Measurement Standards. They are used to calibrate argon ion current ratio measurements in order to obtain SI-traceable argon isotope amount ratio values, independent on any assumptive correction. The methods described are suitable for the determination of the molar mass of argon samples with a total relative combined uncertainty of 0.09×10^{-6}.

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