



Abbasi, Q. H., El Sallabi, H., Chopra, N., Yang, K., Qaraqe, K. A. and Alomainy, A. (2016) Terahertz channel characterization inside the human skin for nano-scale body-centric networks. *IEEE Transactions on Terahertz Science and Technology*, 6(3), pp. 427-434. (doi:[10.1109/TTHZ.2016.2542213](https://doi.org/10.1109/TTHZ.2016.2542213))

This is the author's final accepted version.

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<http://eprints.gla.ac.uk/141057/>

Deposited on: 03 July 2017

Enlighten – Research publications by members of the University of Glasgow
<http://eprints.gla.ac.uk33640>

Re-estimation of argon isotope ratios leading to a revised estimate of the Boltzmann constant

This content has been downloaded from IOPscience. Please scroll down to see the full text.

Download details:

IP Address: 130.209.115.82

This content was downloaded on 03/07/2017 at 15:26

Manuscript version: Accepted Manuscript

de Podesta et al

To cite this article before publication: de Podesta et al, 2017, Metrologia, at press:

<https://doi.org/10.1088/1681-7575/aa7880>

This Accepted Manuscript is: © 2017 BIPM & IOP Publishing Ltd

During the embargo period (the 12 month period from the publication of the Version of Record of this article), the Accepted Manuscript is fully protected by copyright and cannot be reused or reposted elsewhere.

As the Version of Record of this article is going to be / has been published on a subscription basis, this Accepted Manuscript is available for reuse under a CC BY-NC-ND 3.0 licence after the 12 month embargo period.

After the embargo period, everyone is permitted to copy and redistribute this article for non-commercial purposes only, provided that they adhere to all the terms of the licence

<https://creativecommons.org/licences/by-nc-nd/3.0>

Although reasonable endeavours have been taken to obtain all necessary permissions from third parties to include their copyrighted content within this article, their full citation and copyright line may not be present in this Accepted Manuscript version. Before using any content from this article, please refer to the Version of Record on IOPscience once published for full citation and copyright details, as permission will likely be required. All third party content is fully copyright protected, unless specifically stated otherwise in the figure caption in the Version of Record.

When available, you can view the Version of Record for this article at:

<http://iopscience.iop.org/article/10.1088/1681-7575/aa7880>

Re-estimation of Argon Isotope Ratios leading to a Revised Estimate of the Boltzmann Constant

Michael de Podesta^{1*}, Darren F. Mark^{2,3}, Ross C. Dymock², Robin Underwood¹, Thomas Bacquart¹, Gavin Sutton¹, Stuart Davidson¹, Graham Machin¹.

1. National Physical Laboratory, Teddington, TW11 0LW

2. Scottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF

3. Department of Earth & Environmental Science, University of St Andrews, St Andrews, KY16 9AJ, UK

* Communicating Author: michael.depodesta@npl.co.uk

ABSTRACT

In 2013, NPL, SUERC and Cranfield University published an estimate for the Boltzmann constant [1] based on a measurement of the limiting low-pressure speed of sound in argon gas. Subsequently, an extensive investigation by Yang *et al* [2] revealed that there was likely to have been an error in the estimate of the molar mass of the argon used in the experiment. Responding to [2], de Podesta *et al* revised their estimate of the molar mass [3]. The shift in the estimated molar mass, and of the estimate of k_B , was large: -2.7 parts in 10^6 , nearly four times the original uncertainty estimate. The work described here was undertaken to understand the cause of this shift and our conclusion is that the original samples were probably contaminated with argon from atmospheric air.

In this work we have repeated the measurement reported in [1] on the same gas sample that was examined in [2, 3]. However in this work we have used a different technique for sampling the gas that has allowed us to eliminate the possibility of contamination of the argon samples. We have repeated the sampling procedure three times, and examined samples on two mass spectrometers. This procedure confirms the isotopic ratio estimates of Yang *et al* [2] but with lower uncertainty, particularly in the relative abundance ratio $R_{38:36}$.

Our new estimate of the molar mass of the argon used in Isotherm 5 in [1] is $39.947\,727(15)\text{ g mol}^{-1}$ which differs by +0.50 parts in 10^6 from the estimate $39.947\,707(28)\text{ g mol}^{-1}$ made in [3]. This new estimate of the molar mass leads to a revised estimate of the Boltzmann constant of $k_B = 1.380\,648\,60(97) \times 10^{-23}\text{ J K}^{-1}$ which differs from the 2014 CODATA value by +0.05 parts in 10^6 .

[1] M. de Podesta, R. Underwood, G. Sutton, P. Morantz, P. Harris, D.F. Mark, F.M. Stuart, G. Vargha, G. Machin, A low-uncertainty measurement of the Boltzmann constant, *Metrologia*, 50 (2013) 354-376.

[2] I. Yang, L. Pitre, M.R. Moldover, J.T. Zhang, X.J. Feng, J.S. Kim, Improving acoustic determinations of the Boltzmann constant with mass spectrometer measurements of the molar mass of argon, *Metrologia*, 52 (2015) S394-S409.

[3] M. de Podesta, I. Yang, D.F. Mark, R. Underwood, G. Sutton, G. Machin, Correction of NPL-2013 estimate of the Boltzmann constant for argon isotopic composition and thermal conductivity, *Metrologia*, 52 (2015) S353-S363.

1 INTRODUCTION

1.1 BACKGROUND

In 2013, NPL, SUERC and Cranfield University published [1] an estimate for the Boltzmann constant, k_B , based on a measurement of the limiting low-pressure speed of sound, c_0 , in argon gas:

$$k_B = \frac{M_{\text{Ar}} c_0^2}{\gamma_0 N_A T_{\text{TPW}}} \quad (1)$$

In Equation 1, M_{Ar} is the molar mass of the argon gas used in the experiment; γ_0 the adiabatic index of argon in the limit of low pressure; N_A is the Avogadro constant; and T_{TPW} is the temperature of the triple point of water. Our estimate had an overall relative uncertainty of $u_R = 0.71 \times 10^{-6}$ and the component of that uncertainty arising from uncertainty in the molar mass of argon was $u_R = 0.39 \times 10^{-6}$. Throughout this paper, all uncertainties are quoted as standard uncertainties with a coverage factor $k = 1$.

The molar mass of a specific sample of argon depends on the relative abundance, A , of the three stable isotopes ^{40}Ar , ^{38}Ar and ^{36}Ar . In practice the molar mass is determined from two isotope abundance ratios: $R_{38:36} = A(^{38}\text{Ar})/A(^{36}\text{Ar})$ and $R_{40:36} = A(^{40}\text{Ar})/A(^{36}\text{Ar})$ which have typical values of approximately $R_{38:36} = 0.185$ and $R_{40:36} = 298$ [4, 5]. The molar mass can be expressed as:

$$M_{\text{Ar}} = \frac{M_{36} + M_{38} \times R_{38:36} + M_{40} \times R_{40:36}}{R_{40:36} + R_{38:36} + 1} \quad (2)$$

where M_{36} , M_{38} , and M_{40} are the molar masses of the three stable argon isotopes [6-9].

In [1], we showed that the molar mass of argon can vary from one bottle to another due to changes in isotopic composition ([1] Figure 7). Hence it was necessary to determine the isotopic composition of each bottle of gas used. To estimate M_{Ar} we sampled gas from our experiment, reduced its pressure by a factor of approximately 10^9 , and sent the resulting low pressure sample to the *Argon Isotope Facility* (AIF) at the *Scottish Universities Environmental Research Centre* (SUERC) near Glasgow, Scotland.

At SUERC an argon-specific mass spectrometer (GVI ARGUS-V) [10] was used to determine the isotopic abundance ratios by comparison with the isotopic abundance ratios of argon chemically purified from atmospheric air. By this we mean that the raw ion-current ratios in the mass spectrometer were corrected so that argon sampled from atmospheric air matched the composition of atmospheric argon previously determined by Lee *et al* [5]. The global uniformity of the composition of atmospheric argon was confirmed in [5] by measurements of the isotopic abundance ratios in samples of atmospheric argon from around the world. In essence, we used the abundance ratios of argon isotopes in the Earth's atmosphere as a 'transfer standard'. This allowed us to indirectly compare argon samples with Lee *et al*'s gravimetrically-traceable argon isotope mixtures (known as R1 and R3) held at the *Korea Institute of Standards and Science* (KRISS).

After publication of our 2013 k_B estimate [1], an extensive investigation by Yang *et al* [2] revealed that there was very likely to have been an error in our estimate of the molar mass of the argon used in that work. Responding to this, in 2014 de Podesta *et al* [3] sent a sample of gas used in the NPL Boltzmann constant work (labelled Isotherm 5) to KRISS where a *direct* comparison of the gas with the gravimetrically-prepared samples R1 and R3 was made. The revised molar mass estimate led us to revise our estimate of k_B . The revised value was in agreement within experimental uncertainties

1
2
3 with other recent estimates of k_B using both acoustic [11-13] and non-acoustic [14] techniques. But
4 the magnitude of the shift in our estimate of k_B was large: -2.7 parts in 10^6 , nearly four times the
5 original uncertainty estimate.
6

7
8 The work described here was undertaken to understand the origin of our earlier mistake, and so to
9 resolve the apparent conflict between two alternative routes of traceability to gravimetrically-
10 prepared samples R1 and R3. In this work we have repeated the measurement reported in [1] on the
11 same gas sample that was examined at KRISS [2, 3]. This gas was sampled from the bottle of gas
12 used in Isotherm 5 in our 2013 estimate of k_B . The measurements reported here are, like our 2013
13 estimate [1], traceable to KRISS samples R1 and R3 via the Lee *et al* [5] estimate of the argon isotope
14 abundance ratios in air. However in this work we used a different technique for sampling the gas
15 that has allowed us to eliminate the possibility of contamination of the gas. We have repeated the
16 sampling procedure three times, and examined samples on two mass spectrometers. This procedure
17 confirms the isotopic ratio estimates of Yang *et al* [2] but with lower uncertainty, particularly in the
18 relative abundance ratio $R_{38:36}$.
19
20
21

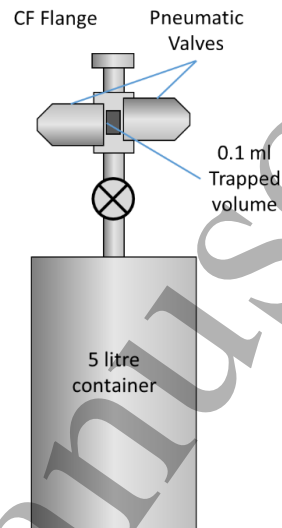
22 In Section 2 we describe the revised sampling procedure and in Section 3 we describe the mass
23 spectrometer measurements and calibration. In Section 4 we discuss the results in the context of
24 previous measurements and estimate the uncertainty of our measurements. In Section 5 we
25 estimate the molar mass of the gas used in Isotherm 5 and conclude with an estimate of the impact
26 of this revised molar mass on our 2013 estimate of the Boltzmann constant [1], and its revision in
27 2015 [3].
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

2 GAS HANDLING

2.1 BACKGROUND

For use with mass spectrometers at SUERC, gas samples were prepared in a 5 litre stainless steel chamber equipped with two pneumatically-actuated valves at the inlet and outlet of a precision 0.1 cm³ sample volume. Collectively this is referred to as a 'pipette' (Figure 1).

Figure 1: A stainless steel 'pipette' used to deliver gas to mass spectrometers used in this work.



In operation, the pipette is filled with argon gas at low pressure and attached to the inlet of the mass spectrometer. The precision 0.1 cm³ volume is then filled with gas from the pipette and for a pipette pressure of 2.5×10^{-3} Pa an aliquot of 10^{-13} mol of gas is released into the inlet of the mass spectrometer. The operation of the mass spectrometer is discussed in Section 4, but here we note that contamination of the gas in the pipette with even a tiny amount of atmospheric argon could result in such small samples appearing to have an isotopic composition similar to atmospheric argon.

2.2 HANDLING OF GAS IN 2013 AND 2017

In our 2013 work [1] an empty 'pipette' was mailed to NPL in a large crate. At NPL it was then baked, evacuated, and filled with gas from a sample bottle in a procedure involving multiple expansions which lowered its pressure to the target 2.5×10^{-3} Pa. The pipette was then mailed back to SUERC where it was attached to the ARGUS-V mass spectrometer. In the work reported here, the sampling procedure has been completely re-designed.

The gas used in Isotherm 5 of [1] was captured from the original cylinder by repeatedly evacuating a 27 cm³ sample bottle, and then filling it with gas at 0.2 MPa. After 4 fillings, the valve was closed and the gas sent to KRIS [2, 3]. Very little of the gas had been used in experiments at KRIS, and the bottle was returned from KRIS in 2017 and transported to SUERC where it was sampled into pipettes using a custom-made apparatus described in Section 2.3. The pipette containing the low-pressure gas sample then only had to be transported 5 metres to the ARGUS-V, rather than 500 km. This significantly reduces the opportunity for contamination by air due to leaks into a container at low pressure. For high pressure gases, the most we might anticipate is a small fractionation effect in which the leak-rate (however small) from the sample bottle might vary with isotopic mass. In fact we saw no evidence of such fractionation.

2.3 SAMPLING

The pressure reduction apparatus (Figure 2) is designed to capture samples into 'pipettes' from source bottles containing gas at pressures in the range 0.1 MPa to 10 MPa. After the source bottle is attached, the apparatus is baked at 80 °C and evacuated to 10^{-4} Pa for 24 hours, with the final pipette being separately baked at 150 °C and pumped for 24 hours to a pressure estimated to be 10^{-8} Pa. Finally, the pumps and pressure gauges are isolated and the entry valve to the first precision 0.1 cm³ volume is opened to capture a gas sample, and then closed to trap gas within the volume. The exit valve is then opened to allow the gas to expand into the communicating pipework, lowering the pressure by a factor ~ 1000 . Then gas within this volume is sampled by a second similar 0.1 cm³ volume and expanded further through a flexible connector into the main volume. Finally, the gas within this volume is sampled by the pipette. During this process, the gas transitions from viscous flow to molecular flow, and so at each stage in the process, valves are left open for at least 30 seconds to minimise the risk of fractionation of the gas.

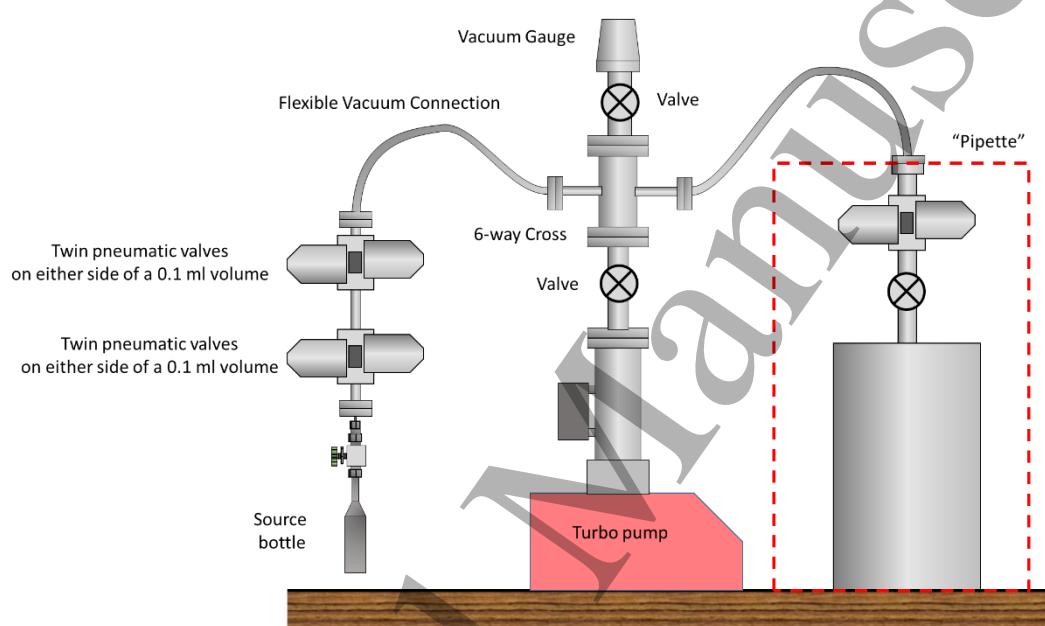


Figure 2: Schematic illustration of apparatus to capture a sample of gas at a pressure of 0.1 to 1 MPa from a source bottle. As explained in the text, a small sample of the gas is sequentially expanded through a series of volumes and is ultimately captured in a pipette (See Figure 1) which is detached and then transferred to the mass spectrometer.

We captured 3 samples of the gas from Isotherm 5 in three separate pipettes and we refer to these samples as Iso5-A, Iso5-B, and Iso5-C. When we prepared Iso5-A, we found the pressure was lower than anticipated and thus the uncertainty in the determination of the ion-current ratios was larger than expected. Subsequently we modified the capture procedure to increase the final pressure resulting in Sample Iso5-B. The efficiency of this procedure can be assessed by the signal in the ⁴⁰Ar ion-current detector which increased by a factor ~ 51 from Iso5-A to Iso5-B (Section 4.2). Iso5-C was prepared using a similar procedure to that used for Iso5-B, but was examined on a second mass spectrometer (MAP 215-50).

3 MASS SPECTROMETERS

3.1 ARGUS-V

Two mass spectrometers have been used in this work, a GVI ARGUS-V [10] and a MAP 215-50 [15]. We have previously described the operation of the ARGUS-V ([3]: Section 2.4) but here we recap the salient features of the procedures, and at the end of this section we highlight the differences between the ARGUS-V and the MAP 215-50.

After filling, the pipette is attached to the ARGUS-V and the sampled gas is directly compared with the argon purified from air in a highly-automated process.

In operation the pneumatic valves take a 0.1 cm^3 sample of gas from the pipette and expand it into a stainless steel 'extraction line' that houses three SAES GP50 getters (one operated at $450 \text{ }^\circ\text{C}$ and two at room temperature). The gas sits within this volume for 5 minutes to facilitate removal of unwanted gas species prior to expansion into the mass spectrometer ionisation chamber. This step is particularly important for the air sample as argon comprises only $\sim 0.9\%$ of the gas.

The ionisation chamber (mass spectrometer source) is a standard Nier-type design [10] in which an electron beam passing through the chamber creates argon ions which are then accelerated out of the chamber to a magnetic sector from which they then travel to the detectors. The ARGUS-V simultaneously measures the ion currents resulting from the five argon isotopes between ^{40}Ar and ^{36}Ar . The ions enter Faraday cups to create currents which are amplified by five independent trans-impedance amplifiers built into the detector head. The trans-impedance amplifier gains are set by $10^{12} \Omega$ feedback resistors for the ^{36}Ar to ^{39}Ar detectors, and a $10^{11} \Omega$ feedback resistor for the ^{40}Ar detector. The relative gain of the amplifiers is measured electronically before each series of measurements and normalised to the sensitivity of the ^{38}Ar channel. The intercomparison has an uncertainty below 1 part in 10^4 and the adjustment factors have not changed detectably over the last 6 months indicating excellent gain stability. The sensitivity is assessed at 10% of full range and at full range to test for linearity of response. Overall we estimate that the equivalence of the sensitivity of each detector is better than 1 part in 10^4 and so adds no significant uncertainty to our ratio estimates.

Data are collected for 300 seconds and baselines are measured for 20 seconds during equilibration to ensure we monitor any pressure effects induced by the expansion of the sample aliquot into the ARGUS-V. During the measurement period, the ion currents decrease with time and analysis of this variation allows the inference of the initial ion current ratios which, after calibration, can be related to the isotopic abundance ratios in the source gas.

For a standard aliquot of 10^{-13} mol , we expect a signal in the ^{40}Ar detector of approximately 1.4 V corresponding to an ion current of approximately 14 pA [10]. For the sample Iso5-B, the signal levels in the ^{40}Ar , ^{38}Ar , ^{36}Ar channels after analysis and gain compensation correspond to initial ion currents of 65 pA, 0.041 pA and 0.222 pA. Despite the small currents, no electron multipliers are used because the higher gain of these devices comes at the expense of stability and results in increased sample-to-sample variability. Background currents are typically 6.1 fA, 0.015 fA and 0.1 fA in the ^{40}Ar , ^{38}Ar , ^{36}Ar channels respectively. The significance of these signal and background levels for assessing the possible level of contamination is discussed in Section 4.2.

The measurement procedure involves cycling through samples from: the background (B) where no gas is in the ionisation chamber; air (A) where an atmospheric air sample is used; and the NPL

1
2
3 samples (X). The actual run order is [B A B X] [B A B X]... and the process is repeated until there have
4 been typically 20 NPL samples measured taking typically 1.5 days. In between measurements the
5 space near the ion source is pumped by turbo-molecular and ion pumps for approximately 20
6 minutes.
7

8
9 The ratio of the signals from the trans-impedance amplifiers in each of the measurement channels is
10 related to the relative abundance of the relevant ions in the ionisation chamber of the mass
11 spectrometer by a series of factors which differ between isotopes. The closely similar electronic
12 structure means that the ionisation efficiency of different isotopes is similar, however the
13 differences in average speed (~5%) between ^{36}Ar and ^{40}Ar , and in the way the source is operated,
14 causes ions to be 'extracted' from the ionisation chamber at differing rates (Section 3.2.1).
15
16

17 3.1.1 MAP 215-5

18 The gas loading procedure, operation with an air comparison, and ion source for the MAP 215-50 are
19 similar to those for the ARGUS-V, but the detection system and mode of operation are different.
20 Instead of five detectors allowing the simultaneous collection of the ion currents from each isotope,
21 there is only a single detector, a Balzers SEV-217 electron multiplier. In operation the magnetic field
22 is scanned to move the ion beams onto the detector in turn. In general, this results in a poorer signal
23 to noise ratio than the ARGUS-V, but there is no requirement to calibrate the relative gains for the
24 different argon isotope detectors. Background currents are similar to those in the ARGUS-V. Further
25 details of the MAP 215-50 can be found in [15, 16].
26
27
28
29

30 3.2 AIR CALIBRATION

31 To calibrate the relative sensitivity of the mass spectrometer to the different argon isotopes, a
32 multiplicative factor (mass discrimination factor) is calculated from the measurement of argon
33 isotope ratios measured in argon which has been chemically purified from air [17, 18]. The factor is
34 chosen to make the ion current ratios ($I_{40:36}$ and $I_{38:36}$) from air samples match the isotopic
35 abundance ratios $R_{40:36} = 298.56(31)$ and $R_{38:36} = 0.1885(3)$ reported by Lee *et al* [5] for air. These
36 adjustments are based on the following two assumptions.
37
38
39

40 Firstly we assume that the isotopic composition of argon in atmospheric air is the same all around
41 the world. This was experimentally verified in [5], and in [3] we argued that if it were not the case,
42 then we would also expect fluctuations in the ratio of atmospheric oxygen and nitrogen, which are
43 not observed.
44

45 Secondly, the adjustments rest on the principle that the physical processes which can discriminate
46 between argon isotopes, can do so only the basis of molecular mass or speed. If this last assumption
47 is correct then we would expect that for a wide variety of processes, the raw ion current ratio $I_{38:36}$
48 should be affected half as much as the raw ion current ratio $I_{40:36}$.
49
50

51 If these assumptions are correct, then we would expect that air sampled anywhere in the world at
52 any time would provide us with argon whose isotopic composition can be related to the composition
53 determined by Lee *et al*. Specifically on a plot of $R_{40:36}$ versus $R_{38:36}$ all observed ion current ratios for
54 argon samples derived from air should lie on a so-called 'fractionation line' that runs through the
55 abundance ratio in atmospheric argon.
56
57

58 Ion current ratios for three groups of air samples examined in the ARGUS-V and MAP 215-50 are
59 shown in Figure 3. The graph plots $I_{40:36}$ versus $I_{38:36}$ for each individual aliquot of gas. It is clear that
60 the 'high pressure' (HP) air provides the lowest uncertainty for calibration of the ARGUS-V. In what

follows we will base our final conclusions on calibration by this sample, but we also include calculations based on the air sample used in the MAP 215-50 for comparison.

The ‘high pressure’ data was acquired by simply adding 10 aliquots of air to the extraction line before opening the extraction line to the mass spectrometer. However we noted that the scatter of the data reduced much more than would be expected ($\sim\sqrt{10}$) if the scatter in the ‘low pressure’ (LP) data arose from random noise in the ‘signal’. Instead the scatter has reduced by a factor of approximately 10. This makes it likely that the scatter substantially arises from difficulty in accurately subtracting backgrounds at low signal levels.

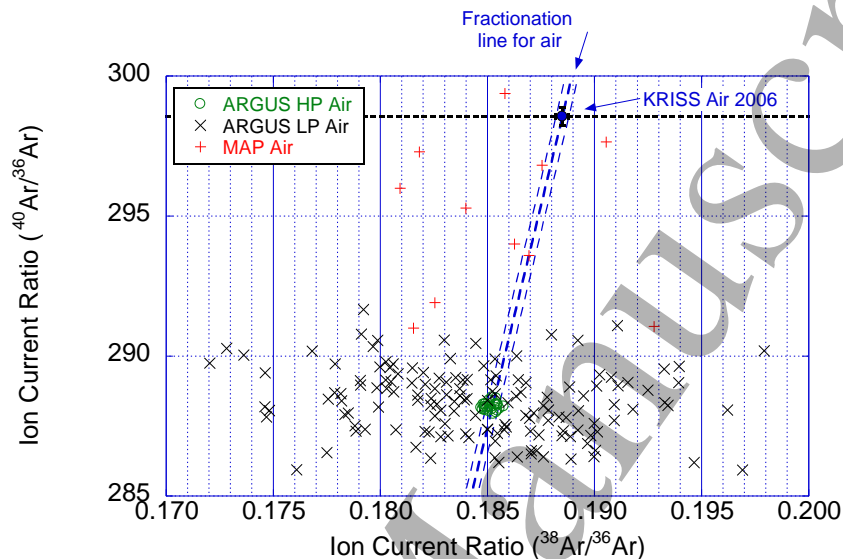


Figure 3: The ion current ratios for each individual aliquot of three samples: low pressure (LP) air in the ARGUS-V, high pressure (HP) air in the ARGUS-V, and low pressure (LP) air in the MAP 215-50.

The averages of the individual aliquots with statistical uncertainties are shown in Figure 4, which covers roughly the central third of Figure 3. We note that the averaged ‘high pressure’ air value lies close to the fractionation line through Lee et al’s estimated composition of atmospheric argon. Given the spread of the individual aliquots, the averaged ‘low pressure’ air estimate agrees reasonably with the ‘high pressure’ estimate, and the difference between the two results might represent a statistical accident. However considering that there was evidence of a possible background subtraction problem for low-pressure data, it is more likely to arise from a systematic error, probably in the horizontal $R_{38:36}$ axis. The data point from the MAP 215-50 also lies close to the fractionation line, but the large statistical uncertainty makes it hard to identify possible background subtraction problems

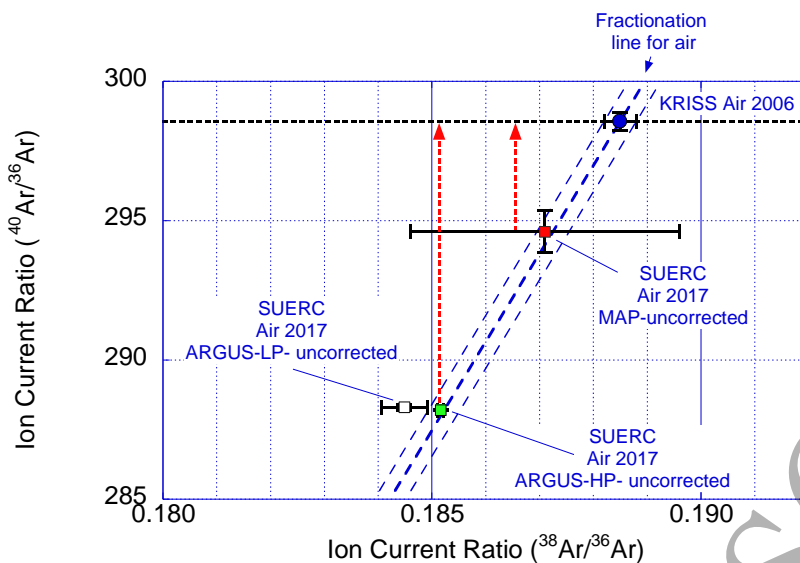


Figure 4: Statistical summaries of the air data sets shown in Figure 3 showing error bars at ± 1 standard uncertainty. It is clear that the averages fall close to the 'air fractionation line' drawn through the abundance ratios for argon isotopes measured by Lee *et al* in 2006 [3]. The dotted red lines show adjustment required in the ratio $I_{40:36}$ to cause it to match the ratio $R_{40:36}$ determined by Lee *et al*.

The data point shown for the 'high pressure' ARGUS-V on Figure 4 ($I_{38:36} = 0.18517(6)$ and $I_{40:36} = 288.20(3)$) is the average of 25 measurements of air. The data point shown for MAP 215-50 on Figure 4 ($I_{38:36} = 0.1871(25)$ and $I_{40:36} = 294.60(75)$) is the average of 14 measurements of air. Significantly, the two mass spectrometers are comparing against different samples of air captured at different times, however within experimental uncertainty, both samples lie on the fractionation line through the Lee *et al* estimate of the isotope abundance ratios. This gives us confidence in the validity of the assumptions outlined above.

To calibrate the ARGUS-V and MAP 215-50 for use with argon of unknown isotopic composition, the factor required to correct the ion current ratio $I_{40:36}$ to the abundance ratio $R_{40:36}$ recommended by Lee *et al* [4] ($R_{38:36} = 0.1885(3)$ and $R_{40:36} = 298.56(31)$) is calculated.

For the ARGUS-V, the factor is estimated to be $F_{40:36} = 1.03596(10)$ and for the MAP 215-50, the factor is estimated to be $F_{40:36} = 1.0134(25)$ where the uncertainty is that arising from the type A uncertainty in the determination of $I_{40:36}$ for air. The correction factor for the ratio $R_{38:36}$ is then calculated as:

$$F_{38:36} = 1 + 0.5(F_{40:36} - 1) \quad (3)$$

i.e. 1.01798(32) for the ARGUS-V and 1.0067(14) for the MAP 215-50. This procedure for estimating the correction factor for $R_{38:36}$ is used because $R_{40:36}$ can generally be measured with lower fractional uncertainty than $R_{38:36}$.

After correction, the air data does indeed agree with the data of Lee *et al* (Figure 5). Please note that in Figure 5 the MAP 215-50 and ARGUS-V data have been vertically offset from the KRIS calibration line by ± 0.1 respectively to allow the error bars to be clearly seen. Also, the error bars shown include only the type A component of uncertainty so that the closeness of the calibration point to the Lee *et al* value can be seen.

We note the low statistical uncertainty of the ARGUS-V calibration point, and the fact that for both calibrations the ratio $R_{38:36}$ falls within the uncertainty range of the Lee *et al* composition for air.

However it is important to remember that both points are plotted *relative* to Lee *et al*'s datum, and the absolute composition of the gas remains uncertain to the same extent that Lee *et al*'s gravimetrically traceable value is uncertain, and this represents a fundamental limit to the overall uncertainty with which the $R_{40:36}$ ratio in an unknown sample can be determined.

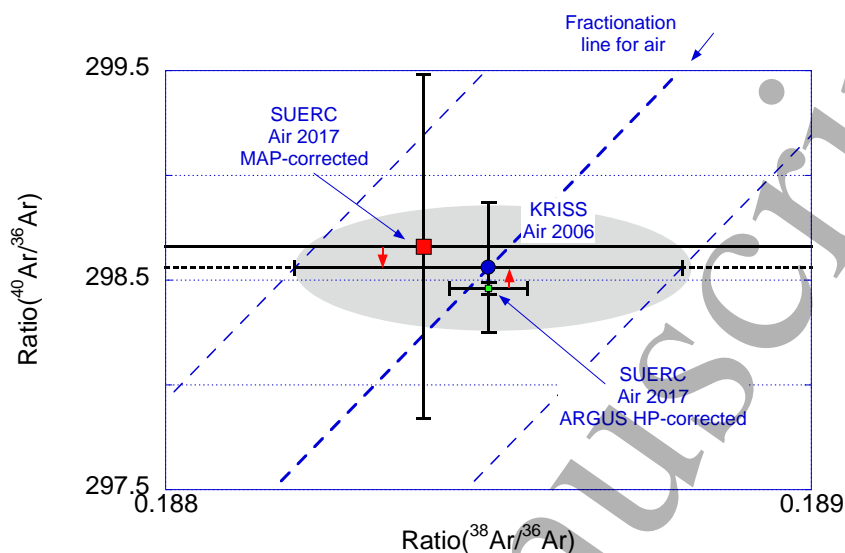


Figure 5: Corrected ion current ratios $R_{40:36}$ versus $R_{38:36}$ for air samples examined in the ARGUS-V and MAP 215-50 mass spectrometers. The data points show the ion current ratios after correction to the composition of air determined by Lee *et al* in 2006. Note that the location on $R_{38:36}$ axis is based entirely on the correction to the $R_{40:36}$ ratio. Thus the fact that the data fall within the uncertainty estimated by Lee *et al* is an indication that the factors fairly correct the fractionation occurring within the instrument – mainly within the ion source. In this figure the MAP 215-50 and ARGUS-V data have been vertically offset from the KRIS calibration line by ± 0.1 respectively to allow the error bars to be clearly seen.

3.2.1 The origin of the fractionation.

It is noticeable on Figure 3 that the data for air are considerably more fractionated in the ARGUS-V than the MAP 215-50 mass spectrometer. This was not always so. In our 2014 paper ([3]: figure 2) the raw ion current ratios for air measured on the ARGUS-V plotted close to the value shown here for the MAP 215-50. The change in behaviour of the ARGUS-V occurred after replacement of the ion source. After replacement, the mass spectrometer settings are optimised, with the most notable adjustment being to the voltage applied to the 'ion repeller': the component of the source that induces ion extraction. Changes to source settings are also common as filaments approach the end of their life and sensitivity deteriorates.

This change in fractionation indicates that – as expected – the ion source is the main cause of the fractionation, and that changes in its design and operating settings can significantly affect the magnitude of the fractionation. However, it also indicates that despite the complex physical processes occurring inside the ion source, the ion current ratios still lie on the fractionation line.

4 RESULTS

4.1 GAS FROM ISOTHERM 5

4.1.1 Samples

Here we discuss the estimated abundance ratios $R_{38:36}$ and $R_{40:36}$ of samples drawn from the Isotherm 5 sample bottle previously examined at KRiSS [3]. The sample bottle was at a pressure of approximately 0.2 MPa and samples were expanded by a factor of approximately 10^8 to produce sample Iso5-A at an estimated pressure of approximately 10^{-3} Pa, lower than we had anticipated. A revised procedure was used for sample Iso5-B which, based on the ratio of ion currents, resulted in an increase in pressure by a factor of approximately 51. Sample Iso5-C was captured in a similar way to Iso5-B, but was examined on the MAP 215-50 machine and compared against a different sample of atmospheric argon.

4.1.2 Data

Figure 6 shows the averages of the three isotherm 5 samples after correcting the ion current ratios as described in Section 3.2. The error bars plotted are the type A uncertainty estimates based on the variability of $I_{40:36}$ and $I_{38:36}$ (Table 1: Section 1). The data cloud formed by the individual aliquot data is similar in extent to that in Figure 3, and Figure 6 shows a selection of the data from individual aliquots which happen to plot close to their averages. We note that all three data points are mutually consistent within their type A uncertainties. However it is clear any low uncertainty estimate of the gas composition will be dominated by the Iso5-B sample.

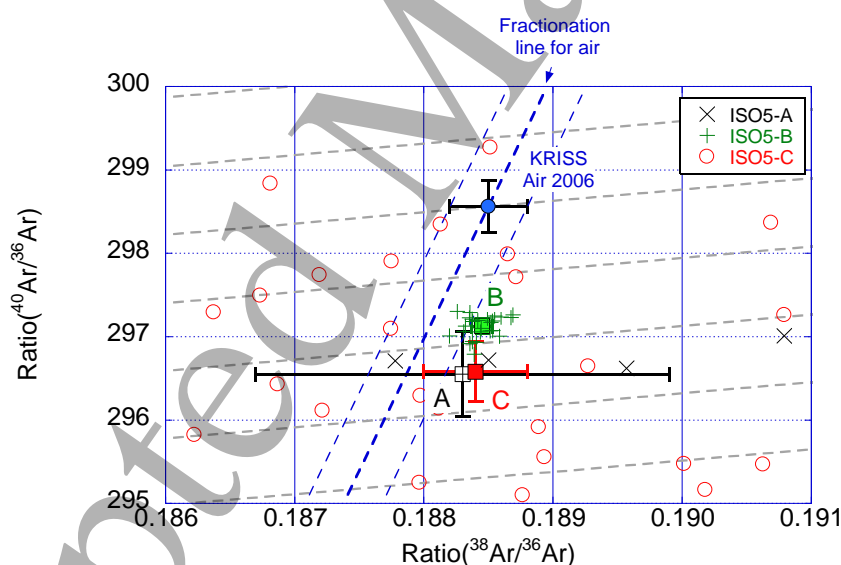


Figure 6: The estimated abundance ratios for three samples of gas from Isotherm 5. Sample A was the first sample and had a low pressure. Samples B and C were captured using a modified procedure to increase the pressure. Samples A and B were examined on the ARGUS-V and Sample C on the MAT 215-50. The data plotted correspond to the data in Section 1 of Table 1

Also shown in Figure 6 and subsequent figures are sloping grey lines which link isotopic compositions of equal molar mass. One of the lines passes through the argon composition of Lee *et al*, and the other lines correspond to molar masses which differ by multiples of 1 part in 10^6 .

Figure 7 shows the same data as Figure 6 but now additionally includes the type A standard uncertainty in the air data (Table 1: Section 2) that was used to estimate the correction factor ($F_{40:36}$

or $F_{38:36}$). The combined uncertainties are shown in Table 1 Section 3. This correction factor uncertainty barely affects the Iso-5 A and B uncertainties, because the air calibration has such low uncertainty. However it increases the uncertainty in Iso5-C because the MAP 215-50 air calibration (Figure 4) has a relatively high uncertainty.

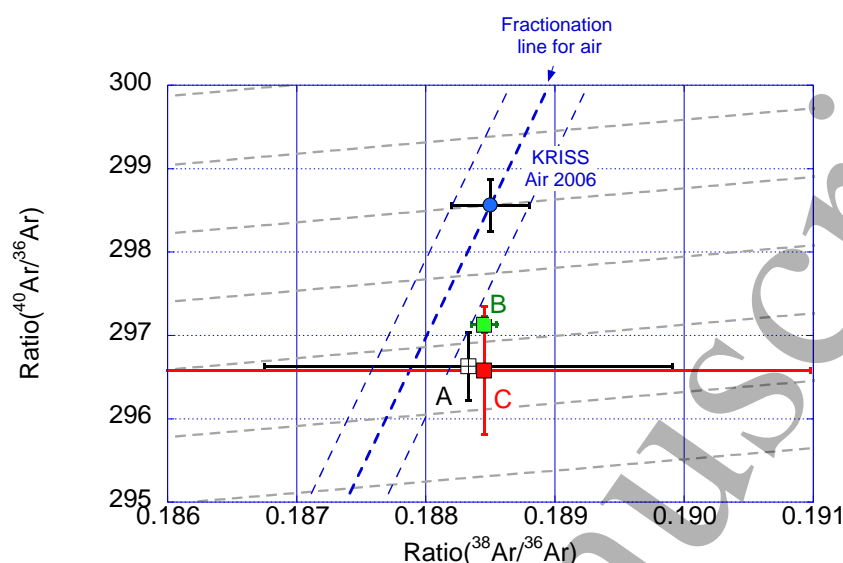


Figure 7: The estimated abundance ratios for three samples of gas from Isotherm 5. Sample A was the first sample and had a low pressure. Samples B and C were captured using a modified procedure to increase the pressure. Samples A and B were examined on the ARGUS-V and Sample C on the MAT 215-50. The data plotted correspond to the data in Section 3 of Table 1

Table 1 Estimates of the isotopic composition of three samples of gas from Isotherm 5 showing the quadrature sum of their type A uncertainty, and the type A uncertainty in the reference sample of air. The data from Section 1 of the table is shown in Figure 6, the data from Section 2 is shown in Figure 4, and the data from Section 3 is shown in Figure 7. The weighted mean value and uncertainty is shown in Figure 8.

Sample	1		2		3		Overall Type A		Weight	
	$R_{38:36}$	$R_{40:36}$	$u(R_{38:36})$	$u(R_{40:36})$	$u(R_{38:36})$	$u(R_{40:36})$	$u(R_{38:36})$	$u(R_{40:36})$	$R_{38:36}$	$R_{40:36}$
Iso5-A	0.18833	296.63	0.00158	0.40	0.00006	0.03	0.00158	0.41	0.4%	5%
Iso5-B	0.18845	297.13	0.00008	0.09	0.00006	0.03	0.00010	0.10	99.5%	93%
Iso5-C	0.18845	296.58	0.00036	0.18	0.00250	0.75	0.00253	0.77	0.1%	1%
Weighted Mean	0.18845	297.10					0.00010	0.09		

Our estimate of the isotopic composition of the gas from Isotherm 5 was produced by taking the weighted average of the 3 estimates on Figure 7 (297.10, 0.18845). The weighted average of each ratio has been calculated separately which means that with regard to $R_{40:36}$, the three samples (A:B:C) are weighted (5%:93%:1%) whereas with regard to $R_{38:36}$, the samples are weighted (0.4%:99.5%:0.1%). The type A weighted uncertainties of the weighted mean (0.0001, 0.09) are plotted in Figure 7. Unsurprisingly, this weighted average differs by only a small amount ($\Delta R_{40:36} = 0.03$ and $\Delta R_{38:36} = 0$) from the Iso5-B estimate.

Significantly, the ratio $R_{40:36}$ is in good agreement with the estimate from KRISSE produced in 2014 [2] which was based on direct comparison of Isotherm 5 gas with gravimetrically-prepared isotope mixtures R1 and R3. However, the new data lie close to the fractionation line unlike the

measurement at KRISS and our uncertainty in this ratio is smaller than that achieved at KRISS. Close association with the mass fractionation line is expected since the argon in the Isotherm 5 samples was ultimately derived from atmospheric air.

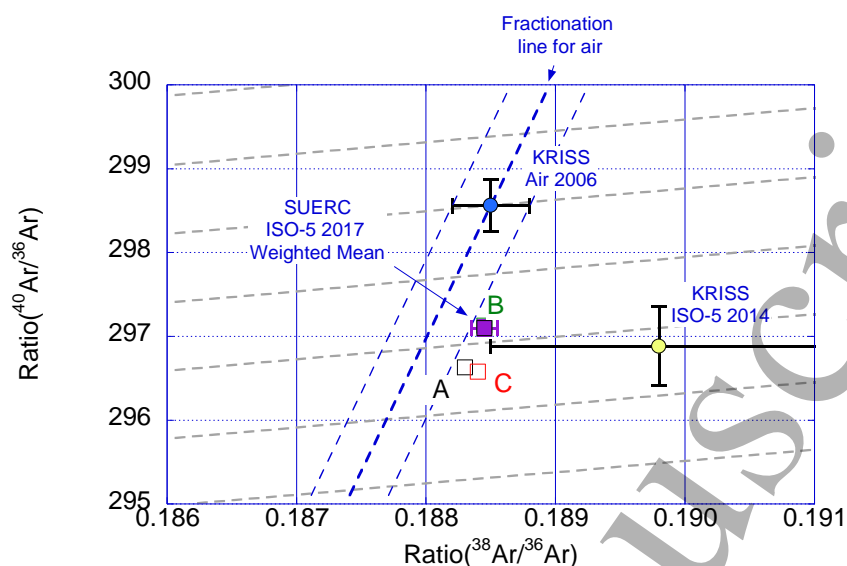


Figure 8: The weighted mean of the three samples (A, B, C) shown alongside the estimated isotopic ratios deduced by KRISS in 2014. The type A error bars on the SUERC weighted mean are shown, but the error bars on the individual estimates (A, B, C) shown in Figures 6 and 7 are omitted for clarity.

4.1.3 Reference to gravimetric samples

The isotope abundance ratios are all estimated with respect to the isotopic abundance ratios in air determined by Lee *et al* [5] and our results can never have an uncertainty lower than that reported in [5]. To estimate the overall uncertainty we need to combine the type A uncertainty of the weighted mean in Table 1 with the Lee *et al* uncertainty in $R_{40:36}$ (0.31) and $R_{38:36}$ (0.0003): we find $u(R_{40:36}) = 0.32$ and $u(R_{38:36}) = 0.0003$. The weighted mean value and overall uncertainty are shown in Figure 9.

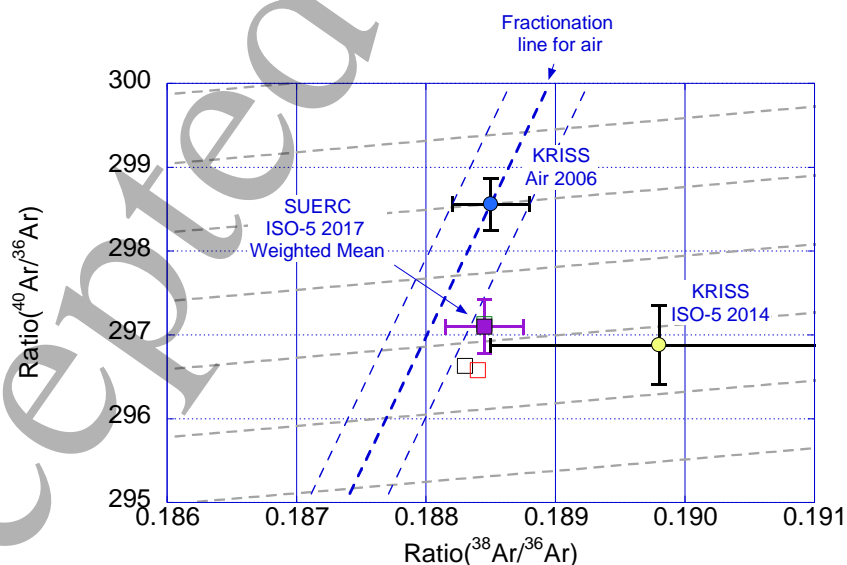


Figure 9: The same data as shown in Figure 8 but re-plotted after including the uncertainty of the reference to the gravimetrically-validated isotopic abundance ratios of Lee *et al*.

4.2 SIGNAL LEVELS, BACKGROUNDS AND CONTAMINATION CHECKS

There are two potential ways in which contamination of the sample gas might lead to errors in the data.

The first source of contamination might occur within the sampling system if, for example, significant amounts of residual argon mixed with the sample gas in the sampling procedure (Section 2.3). We can assess the maximum possible extent of this by comparing the argon isotope ratios measured in samples Iso5-A and Iso5-B, which differed in pressure by a factor 51. Despite the large difference in pressure, the argon-isotope ratios agree within their combined uncertainties. If we ascribe significance to the small difference in the measured $R_{40:36}$ ratios and consider this to be evidence of contamination, then it can affect the Iso5-B sample by at most a fraction 1/51 of this difference i.e. it would affect $R_{40:36}$ by at most 0.01, which is 32 times smaller than the final type A uncertainty. Further consideration of the ‘high pressure’ sample Iso5-C, further reduces the plausible level of contamination within the sampling system. Overall, we consider that contamination within the sampling system is insignificant compared to the type A uncertainties.

Table 2. Typical signal levels achieved in this work. For the ARGUS-V mass spectrometer the ion currents are 1 pA per volt. For the MAP 215-50 mass spectrometer the ion currents are 10 pA per volt. Also shown is the signal-to-background ratio.

Spectrometer	Sample	N	Average Signal Level			Signal-to-background Ratio		
			^{40}A /V	^{38}Ar /mV	^{36}Ar /mV	^{40}A	^{38}Ar	^{36}Ar
ARGUS-V	Air	126	2.365	1.513	8.2016	388	101	82
ARGUS-V	Air	25	26.924	17.298	93.4209	4414	1153	934
MAP215-50	Air	14	3.367	2.135	11.425	387	107	286
ARGUS-V	Iso 5-A	21	1.254	0.8085	4.379	206	54	44
ARGUS-V	Iso 5-B	25	63.798	41.177	222.440	10459	2745	2224
MAP215-50	Iso 5-C	40	32.307	20.652	110.363	3713	1033	2759

The second possible source of contamination – or more properly bias – is in the subtraction of backgrounds. Table 2 shows the average signal levels and the signal-to-background ratio for the air samples and Isotherm 5 samples used in this work. By looking at the measured $R_{40:36}$ ratios for samples with the same gas but different ratios of ‘signal’ to ‘background’ ion current ratios, we can assess the possible extent of bias due to background subtraction. The background subtraction is most challenging for the measurements with the smallest ion currents i.e. $R_{38:36}$. Considering once again samples Iso5-A and Iso5-B we note that the signal-to-background ratios for the ^{38}Ar channel are 54 and 2745 respectively. Similarly, the signal-to-background ratios for the ^{36}Ar channel are 44 and 2224 respectively. If the background subtraction were mis-estimated, then we might expect a significant difference between the estimated $R_{38:36}$ for Iso5-A (0.1883(16)) and Iso5-B (0.1884(2)). However (Table 1) the two estimates of the ratio differ by just 1 part in 1880, providing strong evidence that the background subtraction introduces no bias at a level comparable with the type A uncertainties.

However we note that in Figures 6 to 9, the weighted means and individual averages fall significantly to one side of the fractionation line, albeit with a much smaller displacement than in [2]. The question we need to consider is whether this is really the case, with the offset from the fractionation line being caused by some unknown feature of the argon processing procedure. Or whether there is a problem with background subtraction in the $R_{38:36}$ ratio, despite the large signal-to-background ratio. We consider this an open question, and we follow Yang *et al* [2] in adding a component of uncertainty to account for this displacement (Section 5.2).

5 CONCLUSIONS

5.1 ISOTOPIC COMPOSITION OF GAS USED IN ISOTHERM 5

The general conclusion of this work is that our best estimate of the isotopic abundance ratios in the gas used in Isotherm 5 of our Boltzmann constant estimate [1] are $R_{38:36} = 0.18845(32)$ and $R_{40:36} = 297.10(32)$. These estimates are consistent with the isotopic composition determined by Yang *et al* [2], but the data do not show the large $R_{38:36}$ offset seen in that work.

Significantly, the data also confirm that the isotopic composition determined by us in 2013 [1] was wrong. Given that both this study and that in [1] were carried out with the same mass spectrometer and using similar analytical procedures, it seems likely that the origin of the error was contamination of the low pressure gas with atmospheric air during the sampling procedure.

This suggestion is further supported by the fact that in [1], the isotopic composition of Isotherm 5 gas appeared to be similar to that of atmospheric argon, but argon gas sampled using the procedures described here is distinctly different from atmospheric argon.

To check this conclusion we have examined three independently-prepared samples at a range of pressures and examined the gas in two mass spectrometers with significantly different mass fractionation characteristics, each comparing the gas against its own independently-captured air sample. Together these checks give us confidence that the gas samples measured in this work have not been affected by the contamination that appears to have affected our previous work.

Finally we note that Yang *et al* [2] also measured a range of argon samples from experiments used to determine the Boltzmann constant using acoustic thermometry. They showed a correlation between the molar mass determined from the isotopic composition and the speed of sound at the temperature of the triple point of water. Thus consistency with their results is especially significant in terms of demonstrating consistency with other acoustic measurements of the Boltzmann constant.

5.2 MOLAR MASS OF GAS USED IN ISOTHERM 5

From the data in Table 2 we can calculate a revised value for the molar mass of the Isotherm 5 gas. Using the CODATA 2006 values for the molar masses of the pure isotopes [8, 9], we can use Equation 2 to estimate that the molar mass of the argon used in Isotherm 5 is $39.947\,727(15)\text{ g mol}^{-1}$, a relative uncertainty of $u_R = 0.37 \times 10^{-6}$. This differs by +0.50 parts in 10^6 from the estimate $39.947\,707(28)\text{ g mol}^{-1}$ made in [3], and the two results are consistent within combined uncertainties.

However as noted in Section 4.2, the isotopic composition we have determined has a small offset from the fractionation line for an unknown reason. Following Yang *et al*, we add a small additional uncertainty component to allow for this offset. In our case, the shift amounts to only 0.07 parts in 10^6 in mass and the uncertainty quoted above is negligibly affected.

We note that these two estimates were made using a total of three different mass spectrometers with different fractionation characteristics and detector technologies; with different reference gases; and with different independent sampling techniques. We thus consider our estimate to be reasonably robust. However our work is referenced to the Lee *et al* [5] estimate of the isotopic composition of air, and if future work were to revise that estimate, then this estimate would also change.

5.3 REVISED VALUE OF NPL ESTIMATE OF THE BOLTZMANN CONSTANT

Our new estimate of the molar mass in Equation 1 allows us to re-estimate the molar gas constant, R , and the Boltzmann constant, $k_B = R/N_A$. The calculation is summarised in Table 3 which is an updated version of Table 11 in [1]. The relative standard uncertainty in R is estimated as the quadrature sum of the relative standard uncertainties in M_{Ar} , c_0^2 and T . The standard uncertainty in k_B additionally includes the standard uncertainty in N_A .

We find $R = 8.314\,460\,3\,(58)\text{ J K}^{-1}\text{ mol}^{-1}$ which corresponds to $k_B = 1.380\,648\,60\,(97) \times 10^{-23}\text{ J K}^{-1}$. Both values have the same relative standard uncertainty $u_R = 0.70 \times 10^{-6}$. Our estimates of R and k_B are higher than their values in CODATA 2014 [6, 7] by 0.062 and 0.054 parts in 10^6 respectively.

		Estimate	$u_R/10^{-6}$	Weight
M	g mol^{-1}	39.947 727(19)	0.373	28.3%
T	K	273.160 000(99)	0.364	26.8%
c_0^2	$\text{m}^2\text{ s}^{-2}$	94756.245(45)	0.470	44.9%
R	$\text{J K}^{-1}\text{ mol}^{-1}$	8.314 460 3 (58)	0.702	
N_A	mol^{-1}	$6.022\,140\,857\,(74) \times 10^{23}$	0.012	0.0%
k_B	J K^{-1}	$1.380\,648\,60\,(97) \times 10^{-23}$	0.702	

Table 3. Estimates of the molar gas constant R and the Boltzmann constant k_B and their associated uncertainty. The last column labelled 'weight' shows the percentage contribution of each term to the overall uncertainty.

6 ACKNOWLEDGEMENTS

The authors would especially like to thank: Inseok Yang for many helpful and insightful comments during this work, and for carefully looking after the sample of Isotherm 5 gas; and Peter Harris for advice on the assessment of uncertainties. Additionally we are grateful to the reviewers for their detailed and helpful comments.

The *Argon Isotope Facility* at SUERC is funded by the Natural Environment Research Council. This work was partly funded by the UK Department for Business, Energy and Industrial Strategy and by the European Metrology Research Program (EMRP). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

7 REFERENCES

- [1] M. de Podesta, R. Underwood, G. Sutton, P. Morantz, P. Harris, D.F. Mark, F.M. Stuart, G. Vargha, G. Machin, A low-uncertainty measurement of the Boltzmann constant, *Metrologia*, 50 (2013) 354-376.
- [2] I. Yang, L. Pitre, M.R. Moldover, J.T. Zhang, X.J. Feng, J.S. Kim, Improving acoustic determinations of the Boltzmann constant with mass spectrometer measurements of the molar mass of argon, *Metrologia*, 52 (2015) S394-S409.
- [3] M. de Podesta, I. Yang, D.F. Mark, R. Underwood, G. Sutton, G. Machin, Correction of NPL-2013 estimate of the Boltzmann constant for argon isotopic composition and thermal conductivity, *Metrologia*, 52 (2015) S353-S363.
- [4] A.O. Nier, A Redetermination of the Relative Abundances of the Isotopes of Carbon, Nitrogen, Oxygen, Argon, and Potassium, *Physical Review*, 77 (1950) 789-793.
- [5] J.Y. Lee, K. Marti, J.P. Severinghaus, K. Kawamura, H.S. Yoo, J.B. Lee, J.S. Kim, A redetermination of the isotopic abundances of atmospheric Ar, *Geochim Cosmochim Acta*, 70 (2006) 4507-4512.
- [6] P.J. Mohr, D.B. Newell, B.N. Taylor, CODATA Recommended Values of the Fundamental Physical Constants: 2014, *J Phys Chem Ref Data*, 45 (2016).
- [7] P.J. Mohr, D.B. Newell, B.N. Taylor, CODATA recommended values of the fundamental physical constants: 2014, *Rev Mod Phys*, 88 (2016).
- [8] P.J. Mohr, B.N. Taylor, D.B. Newell, CODATA recommended values of the fundamental physical constants: 2006, *J Phys Chem Ref Data*, 37 (2008) 1187-1284.
- [9] P.J. Mohr, B.N. Taylor, D.B. Newell, CODATA recommended values of the fundamental physical constants: 2006, *Rev Mod Phys*, 80 (2008) 633-730.
- [10] D.F. Mark, D. Barfod, F.M. Stuart, J. Imlach, The ARGUS multicollector noble gas mass spectrometer: Performance for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, *Geochemistry, Geophysics, Geosystems*, 10 (2009) Q0AA02.
- [11] L. Pitre, L. Risegari, F. Sparasci, M.D. Plimmer, M.E. Himbert, P.A.G. Albo, Determination of the Boltzmann constant k from the speed of sound in helium gas at the triple point of water, *Metrologia*, 52 (2015) S263-S273.
- [12] H. Lin, X.J. Feng, K.A. Gillis, M.R. Moldover, J.T. Zhang, J.P. Sun, Y.Y. Duan, Improved determination of the Boltzmann constant using a single, fixed-length cylindrical cavity, *Metrologia*, 50 (2013) 417-432.
- [13] R.M. Gavioso, D.M. Ripa, P.P.M. Steur, C. Gaiser, D. Truong, C. Guianvarc'h, P. Tarizzo, F.M. Stuart, R. Dematteis, A determination of the molar gas constant R by acoustic thermometry in helium, *Metrologia*, 52 (2015) S274.
- [14] C. Gaiser, B. Fellmuth, N. Haft, A. Kuhn, B. Thiele-Krivoi, T. Zandt, J. Fischer, O. Jusko, W. Sabuga, Final determination of the Boltzmann constant by dielectric-constant gas thermometry, *Metrologia*, 54 (2017) 280.
- [15] D.F. Mark, M. Petraglia, V.C. Smith, L.E. Morgan, D.N. Barfod, B.S. Ellis, N.J. Pearce, J.N. Pal, R. Korissettar, A high-precision $\text{Ar-40}/\text{Ar-39}$ age for the Young Toba Tuff and dating of ultra-distal tephra: Forcing of Quaternary climate and implications for hominin occupation of India, *Quaternary Geochronology*, 21 (2014) 90-103.
- [16] D.F. Mark, C.M. Rice, A.E. Fallick, N.H. Trewin, M.R. Lee, A. Boyce, J.K.W. Lee, $\text{Ar-40}/\text{Ar-39}$ dating of hydrothermal activity, biota and gold mineralization in the Rhynie hot-spring system, Aberdeenshire, Scotland, *Geochim Cosmochim Acta*, 75 (2011) 555-569.
- [17] P.R. Renne, W.S. Cassata, L.E. Morgan, The isotopic composition of atmospheric argon and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology: Time for a change?, *Quaternary Geochronology*, 4 (2009) 288-298.
- [18] P.R. Renne, W.S. Cassata, L.E. Morgan, The isotopic composition of atmospheric argon and $^{40}\text{Ar}/\text{Ar-39}$ geochronology: Time for a change? (vol 4, pg 288, 2009), *Quaternary Geochronology*, 5 (2010) 82-82.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Accepted Manuscript