Determination of Ar molar mass for the Boltzmann constant

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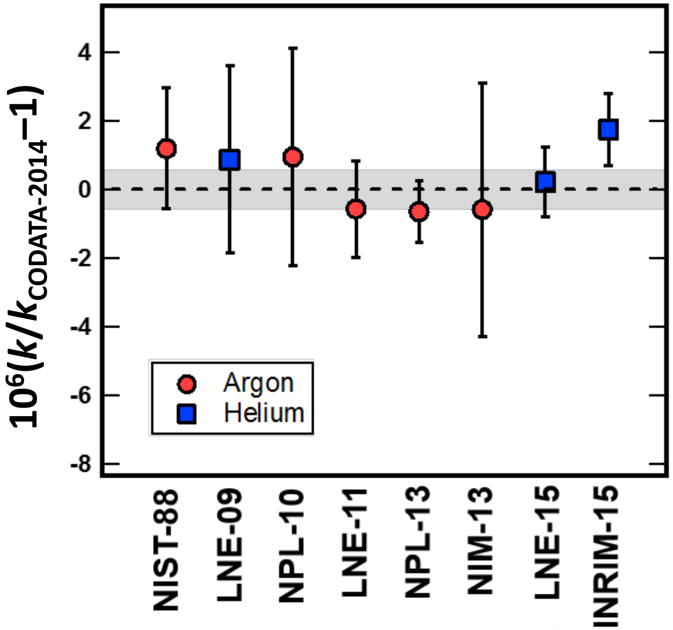
IPQ, 13 October 2016

Acoustic determination of *k* and molar mass of argon

$$k = \frac{{c_0}^2 M}{T \gamma_0 N_A}$$

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



Acoustic determination of *k*

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

Yang, Pitre, Moldover, Zhang, Feng, Kim, Metrologia, **2015**, Vol. 52, S394-409

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

Motivation of the work

- **Provide better *M* measurement (lower uncertainty) for acoustic determination of *k*, if needed.**
- **Complete a procedure of the molar mass measurement, to make sure the method and uncertainty assessment are sound from perspective of thermometry.**

Lee, Marti, Severinghaus, Kawamura, Yoo, Lee, Kim, Geochimia et Cosmochimima Acta, **2006**, Vol. 70, 4507-4512

Gravimetric method

→

Reference "R3"
$^{40}Ar/^{36}Ar = 330.30 \pm 0.34$

Reference "R2"
$^{40}Ar/^{36}Ar = 39.596 \pm 0.037$

→

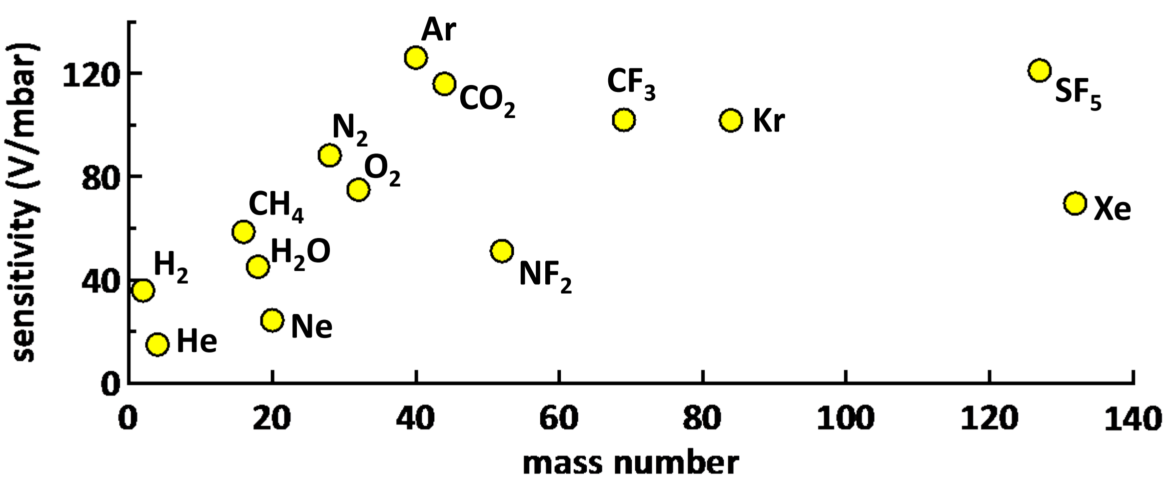
Molar mass of argon determination for Boltzmann project in 2014

Mass spectrometer at KRISS

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

"Partial pressure" machine

Pressure of certain gas in the sample → Ion current (Number of ion per second) (Output voltage)



- Sensitivity slowly changes over time.
- Sensitivity of isotopes are not the same.

➢ **We need reference gas.**

"Calibration of mass spectrometer"

Reference of known

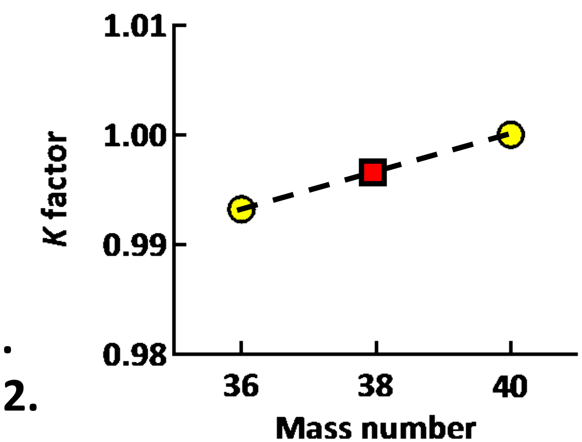
$R_{40/36}$ ratio (= $\dfrac{\text{amount of } ^{40}\text{Ar}}{\text{amount of } ^{36}\text{Ar}}$)

Measure Ion current ratio I_{40}/I_{36}

$$K_{36} = \frac{\text{known } R_{40/36} \text{ ratio}}{\text{Measured ion current ratio } I_{40}/I_{36}}$$

K_{36} is very closed to 1, but not identical to 1.
(K_{36} = 0.9932, for example, and changes with time)

For samples,
$R_{40/36} = K_{36} \times I_{40}/I_{36}$



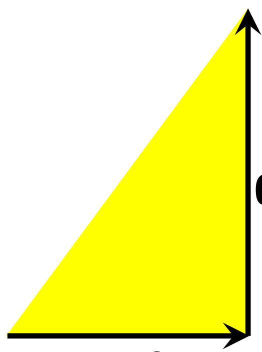
- Ideally, with a similar procedure, we can obtain K_{38} .
- But for all practical reasons, we use $K_{38} = (1 + K_{36}) / 2$.

Assumed linearity of sensitivity change
narrow range
same kind of molecule (argon)

Sensitivity of isotopic ratio and target uncertainty of molar mass

$$M_{Ar} = \frac{M_{36} + R_{38/36} M_{38} + R_{40/36} M_{40}}{1 + R_{38/36} + R_{40/36}}$$

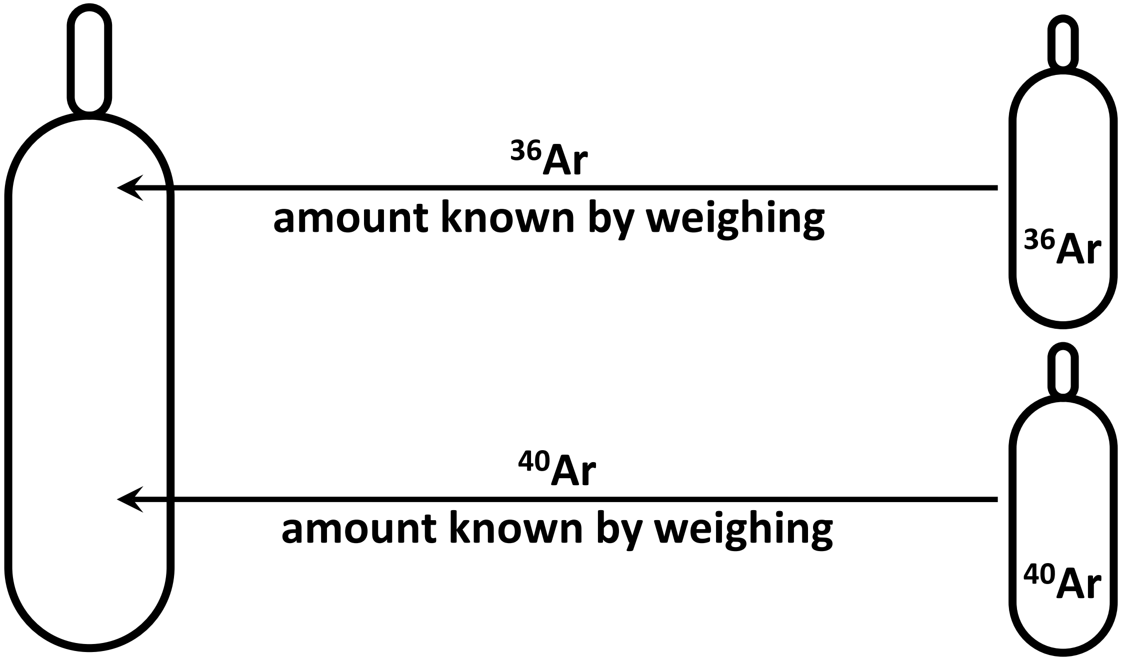
Near a "natural" isotopic composition,



We want to determine $R_{40/36}$ of sample within 0.05 %
→ $u(R_{40/36})_{sample} = 0.15$ (0.156 % in 2014 measurement)

For this, we need reference of known $R_{40/36}$ better than 0.05 %
$(R_{40/36})_{reference} = 300 \pm 0.1$

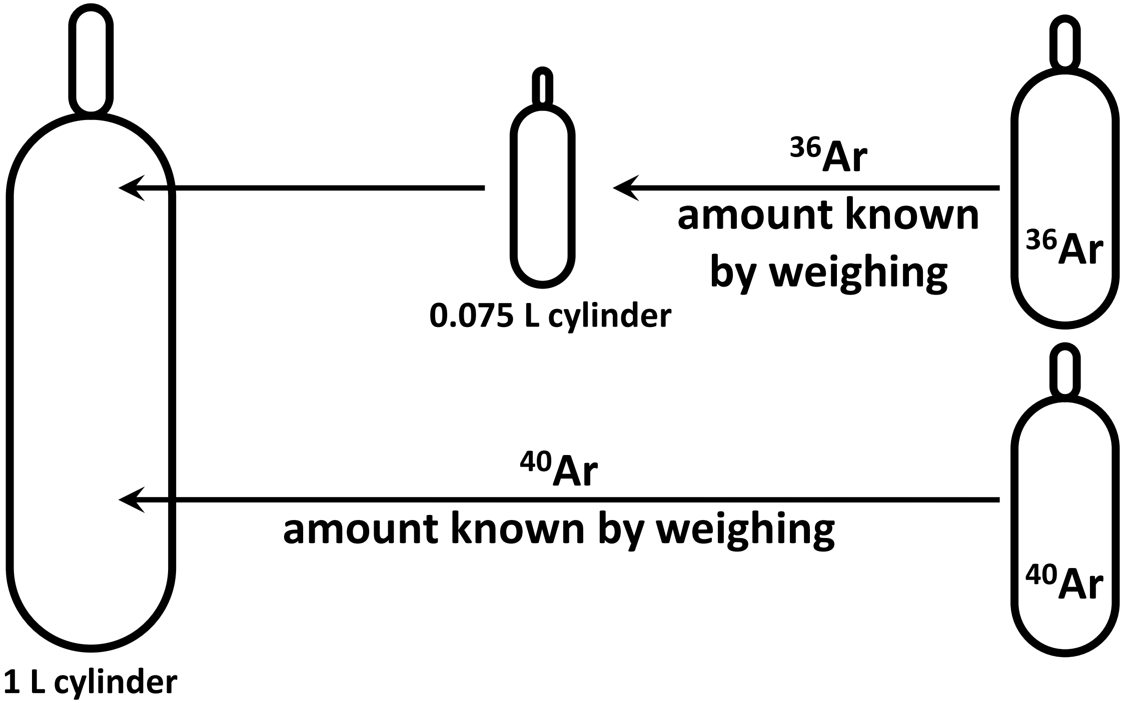
Gravimetric method



Known $R_{40/36}$ ratio by gravimetric method

ISO 6142-1 Gas Analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for class 1 mixtures

Gravimetric method



Known $R_{40/36}$ ratio by gravimetric method

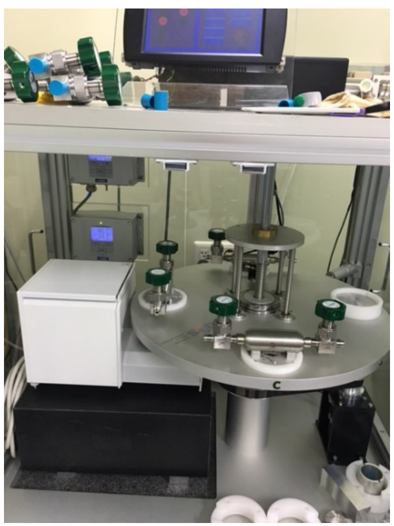
Two references were prepared:
one with $R_{40/36}$ slightly above atmospheric ratio (R4),
one slightly below (R5)

ISO 6142-1 Gas Analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for class 1 mixtures

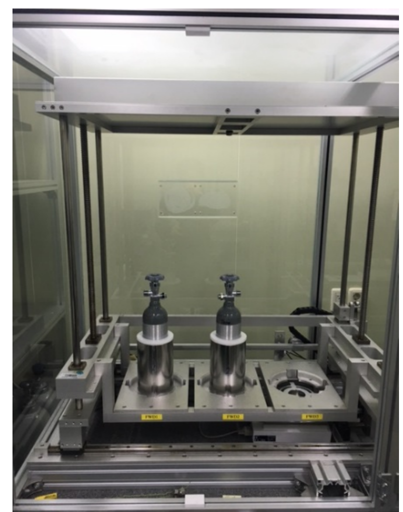
Weighing cylinders: comparison against “tare” cylinder

- Always comparison against a tare cylinder
- Tare always moves together with cylinders to be measured. (buoyancy compensation)
- Tare → cylinder 1 (→ cylinder 2) → Tare → cylinder 1 (→ cylinder 2) → Tare → … cycle repeated
- Automatic weighing system to minimized interference

Balances (mass comparator) used:



Mettler Toledo AX1005
1.1 kg capacity, 0.01 mg resolution



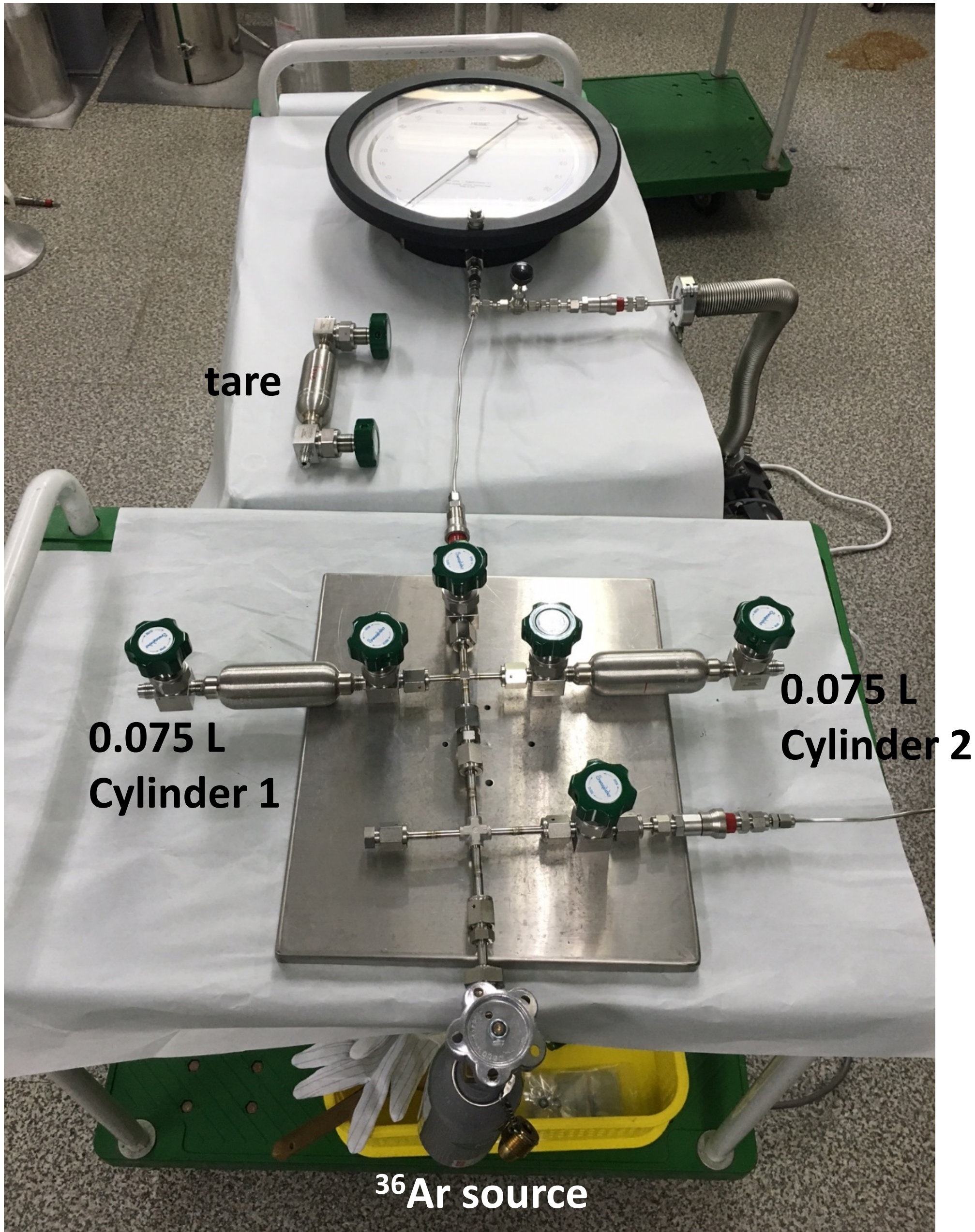
Mettler Toledo XP10003S:
10.1 kg capacity, 1 mg resolution

Source gas

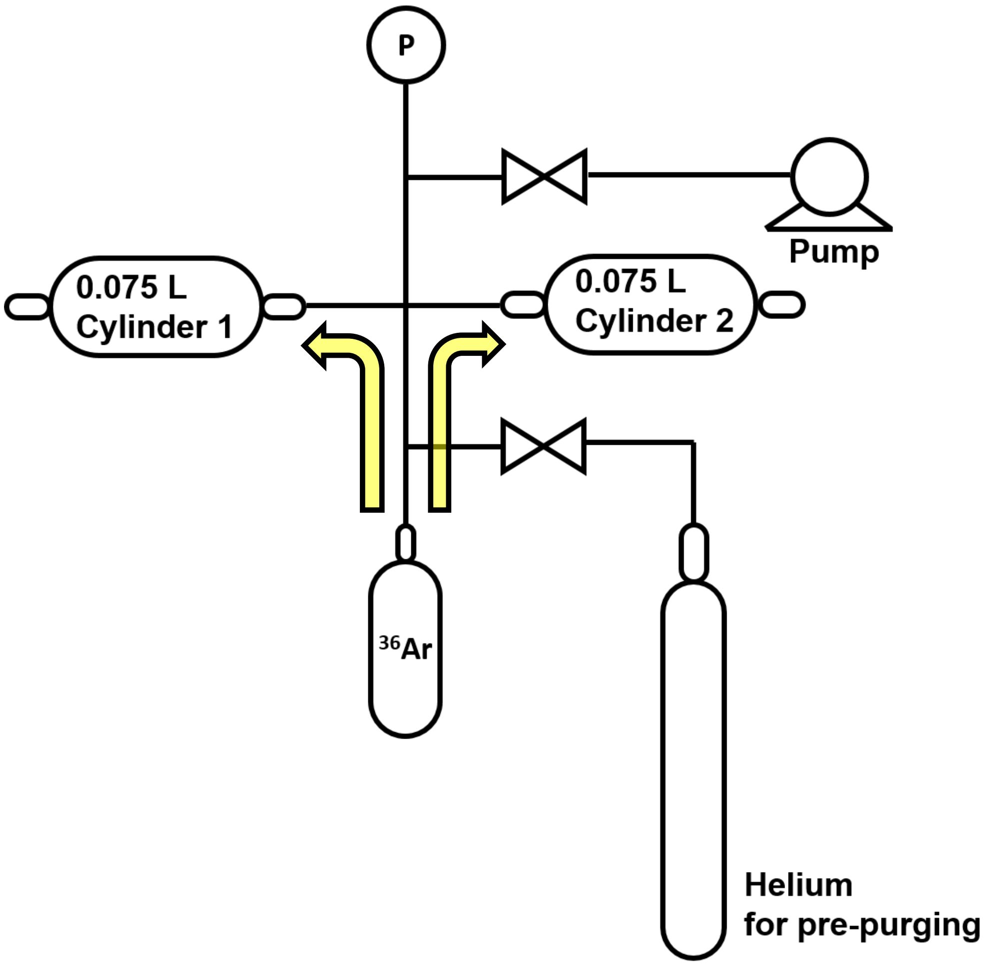
Enriched argon sources purchased from ICON services Inc. (NJ, USA)

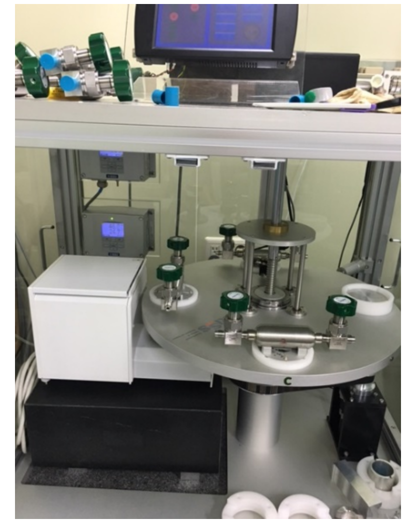
Element	Container	Pressure	Nominal chemical purity	Nominal isotopic purity	Usage
^{40}Ar	1.4 L	7.1 MPa	99.9 %	99.96 %	For purging only
^{40}Ar	3.03 L	6.6 MPa	99.9 %	99.96 %	Source gas
^{36}Ar	0.5 L	1 MPa	99.9 %	99.95 %	Purging and source gas

Filling ^{36}Ar and weighing



Filling ^{36}Ar and weighing

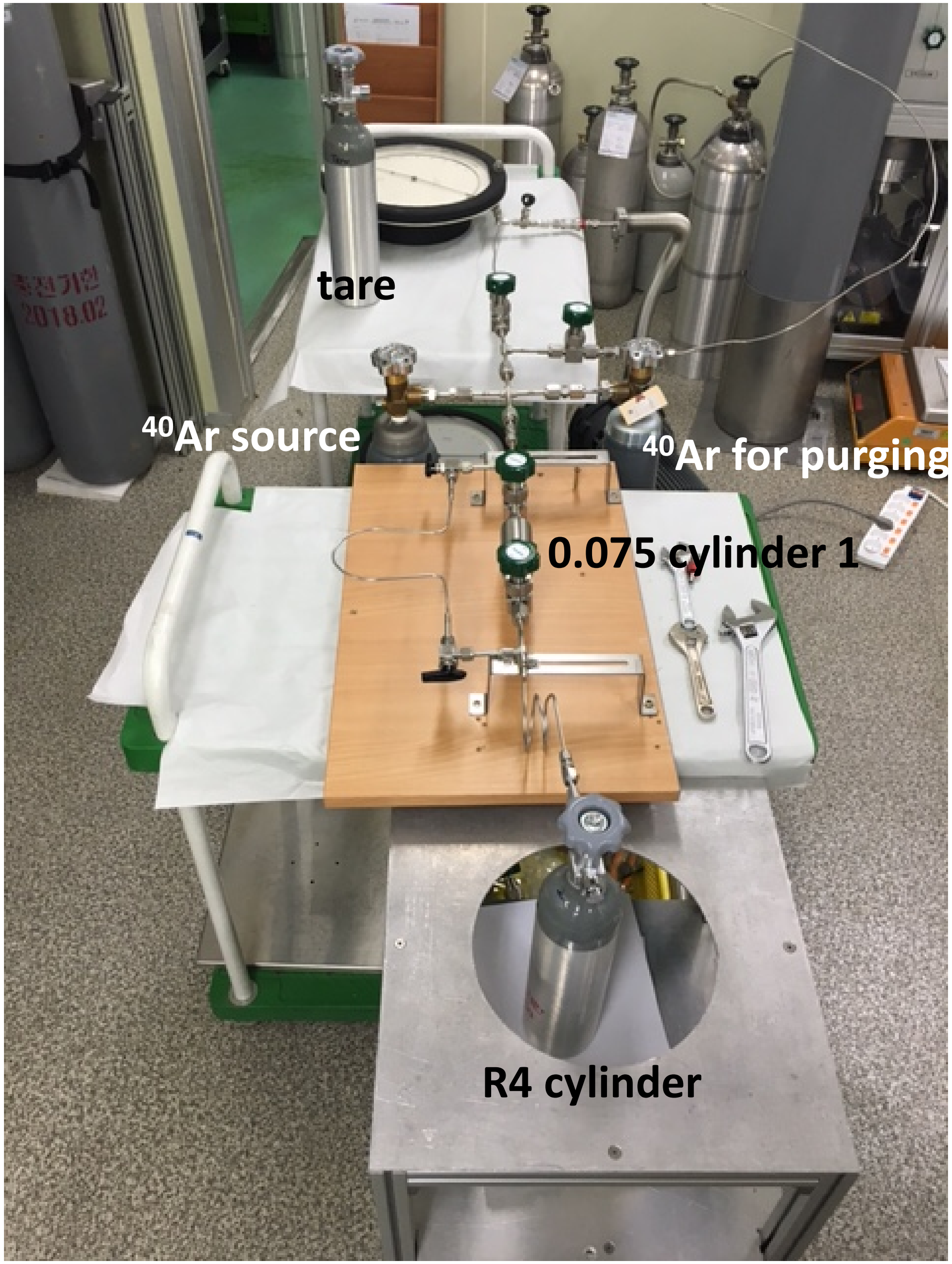




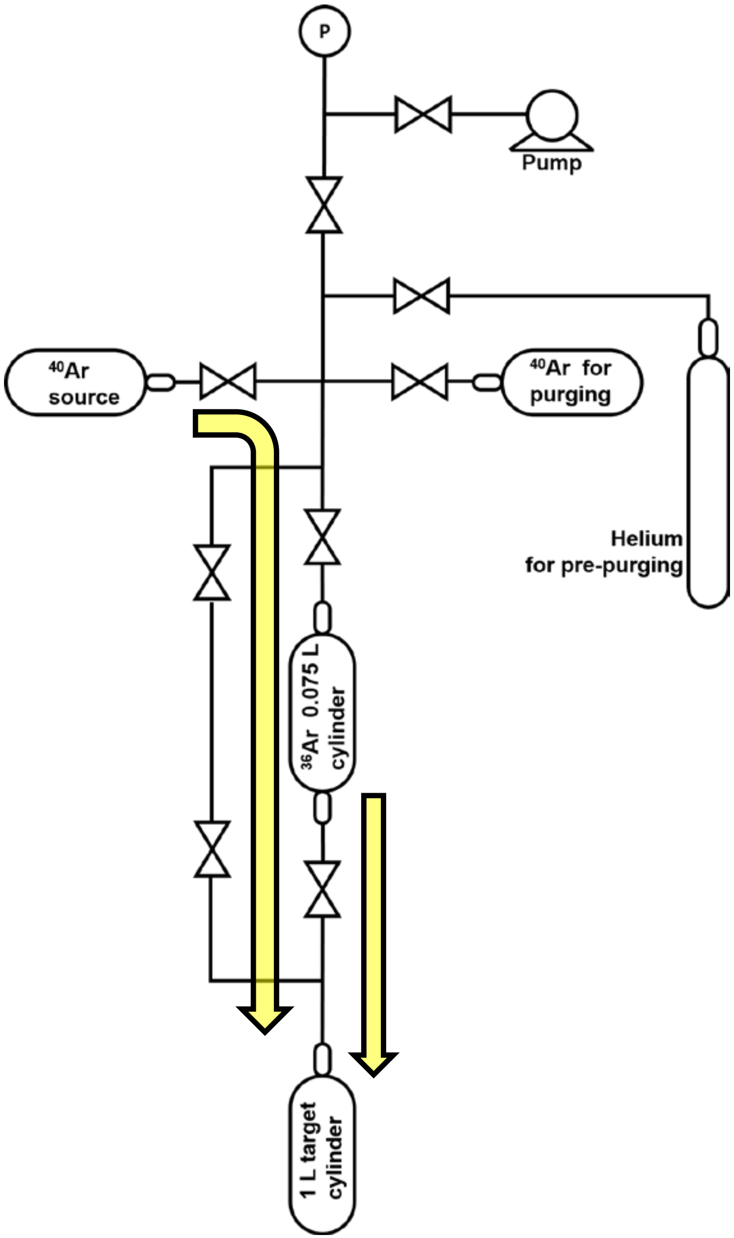
Mass of ^{36}Ar measured by differential measurements of 0.075 L cylinders

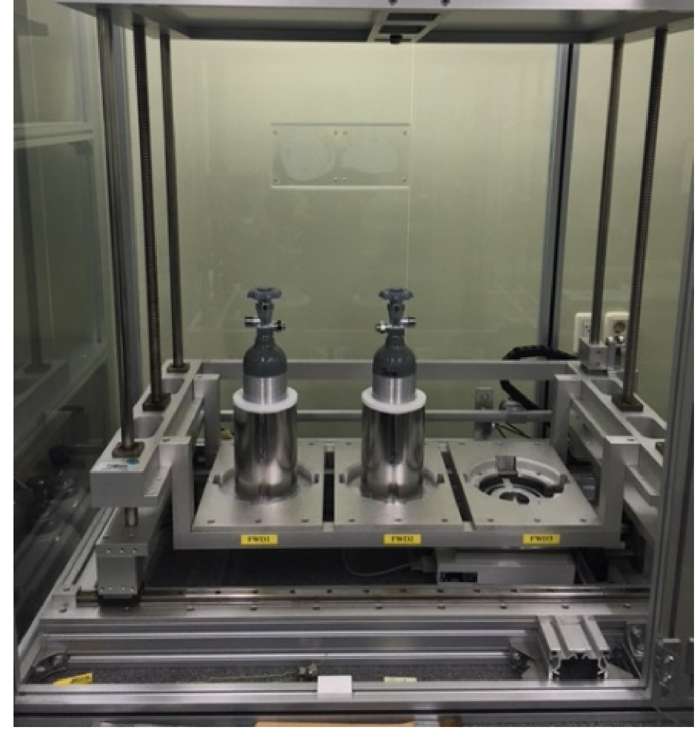
^{36}Ar in cylinder 1: 0.147 07 g
^{36}Ar in cylinder 2: 0.147 75 g

Filling ^{40}Ar and weighing



Filling ^{40}Ar and weighing





- ^{36}Ar transferred from 0.075 L cylinder to 1 L cylinder
- Mass of ^{40}Ar measured by differential measurements of 1 L cylinder

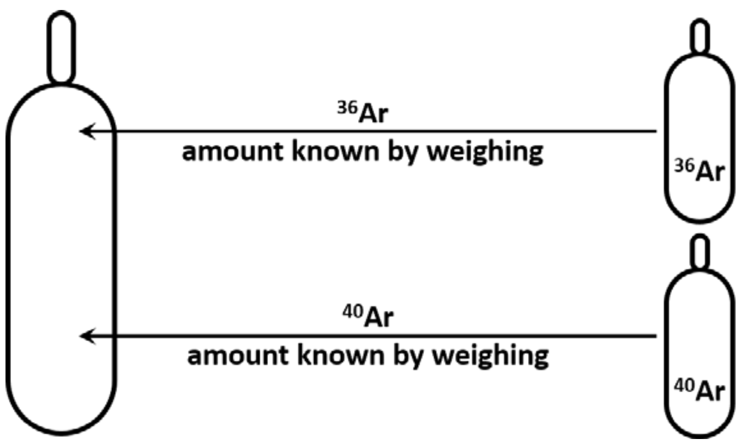
^{40}Ar in cylinder R4: 50.852 68 g
^{40}Ar in cylinder R5: 49.684 83 g

Mechanical mixing

Rolling for a few hours for homogeneous mixture

Effect of chemical impurity and isotopic impurity

$$y_k = \frac{\sum_{j=1}^{r} \left(\frac{x_{k,j} \times m_j}{\sum_{i=1}^{q} x_{i,j} \times M_i} \right)}{\sum_{j=1}^{r} \left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j} \times M_i} \right)}$$



Remember: target uncertainty of $R_{40/36}$ is 0.1

For 10 μmol/mol existence in the source, the shift in $R_{40/36}$ is …

Element	In ^{40}Ar cylinder	In ^{36}Ar cylinder
H_2	0.0002	0.0002
H_2O	0.0014	0.0014
CO	0.0021	0.0023
N_2	0.0021	0.0023
O_2	0.0024	0.0026
^{36}Ar	0.8729	-
^{38}Ar	0.0028	0.0030
^{40}Ar	-	0.0032
CO_2	0.0032	0.0035
Kr	0.0061	0.0067
Xe	0.0095	0.0105

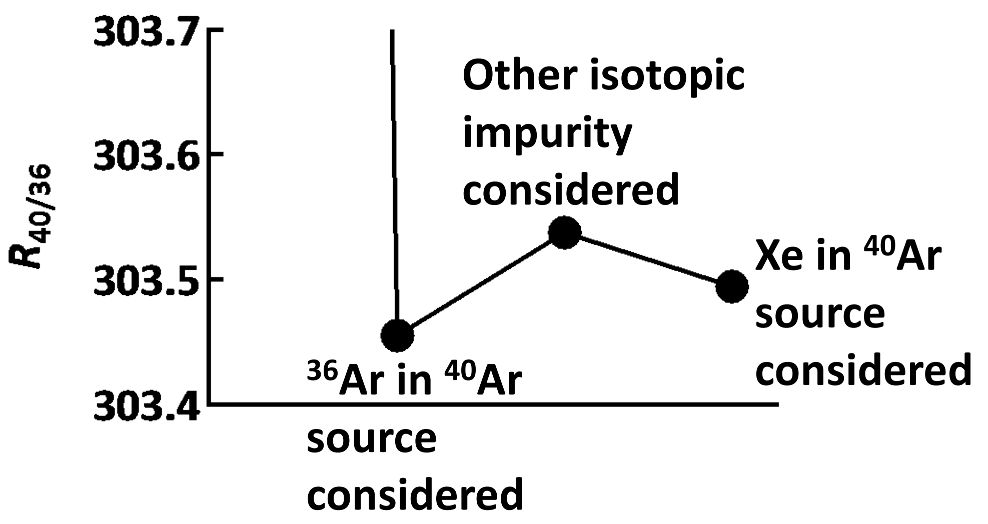
The most significant "impurity" is ^{36}Ar in ^{40}Ar cylinder.

Preliminary analysis

Element	Concentration in ^{40}Ar cylinder (µmol/mol)	Concentration in ^{36}Ar cylinder (µmol/mol)
^{36}Ar	81.9	balance
^{38}Ar	265.1	495.0
^{40}Ar	balance	13.2
Xe	44	0

For reference R4:

When 100 % nominal source gases are assumed: $R_{40/36}$ = 311.216



In reference R4:

$R_{40/36}$ = 303.494

In reference R5:

$R_{40/36}$ = 295.349

Expected uncertainty of reference mixture

Factors	$u(R_{40/36})$	Comment
Weighing ^{36}Ar	0.061	0.03 mg uncertainty in weighing
^{36}Ar in enriched ^{40}Ar	0.014	Uncertainty of 0.002 in K36 assumed
Xe in enriched ^{40}Ar	0.004	10 % uncertainty in Xe assumed
Total	0.063	Better than 5-fold from previous reference

Samples near "natural" composition will be measured using MAT 253 using the prepared reference in this work.

- This cannot measure all of the mass numbers.
- Only recently it was configured to measure argon isotopes.
- Much better repeatability than MAT 271.
- Limited linearity: only can be used near "natural" composition.

Expected uncertainty in M_{Ar}: 0.2×10^{-6}

- We hope that using MAT 252 we can resolve $R_{38/36}$ shift from the natural fractionation line, which added 0.35×10^{-6} relative uncertainty in 2014 work.

Helium isotopic reference gas at KRISS

- **^{3}He/^{4}He mass ratio is 0.75**
- **Sensitivity difference of ^{3}He and ^{4}He is larger: *K* factor further away from 1**
- **Three isotopic reference mixtures were created:**

  $$R_{4/3} = 18.905 \pm 0.036,\ 98.78 \pm 0.21,\ 209.82 \pm 0.44$$

- **Helium isotopic concentration from different commercial sources will be investigated.**

J. Tshilongo, D. Min, J. B. Lee, J. S. Kim, Bull. Korean Chem. Soc., **2015**, Vol. 36, 591-596

Things to be done and summary

- Finalize the analysis on both source gases and prepared reference R4 and R5.
- Validate the consistency between R4 and R5.
- Check the consistency with 2005 prepared references (R2 and R3).

- With new isotopic mixtures and enhanced MAT 253, KRISS will be able to provide molar mass of argon measurement with the relative uncertainty of 0.2×10^{-6}.
- With new helium isotope reference, KRISS can also provide traceable helium isotopic composition measurements.

- Thank you.