Comparison between the mass spectrometer and speed-of-sound measurements of M_{Ar} for the k_B determination

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Contribution

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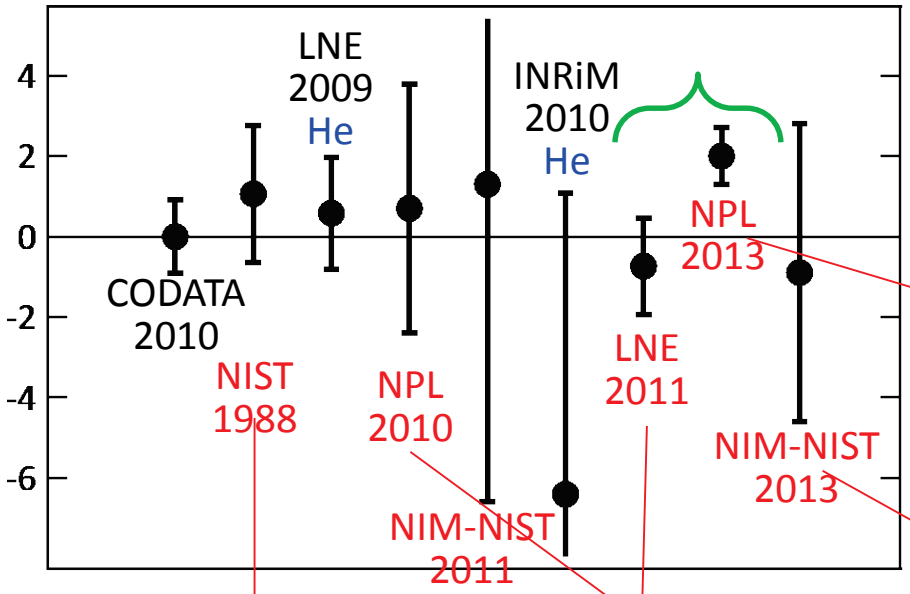
k_B measurement and argon molar mass



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

Argon, by SUERC mass spectrometer (referenced to atmospheric Ar measurement Lee *et al.*)

Argon, by IRMM mass spectrometer

Argon, by KRISS mass spectrometer/ KLPRR CAS mass spectrometer referenced to KRISS result

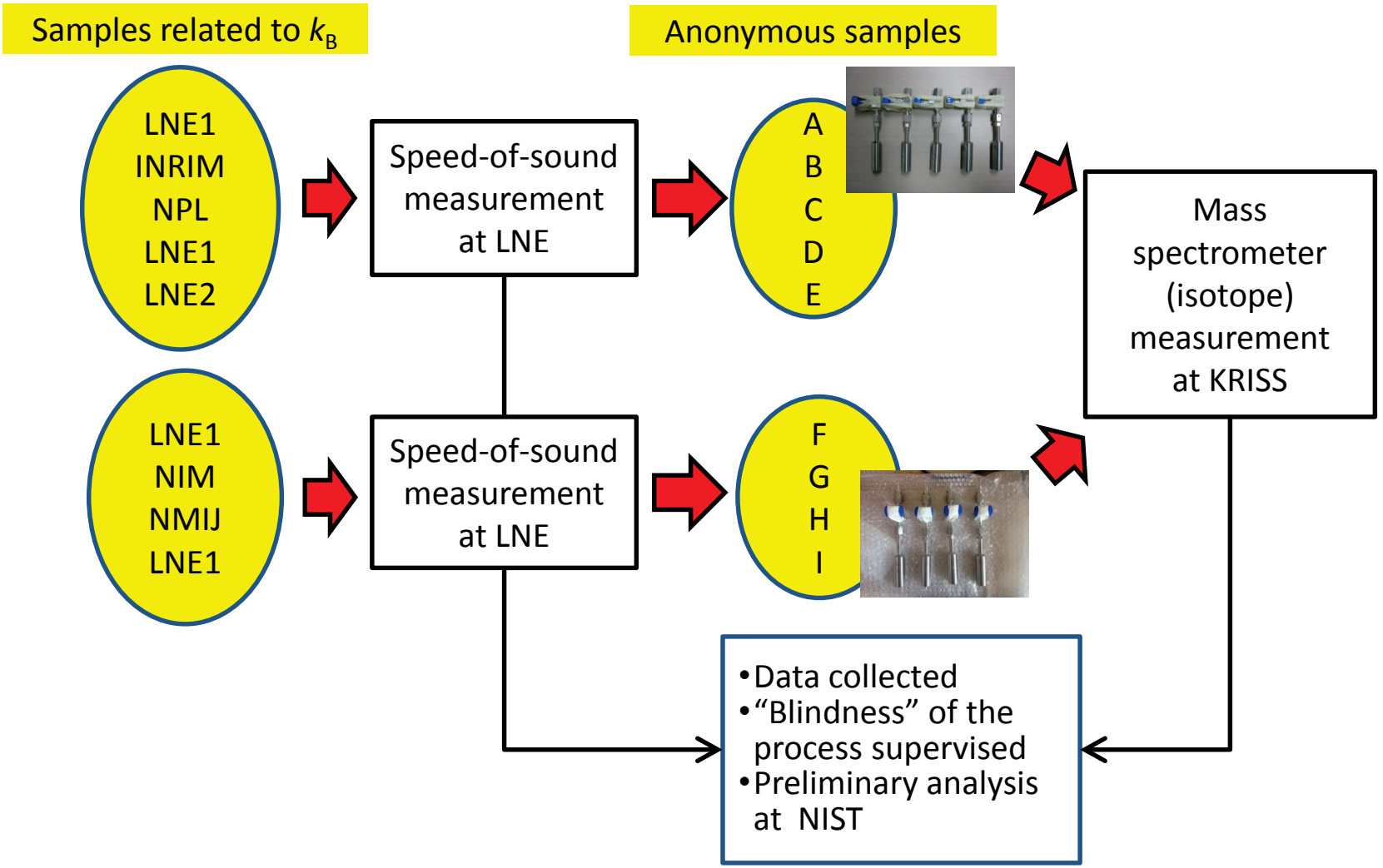
Argon, by Speed-of-sound comparison with Ar-40

Argon, by KRISS mass spectrometer

- Molar mass measurement M_{Ar} may be the weakest point in k_B determination.
- M_{Ar} measurement is suspected as source of the discrepancy in the key k_B measurements.

Measurement Protocol

- Following the protocol drawn by Laurent Pitre (LNE)

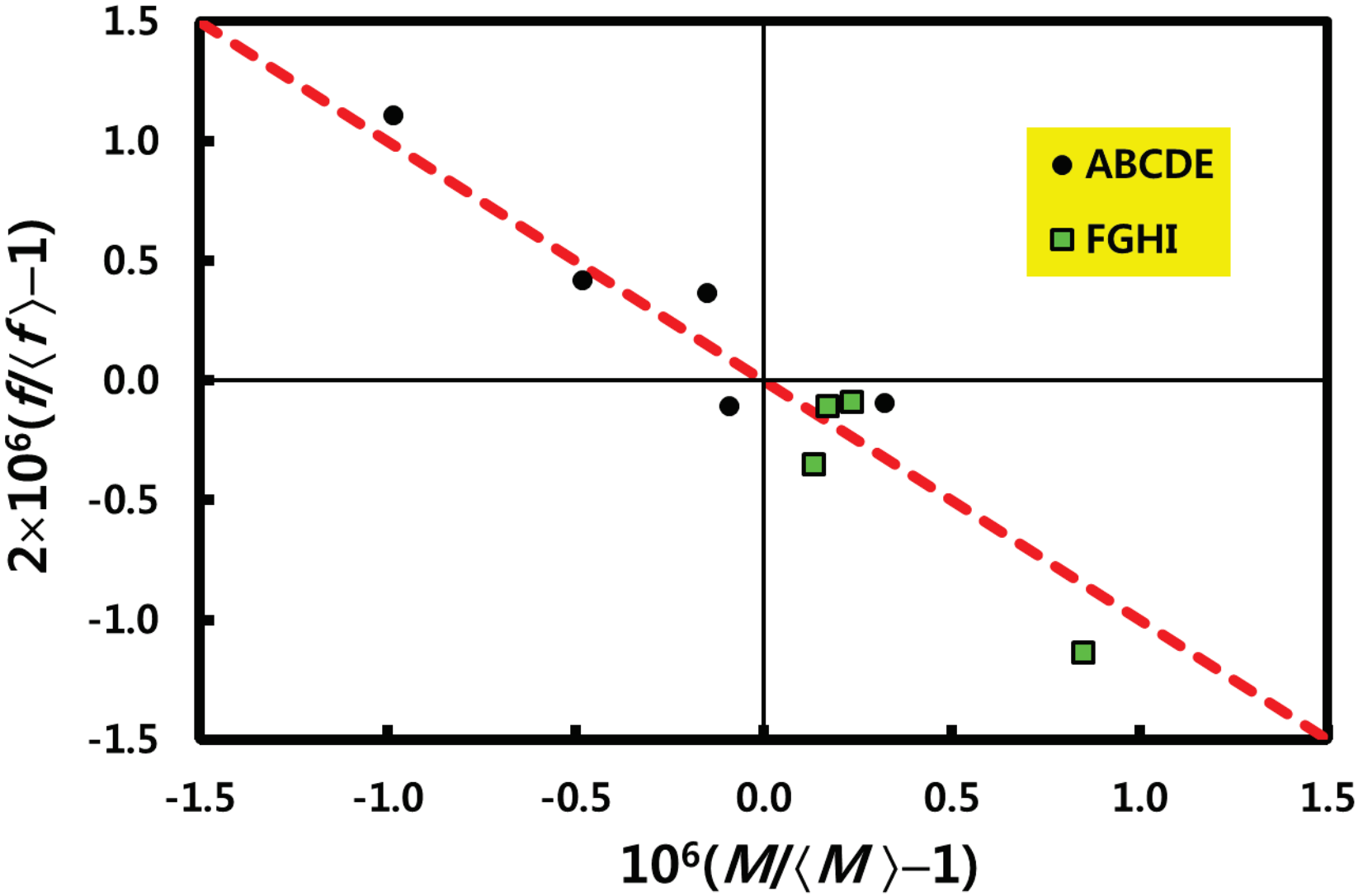


KRISS mass spectrometer

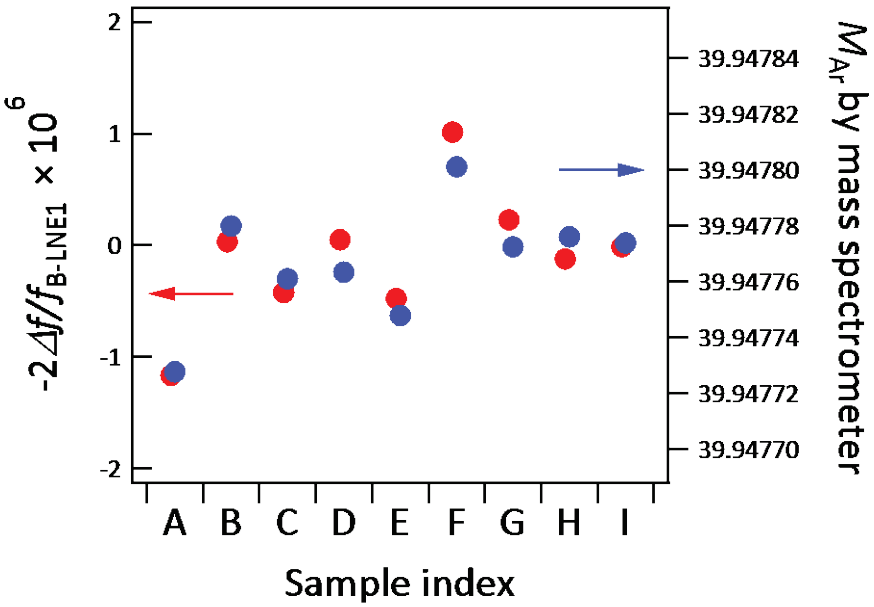
- Finnigan MAT 271 precision gas mass spectrometer

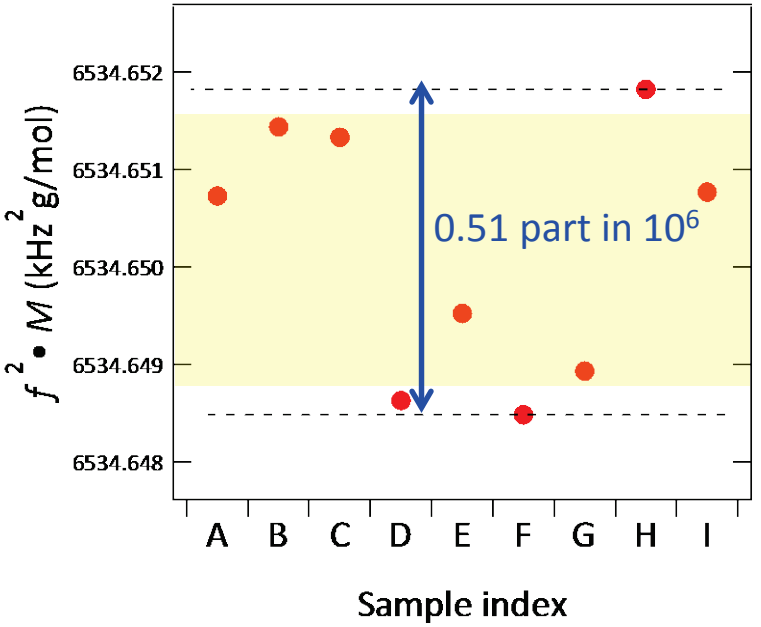
- Sample gas of < 1 mbar is ionized and diffused through a small orifice, then detected by an ion detector.
- Measures ion current at specific mass-to-charge ratio (m/z).
- Gravimetric standard of argon isotopes used as reference
- Has been used for the redetermination of the isotopic composition of Atmospheric Ar (Lee *et al*. 2006), and NIM-NIST 2011 k_B determination

Gas Samples Span the Range $\pm 10^{-6}$ *M*
Frequencies and Mass have expected Correlation



Result

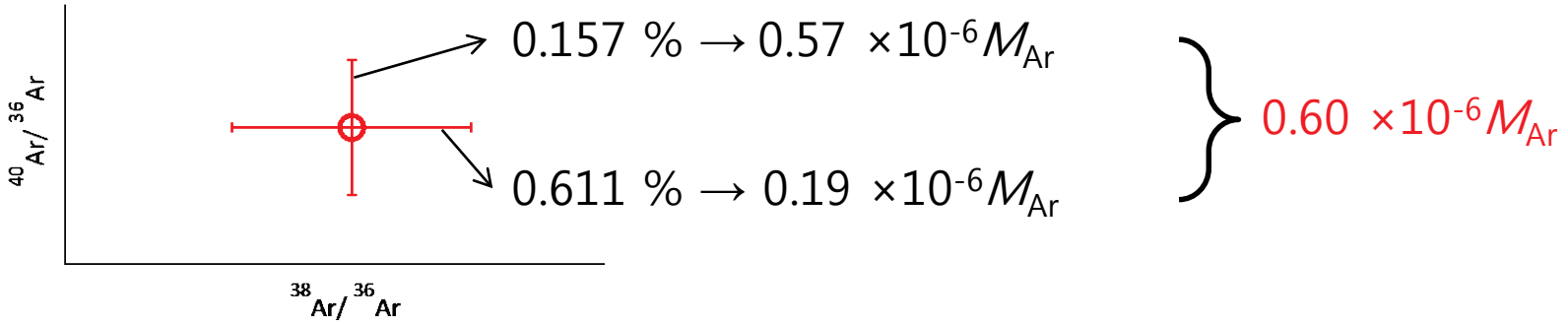




- Speed-of-sound and mass spectrometer measurement of M_{Ar} is mutually consistent (maximum deviation of 0.51 $\times 10^{-6}$)
- Relative standard deviation of $f^2 \cdot M$ is 0.2 $\times 10^{-6}$
- 9 pairs of measurements that are mutually consistent ⇨ Both measurements seem to be internally consistent.

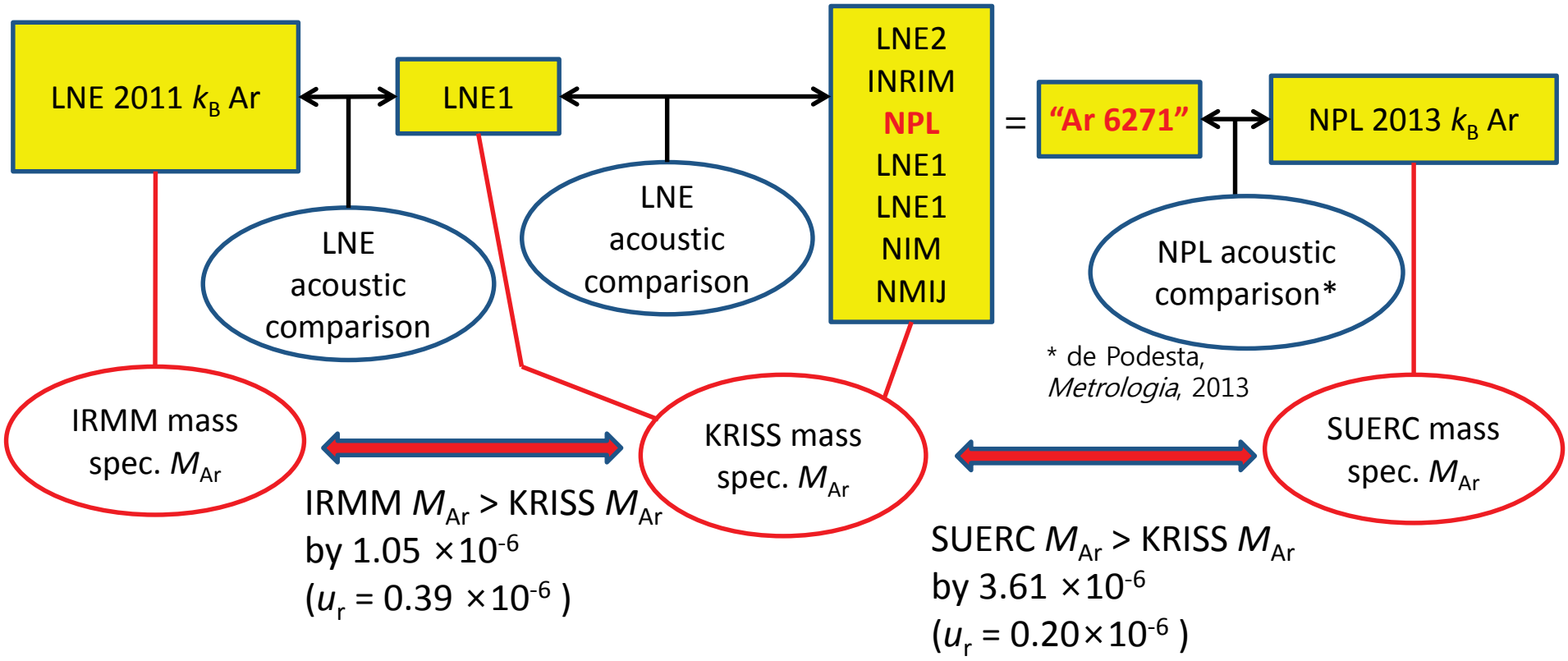
Uncertainty of isotopic M(Ar)

Uncertainty factor	$^{38}Ar/^{36}Ar$ Relative uncertainty	$^{40}Ar/^{36}Ar$ Relative uncertainty
Determination of f_{MD}	0.053 %	0.107 %
from reference gas	0.051 %	0.103 %
from the Determination of I(^{40}Ar)/I(^{36}Ar) of the reference gas	0.015 %	0.029 %
Determination of the ion current ratio of the sample	0.195 %	0.029 %
Detection limit	0.577 %	0.110 %
Combined uncertainty (k=1)	0.611 %	0.157 %



- The uncertainty of the M_{Ar} for mass spectrometer measurement: $0.60 \times 10^{-6}\ M_{Ar}$
- If correlation through f_{MD} considered ⇨ uncertainty becomes smaller.
- The short-term repeatability of the measurement: $0.164 \times 10^{-6} M_{Ar}$ from pooled standard devotion of 37 measurements on 15 samples (ν = 22)

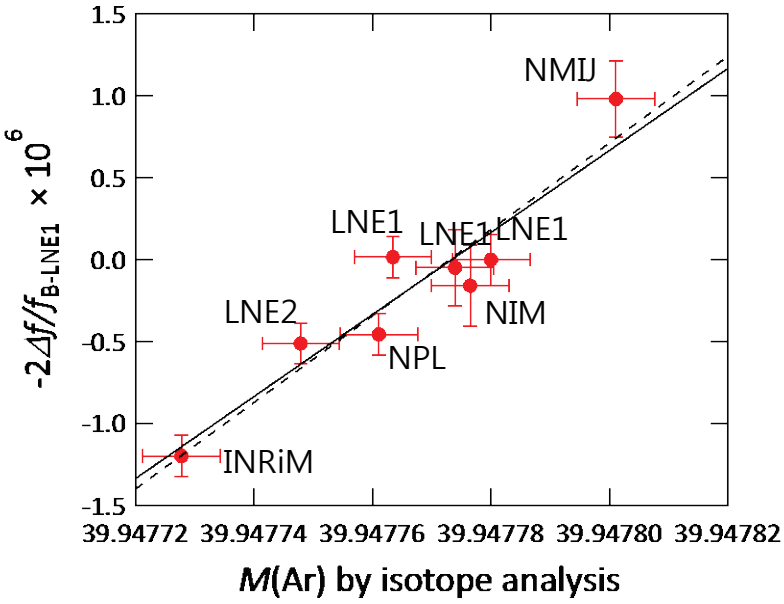
Linkage to other mass spectrometer measurements



- SUERC measurement (on NPL 2013 k_B Ar) has offset of +2.56 $\times 10^{-6}$ from the IRMM measurement (on LNE 2011 k_B Ar)
- Link can be also established only through speed-of-sound comparison: the offset from this link is +2.71 $\times 10^{-6}$

Key finding

- SUERC measurement (on NPL 2013 k_B Ar) has offset of +2.56 $\times 10^{-6}$ from the IRMM measurement (on LNE 2011 k_B Ar)
- This was also confirmed by speed-of-sound comparison.
- Therefore, 2.74 $\times 10^{-6}$ discrepancy between the two k_B determination was from the molar mass measurement.
- The above statement does not rely on the accuracy of the absolute values of KRISS M_{Ar}
- It only relies on
  - internal consistency of KRISS M_{Ar} measurement (short-term repeatability)
  - LNE speed-of-sound ratio measurement
  - NPL speed-of-sound ratio measurement (de Podesta, *Metrologia*, 2013)
- KRISS isotope measurement and LNE acoustic comparison support each other's consistency.



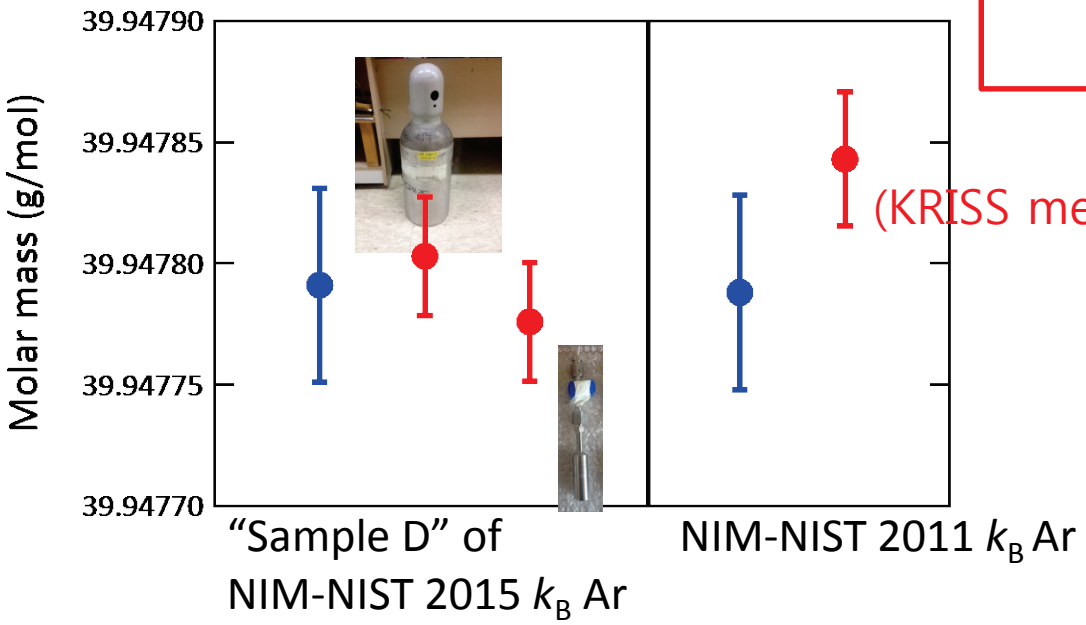
Comparing absolute values of M_{Ar}

Speed-of-sound measurement Comparison with NIST Ar-40 at NIM

NIM-NIST 2011 k_B Ar "Sample D" of NIM-NIST 2015 k_B

Isotope measurement at KRISS (2010)

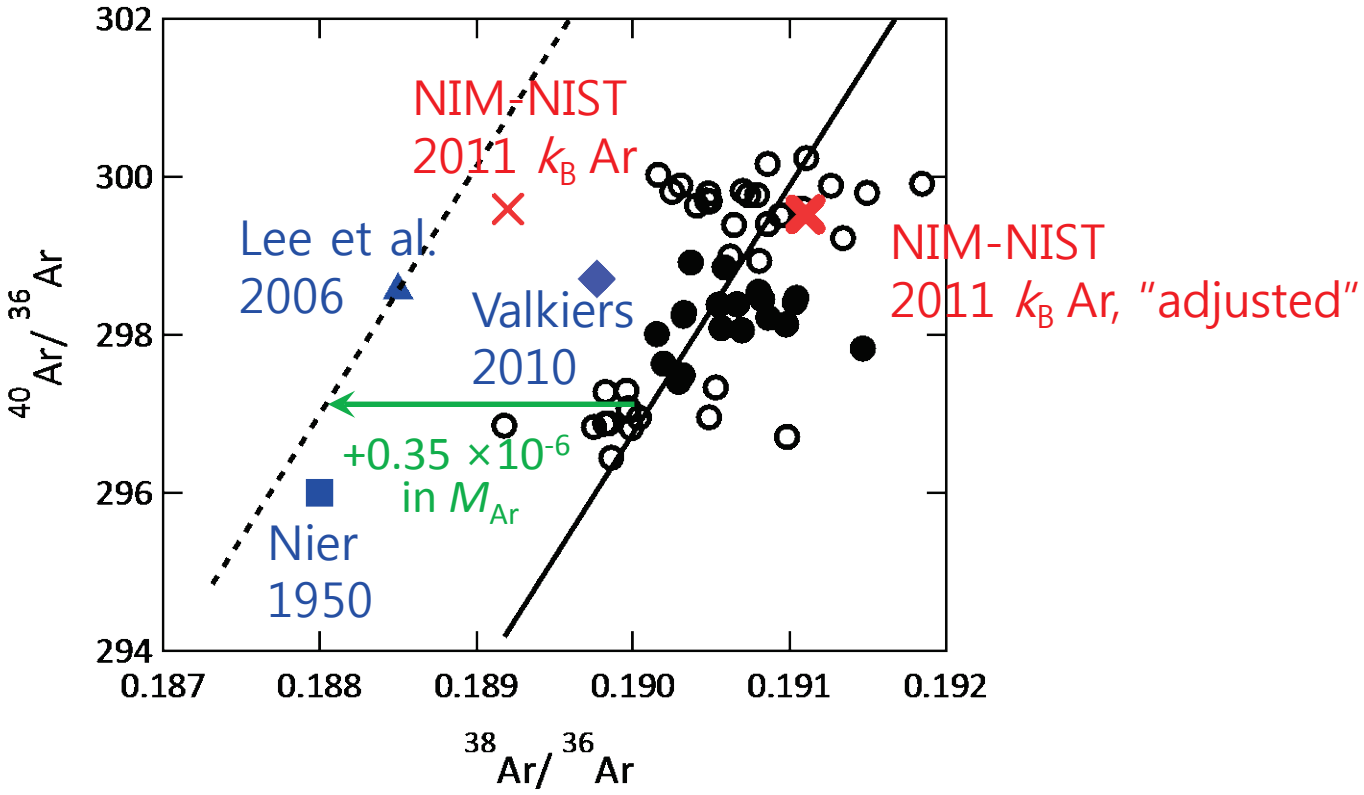
Isotope measurement at KRISS on large bottle (Oct. 2014)
Isotope measurement at KRISS on 25 cm^3 cylinder (Nov, Dec. 2014)



(KRISS measurement in 2010)

- KRISS absolute measurement M_{Ar} consistent with the NIM acoustic comparison with NIST Ar-40 within the claimed uncertainty
  (1.0 $\times 10^{-6}$ for NIM comparison, (0.6-0.7) $\times 10^{-6}$ for KRISS M_{Ar})

Mass fractionation and M_{Ar}



- Assuming mass fractionation of Lee *et al.* (2008) on atmospheric Ar is "correct" ⇨ may need +0.35 ×10^{-6} correction in M_{Ar}

Summary

- The discrepancy of 2.74 $\times 10^{-6}$ between LNE 2011 k_B and NPL 2013 k_B was due to the inconsistent determination of M_{Ar}
- This was confirmed both by KRISS mass spectrometer and LNE speed-of-sound comparison.
- Chain of speed-of-sound comparisons indicates that
  - IRMM measurement higher than KRISS by 1.05 $\times 10^{-6}$;
  - SUERC measurement higher than KRISS by 3.61 $\times 10^{-6}$.
- The absolute value of KRISS molar mass measurement is consistent with NIM acoustic comparison with NIST Ar-40.
- The uncertainty of KRISS mass spectrometer M_{Ar} is 0.60 $\times$ 10^{-6}.