Evaluation of Measurement Uncertainty associated with the Avogadro Constant

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Agenda

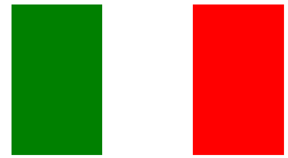
- Importance of the Avogadro Number
- The international approach in 2002
- The Avogadro Number
- The task: establishing the final value
  - Sub-problem: molar volume
  - Removing inconsistencies
  - Treating correlations
  - Uncertainty budget
- Discussion of the final approach

Importance of the Avogadro Number

- Why do we need it?
- Why do we need to measure it?
- How do we measure it ?
  - Molar mass
  - Volume
  - Mass
  - Lattice parameter
- Why is silicon used?

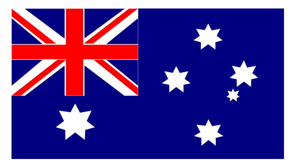
The international approach in 2002

EU/IRMM
Molar Mass

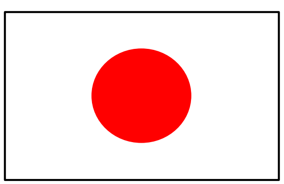


INRIM (IMGC)
Lattice parameter, Density

PTB
Density



NMI-A
Density



NMIJ
Density,
Lattice parameter

The Avogadro Number

$$N_A = \frac{n \cdot M_{Si}}{\frac{m}{V} \cdot a^3} = \frac{M_{Si}}{m} \cdot \frac{V}{\frac{a^3}{n}}$$

(Si: $n = 8$)

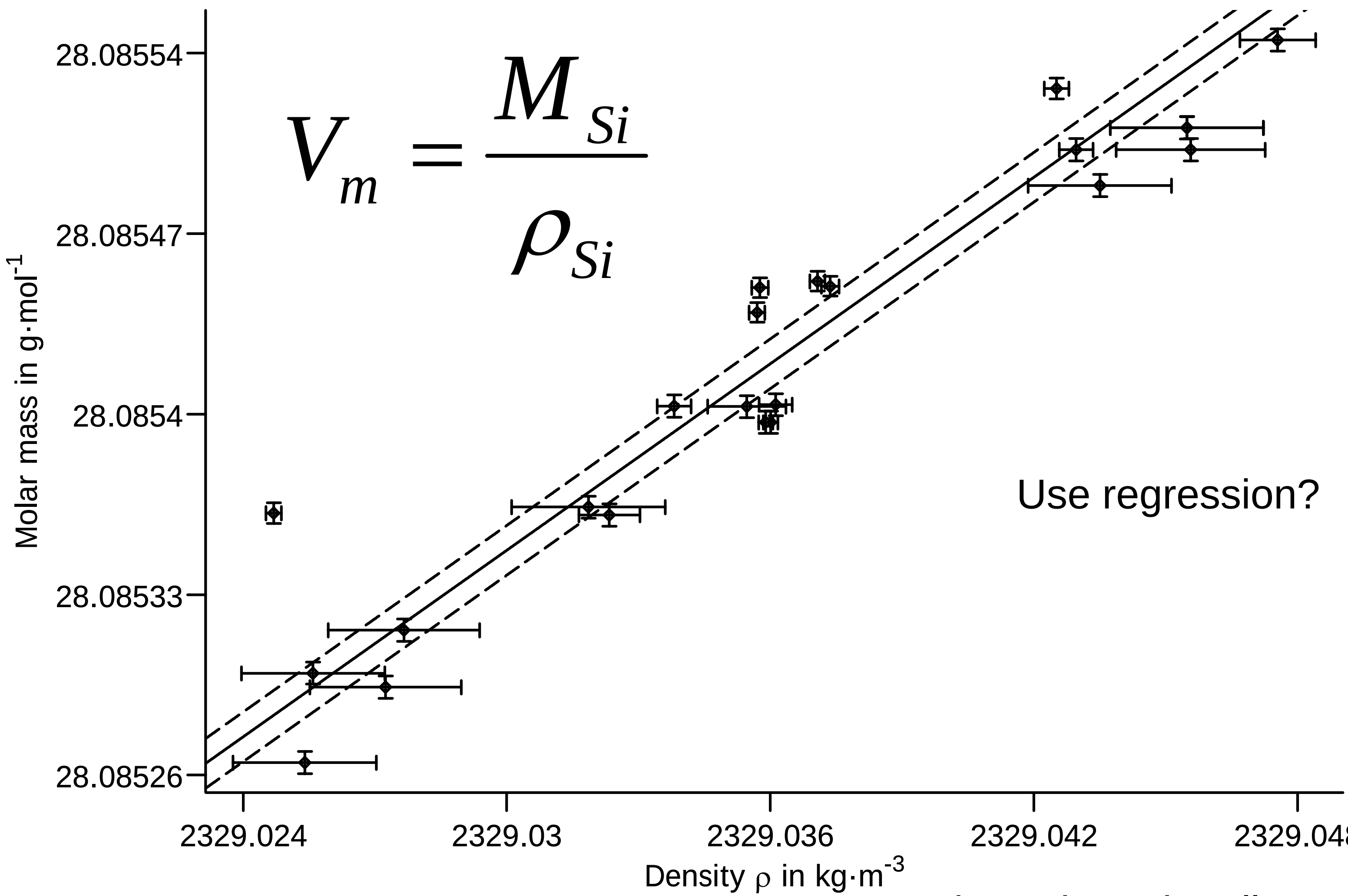
Mass Spectrometer at IRMM

Establishing the final value

- Results and uncertainty budget have been provided for all measurements of:
  - Density
  - Molar mass
  - Lattice parameter
- Two main questions:
  - What is the measurement function?
  - How to combine different data?

Sub-problem: molar volume

$$V_m = \frac{M_{Si}}{\rho_{Si}}$$



Use regression?

(Data intentionally modified)

Why not use regression?

- Regression leads to a complicated model equation.
- The zero point need to be included.
- With the zero point the regression degenerates.
- Check of pairwise consistency is difficult.

Use of the weighted mean value

$$V_{m,i} = \frac{M_{Si,i}}{\rho_{Si,i}} + \delta V_{m,i}$$

Individual molar volume

$$M_{Si,i} = \frac{M_{28Si} + r_{29/28,i} \cdot K_{29/28} \cdot M_{29Si,i} + r_{30/28,i} \cdot K_{30/28} \cdot M_{30Si}}{1 + r_{29/28,i} \cdot K_{29/28} + r_{30/28,i} \cdot K_{30/28}}$$

Individual molar mass

$$V_m = \frac{\sum_i \frac{1}{u^2(V_{m,i})} V_{m,i}}{\sum_i \frac{1}{u^2(V_{m,i})}}$$

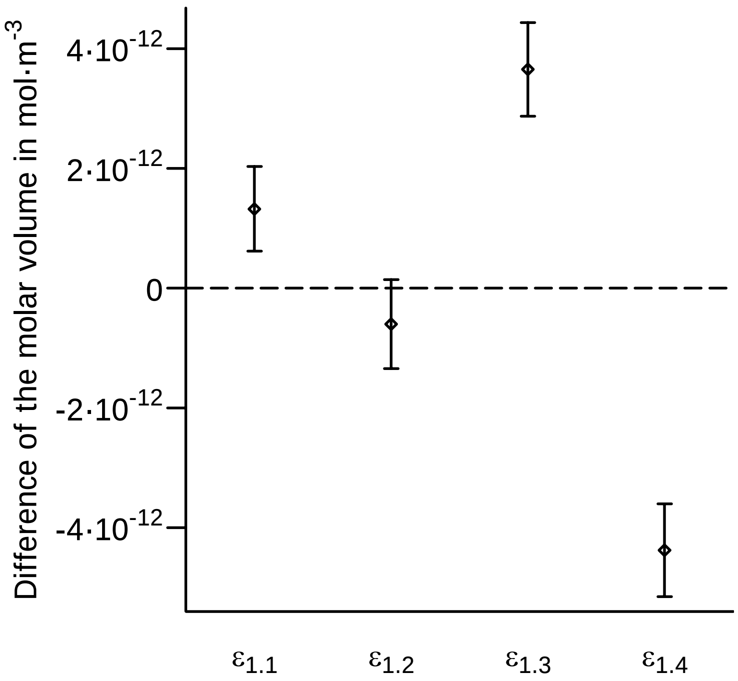
Weighted mean for the overall molar volume

$$\varepsilon_i = V_{m,i} - V_m$$

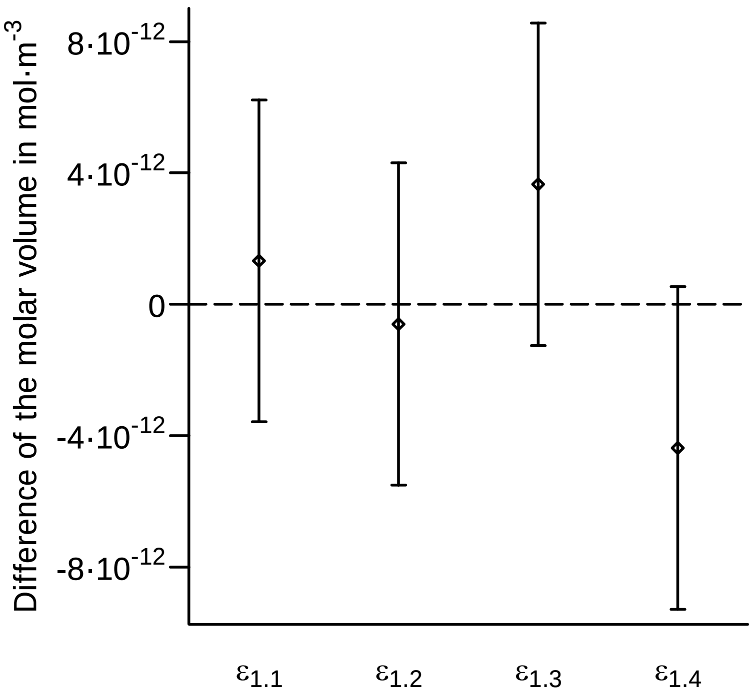
Difference between individual and overall molar volume

Removing inconsistencies

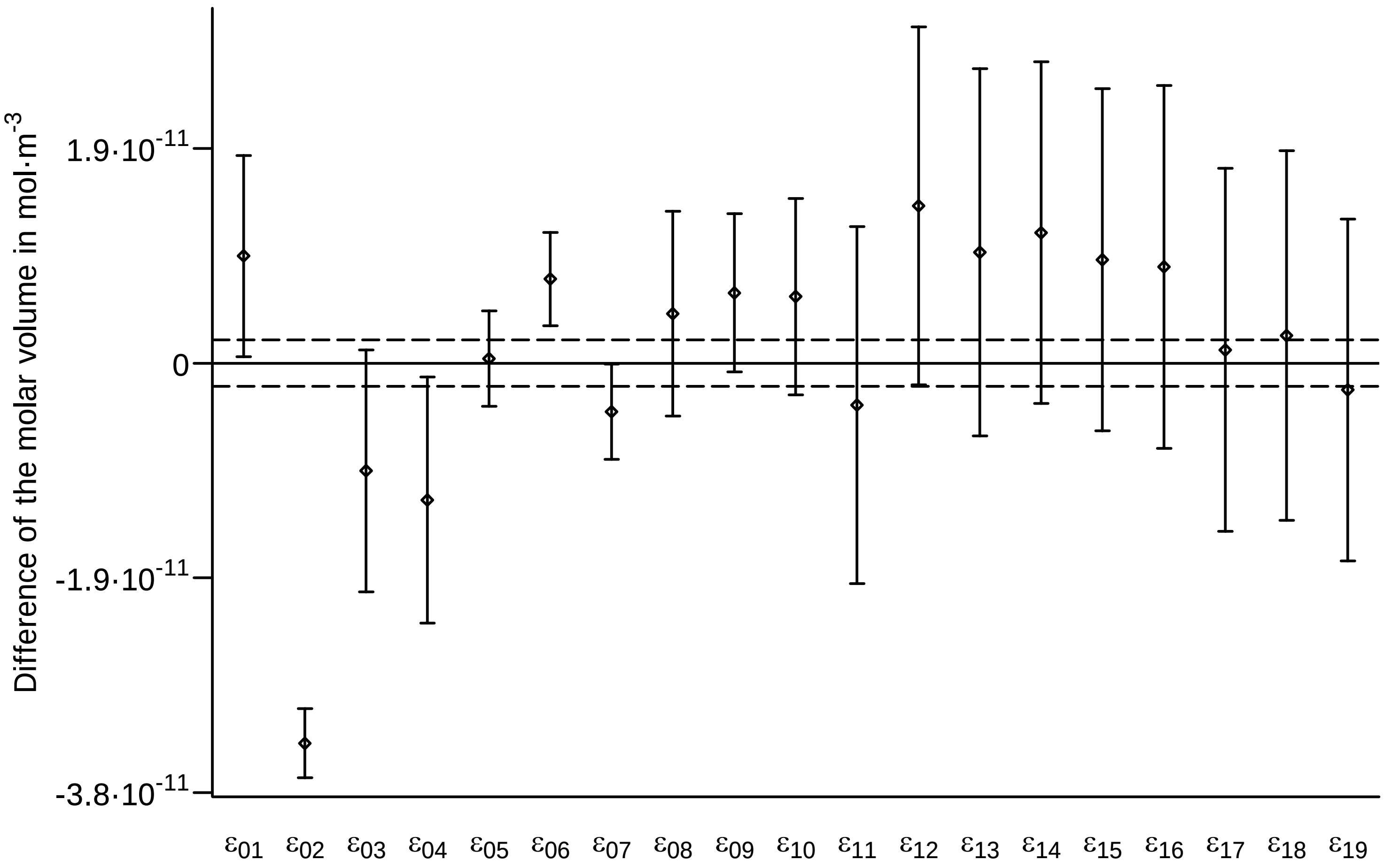
Before…



After…



Overall data consistency



Treating correlations

- Correlations are important because we average over large number of molar volume values
- Correlations arise because the laboratories use common quantities for different results (e.g. calibration factor for molar mass)
- Results from different laboratories are considered to be independent

Uncertainty budget

Quantity	Value	Standard Uncertainty	Sensitivity Coefficient	Uncertainty Contribution	Index
a_0	$543.1020880 \cdot 10^{-12}$ m	$16.0 \cdot 10^{-18}$ m	$-3.3 \cdot 10^{33}$	$-53 \cdot 10^{15}$ mol^{-1}	21.0 %
$K_{29/28Si}$	1.0013060 mol/mol	$37.0 \cdot 10^{-6}$ mol/mol	$890 \cdot 10^{18}$	$33 \cdot 10^{15}$ mol^{-1}	8.1 %
$K_{30/28Si}$	0.9963150 mol/mol	$58.0 \cdot 10^{-6}$ mol/mol	$1.3 \cdot 10^{21}$	$73 \cdot 10^{15}$ mol^{-1}	39.3 %
M_{28Si}	27.976926490 g/mol	$220 \cdot 10^{-9}$ g/mol	$20 \cdot 10^{21}$	$4.4 \cdot 10^{15}$ mol^{-1}	0.1 %
r_{30}	0.03360280	$1.00 \cdot 10^{-6}$	$12 \cdot 10^{21}$	$12.0 \cdot 10^{15}$ mol^{-1}	1.2 %
δV_m	0.0	$5.60 \cdot 10^{-12}$	$2.2 \cdot 10^{27}$	$12.2 \cdot 10^{15}$ mol^{-1}	1.2 %
ρ	2329.035464 kg/m^3	$900 \cdot 10^{-6}$ kg/m^3	$-70 \cdot 10^{18}$	$-62.6 \cdot 10^{15}$ mol^{-1}	29.1 %
N_A	$6.0221353 \cdot 10^{23}$ mol^{-1}	$100 \cdot 10^{15}$ mol^{-1}			

- 50% of the uncertainty arises from molar mass measurements
- 20% from lattice parameter measurements
- 30% from density measurements

Discussion of the final approach

$$V_{m,i} = \frac{M_{Si,i}}{\rho_{Si,i}} + \delta V_{m,i}$$

$$V_m = \frac{\sum_i \frac{1}{u^2(V_{m,i})} V_{m,i}}{\sum_i \frac{1}{u^2(V_{m,i})}}$$

$$N_A = \frac{8 \cdot V_m}{a^3}$$

- clear measurement function
- every lab is contributing
- weighting based on uncertainties
- check for consistency

Acknowledgement

I would like to thank Prof. Paul De Bievre (IRMM, retired) for involving me in the project.

I would like to thank Dr. Peter Becker (PTB) for providing me with detailed data and some photos.

Thank you for you attention!