Determination of the Avogadro constant by counting $^{28}\text{Si}$ atoms

Horst Bettin
Physikalisch-Technische Bundesanstalt
Germany
Definition of Avogadro constant $N_A$

- Number of molecules per mol
- $6.022... \times 10^{23} \text{ mol}^{-1}$

Current definition of mol

- Number “entities” like $^{12}\text{C}$ atoms in 12 g
- i.e. $6.022... \times 10^{23} ^{12}\text{C}$ atoms have a mass of 12 g
How to count $10^{23}$ atoms?

With a crystal!

1. Volume $a_0^3$ of the unit cell
2. Volume of an atom: $a_0^3/8$
3. Volume $V$ of a sphere
4. Number $n$ of the atoms

\[ N_A = \frac{8 \times V}{a_0^3} \times \frac{M_{\text{mol}}}{m_{\text{sphere}}} \]
Lattice parameter measurement

Combined optical and X-ray interferometry
INRIM X-ray interferometer

Si crystal

X-rays

Crystal translation devices

Laser interferometer
Lattice parameter results (INRIM)

Variations of the (220) lattice-plane spacing along the 50 mm, 5 mm from top

\[ u_r(d_{220}) = 3.5 \times 10^{-9} \]
Principle of MC-ICP-MS

MC-ICP-MS
multicollector inductively coupled plasma mass spectrometer

Isotope dilution method
PTB, NIST, NRC, NMIJ, …
Molar mass results (PTB)

\[ u_r(M) = 8 \times 10^{-9} \]
Why spheres?

Spheres:
- no edges
- highly symmetric
- “easy” to polish
Spherical waves:
With the Fizeau interferometer thousands of diameters are measured simultaneously.
The uncertainty is 0.7 nm.
PTB's sphere interferometer enables complete topographies of spheres, $n_{\text{diameter}} \approx 500,000$. 
Sphere topographies

Diameter topographies of the Avogadro spheres
AVO28-S5  AVO28-S8
Sphere interferometer of NMIJ

- Optical interferometer with flat etalons
- Active radiation shield for thermal uniformity
- Volume determination from 770 directions
- $u (D) = 1 \text{ nm}$
- Results consistent with PTB
Sartorius CCL 1007 mass comparator with its vacuum transfer system

Surface artefacts $\Delta S = 186 \text{ cm}^2$
Mass determination: Results

- AVO28–S5
  - BIPM
  - NMIJ

- AVO28–S8
  - BIPM
  - PTB

Mass difference to weighted mean / μg

10^{-8} kg
Mass of the core of the silicon sphere:

\[ m_{\text{core}} = m_{\text{meas}} - m_{\text{oxide}} - m_{\text{ads}} \]

\[ m_{\text{ads}} = m_{\text{hydrocarbon}} + m_{\text{water(\text{rev})}} + m_{\text{water(\text{irrev})}} \]

- **Contamination**: Can be removed by cleaning
- **Physisorption**: Can be removed by vacuum
- **Chemisorption**: Could be removed only at high temperature under vacuum
Surface model

<table>
<thead>
<tr>
<th>Surface</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carb. Cont.</td>
<td>XRF</td>
</tr>
<tr>
<td>Water</td>
<td>Gravimetric</td>
</tr>
<tr>
<td>Metals</td>
<td>XRF</td>
</tr>
<tr>
<td>Si oxide</td>
<td>XPS, XRF, XRR, SE</td>
</tr>
<tr>
<td>Si crystal</td>
<td></td>
</tr>
</tbody>
</table>
### Surface layer results

<table>
<thead>
<tr>
<th>Layer</th>
<th>Sphere</th>
<th>$d_{SL}$ (nm)</th>
<th>$m_{SL}$ (µg)</th>
<th>$u(SL)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonaceous layer (CL)</td>
<td>AVO28-5</td>
<td>2.88(33)</td>
<td>222,1(14,5)</td>
<td>0.3 nm</td>
</tr>
<tr>
<td>Chemisorbed water layer (CWL)</td>
<td>AVO28-8</td>
<td>2.69(32)</td>
<td>213.6(14,4)</td>
<td></td>
</tr>
<tr>
<td>Metal silicide layer (ML)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbon liquid (0.47 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O (0.28 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiSi (0.54 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMIJ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si crystal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si crystal (Avo28 S8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO (0.1 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: $u(SL)$ is the uncertainty in the surface layer.
Avogadro constant values

![Graph showing the Avogadro constant values over the years with different sources indicated.]
## Uncertainty budget 2011

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Relative uncertainty $10^{-9}$</th>
<th>Contribution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Sphere mass</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Surface</td>
<td>14</td>
<td>22</td>
</tr>
<tr>
<td>Sphere volume</td>
<td>23</td>
<td>57</td>
</tr>
<tr>
<td>Lattice parameter</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>Point defects</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Partners</td>
<td>Lattice parameter</td>
<td>Sphere volume</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------</td>
<td>---------------</td>
</tr>
<tr>
<td></td>
<td>Abs.</td>
<td>Rel.</td>
</tr>
<tr>
<td>BIPM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>INrim</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Metas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nist</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nim-A</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>NmiJ</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Nrc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtB</td>
<td>2015</td>
<td>X</td>
</tr>
</tbody>
</table>
Resolving discrepancies

- Resolving the discrepancy in molar mass: Measurements at PTB, NRC, NIST, NMIJ, NIM

Confirmation of results

- Independent lattice parameter measurement (PTB)
- Impurity concentrations: all chemical elements (INRIM)
- More Si28 crystals (at least 3)
Future of the Avogadro project

Reduction of uncertainty

- Improved surface characterisation
- Sphere manufacturing: unroundness 10 nm
- New sphere interferometer at PTB
- Target: uncertainty of $1.5 \times 10^{-8} N_A$
PTB purchases 11 kg new $^{28}\text{Si}$ from Russia

- 2 different single crystals of 5 kg each
- 2 spheres (1000 g) from each crystal
- First 2 spheres will be ready for measurements end of 2014
- Second 2 spheres will be available in 2015
The kilogram, kg, is the unit of mass; its magnitude is set by fixing the numerical value of the Planck constant to be equal to exactly $6.626\,06\times 10^{-34}$ when it is expressed in the unit $\text{s}^{-1} \, \text{m}^2 \, \text{kg}$, which is equal to $\text{J} \, \text{s}$.

$E = m \, c^2$ and $E = h \nu$

Consequence:
The mass of the kg prototype $m(K)$ has to be determined experimentally and will have an uncertainty.

*) X represents one or more digits to be added at the time the new definition is finally adopted.
Molar Planck constant

Avogadro constant · Planck constant

\[ N_A h = \frac{M(e)}{m(e)} \cdot \hbar = \frac{M(e) c \alpha^2}{2 R_\infty} \]

\[ m^{(28)\text{Si}} = 2 \hbar \frac{A^{(28)\text{Si}}}{A^*(e)} \frac{R_\infty}{\alpha^2 c} \]

CODATA 2010:

\[ N_A h = 3.990\ 312\ 7176(28) \times 10^{-10}\ \text{J s mol}^{-1} \]

quoted relative uncertainty: 7 \times 10^{-10}!
Kilogram realisation by XRCD method

Measurements for the realisation of the new kg

- Lattice parameter
- Molar mass (isotopic composition)
- Crystal perfection (impurity contents)

Duration of all values for one crystal: about 6 months.

Have to be measured only once!
Kilogram realisation by XRCD method

Measurements for the realisation of the new kg

- Volume of the sphere: Duration about 1 month.
  Has to be repeated only every few years

- Surface layers (oxide etc.): Duration about 1 week.
  Has to be repeated for each realisation!

Thus, realisation of the new kg by the XRCD method usually takes about 1 week.
Summary

The XRCD method

- is suitable to realise the kg after redefinition,
- has reached a relative uncertainty of $3.0 \times 10^{-8}$,
- is able to reach a relative uncertainty of $1.5 \times 10^{-8}$
Thank you very much for your attention!

Questions?

Comments?
Uncertainty of kg realization

Consequences of the redefinition

- $20 \times 10^{-9}$ No damage to customers of NMIs
- $10 \times 10^{-9}$ No damage to NMIs
- $5 \times 10^{-9}$ Advantages and disadvantages cancel
- $2 \times 10^{-9}$ Improvement of mass metrology
The CCM roadmap towards a redefinition in 2018

- **Now**
  - 14 CCM
  - 21 CCU
  - NMI directors meeting

- **2013**
  - BIPM calibration with IPK (preparation, support group)

- **2014**
  - Mise en pratique (mep kg)
  - Convocation-
    - CGPM

- **2015**
  - mep kg approved

- **2016**
  - Initial pilot study (kg)
  - (preparation, measurements & report)

- **2017**
  - Updated mep kg approved

- **2018**
  - Consultation/announcement
  - CODATA (final LSA)
  - Convocation

- **Redefinition**
  - CIPM

- **2013**
  - EMRP kNOW and NewKILo projects

- **2014**
  - Pool established
  - Pool characterized

- **2015**
  - XRC and WB publish consistent results

- **2016**
  - Pool linked to experiments

- **2017**
  - CCM
  - R3

- **2018**
  - CCM
  - R4

**Conditions from CCM G1 (2013)**

**Metrologia special edition**
- (with references for the mep)

**METAS 05.07.2013**
Preconditions for a new kg definition

- *Mise en pratique*
- New calibrations using the IPK
- 3 determinations of \( h \) with rel. unc. \( \leq 5 \times 10^{-8} \)
- Two different methods
- 1 determination of \( h \) with rel. unc. \( \leq 2 \times 10^{-8} \)
- Consistent results
- Procedures of realization\&dissemination validated
- Key comparison (CIPM-MRA)
Kilogram redefinition

CCM conditions for the new kg definition

- 3 determinations of $h$ with rel. Unc. $\leq 5 \times 10^{-8}$
- 1 determination of $h$ with rel. Unc. $\leq 2 \times 10^{-8}$
- Consistency

CCM:

Comité consultatif pour la masse et les grandeurs apparentées

Consultative Committee for Mass and Related Quantities
Confirmation of Measurements

- Molar mass measurements at NIST, NRC
- Lattice parameter determination at PTB
- Surface characterisation at NMIJ and NIM
- Impurities and crystal defects
- Homogeneity of the crystal: Density comparisons
- New (small) crystals
- Temperature comparison measurements with an electronic temperature reference point
X-ray Fluorescence Analysis (XRF)

- Excitation of atoms by X-rays
- Atoms emits characteristic X-rays
- Following Moseley’s law, this emitted radiation is used to identify the different elements
X-ray Photoelectron Spectroscopy (XPS)

- Excitation of atoms by X-rays
- Atoms emits a characteristic photoelectron
- The emitted electron has a specific energy for the element and the binding state of the atom
S.E. is a non destructive optical technique that is able to measure optical properties and thickness of single and multi layer(s) without any contact.

Potential of Spectroscopic Ellipsometry

\[ \rho = \frac{r_p}{r_s} = \text{Tan}(\Psi) \cdot e^{j\Delta} \]

Measured Parameters:
- \( \text{Tan}(\Psi) \)
- \( \text{Cos}(\Delta) \)

\( \rho \) (spectral range)

Detection

\( \lambda \)

Ambient \( (n_0, k_0) \)

Thin Film 1 \( (n_1, k_1, T_1) \)

Thin Film 2 \( (n_2, k_2, T_2) \)

Thin Film i \( (n_i, k_i, T_i) \)

Substrate \( (n_s, k_s) \)

1. SE Measurement

We find:
- \( T_i, n_i, k_i \)

2. Physical Model Simulation

- Film Stack and structure
- Material \( n, k \), dispersion
- Composition Fraction of Mixture

Experimental Measurement = Model Simulation?

Yes!

No

REAL SAMPLE STRUCTURE

© Sopra
Optical scheme of an ellipsometer
Système International d'Unités (SI)

- Luminous intensity
  - $K_{cd}$
  - $1979 / 10^{-3}$
  - $1983 / 10^{-10}$

- Amount of substance
  - $N_A$
  - $1971 / 10^{-6}$

- Tripelpunkt-Zelle
  - $k_B$
  - $1967 / 10^{-6}$

- $H_2O$

- kg-Prototyp
  - $1889 / 10^{-8}$
  - kg

- $133$ Cs
  - $1967 / 10^{-14}$

- Atomuhr
  - $1948 / 10^{-8}$

- "SI"
  - $1967 / 10^{-6}$

Note: A, mol and cd depend on kg!

Opens the door for quantum standards
Avogadro constant: Relative uncertainty and deviation from CODATA value 2006
Status

- Publication in *Phys. Rev. Lett.*
- Special Issue of *Metrologia*: „Dedicated to Peter Becker“
  14 publications (119 pages)
- Uncertainty: $3,0 \times 10^{-8} \, N_A$
- Largest uncertainty contributions:
  - Mass of surface layers: $1,4 \times 10^{-8} \, N_A$
  - Diameter of spheres: $2,3 \times 10^{-8} \, N_A$
### Mass unit: Dissemination chain

<table>
<thead>
<tr>
<th>Present system</th>
<th>After redefinition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0 µg</strong></td>
<td><strong>20 µg</strong></td>
</tr>
<tr>
<td>Best realisation of the kilogram</td>
<td><strong>30 µg</strong></td>
</tr>
<tr>
<td>BIPM reference standards</td>
<td><strong>30 µg</strong></td>
</tr>
<tr>
<td><strong>6 µg</strong></td>
<td><strong>42 µg</strong></td>
</tr>
<tr>
<td>BIPM working standards</td>
<td><strong>43 µg</strong></td>
</tr>
<tr>
<td><strong>6 µg</strong></td>
<td><strong>32 µg</strong></td>
</tr>
<tr>
<td>National standards of NMIs</td>
<td><strong>71 µg</strong></td>
</tr>
<tr>
<td><strong>14 µg</strong></td>
<td><strong>30 µg</strong></td>
</tr>
<tr>
<td>Secondary standards of NMIs and best standards according to CMC</td>
<td><strong>43 µg</strong></td>
</tr>
<tr>
<td><strong>25 µg</strong></td>
<td><strong>53 µg</strong></td>
</tr>
<tr>
<td>Reference standards of E1 accredited laboratories</td>
<td><strong>77 µg</strong></td>
</tr>
<tr>
<td><strong>≥83 µg (E1)</strong></td>
<td><strong>6 µg</strong></td>
</tr>
<tr>
<td>Standards of customers of E1 accredited laboratories</td>
<td><strong>43 µg</strong></td>
</tr>
<tr>
<td><strong>≤83 µg (E2)</strong></td>
<td><strong>85 µg (E2)</strong></td>
</tr>
<tr>
<td><strong>100 µg (E2)</strong></td>
<td><strong>71 µg</strong></td>
</tr>
</tbody>
</table>

Ex. 1 (CCM req.) | Ex. 2 | Ex. 3

- Present system:
  - 0 µg: Best realisation of the kilogram
  - 6 µg: BIPM reference standards
  - 6 µg: National standards of NMIs
  - 14 µg: Secondary standards of NMIs and best standards according to CMC
  - 25 µg: Reference standards of E1 accredited laboratories
  - ≥83 µg (E1): Standards of customers of E1 accredited laboratories

- After redefinition:
  - 20 µg
  - 30 µg
  - 50 µg
  - 30 µg
  - 42 µg
  - 71 µg
  - 32 µg
  - 43 µg
  - 71 µg
  - 30 µg
  - 43 µg
  - 71 µg
  - 44 µg
  - 53 µg
  - 77 µg
  - 6 µg
  - 85 µg (E2)
  - 100 µg (E2)
IAC

\[ N_A = \frac{M_{Si} \cdot V_{sphere}}{\sqrt{8} \cdot d_{220}^3 \cdot m_{sphere}} \]
XRF-spectra of the Ni and Cu contamination on AVO28-S5:

- CSIRO-ACPO polished
- Freckle etch 1 min
- Freckle etch 2 min

Counts in h⁻¹

Energy in keV

Ni-Kα, Ni-Kβ, Cu-Kα, Cu-Kβ
Mass drift of the official copies between 1889, 1946, 1989
Mass values of the prototypes in 1889, 1950 and 1990

- red: International Prototype
- green: BIPM, Official Copies
- orange: no.25, BIPM, for special use
- black: national prototypes

Mass drift of the national prototypes between 1889, 1950, 1990

50 µg = 0.05 ppm

50 µg is the mass of a dust particle of 0.34 mm in diameter
X-ray Reflectometry (XRR)

Oscillation → Thickness
Amplitude → Density
Slope → Interface/Roughness

\[ 4l \left( \alpha_i^2 - \alpha_k^2 \right) = m^2 \lambda^2 \]

\[ \Delta q_z \cdot d \]

- Incident beam
- Reflected beam

\( d \) : film thickness
\( m \) : interference order
\( \lambda \) : wavelength
\( \alpha_i, m \) : angle of \( m^{th} \) order
\( \alpha_k \) : critical angle
\( \Delta q_z \) : distance of two maxima (in reciprocal space)
X-ray reflectometry at BESSY
Spectral ellipsometry
Vacuum mass comparator
Nominal load: 1 kg
Pressure range: \(10^{-2}\text{ Pa} \leq \text{10^5 Pa}\)
Weight exchange mechanism with 6 positions
Weighing range (electr.): 1.5 g
Resolution: 0.1 µg
Linearity error: \(\leq 2\) µg
Standard deviation (typ.): \(\leq 0.4\) µg
Mass determination

Problems for comparison to PtIr: density and surface area of sphere
Vacuum (1 mPa): no air buoyancy but desorption effects!

Sorption artefacts:
- Same mass
- Same volume
- Same polishing
- Different surface area
Surface layer topographies of spheres

AVO28-S5

AVO28-S8