IAC Report to CI PM 2009

Micro. Density = Macro. Density

\[
\left( \frac{M}{N_A} \right) / d^3 = \rho = \frac{m}{D^3}
\]

\[
N_A = M \left( \frac{2^{3/2} \times \rho \times d_{220}^3}{d^3} \right)
\]

<table>
<thead>
<tr>
<th>Material Evaluation</th>
<th>2008/10</th>
<th>2009/10</th>
<th>2009/10</th>
<th>2011/3</th>
<th>Final Target</th>
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<td>Molar Mass</td>
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<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Volume of Sphere</td>
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<td>2.8</td>
<td>1.7</td>
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<tr>
<td>Lattice Parameter</td>
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<td></td>
<td>1.0</td>
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<tr>
<td>Material Evaluation</td>
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<tr>
<td>Surface oxide</td>
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<td>?</td>
<td>?</td>
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<td>1.0</td>
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<tr>
<td>Mass of Sphere</td>
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<tr>
<td>Avogadro Constant</td>
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<td>Discrepancy XRCD/WB</td>
<td>-110</td>
<td>20.1</td>
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</table>
Molar Mass Measurement

1) Shift $+120 \times 10^{-8}$ in Nat.Si?
   - Task Force for Un
   - No Evidence.
   - Contamination.
   - Different K-factors. (Mole/Current)

2) IMR(Beijing): Direct Conversion to SiF4.

3) PTB application of IDMS
   - No Conversion.
Cu and Ni contamination on Silica layer of Sphere
XPS(METAS) found, XRF(PTB) confirmed.
Influential to $N_A$ through Silica layer.
Caused by polishing.

IAC Report to CIPM 2009

BESSY XRF Sphere on AVO28-S8
significant Ni and Cu contamination

IAC Report to CIPM 2009

Relative difference in $N_A (10^4)$

CODATA 2006 Natural Si Avo28
IAC Report to CIPM 2009

2. Addendum to
Consortium Agreement on cooperation to facilitate
“New determination of the Avogadro Constant”
dated from 24 March 2004

BY THE

INTERNATIONAL AVOGADRO COORDINATION (IAC)

CONSULTATIVE COMMITTEE OF MASS (CCM)
# INTERN. AVOGADRO COORDINATION PROGRESS REPORT

| 1. | **Year**: 2008/2009  
**October 2008 – September 2009** | **Coordinator**: Peter Becker |
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>2.</td>
<td><strong>Pilot Laboratory</strong>: PTB</td>
<td><strong>3.</strong> <strong>Partner Laboratories</strong>: BIPM, INRIM, IRMM, NMIA, NMIJ, NIST, PTB</td>
</tr>
</tbody>
</table>
| 4. | **Research Topic**: Report of scientific activities of IAC until September 2009 | **4.** **Progress**:

## Summary

* **Re-evaluation of natSi**
  - Relative standard uncertainty in $N_A$: 0.299 ppm
  - Difference from CODATA 2006: +0.201 ppm

* **Preliminary results for $^{28}$Si**
  - Relative standard uncertainty in $N_A$: 0.052 ppm
  - Difference from CODATA 2006: +0.133 ppm

* **Independent molar mass measurements**
  - Institute for Mineral Resources (Beijing): chemical conversion with BrF$_5$
  - Isotope Dilution Mass Spectrometry (IDMS) at PTB

* **Absolute lattice parameter measurements** on WASO 04 at INRIM: 0.005 ppm
  - (Test of performances)

* **Intercomparison of diameter measurements**
  - Agreement between NMJ, PTB, and NMIA: better than 1 nm (?)

* **Intercomparison of mass measurements 1 kg Si spheres**
  - Agreement between BIPM, NMJ, PTB: better than 20 $\mu$g
  - Standard uncertainty at the BIPM: 5.4 $\mu$g

* **Intercomparison of density measurements**
  - Agreement between PTB and NMJ: better than 0.1 ppm

* **Oxide layer determination**
  - Unexpected oxide contamination by metals on CSIRO polished spheres

## Publications


Preliminary data available so far have been used to calculate a value for the Avogadro constant to compare it with the CODATA or watt balance results. As regards as the nat-Si measurements the values derived from sphere PTB AVO#1, and from NMIJ spheres S6 and S7 agree, to within their uncertainties, with the NIST watt balance determination. As regards as the $^{28}\text{Si}$ measurement, the $N_A$ value obtained is in agreement with the NIST watt balance, too. The data are compiled in Figure 1.

For all the quantities involved in the $N_A$ determination, the measurement capabilities have nearly reached the targeted resolution ($2 \times 10^{-8}$); only a factor from two to three is missing, in the worst case. However, at the new resolution level (below 0.1 ppm) some new problems, in particular the oxide contamination by metal impurities, are emerging which have to be investigated and eliminated.

**$^{28}\text{Si}$ material**

The 5 kg enriched material fulfils almost perfectly the requirements of the IAC due to enrichment and chemical purity. Two 1 kg spheres were prepared at CSIRO in 2008, named AVO28-S5 and AVO28-S8.

At NMIJ, a self-referencing lattice comparator was developed at the beamline BL3C in KEK, Japan [Xiaowei Zhang et. al., *J. Appl. Cryst.* 36 (2003) 188-192]. Newly improved apparatus has been operational. It can map (100), (110) and (111) ingot (10 cm in diameter) combined with monolithic monochromators of relevant indices. The resolution (standard deviation) achieved is 0.005 ppm. High resolution 3D x-ray diffraction microscopy measurement at SPring-8 is expected to detect very
small defects and voids (10 nm). Sample preparation for Cu-decorated nat-Si crystals (NRLM3, NRLM4 and WAS004) is proceeding. Special etching is needed to have a very thin film for the measurement and was finished at Osaka university. Next measurement will be performed when beam time is available. Ultrasonic measurement at low temperatures at Niigata university can measure the vacancy in Si crystals. Preliminary results for IKZ test ingot and Si28 crystal show no signal of vacancy existence. Further measurement is conducted to characterize the silicon crystals.

Volume determination
Volume measurements were performed at NMIJ, PTB and NMIA. PTB and NMIJ have reached a measurement uncertainty of 0.03 ppm (target 0.01 ppm by further improvements in temperature shielding at NMII and by using a new Fizeau interferometer at PTB). Test measurements of a single diameter at PTB and NMIJ disagreeing in the past by about 3 nm are now consistent due to more precise phase shift corrections. Comparison measurements are ongoing, as well as simulations of optical phase shifts in this kind of interferometers.
At NMIJ, the volume of AVO28-S8 has been measured with a relative uncertainty of 2.8 x 10⁻⁸. At present, the most dominant uncertainty source is the chemical composition analysis in the oxide layer thickness determination. Taking account of the XPS measurement results, this uncertainty will be reduced significantly. The uncertainty in the volume determination will be reduced to 1.7 x 10⁻⁸.

Oxide Layer determination
At PTB, the XRR method is directly applied on the sphere at selected points and acts as calibration. For the complete mapping of the native oxide directly on the AVO28-S8 sphere, a new ellipsometer, with a shorter measuring time, is now in function. A full measurement circle on ²⁸Si spheres has been accomplished. Additional XPS measurements on the ²⁸Si and natSi spheres have been performed at METAS with following unexpected results: a) On all spheres XPS data indicate a pure SiO₂ stoichiometry. b) All spheres polished at CSIRO including ²⁸Si spheres show a significant Cu and Ni oxide contamination which will probably influence the optical constants both in x-ray and optical diffractometry, see Fig. 2. The thermal oxidation on CSIRO-polished sphere – necessary for the target uncertainty 2 x 10⁻⁸ – is still a risk probably due to the metallic contamination of the oxide. A light repolishing with Syton at PTB is in discussion to avoid this problem. The data for the oxide layer are presently not XRR calibrated due to the – so far - uncertain optical constants.
NMIJ measurement results of the oxide layer thickness (ellipsometry, 20 data points) are available for AVO28-S5 and AVO28-S8. The ellipsometric measurements were calibrated via flat test-samples whose oxide thickness was determined via XRR using a conventional x-ray source. A comparison between PTB and NMIJ for oxide thickness measurements by XRR and ellipsometry via calibrated flat samples will be a next step for finalizing the uncertainty reached so far. NMIJ and PTB have measured the oxide thickness on a specified position on AVO28-S8 by ellipsometry. The results show good agreement each other within their uncertainties.
Mass determination
The mass measurement of the spheres AVO28-S5 and AVO28-S8 performed at the BIPM, PTB, and NMIJ are in excellent agreement. The only discrepant value is from the NMIA, but the measurement was performed without the aid of a vacuum facility. The target measurement uncertainty of $5 \times 10^{-9}$ could be reached. NMIJ and BIPM are still studying water vapour adsorption of a Si sphere at a low-pressure operation of the balance. A correction due to the metal oxide contamination seems to be necessary.

BIPM
The BIPM is pilot laboratory for the international mass comparison under vacuum of the two isotopically enriched silicon 1 kg spheres named AVO28-S5 and AVO28-S8. The other laboratories involved in this comparison are the NMIJ/AIST and the PTB. The protocol of this comparison is based on experience gained from the previous comparison, reported two years ago. In September 2008, the BIPM received the AVO28-S8 sphere and in October 2008, the AVO28-S5. Comparisons were carried under vacuum with respect to our sorption artefacts, and these could be transferred to air for comparison against our working standards (thereby effecting an indirect comparison between silicon artefacts maintained in vacuum and Pt-Ir artefacts maintained in air). Such comparisons were carried out four times and three times for the spheres AVO28-S8 and AVO28-S5, respectively. First results obtained at the BIPM demonstrate that the relative uncertainty target fixed by the IAC, which requires a mass determination with an accuracy of about 5 µg for a 1 kg silicon sphere has been reached. Indeed, the combined uncertainty for the mass determination under vacuum for both spheres, is 5.4 µg. This international mass comparison is ongoing.

We received delivery of the vacuum transfer system (VTS) that was ordered from Sartorius AG. This accessory to our CCL 1007 comparator will permit us to load artefacts, stored in inert gas or under vacuum, into the comparator without any contact with ambient laboratory air. An automatic loadable container (ALC) permits the transfer between an external glove box and the VTS. The ensemble of the mass comparator, the VTS, the glove box with its associated vacuum oven and the ALC are essential for the IAC mass comparisons. With this equipment we will be able to determine the irreversible amount of water adsorbed on the surface of a silicon sphere. The first vacuum-vacuum transfer of artefacts has been successfully carried out during the commissioning of the new equipment.

PTB
Because of a reconstruction of the climate system, the PTB mass laboratory could not participate in the first comparison measurements of the 1 kg $^{28}$Si sphere AVO28-S8, which were scheduled for autumn 2008. Between the end of March and the beginning of May 2009 the mass of the silicon sphere...
AVO28-S5 was determined in air and under vacuum with a standard uncertainty of 13 µg. In addition to the uncertainty of the reference mass (6 µg) the main contribution to the uncertainty budget results from the uncertainty of the buoyancy correction (9 µg) for the mass determination in air and the uncertainty of the sorption correction (9 µg) for the mass determination under vacuum. In the near future, it will be possible to reduce the uncertainty contribution of the sorption correction of the reference mass under vacuum significantly by applying sorption artefacts made from Pt–Ir similar to the approved BIPM design. The raw material for the manufacture of the artefacts was delivered by the BIPM. The polishing and adjustment procedure was performed at PTB. A mean surface roughness of 2 nm < Rₐ < 4 nm was achieved. Results of first measurements indicate that the mass desorbed from the Pt–Ir cylinder during the transfer between air and vacuum amounts to about 3 µg (40 ng/cm²), which is comparable to the results obtained by the BIPM.

**NMIJ**

The mass of the silicon sphere (AVO28-S8) was measured in air and under vacuum in February 2009. The measurement results were reported in March 2009. The measurement uncertainties were 0.018 mg for the result in air and 0.017 mg for the result under vacuum. These measurement results will be re-evaluated after the recalibration of the reference weight, which is planned this year.

**Relative Density**

The densities of the two ²⁸Si spheres AVO28-S5 and AVO28-S8 were compared in the pressure-of-flotation apparatus of PTB, yielding:

\[
\text{Density(AVO28-S8)} - \text{density(AVO28-S5)} = 0.020(10) \text{ ppm.}
\]

This new determination has a far lower uncertainty, since the spheres were compared directly and not via a very small sphere of only 10 g as during the comparison in 2008. This comparison will be repeated soon at NMIJ.

**Lattice parameter determination**

First results for the lattice parameter of ²⁸Si have been derived by comparison with samples from natSi-WASO04 using the NIST lattice comparator. Measurement uncertainty is 1.2 x 10⁻⁸.

X-interferometric test measurements at INRIM on the nat-Si crystal MO*4 (INRIM), WASO 4.2A (PTB), and WASO04 have been completed. The accuracy achieved is 0.005 ppm, to be compared with a targeted accuracy of 0.003 ppm. The manufacturing of the ²⁸Si interferometer at the PTB is now completed. The INRIM carried out some upgrade to the experimental apparatus to solve the problems pinpointed during the test measurements. First measurement results are expected to be available by the end of the year.

**Molar Mass determination**

In the meantime 3 independent measurements for the molar mass are established:

1) IRMM has finished the re-measurement of the molar mass of natural silicon using new synthetic mixtures, new results differ by +1.2 ppm from previous ones. It is not possible to illuminate fully the reason for this shift.

2a) The IRMM completed a first calibration with a ²⁸Si enriched mixture and first test calibrated measurements of the ²⁸Si crystal molar mass. Measurement uncertainty 0.01 ppm (target). Further problems to be investigated: a) Different calibration factors have been found with the use of nat-Si and enriched ²⁸Si mixtures; this might be not consistent with an assumption of a constant calibration factor. b) The nat-Si contamination is rather high (~ 0.5 ppm) and must be corrected, based on calibrated measurements of the nat-Si content in the chemicals (calibration via Merck standards (PTB)).

2b) A contract has been issued by INRIM, PTB and the Institute of Mineral Resources (Beijing, China, ref. T. Ding) to convert ²⁸Si directly into ²⁸SiF₄ via BrF₅ – so reducing the chemical processing and, consequently, the risk of nat-Si contamination – and to perform independent measurements of the molar mass.

3) At PTB the molar mass measurement is performed using multicollector ICP mass spectrometry. First experiments have been applied using a sample of a highly enriched Si₂⁸ crystal. The relative repeatabilities of the preliminary measurements of the molar mass are in the order of 1·10⁻⁸ (k = 1).
However, the determination of an absolute value needs careful elimination of bias effects in the near future. Theoretical investigations in calibration and limit uncertainty of the mass spectrometry are ongoing to supply guidelines for optimal molar mass measurements.

Remarks:

Paper on re-measurement of natSi in preparation. Extension of IAC contract (without financial commitments) by 1 year until March 2011 is proposed.

<table>
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<th>6. Completion date:</th>
<th>7. Coordinator’s signature:</th>
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<tr>
<td></td>
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<td>30 September 2009</td>
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