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Primary mass standard based on atomic masses

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Abstract

The paper summarises the activities of several national and international Metrology Institutes in replacing the kilogram artefact, the unit of mass, by the mass of a certain number of atoms, in particular the atomic masses of silicon or bismuth. This task is based on two different experiments: a very accurate determination of the Avogadro constant, N_A, measuring the density and lattice parameter of an enriched silicon-28 crystal, and the accumulation of decelerated bismuth-209 ions by using a mass separator.

The relative measurement uncertainties reached so far are in the first case 2 parts in 10^7, and in the latter several part in 10^4. The bismuth experiment is still in an early state of the work. The ratios between the masses of ^{28}Si or ^{209}Bi, respectively, and the present atomic mass standard, the mass of ^{12}C, can be determined with an accuracy now approaching 10^{-10} using high precision Penning traps mass spectrometers.

Keywords: Silicon; Bismuth; Avogadro constant; Penning trap; Relative atomic mass

1. Introduction

About 200 years ago, during the period of the French Revolution, several well-known French scientists were discussing a new system of basic physical units. They agreed that – in accordance with the spirit of the age – the new metrological units should be the same all over the world, and should be based not on artefacts but on natural standards. Thus the unit of length, the "meter", was defined as one ten millionth of the earth's quadrant and the unit of mass, the "kilogram", as the mass of one cubic decimeter of water, considering the density of water to be constant by nature. As the representation of the unit, a piece of platinum was linked to the density of water by careful experiments. Lavoisier, one of the most important experimenters and promoters of the new unit of mass, tried to collect and stockpile all the platinum available in the country. Even though the meter and the kilogram were derived from natural quantities, their final definition by the prototypes of platinum returned to artefacts being subjected to changes by handling, by ambient influences and with time.

The kilogram standard which we use today is about 100 years younger. During the years from 1883 to 1889, a prototype and a large number of copies were moulded from one charge of platinum–iridium. The international prototype and some of the copies acting as secondary standards remained at the Bureau International des Poids et Mesures (BIPM) in Sèvres near Paris, while the remaining ones were delivered to other countries.

The first Conférence Général des Poids et Mesures in 1889 sanctioned the international prototype of the kilogram and declared that "this prototype shall henceforth be considered the unit of mass". This definition is still valid.

The kilogram is now the only base unit of the International System of Units (SI) being still defined in terms of a material artefact. The main problems associated with this definition are well known and can be summarised as follows:

- It can be damaged or even destroyed.
- It is not well defined (it accumulates foreign material and has to be cleaned with unknown effect).
- It is probably aging (perhaps 50 μg change within the last 100 years). A significant averaged drift of about 50 μg of the official and national copies of the international prototype has been observed over 100 years. Because of the number of these secondary standards (about 40) it is rather probable, that the international prototype itself is the source of this drift.
- It limits the stability of the kilogram relative to fundamental constants to a few parts in 10^8 at best.

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As early as 1870, when Maxwell [1] defined the well-known requirement that the physical units should not be founded on macroscopic quantities but on the properties of these “imperishable and unalterable molecules”, metrologists were called upon to consider the possibilities of redefining the kilogram.

One of the possibilities discussed among metrologists today is to trace back the unit of mass to an atomic mass, just as Maxwell would have done. The kilogram would then be defined as the mass of a fixed number of atoms of a definite species. For this, the number of atoms in a macroscopic mass of a substance has to be known, or the mass of the individual atom expressed in the present-day unit of mass has to be known with sufficient accuracy for the new mass scale to agree with the former one.

Another approach by the watt-balance experiment determines the relation of the Planck constant to the kilogram, based on condensed matter physics and mechanical measurements, with a relative uncertainty of 5.1×10^{-8} [2], the most advanced one among the experiments aimed at a new definition of the kilogram.

The direct determination of the mass of an atom can be performed either by an accurate determination of the Avogadro constant N_A, using a silicon crystal or by an accumulation of ions from an ion beam, e.g., bismuth ions, to a weighable mass m and determining their number by measuring the total charge of the ions, with relative uncertainties in the order of 10^{-8}. While the first method makes use of the perfection of a crystal structure counting all particles in the silicon molar volume, the second one is based on counting ions of a certain mass.

The new definition of the unit of mass, the kilogram could read as follows.

“The kilogram is the mass of N_{kg} free ^{12}C atoms at rest and in their ground state” with

$$N_{kg} = \frac{\{N_A\}}{A_r(^{12}C)} \times 10^3 \tag{1}$$

or

$$N_{kg} = \frac{1\,kg}{A_r(^{12}C)m_u} \tag{2}$$

where in both cases, N_A, $\{N_A\}$ numerical value, would become a fixed constant whose value will be based on the best experimental determinations as described below, and $A_r(^{12}C)$ is the relative atomic mass of ^{12}C with $A_r(^{12}C) = m(^{12}C)/m_u$, m_u unified atomic mass constant.

A combined relative uncertainty in the order of 10^{-8} in the determination of N_{kg} is required. An agreement of the Consultative Committee for Mass and Related Quantities found that at its meeting in 2005 a relative uncertainty of 2×10^{-8} (1σ) of the realisation of a new definition of the SI kilogram would be acceptable. It would not change the best uncertainties given today to stainless steel standards. Larger uncertainties would cause problems with the dissemination chain, the present system of accuracy classes and the fact that even some private calibration laboratories are certifying according to the best class (E_1) with 8×10^{-8} (1σ) relative uncertainty for 100 g and larger weights.

A discussion on the best time for a new definition has been raised by a proposal made in January 2005 [3], which shows the advantages for the system of fundamental constants in case that the Planck constant or the Avogadro constant were fixed by definition. A number of at least 10 constants would be known with relative uncertainties better by more than a factor of 10 than today. The authors proposed therefore to redefine the kilogram as soon as possible, that means at the next CGPM meeting in 2007, and not to wait for improved experimental results. This proposal was supported by the CODATA task group and by the CCU at first. Other consultative committees, such as the CCM, the CCEM and others discussed this proposal on their meetings and found that 2007 is too early, because it cannot be expected that the experiments will attain sufficiently low uncertainty and satisfying agreement among each other. The CCU took over these concerns in its Recommendation to the CIPM, where a redefinition of the kilogram, the ampere and the kelvin in 2011 is envisaged in case the experimental measurements are indeed acceptable and the relevant committees agree. The CIPM finally agreed with the CCU as documented in the CIPM Recommendation (CI-2005) of October 2005.

The paper is organised as follows.

After a short overview in Section 2 about the measurement of relative atomic masses in Section 3 the principles of the determination of the Avogadro constant using a silicon crystal are described while In Section 4 the ion accumulation experiment is presented. The paper closes with an evaluation of the experiments, together with other experiments devoted to a new kilogram definition.

2. Determination of the relative atomic mass

If the dream of a redefinition of the kilogram in terms of $A_r(^{12}C)$ on the basis of accumulated ions of an appropriate nuclide or of Si single crystals could ultimately be realised, we should be able to determine the ratio of the corresponding nuclide masses to that of ^{12}C, which is the present reference of the relative atomic masses, with $A_r = 12$ exactly.

Penning traps are presently the most accurate mass spectrometers [4–7]. The high accuracy that can be achieved with these devices, now approaching relative uncertainties of 10^{-10}, is due to the long storage time and the confinement of ions in a small volume in well-defined electric and magnetic fields.

In a magnetic field B the mass of an ion with charge q and mass m can be determined via its cyclotron frequency

$$\omega_c = \frac{qB}{m}. \tag{3}$$

The Penning trap consists of a uniform magnetic field together with a weak quadrupole electrostatic field which confines the ions. A mass ratio is determined by comparing the cyclotron frequencies of two ions repeatedly alternating between them. Table 1 lists the experimental data for the relevant atomic masses of the isotopes ^{28}Si and ^{209}Bi, together with the accepted values from conventional mass spectroscopy.

Table 1
Determination of the atomic mass of ^{28}Si and ^{209}Bi

Laboratory/author	$A_r(^{28}\text{Si}) = m(^{28}\text{Si})/\text{u}$	u	$A_r(^{209}\text{Bi}) = m(^{209}\text{Bi})/\text{u}$	Remarks
Univ. Mainz/Stockholm [38]	27.976 926 57 (30)			Penning trap
MIT Cambridge USA [4]	27.976 926 532 4 (20)			Penning trap
Audi et al. [23]	27.976 926 532 5 (19)		208.9803987 (16)	
CODATA [22]		$1.660\,538\,86\,(28) \times 10^{-27}$ kg		$1\,\text{u} = 1/12\, m(^{12}\text{C})$

3. Determination of the Avogadro constant

The desired number N_A can be obtained by counting all silicon atoms in a mole. To realise this to very high accuracy, a practically perfect single crystal is required. We have chosen silicon crystals which are commercially available and which are almost perfect in structure and purity. The Avogadro constant N_A can be derived from

$$N_A = \frac{M_{\text{mol}}}{m_{\text{Si}}} = \frac{n M_{\text{mol}} V}{v_0 m} \tag{4}$$

with V, volume, and m, mass of a sample, M_{mol}, silicon molar mass, v_0, volume of the unit cell (with n atoms) and m_{Si} the mass of a silicon atom. From Eq. (4) it can be seen that the Avogadro constant relates quantities on the atomic scale to those on the macroscopic scale: N_A is the ratio between the molar volume V_m and the atomic volume V_a, and the following quantities must be measured:

1. the volume occupied by a single Si atom, derived from the knowledge of the structure and the lattice spacing of an almost perfect, highly pure silicon crystal. These measurements therefore include precise determinations of the content of impurity atoms and Si self-point defects,
2. the macroscopic density of the same crystal, and
3. the isotopic composition of the Si crystal (Si has three stable isotopes ^{28}Si, ^{29}Si, ^{30}Si). Most of the reported results were obtained with silicon of natural isotopic composition. Final experiments will be performed with an isotopically enriched ^{28}Si crystal.

The three tasks have been attempted by several national laboratories, first in scientific competition but today in a cooperative project under the umbrella of the Comité International des Poids at Mesures (CIPM) [8]: the National Institute of Standards and Technology (NIST) in USA, the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig (Germany), the Istituto Nationale di Ricerca Metrologica (INRM, former IMGC) in Torino (Italy), the National Measurement Laboratory (NML) of Australia, the National Metrology Institute of Japan (NMIJ) in Tsukuba, the National Physical Laboratory (NPL) in Teddington (UK), and the Bureau International des Poids et Mesures (BIPM) in Sèvres near Paris. The third point has been actively pursued at the Institute for Reference Materials and Measurements (IRMM) of the European Community in Geel (Belgium).

3.1. Measurement procedure

3.1.1. The atomic volume of silicon

Information on the atomic volume can generally be deduced from interatomic spacings measured by X-ray diffraction, investigating also the homogeneity in structure and the chemical purity of the material, in other words, a highly accurate determination of the departure from an ideal crystal structure is required. Early measurements of the lattice plane spacing were based on Bragg's equation

$$\lambda = 2d \sin\theta \tag{5}$$

where λ is the X-ray wavelength, d the lattice plane spacing and θ is the angle formed by the incident beam with the diffracting planes. d is related to the unit cell volume by simple analytical geometry according to the Bravais lattices. The accuracy of this method was limited by the absence of sharp lines with calculable wavelengths in the X-ray region. In 1965, with the discovery of X-ray interferometry by Bonse and Hart [9] using silicon crystals, a radical improvement came about with a method which was independent of the X-ray wavelength used and traceable to the unit of length, the meter.

The principles of these measurements are similar and the basic components, shown in Fig. 1. The X-ray interferometer consists of three thin crystal lamellae with rows of atoms well orientated with respect to one another. The X-ray beams reaching the entrance surface of the third lamella form a periodic X-ray standing wave-pattern, reproducing the lattice period.

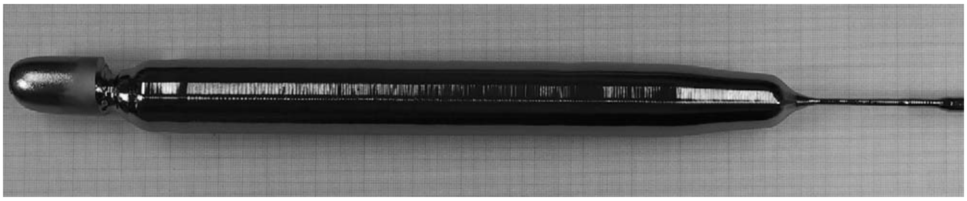

Fig. 1. ^{28}Si enriched single crystal.

Moving this lamella perpendicularly through the pattern results in a sinusoidal intensity modulation behind the interferometer. Measuring the travel distance using the meter as the unit of length, for instance with an optical laser interferometer, and simultaneously counting the X-ray intensity maxima leads to a calibrated-mean-silicon lattice parameter a, averaged over the cross-section of the X-ray beam. Assuming the unit cell to be cubic in shape and of no more and no less than eight atoms, the atomic volume is $V_a = a^3/8$.

Up to a resolution of several femtometers ($1\,\text{fm} = 10^{-15}\,\text{m}$) the purity of semiconductor-grade silicon is high enough for the above-stated assumptions to remain valid. For resolutions better than 1 fm, the actual content of impurity atoms, Si self-point defects and, of minor importance, the actual isotopic composition have to be taken into account. Whereas the element specific analysis of the impurities is made spectroscopically (see Section 3.1.2), their influence on the lattice homogeneity and the average interatomic distance can be measured with special X-ray crystal arrangements.

3.1.2. Actual number of atoms in the unit cell

Fortunately, the lattice defects in semiconductor-grade silicon are reduced to nearly zero dimensional point defects, which include:

1. impurity atoms occurring on regular lattice sites by substituting of silicon atoms,
2. impurities on interstitial lattice sites increasing the average number of atoms per unit cell, and
3. Si-vacancies and Si self-interstitials favoured by the relatively small packing density of the lattice.

Under these assumptions the average number, n, of atoms per unit cell in Eq. (4) is no longer an integral number. n has to be slightly modified by $n = (N_0 \pm \delta)$, with $N_0 = 8$ and δ a correction for the impurity content in the order of 1×10^{-8}.

Fortunately, the number density of the defects is quite low in undoped silicon and therefore in many cases close to the detection limits of the analysing methods. Only a fraction of 1×10^{-8} of the atoms are not silicon atoms [10]. This negligibly small amount is achieved by the highly efficient purification process during the floating zone (FZ) refining of crystal growth.

The concentration of the main residual impurities in undoped FZ-purified Si, either electrically active or inactive, can be measured by optical (IR) spectroscopy. For inactive impurities the method is not so sensitive and the detection limits are close to the residual C and O concentrations in the best crystals ($<3 \times 10^{14}\,\text{cm}^{-3}$). Besides optical spectroscopy, a wide range of mass spectrometric methods can also be used to obtain impurity concentrations. The concentrations of intrinsic structural defects, i.e., vacancies or interstitial atoms, are limited to about $0.2 \times 10^{15}\,\text{cm}^{-3}$. In a crystal they appear as agglomerations of 10–100 nm size voids or as swirls, resulting in a relative deviation in the measured molar volume of less than 2.2×10^{-8}.

When impurities enter regular lattice sites, the real silicon lattice parameter is affected by the difference in atomic size between the atoms of the host lattice and the impurities. In the case of silicon each atom has four close neighbours, their bonds are covalent, and their interatomic distances are determined by the corresponding covalent radii. In the case of a substitutional replacement of silicon atoms, the value of the covalent radius r compared with that of silicon, r_{Si}, directly shows the trend of the volume change of the unit cell, and this changes linearly with the atomic concentration N_i of the impurities [11]:

$$\frac{\Delta a}{a} = \frac{\Delta r}{r_{\text{Si}}} \times \frac{N_i}{N_{\text{Si}}} \tag{6}$$

with $r_{\text{Si}} = 0.117\,\text{nm}$ and $N_{\text{Si}} = 5 \times 10^{22}\,\text{cm}^{-3}$ for the covalent radius and atomic density of silicon.

If the impurities enter interstices between the host silicon atoms, the corresponding lattice deformation was investigated experimentally. Doped samples were compared with a highly pure silicon crystal using X-ray diffraction methods.

3.1.3. Determination of the molar mass

The molar mass $M(\text{Si})$:

$$M(\text{Si}) = \Sigma f(^{\text{i}}\text{Si}) M(^{\text{i}}\text{Si}) = \frac{\Sigma M(^{\text{i}}\text{Si}) R_{\text{i}/28}}{\Sigma R_{\text{i}/28}} \tag{7}$$

is obtained from the measurement of the isotope abundance ratios $R_{\text{i}/28}$ of the three stable Si isotopes ^{28}Si, ^{29}Si, and ^{30}Si which are then combined with the molar mass values $M(^{\text{i}}\text{Si})$, all available with an uncertainty $<10^{-8} \times M(^{\text{i}}\text{Si})$, for ^{28}Si with $<10^{-9}$, always with $\Sigma f(^{\text{i}}\text{Si}) \equiv 1$. Although a three-isotope amount-of-substance system is fully determined by two isotope amount ratios, the ratio $R_{29/30}$ is also measured to check that $R_{29/28}/R_{30/28}/R_{29/30} = 1$. Any deviation from 1 indicates systematic errors in the measurement of one isotope which would show up in two amount ratios but not in the third one. The value for "1" observed experimentally is 0.999 927 (57). To calibrate the measurement of $R_{\text{i}/28}$, IRMM used synthetic mixtures prepared gravimetrically from highly enriched ^{30}Si, ^{29}Si, and ^{28}Si. These were kept in the form of BaSiF_6, carrying the isotope amount ratios $n\,(^{\text{i}}\text{Si})/n\,(^{28}\text{Si})$ synthesized gravimetrically. The abundance ratio measurements are performed by means of an isotope ratio gas mass spectrometer, which compares the number of atoms of the various isotopes with each other through precise measurements of the ratios of the ion currents of the isotopes. In order to apply this method, the single crystals are converted to the gaseous compound SiF_4 All measurements were done relative to a standard material (WASO 17.2 crystal) with a relative uncertainty of 1.5×10^{-7}, still constituting one of the major contributions to the present uncertainty of the Avogadro constant.

A further reduction of the uncertainty on measured molar mass values (and hence on the value of N_A) has been started already 2004 by fabricating a Si single crystal sphere of $\geq$99.99% enriched ^{28}Si, which means ^{29}Si and ^{30}Si abundances of the order of 0.005% [12]. A relative combined uncertainty of $\leq$1% on each of these abundance-value corrections contributes to a relative uncertainty on the molar mass value of the highly enriched ^{28}Si with $\leq 3 \times 10^{-8}$. For the molar mass it means that the calibrated measurement of the isotope amount ratios in Si of the natural isotopic composition using synthetic isotope mixtures can be replaced by the measurement of (very) small ^{29}Si and ^{30}Si abundances in the highly enriched ^{28}Si. That results in (very) small corrections to the molar mass value of ^{28}Si, known to a relative combined uncertainty (see Ref. [3]) of $\leq 10^{-9}$. As these corrections will be measured, only the uncertainty of these (very) small corrections will enter the uncertainty budget of the molar mass of the highly enriched ^{28}Si in the Avogadro crystal [13]. This approach is possible because a potential source of very highly enriched Si isotopes in Russia is being evaluated. From this enriched Si material, a 5 kg single crystal will be grown. It must be isotopically homogeneous which means that during the transformation of gaseous SiF_4 (the form in which the Si is enriched for the isotope ^{28}Si), through the several wet-chemical steps to polycrystalline Si (from which the single crystal is grown), isotopic contamination must be minimised. The requirements on the chemical purity of this enriched ^{28}Si material are very stringent. Fig. 1 shows a 440 g test crystal with an enrichment of more than 99.99% ^{28}Si and a chemical purity close to the required data. Therefore one expect rather pure enriched isotope materials at the end of the growth process in 2006.

3.1.4. Density of silicon volume standards

Highly accurate density measurements within the scope of the investigations discussed here are performed either directly by determining the mass and volume of nearly perfect silicon spheres, the latter by optical interferometry, or traced back to well-known volume or density standards. These standards serve to compare unknown specimens by hydrostatic weighing or by the flotation method where an almost ideal shape is not necessary.

A suitable three-dimensional artefact, the volume of which can be accurately calculated, is a sphere because cubes and cylinders have sharp edges and corners that are susceptible to damage. The mass of the sphere should be comparable with the 1 kg prototype, so 1 kg silicon volume standards are needed. Their diameters of about 10 cm have to be measured with subnanometer resolution. The surface quality of the sphere must therefore be checked with the same accuracy. The ultimate roundness achievable on a 90 mm diameter sphere made from single-crystal silicon depends largely on the mechanics of the grinding and polishing process. It is also necessary to have roundness and roughness measurement capabilities to resolve and reliably characterise surface topography down to nanometer level. The best spheres have deviations from ideal roundness in the order of 30 nm and a surface roughness of about 0.5 nm (peak to valley) [14].

The volume is being determined by measuring diameters either with a Fizeau interferometer that measures about 16,000 phase differences (diameters) simultaneously or with a Fabry-Perot etalon coupled with a large number of single measurements [15]. In order to fit the wave fronts to the curvature of the sphere, two different modifications are used, respectively: expanded light beams with spherical wave fronts in order to obtain a topographical map simultaneously or light beams with a very small beam diameter collimated by a lens so that concentric circular fringes are observed. From the phase difference of the interfering beams with and without the sphere, the diameter can be determined. Reproducibility in diameter measurements of about 1 nm could be achieved.

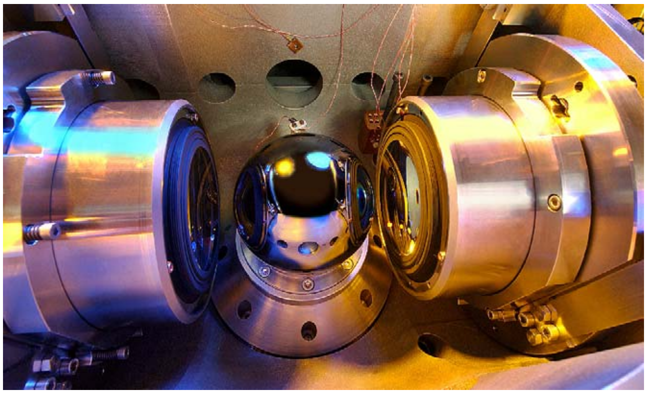

Fig. 2. Spherical Fizeau interferometer for diameter determinations.

Fig. 2 shows the PTB interferometer for diameter measurements of the silicon spheres. The sphere is placed in a quartz etalon consisting of lenses with spherical surfaces. A light beam from a frequency-stabilized He–Ne laser is divided into two beams pointing at opposite ends of the interferometer.

Today, two methods are possible for transferring absolute volume values from one sample to another: a density comparison by means of hydrostatic weighing [16] or floatation in a fluid of equal density [17]. The hydrostatic comparison can be carried out with standard deviations already smaller than 10^{-7} but the accuracy is limited by temperature gradients in the bath. The principle of the floatation method is rather simple: a fluid and a body floating in it have the same density. For comparisons, the density of the fluid can be changed by temperature or pressure variations. The sensitivity of this comparison is well below the 10^{-8} level, but limited by instabilities of the equilibrium condition and instabilities in the density of the fluid, which is a mixture of organic compounds.

Both density and diameter measurements are influenced by the real structure of the surfaces. Surface contaminants such as oxide, water vapour, hydrocarbons affect the density. The thickness and composition of the oxide layer depend on the polishing process, crystal orientations and may vary with time, thus contributing to the long-term instability of the silicon crystal's mass. There are a large number of analytical methods for investigating the surface structure: scanning tunnelling microscopy, optical ellipsometry, IR and X-ray spectroscopy and reflectometry, low-energy electron diffraction, etc. The BIPM is following the evolution of the mass difference between two silicon crystals of different surface areas as a function of relative humidity, atmospheric pressure, air temperature and time. Recontamination of surfaces with time is also monitored. So far, observed changes in mass are negligible. In addition, the reproducibility of the mass difference between the measurement in air and in vacuum has been evaluated. Desorption on silicon artefacts is about 200 ng cm^{-2} for the first vacuum. Subsequent weighing in air and vacuum show that the adsorption of water at atmospheric pressure and the desorption of water in vacuum at 0.01 Pa are

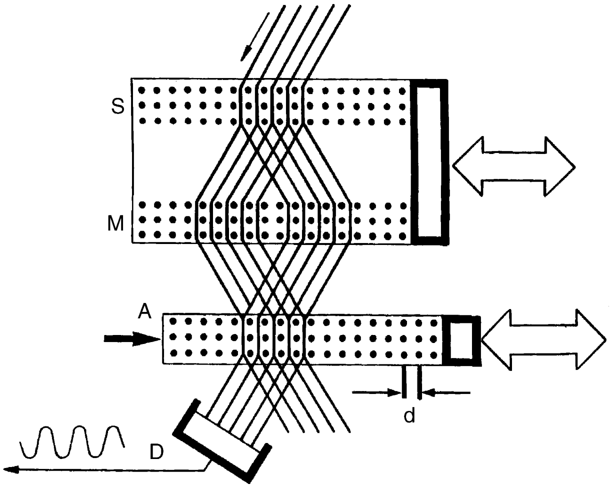

Fig. 3. Scheme of the X-ray interferometer, according to Ref. [8].

reversible and they point to ≤3 layers of water. The study will be completed by replacing the natural oxide on the crystals with an thermal grown oxide. Layer characterisation of natural oxide led to measurement uncertainties of the order of 0.4 nm.

The masses of the silicon volume standards are compared with the national kilogram using the prototype balance. Weighing in air requires a buoyancy correction and in vacuum the effect of adsorbed water molecules on the silicon surfaces must still be studied. At present, a total uncertainty of better 1×10^{-8} is reached.

3.1.5. *Determination of lattice spacing*

Up to now four experiments on the precision measurement of the (2 2 0) silicon lattice spacing have been completed: at NIST [18], at PTB [19], at INRM [20], and at NMIJ [21]. The principles of these measurements are similar and the basic experimental components are shown in Fig. 3. The X-ray interferometer consists of three thin crystal lamellae with rows of atoms well orientated with respect to one another. The X-ray beams reaching the entrance surface of the third lamella form a periodic X-ray standing wave-pattern, reproducing the lattice period. Moving this lamella perpendicularly through the pattern leads to a sinusoidal intensity modulation in the exit beams. Measuring the path length in the unit of length, meter, for instance with an optical laser interferometer, and simultaneously counting the X-ray intensity maxima yields a calibrated-mean-silicon lattice parameter a, averaged over the cross-section of the X-rays. Technical improvements at INRM in 2004 were the basis for relative measurements uncertainties of the order of 10^{-8}.

3.2. *Results*

The results for the lattice parameter so far are equal to within 1×10^{-7}, relatively, whereas the results obtained for the molar volume of the various samples show differences within several parts in 10^7. The data of these measurements agree with the CODATA values obtained from independent measurements of fundamental constants in 2005 [22] only to within 1×10^{-6}, see Table 2. This discrepancy gives rise to a more intensive search for hidden and unexpected systematic errors in the determination of fundamental physical quantities.

4. Determination of the mass of an atom by the accumulation of ions

The mass of an atom, or better of a nuclide, in the unit kilogram is usually obtained by the product of the relative atomic mass A_r of a nuclide and the atomic mass unit m_u. Relative atomic masses are referred to the nuclide ^{12}C and are measured, e.g., by nuclear reactions, mass spectrometry or Penning traps experimentally [23]. The atomic mass unit results itself from a least squares adjustment of the physical fundamental constants, see Ref. [22]. Because the atomic mass unit is linked to the Avogadro constant N_A by the relation:

$$1\,\text{kg} = 10^3\{N_A\}m_u \tag{8}$$

an experiment determining the atomic mass unit results also in a value of the Avogadro constant and vice versa.

4.1. *Experimental concept*

The idea of the ion accumulation experiment is very simple, even though its realisation requires some skill to manage moving atomic particles [24]. An ion source generates an ion beam in vacuum and the ions are then trapped in a collector until a weighable mass has been accumulated. Because moving ions represent an electrical current, this current is measured and integrated over the whole accumulation time (see Fig. 4). It is evident, that the mass-to-charge ratio of a single ion is equal to that of all accumulated ions:

$$\frac{m_a}{q} = \frac{m}{Q} \tag{9}$$

with

$$Q = \int I\,dt \tag{10}$$

Table 2
Summary of results for the Avogadro constant, present state

Laboratory	Sample	Year/reference	Avogadro constant ($\times 10^{23}$ mol^{-1})	Difference in 10^{-6} to CODATA
INRM (I)	Several	1995 [39]	6.022 1379 (25)	−0.68
CSIRO (AU)	WASO 04 #3	2001 [40]	6.022 1331 (18)	−1.48
PTB (D)	WASO 04 #1	2003 [19]	6.022 1353 (20)	−0.91
NMIJ (JP)	NRLM 1, 2, 4	2003 [41]	6.022 1375 (12)	−0.75
CCM working group	NRLM 4, WASO 04 #1	2005 [42]	6.022 1353 (18)	−1
CODATA		2002 [22]	6.022 141 5 (10)	

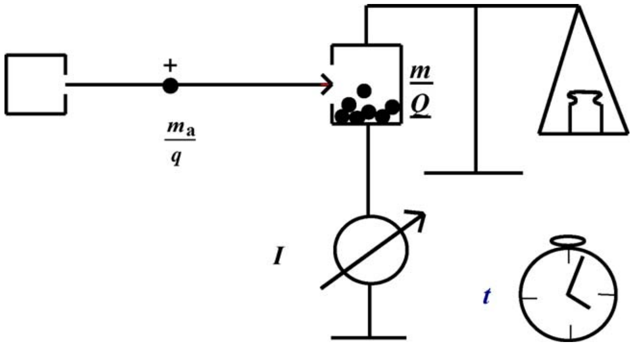

Fig. 4. Idea of the ion accumulation experiment for measuring the mass of a single atom. Ions with a mass m_a and a charge q are travelling from a source to a collector. The ion current I is measured and integrated over the accumulation time t representing a total charge Q of the collected ions. Weighing the collector before and after the accumulation gives a mass m of all collected atoms.

m_a, q mass and charge of a single ion, m, Q mass and charge of all accumulated ions, I ion current, t time. The accumulated ions of course are neutral atoms, when the current stops running. The atomic mass unit is obtained from:

$$m_u = \frac{q}{Q}\frac{m}{A_r} \tag{11}$$

where A_r is the relative atomic mass of the nuclide used for the ion beam. The number of the accumulated ions is:

$$N = \frac{m}{m_a} \quad \text{or} \quad N = \frac{Q}{q} \tag{12}$$

and its relation to the Avogadro constant and the molar mass $M = A_r \times 10^{-3}\,\text{kg}\,\text{mol}^{-1}$ of the nuclide is:

$$\frac{N}{N_A} = \frac{m}{M} \tag{13}$$

We may consider to count this number by using, e.g., a secondary-electron multiplier (SEM) or a channeltron. The problem is the great number of atoms required for weighable mass of 1 kg or even several gram. A corresponding particle detector always needs a time period, even though a small one, after one signal and before the next can be registered, the dead time within which ions impinging on the detector do not generate a signal. For an ion current that can be used to accumulate a sufficiently large and weighable mass, this dead time would have to be about 7–8 orders of magnitude smaller than is possible with today's detectors (approximately 10^{-9} s). The alternative of current and time measurements is therefore certainly more realistic.

From Eqs. (9) and (10) we see that we need to measure the accumulated mass m, the current I, the time t, and the charge q for calculating the mass of a single atom. The charge q is an integer multiple z of the elementary charge e. The multiple z can be defined by selecting ions for their mass-to-charge ratio using a mass separator, e.g., a dipole magnet. The value of the elementary charge is tabulated in the list of the fundamental constants with a relative uncertainty of 8.5×10^{-8} [22], which is too large in view of 10^{-8}, needed for a new determination of the atomic mass unit. However, if we measure the ion current by the voltage drop over a known resistance and measure the voltage in terms of the Josephson voltage, quantized in steps of $fh/(2e)$ and the resistance in terms of the Quantum-Hall resistance, quantized in steps of h/e^2 (f microwave frequency, h Planck constant), Eq. (9) becomes:

$$m_a = \frac{2zm}{n_1 n_2 \int_{t=0}^{t_m} f\,\mathrm{d}t} \tag{14}$$

n_1, n_2 are multiples of the quanta of the Josephson voltage and of the Quantum-Hall resistance, respectively. Now, we do not need either a value of the elementary charge e or an absolute measure of the current I. If we measure time t and frequency f, both based on the same atomic clock with sufficient reproducibility, we need not care about the clock's possible offset from the SI unit second. The only absolute measurement required is that of the mass m of the accumulated atoms – traceable to the international prototype of the kilogram.

4.2. *Measurement details*

When such an experiment is carried out in practice, a number of boundary conditions must be fulfilled if relative uncertainties of about 10^{-8} have to be reached. The following parameters should be observed:

1. accuracy of the mass determination, sorption and air buoyancy effects when changing between air and vacuum,
2. size of the ionic current. It must allow the required mass to be accumulated in a reasonable time,
3. resolution of the mass-to-charge separator,
4. electrical conductance, vapour pressure and mass of the element, the ions of which are accumulated,
5. lost collector particles, sputtered by the ions and lost ions being reflected from the collector and having changed their charge number,
6. accumulated foreign particles with a wrong mass-to-charge ratio,
7. lost or captured free electrons, and
8. accuracy and reproducibility of the standards for measuring the ion current.

PTB has set-up an experimental device for accumulating ions and will be modifying it in the future for improving the results [25–28]. The conditions numbered above will be met as follows:

1. Mass determination will be carried out by using a special mass comparator, similar to the BIPM flexure-strip balance [29] and modified for the particular ion collection requirements. It is an equal armed beam balance used for comparing the mass of the accumulated ions with mass standards in the order of 10 g or less. The ion collector with a mass of about 1 kg will be suspended from one of the arms an weighed inside the ion collection apparatus under vacuum conditions by using the substitution method. The mass of the collector will be substituted by a weight with the mass of the empty collector and additional weights from 1 mg up to 10 g that will be added using piezo-electric transducers after the

accumulation. The mass difference of two of these additional weights that have the same surface area will be compared in vacuum and in air and will be scaled up to the national prototype of the kilogram in air. The relative standard deviation of this balance will be less than 10^{-10}, that is 0.1 μg of 1 kg.

Surface sorption effects from linking the mass standards in vacuum with those in air will be eliminated by linking the mass of the accumulated atoms to the difference of two mass standards having the same surface area. Buoyancy effects will be minimised by using mass standards of the same density in vacuum and in air up to the national kilogram prototype made of platinum–iridium.

2. A high-current ion source (CHORDIS) with a sputter electrode for gold has been investigated and used for previous measurements [26,27], an oven version of this source for bismuth is running with 5 mA ion current with expectation for achieving about 10 mA [30]. Using the mentioned heavy elements, a mass of 10 g can be accumulated within about a week.
3. An element with only one natural stable isotope will be used to avoid the need for isotope separation. Inside the vacuum apparatus, the only elements being present will have atomic masses well away from that of the ions. A resolution of 1:300 may then be sufficient for the separator.
4. There are 20 elements with only one natural isotope. Some of them are not considered because of their high vapour pressure (^{19}F, ^{127}I, ^{23}Na, ^{133}Cs, ^{31}P, ^{75}As). Heavy elements are preferred, because they require lower ion currents than the lighter ones. The heaviest ones are ^{209}Bi and ^{197}Au. The measurements made with ^{197}Au have shown that it is difficult to obtain ion currents in the order of several mA. Therefore ^{209}Bi is used at present. Ion beams with bismuth of more than 30 mA have already been achieved [31]. Its vapour pressure is many orders of magnitude higher than that of gold (see Table 3). Bismuth can therefore be evaporated using an oven.
5. Sputtering of surface atoms by ion bombardment cannot completely be avoided in the present experiment. The ions leaving the ion source have energies of about 25 keV. Comparing such energies with the binding energies of surface atoms (about 2 eV for Bi), mass would be lost rather than gained when the ions encounter a surface, even when implantation is taken into account. The sputter rate for Bi^+-ions of 25 keV on a Bi surface is in the order of 10 (TRIM simulations), that means that 10 surface atoms per incident ion are sputtered. Acceleration up to MeV energies would enhance implantation and reduce sputtering, but thermal power would pose larger problems. A reasonable solution is to decelerate the ions well below 1 keV where the sputter and the reflection effects are small (the reflection coefficient has a maximum of about 0.1 at about 1 keV). First measurements have shown that a net accumulation with gold ions on a flat surface occurs at energies below 150 eV [26].

   A decelerated ion beam diverges due to the transverse energy components and due to electrostatic repulsion between the ions. Beam spreading due to such space charge effects is described in several charged particle books, see, e.g. [32]. Suitable focusing and beam guiding devices will be installed such that divergence will occur mostly inside the collector. The shape of the collector will be designed for catching most of the sputtered and reflected particles. Particles leaving the entrance aperture of the collector will be measured by oscillating quartz arrays or by analysing layers of backscattered particles using X-ray photoelectron spectroscopy (XPS) or optical transmission measurements. In addition, the collector will be arranged in a transverse magnetic field that directs the ion trajectories onto surface areas from which no straight way to the entrance aperture is possible for (electrically neutral) sputtered or reflected particles.

Table 3
Some data of gold and bismuth

	^{197}Au	^{209}Bi
Z	79	83
A_r(u)	196,966 568 7 (6)	208,980 398 7 (16)
a (nm)	0.144	0.182
E_{ioniz} (eV)	9.23	8.8
ρ (kg m^{-3}), $t = 0\,°$C	19290	9800
t_{m} (°C)	1065	271
t_{b} (°C)	2707	1560
ρ_{el} (10^{-8} Ωm), $t = 0\,°$C	2.06	110
p (mbar at 800 °C)	1×10^{-8}	2×10^{-1}
t (°C at $p = 10^{-14}$ mbar	520	170

Z: number of protons, A_r(u): relative atomic mass (uncertainty) [23], a: atomic radius, E_{ioniz}: ionization energy, ρ: density, t_{m}: melting temperature, t_{b}: boiling temperature, ρ_{el}: specific resistance, and p: vapour pressure (an evaporation rate of 1 μg/dm^2/year occurs at a vapour pressure of about 10^{-14} mbar, these data are extrapolated).

6. Candidates for accumulated foreign particles are:
   - (a) particles that are not separated by the separator,
   - (b) molecules of the residual gas being scattered into the collector by collisions with ions,
   - (c) ions separated by the separator and scattered from the walls into the collector,
   - (d) particles sputtered by the ions from apertures, and
   - (e) ions having changed their charge number by collisions with molecules of the residual gas.

   The number of collected foreign particles of the type 2 and 5 will be reduced by ultra-high vacuum conditions between the mass separator and the ion collector. An estimate for the contribution of residual gas molecules scattered into the collector was made using a classical collision model for hard spheres. The estimates for the relative change of the accumulated mass, μ_{col}, show values below 10^{-8} at pressures below 10^{-6} Pa.

   The contribution of particles of the type 1–4 will be measured by subsequent chemical analysis of the deposit. An alternative method will be replacing the collector by a mass spectrometer and running the ion beam under same conditions. Neutral particles, particular some of the type 5 will be separated from the ion beam by an additional magnetic deflection just in front of the collector.
7. Electrons propagating inside the ion beam will be rejected by an electrode with negative potential. The same electrode rejects electrons released from the collector.

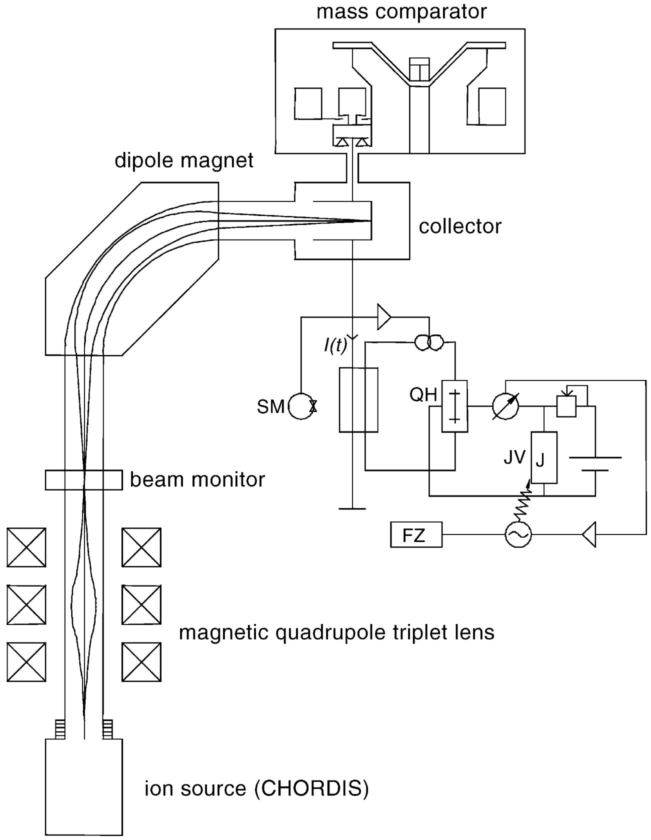

Fig. 5. Scheme of the ion accumulation the set-up as it is planned. SM: squid, *I*(*t*): ion current as a function of time, QH: Quantum-Hall device, JV: Josephson voltage device, and FZ: frequency counter.

8. The current will be measured as the voltage drop over a known resistance. The voltage will be compared with a stable voltage standard, such as a Zener-diode, and this will be traced to the PTB Josephson standard. Similarly, a sufficiently stable resistance will be used and compared with the PTB Quantum-Hall standard. If necessary, Josephson voltage and Quantum-Hall devices can be used for directly measuring the ion current (see Fig. 4). Time measurements and Josephson frequency will be traced to a single, sufficiently stable clock. Fluctuations of the ion current will be averaged over the time interval of data collection.

4.3. Results

The experimental set-up is shown in Fig. 5. The ion source is a plasma discharge source with an internal sputter electrode of gold or an oven evaporating bismuth. The ion beam characteristics as a function of the source parameters, such as discharge voltage, cathode current, pressure, extraction and electron suppression voltages have been investigated in detail [28]. Also TRIM simulations for assessing sputter and reflection processes for collisions of Au$^+$ ions on Au surfaces have been made [33]. The shape of the ion beam has been investigated using a segmented Faraday cup, developed for this purpose [34].

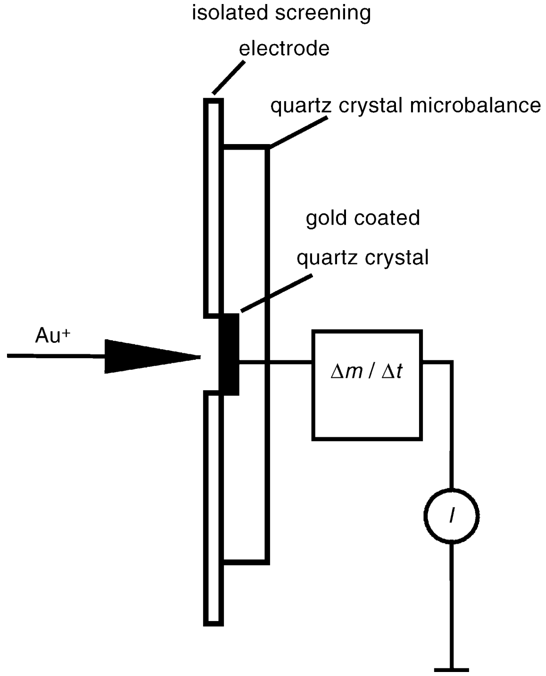

Fig. 6. Single quartz crystal as used for the measurements of a gold ion beam. The crystal gave a signal of the mass change in time $\Delta m/t$. The current I was measured simultaneously.

First accumulation measurements using a $^{197}\mathrm{Au}^{1+}$ ion beam have been done by using a gold plated quartz crystal oscillator as detector for the accumulated mass (see Fig. 6). The ion current of some 10 μA has been measured by using the quartz crystal as a (flat) Faraday detector [26]. The measurements were made when the ions have been decelerated from 20 keV down energies between about 20 and 300 eV. Fig. 7 shows the parameter emQ^{-1} as a function of the ion energy. Extrapolated to zero energy, this

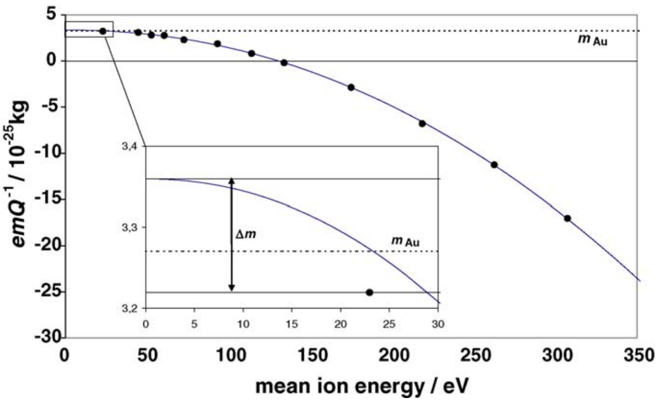

Fig. 7. The mass equivalent emQ^{-1} as a function of the mean ion energy, measured with a gold ion beam [26]. The mass of a gold atom m_{Au} as taken from literature is shown as dotted line. The centre of the range Δm between the extrapolation to zero energy of all measured data and the value at the smallest energy (23 eV) was assumed as measurement result, because of the unknown value of the threshold for sputter and reflection effects.

parameter represents the mass of a single gold atom according to

$$m_{\mathrm{Au}} = e\frac{1}{I}\frac{\mathrm{d}m}{\mathrm{d}t} \qquad (15)$$

or

$$m_{\mathrm{Au}} = e\frac{m}{\int_0^t I\,\mathrm{d}t} \qquad (16)$$

The mass of a gold atom has thus been measured with a relative uncertainty of 1.5% and a deviation from the product of the tabulated values of A_{Au} and m_{u} of 0.6%. Sputter yields of, e.g., 6.2 at 310 eV and of 0.015 at 23 eV have been derived from the measurement results as well. They show reasonable agreement with results of other authors [35,36].

A new experiment is running with a bismuth ion source that delivers now 5 mA ion current with the capability to achieve even 10 mA. A first accumulation measurement with a cylindrical collector and a non-decelerated ion beam of 25 keV energy gave about 40 mg accumulated bismuth and, together with the integrated ion current, a relative deviation of 9×10^{-4} from the expected mass of a bismuth atom. The loss of neutral particles, assessed by XPS at the back of the entrance plate correspond approximately to the mentioned deviation. Further measurements are going on.

5. Conclusion

Using single crystals of natural silicon, the uncertainty attained for that value is now close to a practical limit. The available data are all contained in a – non-public-database [37]. Today, the uncertainty in the value of the Avogadro constant is only one order of magnitude greater than the accuracy to which the mass of the unit kilogram is known and can be reproduced. This is promising. Further reduction of the uncertainty is internationally co-ordinated and ongoing using a 99.99% ^{28}Si crystal. Performing density and lattice measurements, analogous to those on Si of natural isotopic composition as described above, does not present new problems. A structured task distribution between the participating laboratories will be implemented on a world-wide level amongst participants under the aegis of the working group on the Avogadro constant of the Comité Consultatif pour la Masse of the Comité International des Poids at Mesures (CCM-CIPM). It “integrates” – rather than “federates” – the efforts at various Metrology Institutes on a fundamental constant.

The determination of the mass of an atom by accumulation of ions from an ion beam is still in an early state. First measurements with a decelerated gold ion beam of about 10 μA using a quartz crystal oscillator as a mass detector have been made with a relative uncertainty of 1.5%. An improvement of the uncertainty by at more than on order of magnitude is already evident with a new, running experiment using a bismuth ion beam of several mA current and a collector weighed on a balance. Further progress is expected by future developments, such as deceleration and collector design and improvements of measuring techniques. For attaining a level of 10^{-8} in the relative uncertainty will however need some further years.

The authors stress that regardless of which redefinition of the kilogram is chosen, efforts should continue to reduce the measurement uncertainty of both the watt balance and X-ray crystal experiments. Currently, both methods are 5–10 times less precise than the measurement uncertainty produced when comparing the kilogram artefact to national standards. What is more, the results of the two of the three approaches disagree by nearly 1 part per million. Eventually, when uncertainties of experiments with the watt balance or X-ray crystal density method reach a sufficiently low level, the cylinder artefact would no longer be needed.

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