Ultra-high accuracy isotopic measurements:
Avogadro's constant is up!

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Abstract

Ultra-high accuracy isotopic measurements have been achieved on abundance ratios of Si isotopes by achieving 10^{-5} reproducibilities on the ratio measurements and calibrating the results by synthetic isotope mixtures prepared to $2 \cdot 10^{-5}$ combined relative uncertainty. This enabled us to attain a relative combined uncertainty of $3 \cdot 10^{-5}$ on the abundance ratios in natural Si samples and, consequently, 10^{-7} on the Si molar mass. The route to these results is described, followed by a description of the improvement of our knowledge of the Avogadro Constant N_A through these measurements.

Combined with measurements of the lattice constant and density in a near-perfect Si single crystal, Si molar mass measurements lead to a totally independent value of N_A. This value is compared to the authoritative CODATA evaluation of the interrelationships of our fundamental constants. After the year 2000 an improved value of N_A will almost certainly play a key role in a redefinition of the kilogram, our primary standard of mass.

The acquired expertise in measurement instrumentation and measurement procedures for measurements of Si isotope amount ratios can now be extended to a more general use in measurements of isotope amount ratios (*i.e.* in other elements). It can also be combined with isotope dilution. I describe how the latter combination may open the possibility of realising direct traceability of an amount-of-substance measurement to the measurement procedure and instrumentation leading to the Avogadro Constant. Perhaps a "traceability to the mole", *i.e.* to SI, is being developed.

Introduction

Some elements have their abundance ratios known to 10^{-3} combined relative uncertainty, some abundance ratios have been measured to 10^{-4}, but only for one element, silicon, have the abundance ratios been measured to a confirmed relative uncertainty in the 10^{-5} range, all uncertainty components included. It required 10^{-5} reproducibility in abundance ratio measurements, calibrated by $2 \cdot 10^{-5}$ accurate synthetic isotope mixtures, to achieve a $3 \cdot 10^{-5}$ combined relative uncertainty. Since it takes an enormous effort to achieve this, the incentive to do it must be important. Indeed it is.

It is the molar mass M (numerically equal to the atomic weight) which constituted for many years the limiting factor in the knowledge of the Avogadro constant N_A (in mol^{-1}) as determined from X-ray density, lattice constant and molar mass measurements on a near-perfect Si single crystal (an "Avogadro crystal") through the relation

$$N_A = \frac{M(Si) / \rho}{V_a} \qquad \text{(eq. 1)}$$

in which N_A is calculated as the ratio of molar volume $M(Si) / \rho$ (in $m^3 \, mol^{-1}$) to atomic volume V_a (in m^3); M

(Si) is the molar mass in $kg \, mol^{-1}$ and ρ the density in $kg \, m^{-3}$.

The value of V_a is determined through an X-ray interferometric measurement of the lattice constant d_{220}. With the lattice parameter $a_o = d_{220} \sqrt{8}$, the atomic volume $V_a = a_o^3$. Molar masses are derived from isotope abundances f_i ($\Sigma f_i = 1$) and atomic masses $M(^iSi)$. In fact, abundance ratios R_{ij} are measured relative to the abundance f_j of one isotope j as,

$$M(Si) = \Sigma f_i \cdot M(^iSi) = \frac{\Sigma f_i M(^iSi)}{\Sigma f_i}$$

$$= \frac{\Sigma [f_i M(^iSi)]/f_j}{(\Sigma f_i)/f_j} = \frac{\Sigma R_{ij} M(^iSi)}{\Sigma R_{ij}} \qquad \text{(eq. 2)}$$

The isotope abundances (Table 1) and resulting molar mass (Table 2) of natural Si are not constant enough in nature to be used in this approach. Individual calibrated measurements of the Si in the "Avogadro crystal" must be carried out. Combined relative uncertainties which have been achieved on M, V_a and ρ by 1994 in the currently running three Avogadro projects in the world, are summarized in Table 3. A combined relative uncertainty of 10^{-7} on $M(Si)$ requires a combined relative uncertainty of $3 \cdot 10^{-5}$ on the abundance ratios of the Si isotopes in a Si single crystal. Before 1990 this uncertainty was simply the largest uncertainty contributor to the uncertainty of N_A (Table 4).

Table 1

International Union of Pure and Applied Chemistry (IUPAC) isotope abundances of Si.

Isotopes	IUPAC representative isotopic composition of terrestrial material	IUPAC selected "Best Measure-ment"	IUPAC evaluated range of natural occurrences	IRMM 1993 = IUPAC selected "Best Measure-ment" in 1995
$f(^{28}Si)$	0.92231	0.922310446	0.9241-0.9214	0.922310446
$f(^{29}Si)$	0.04671	0.046753633	0.0473-0.0457	0.046753633
$f(^{30}Si)$	0.03101	0.030936036	0.0314-0.0301	0.030936036

Table 2

International Union of Pure and Applied Chemistry (IUPAC) molar masses of Si.

Molar mass (atomic weight)	$M(Si)/g \cdot mol^{-1}$
IUPAC representative atomic weight of terrestrial material	28.08553
IRMM 1993	28.085434976
IUPAC selected "Best Measurement" up to 1995	28.08552
after 1995	28.085434976

Table 3

Achieved combined relative uncertainties on measurements of lattice parameter a_o, density ρ and molar mass M, as measured on near-perfect Si single crystals. IRMM = Institute for Reference Materials and Measurements, Geel; PTB = Physikalisch Technische Bundesanstalt, Braunschweig; NRLM = National Research Laboratory for Metrology, Tsukuba; IMGC = Istituto di Metrologia Gustavo Colonnetti, Torino.

N_A Project	1	2	3
a_o	PTB^1 6×10^{-8}	$IMGC^2$ 3×10^{-8}	
V_a	1.8×10^{-7}	9×10^{-8}	
ρ	PTB^1 7.7×10^{-7}	$IMGC^3$ 1.5×10^{-7}	$NRLM^4$ 1.1×10^{-7}
$M(Si)$	$IRMM^1$ 3.2×10^{-7}	$IRMM^1$ 3.2×10^{-7}	$IRMM^1$ 3.2×10^{-7}

[1]De Bièvre *et al.* (1995); [2]Basile *et al.* (1995); [3]Saccomi *et al.* (1995); [4]Fujii *et al.* (1995)

Table 4

The isotopic composition of natural silicon with combined relative uncertainties compared with uncertainties of measurements at IRMM on "Avogadro Si crystal" samples.

IUPAC values for natural abundances			IRMM 1989/90	IRMM 1992[a]	IRMM 1995[b]
$f(^{28}Si)$	0.92231	$\pm 1 \times 10^{-4}$	$\pm 1 \times 10^{-5}$	$\pm 1 \times 10^{-6}$	$\pm 1 \times 10^{-6}$
$f(^{29}Si)$	0.04671	$\pm 2 \times 10^{-3}$	$\pm 2 \times 10^{-4}$	$\pm 2 \times 10^{-5}$	$\pm 2 \times 10^{-5}$
$f(^{30}Si)$	0.03101	$\pm 3 \times 10^{-3}$	$\pm 3 \times 10^{-4}$	$\pm 3 \times 10^{-5}$	$\pm 3 \times 10^{-5}$
$M(Si)$	28.0855	$\pm 1 \times 10^{-5}$	$\pm 1 \times 10^{-6}$	$\pm 1 \times 10^{-7}$	$\pm 1 \times 10^{-7}$
$n(^{29}Si)/n(^{28}Si)$	0.0506	$\pm 2 \times 10^{-3}$	$\pm 2 \times 10^{-4}$	$\pm 2 \times 10^{-5}$	$\pm 2 \times 10^{-5}$
$n(^{30}Si)/n(^{28}Si)$	0.0336	$\pm 3 \times 10^{-3}$	$\pm 3 \times 10^{-4}$	$\pm 3 \times 10^{-5}$	$\pm 3 \times 10^{-5}$

[a]Seyfried *et al.* (1992); [b]De Bièvre *et al.* (1995)

Measurement of *M*(Si) and its relative uncertainty

The Si crystal samples were converted to SiF_4 gas as described by De Bièvre *et al.* (1995). The Avogadro I Mass Spectrometer (an IRMM upgraded MAT-CH5) had yielded a 1×10^{-6} *M*(Si) uncertainty which had led to 1.1×10^{-6} relative uncertainty on the 1992 N_A value (Seyfried *et al.*

1992). Using the acquired experience, an Avogadro II Mass Spectrometer was assembled, essentially based on a standard MAT 271 instrument, into what is now known as the IRMM/MAT 271 Avogadro II mass spectrometer. The development of appropriate measurement procedures in which correction for every single significant error as well as a full orthodox calculation of every

uncertainty contribution was properly incorporated, proved to be of overriding importance. Creating near-to-ideal vacuum conditions, realizing close-to-ideal circumstances for the SiF_4 gas, also proved to be crucial for the ultimate quality of the results and has been described elsewhere (De Bièvre *et al.* 1994). Then, of course, synthetic isotope mixtures had to be made to calibrate the isotopic measurements on the Si of the "Avogadro" crystal. They were made from enriched isotopes (see Table 5) which were incorporated in higly stable, non-hygroscopic, pure Cs_2SiF_6 molecules. This enabled the preparation of isotope mixtures of about "natural" isotopic composition (Fig 1). Typical values of such a mixture with their uncertainties are given in Table 6, which also shows a full analytical uncertainty budget that will ultimately contribute to the uncertainty of the Avogadro constant. The complete correct formula to calculate the value of such a mixture is (De Bièvre *et al.* 1995);

Table 5

Isotopic composition of the enriched starting materials "iSi" (after chemical purification and assay) as measured on their SiF_3^+ ions. Combined standard uncertainties (u_c) are given below the digits to which they apply.

	Enriched "^{28}Si"	Enriched "^{29}Si"	Enriched "^{30}Si"
$f(^{28}Si)$	0.9953463 10	0.0343310 200	0.0364759 44
$f(^{29}Si)$	0.0028138 5	0.9639600 210	0.0028005 43
$f(^{30}Si)$	0.0018399 8	0.0018090 11	0.9607236 63

$$\frac{n(^{29}Si)}{n(^{28}Si)} = \frac{\frac{m("Cs_2{}^{28}SiF_6")\cdot f(29."28")}{M("Cs_2{}^{28}SiF_6")} + \frac{m("Cs_2{}^{29}SiF_6")\cdot f(29."29")}{M("Cs_2{}^{29}SiF_6")} + \frac{m("Cs_2{}^{30}SiF_6")\cdot f(29."30")}{M("Cs_2{}^{30}SiF_6")}}{\frac{m("Cs_2{}^{28}SiF_6")\cdot f(28."28")}{M("Cs_2{}^{28}SiF_6")} + \frac{m("Cs_2{}^{29}SiF_6")\cdot f(28."29")}{M("Cs_2{}^{29}SiF_6")} + \frac{m("Cs_2{}^{30}SiF_6")\cdot f(28."30")}{M("Cs_2{}^{30}SiF_6")}} \qquad \text{(eq. 3)}$$

Table 6

Calculated values with combined relative uncertainties for one of the Si synthetic isotope mixtures as propagated from the contributing uncertainty sources. Also listed are the chemical uncertainties for A_r(Si):18.

	abundance (amount of substance fraction) in the synthetic mixture	10^7 combined relative standard uncertainty					
			as contributed to the total by the measurements of the:				
		total	abundances of enriched isotope materials[a]	chemical impurities	stoichiometry	weighings	atomic masses of the isotopes
$f(^{28}Si)$	0.9233923 18	18	12	6.5	6.5	8.4	0.2
$f(^{29}Si)$	0.0463008 14	14	10	4.6	4.6	6.1	0.14
$f(^{30}Si)$	0.0303069 11	11	7.9	3.0	3.0	6.1	0.09
A_r(Si)[b] = 28.0837260 27	1.0000000 1[c]	25	18	9	9	12	<1

[a]from measurements of the enriched isotopes; [b]this "sample atomic weight" applies only to this synthetic mixture; [c]rounding off uncertainty only.

Table 7

Isotopic composition and silicon atomic weight of the "test material" which is now a certified isotopic reference material (IRMM 018). Combined standard uncertainties (u_c) are given below the digits to which they apply.

Abundance ratio		Abundance (amount of substance fraction)			Atomic weight (relative atomic mass)
$n(^{29}Si)/n(^{28}Si)$	$n(^{30}Si)/n(^{28}Si)$	$f(^{28}Si)$	$f(^{29}Si)$	$f(^{30}Si)$	A_r(Si)
0.0508442 24	0.0335851 33	0.9221440 35	0.0468857 21	0.0309703 29	28.085635 6
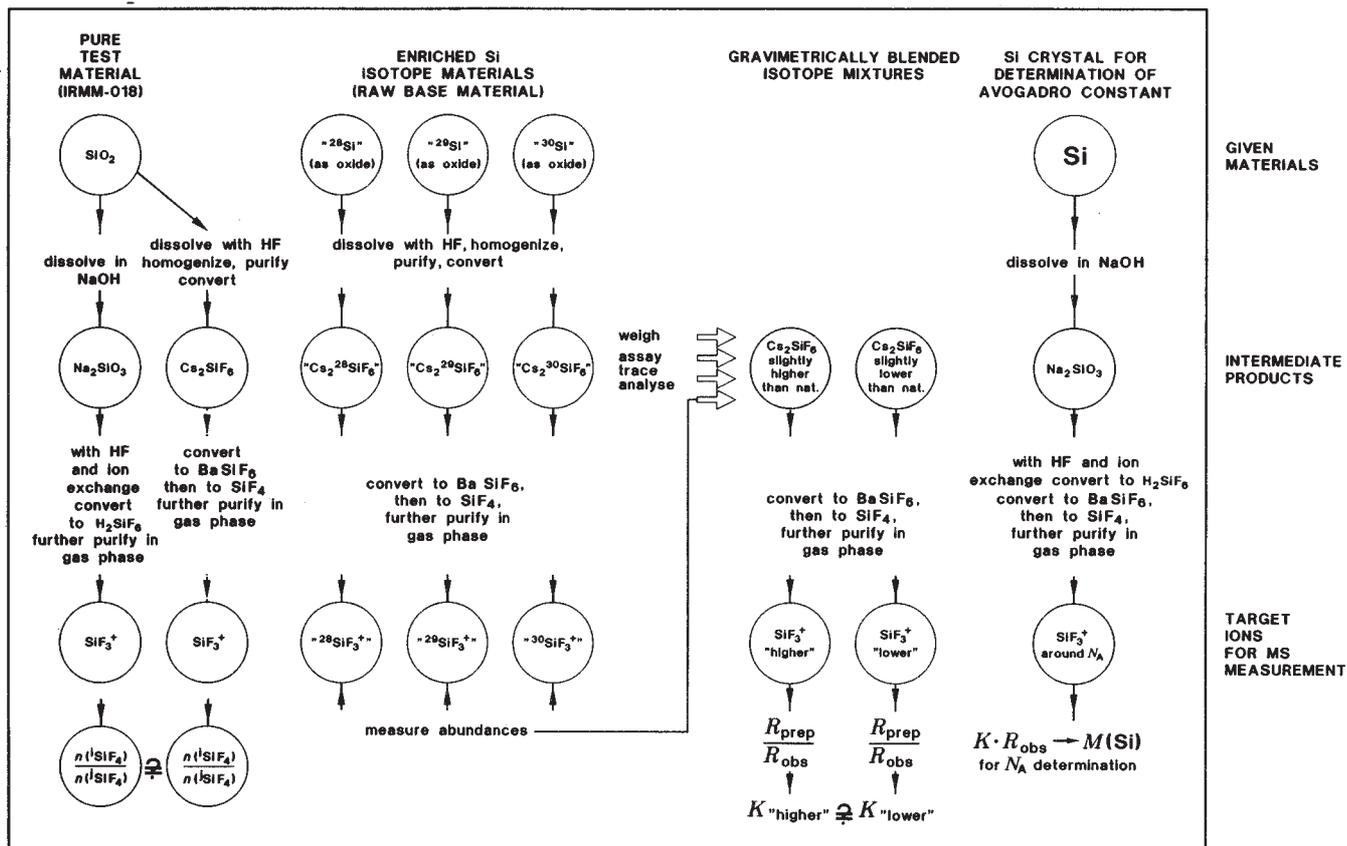
Figure 1. General layout of preparation and measurements of Si isotope mixtures.

$$N_A / 10^{23} \cdot \text{mol}^{-1}$$
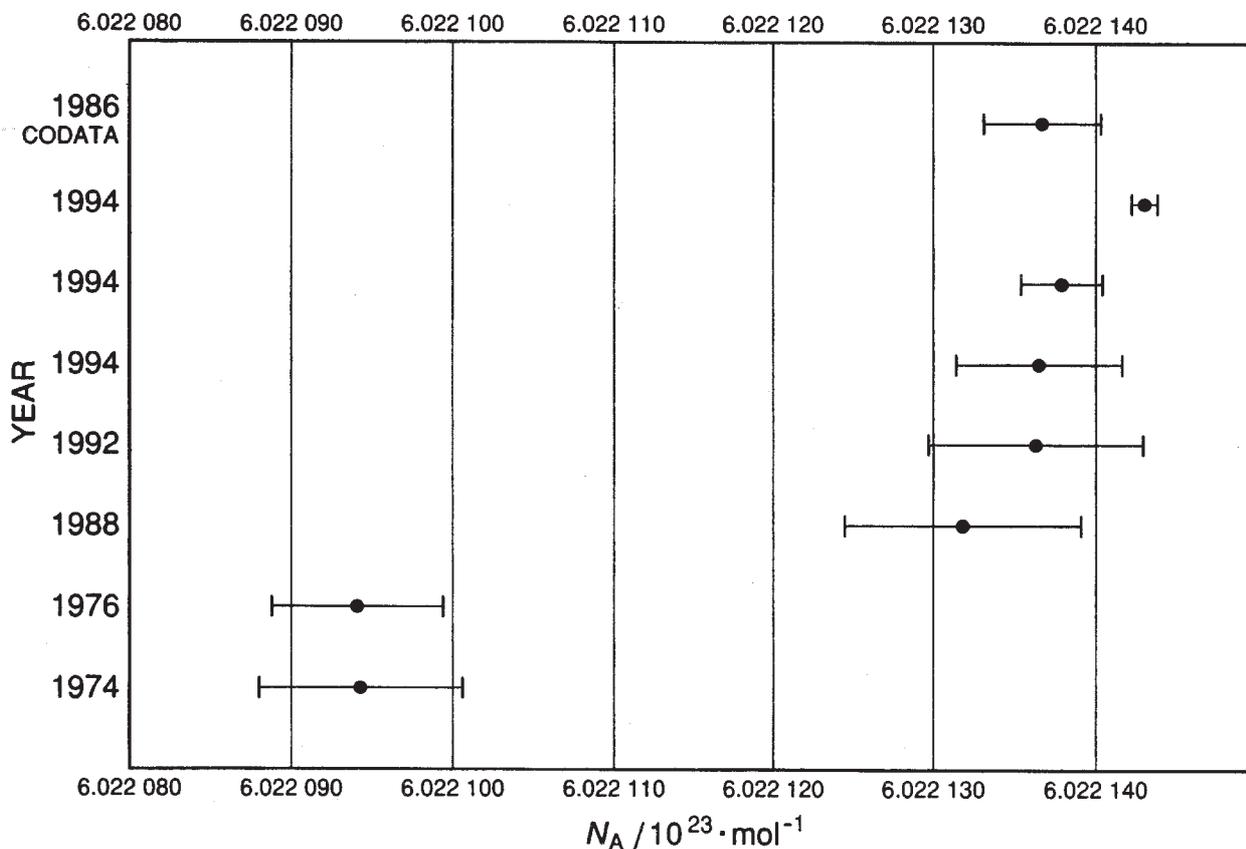
Figure 2. Values and uncertainties (as stated by authors) for N_A in the period 1974-1986. Values are from Deslattes *et al.* (1974, 1976), Cohen & Taylor (1987), Deslattes (1988), Seyfried *et al.* (1992), Basile *et al.* (1995), De Bièvre *et al.* (1995).

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where " indicates the isotopically enriched materials, not pure isotopes. In the course of the project, a 10 kg SiO_2 batch was measured and calibrated and made into a certified reference material, IRMM-018 (De Bièvre *et al.* 1994), the values of which are given in Table 7.

What now is Avogadro's Constant?

The various determinations of N_A over the last 20 years are given in Table 8 and Figure 2. They show the gradual "tuning in" of the value as well as the reduction of the uncertainty. As is apparent from the CODATA evaluation of the interrelationships of the fundamental constants (Cohen & Taylor 1987; Taylor & Cohen 1990), the Avogadro constant obtained through the molar mass/lattice constant/density route is consistent at the $10^{-6} \cdot N_A$ level with other fundamental constants such as the Planck constant, the Boltzmann constant, the Universal gas constant *etc.* It is interesting to note (De Bièvre & Peiser 1994) how this uncertainty has been decreasing at a steady rate of a factor of 10 every 15 years since about 1860 (Fig 3).

Table 8

Values of N_A with their combined relative uncertainties as detemined in the period 1974-1994, compared to the 1986 CODATA evaluation.

Year	N_A with uncertainty
1974[a]	6.0220943 10^{23} 63
1976[b]	6.0220941 10^{23} 53
1988[c]	6.0221318 10^{23} 73
1992[d]	6.0221363 10^{23} 66
1994[e]	6.0221365 10^{23} 51
1994[f]	6.0221379 10^{23} 25
1994[f]	6.0221430 10^{23} 8
CODATA[g] 1986	6.0221367 10^{23} 36

[a]Deslattes *et al.* (1974), [b]Deslattes *et al.* (1976), [c]Deslattes (1988), [d]Seyfried *et al.* (1992), [e]De Bièvre *et al.* (1994), [f]Basile *et al.* (1994), [g]Cohen & Taylor (1987).
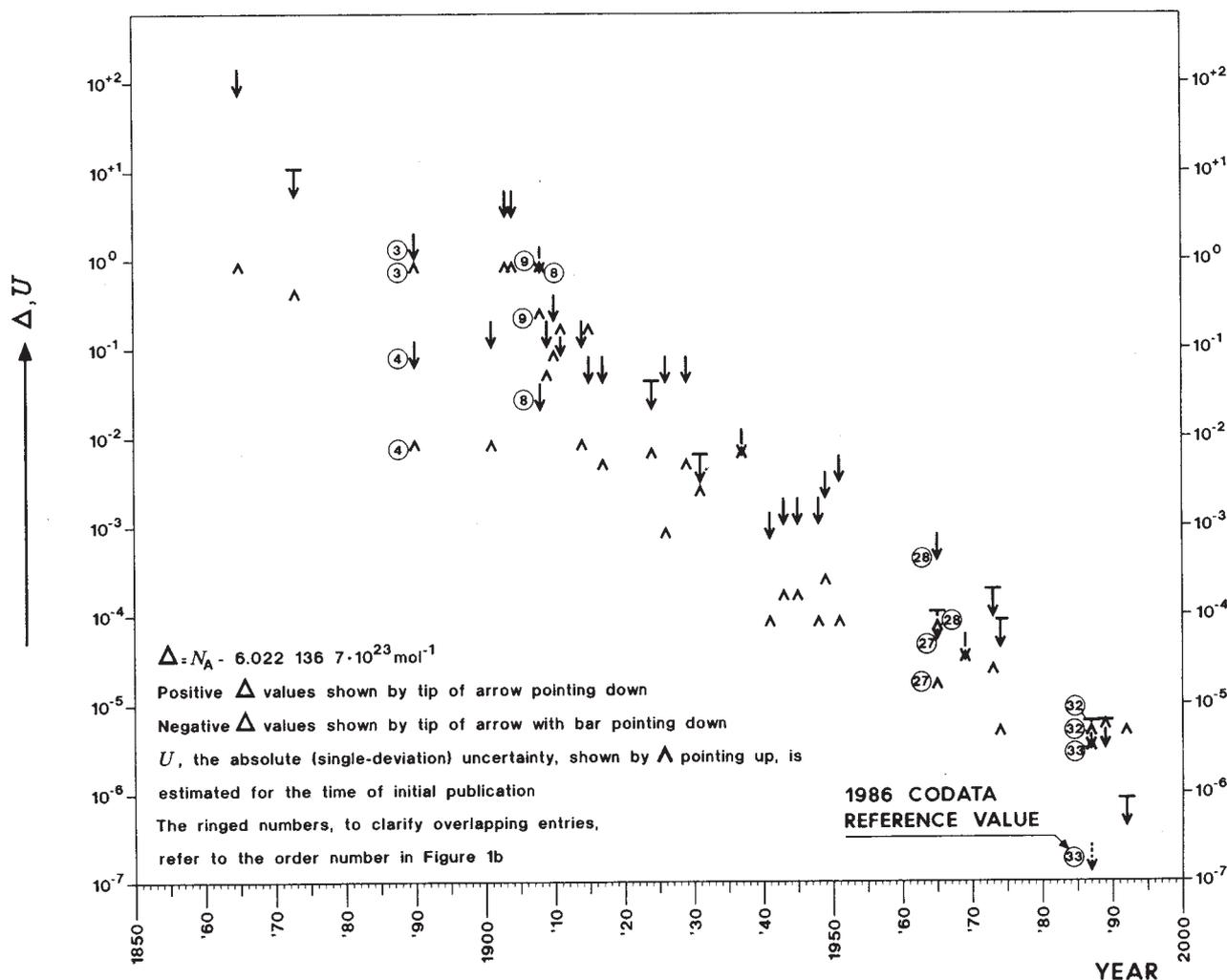
Figure 3. Uncertainties of published values for Avogadro's constant.

Possible consequences of the achieved uncertainty on N_A

It is now well accepted (Kind & Quinn 1995) that there are variations of the order of $5 \ 10^{-8}$ kg in the mass of the prototype of the kilogram, our primary standard of mass (see Fig 4). Hence, a new definition of the kilogram is needed. It will probably evolve around "$1/12$ of the mass of $\{N_A\}$ atoms of ^{12}C ($\times$ 1000)". For a smooth transition of definitions, an uncertainty of at least $5 \ 10^{-8} \ N_A$ must be attained on N_A. Work is in progress to achieve this.

Inversely, the observation that N_A is consistent with other fundamental constants to better than $10^{-6} \ N_A$, one could say that the closely-knit network of fundamental constants supports a value of N_A to at least $10^{-6} \ N_A$ combined relative uncertainty and therefore also supports the claimed combined relative uncertainty of the molar mass, lattice constant and density measurements as a group – not necessarily singly. Hence, this network also supports the measurements of the isotope amount ratios R_i of Si at the $3 \ 10^{-5} \ R$ level. Apart from the fact that the molar mass measurements are traceable to prepared isotope amount ratios (synthetic isotope mixtures), the entire measurement procedure to achieve $3 \ 10^{-5}$ uncertainty on an isotope amount ratio can be said to be, so to say, under the supreme quality control of the Avogadro constant and its interrelationships with other fundamental constants.

There is indeed a strong "quality assurance"; the measurement procedure and instrumentation appear to be monitored by the "network" of inter-related fundamental constants.

Are the measurement methods leading to the Avogadro constant useable for other metrological purposes?

Given the supreme "quality assurance" exerted by the network of fundamental constants on the measurement methods used, the results obtained with these methods are indeed confirmed by this network within the stated uncertainties. Are results of measurements, by these methods, not reliable and credible in other fields of application to within the stated uncertainties? Does the X-ray interferometric method used not yield a result of the same uncertainty in other lattice constant measurements? Are density measurements using the same method on other materials not credible to the stated uncertainty? Are molar mass determinations not reliable to the stated uncertainty when performed on other (ideal) gases? The underlying reasoning for these questions is that measurement methods which are monitored by a quantified connection to the network of interrelated fun-
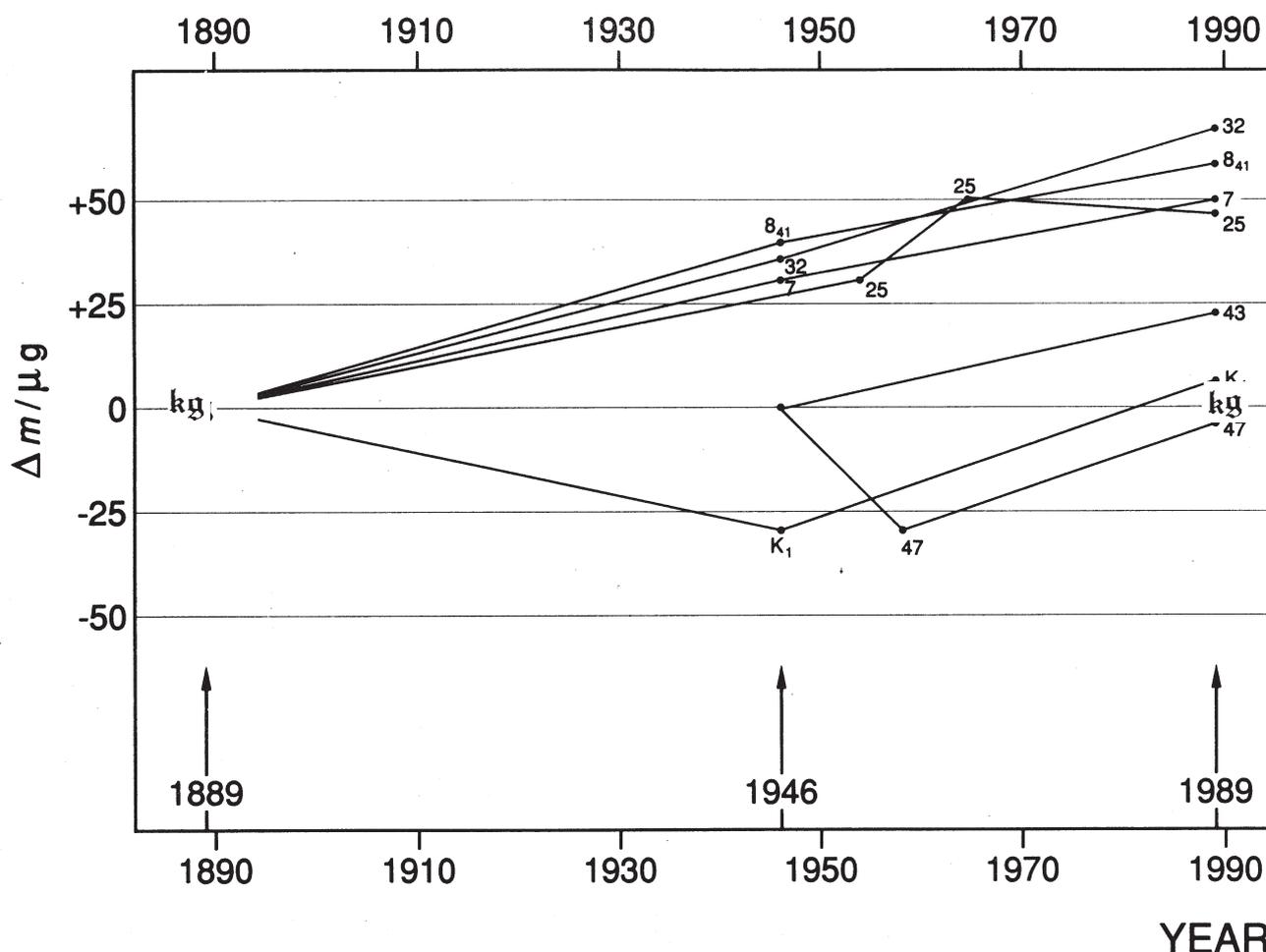
Figure 4. Observed variations in mass of realisations of the kilogram (indicated by their number identification) against the mass of the prototype kg of the kilogram.

damental constants are subject to the highest "quality assurance" programme imaginable, one which does not make use of a human convention (written procedure or other) as the ultimate judge but of nature itself by referring to its unalterable fundamental constants.

What is more, all quantities measured in equation 1 are properly traceable to SI units, and, in addition, equation 1 only contains ratios of values expressed in SI units,

$$N_A = \frac{kg\ mol^{-1}/kg\ m^{-3}}{m^3} = mol^{-1} \qquad \text{(eq. 4)}$$

This ultimately delivers a number per mole, only based on ratios of values which are expressed in SI units. Isotope mass spectrometrists have always made calibrated measurements of a molar mass (numerically equal to atomic weight or mean relative atomic mass) which were in fact traceable to ratios of amounts of pure isotopes in gravimetrical preparations from enriched isotope materials. Through various corrections ε, such as for the lack ε_{is} of 100% isotopic purity of the enriched isotopes, for impurities ε_{imp} and for deviations of stoichiometries ε_{st} of the compounds containing the enriched isotopes, the weight or mass ratio of isotopically enriched materials (^iE) leading to synthetic isotope mixtures, is converted into an amount ratio of (pure) isotopes;

$$\frac{n(^iE)}{n(^jE)} = \frac{m\ (^iE)}{m\ (^jE)} \cdot \frac{M\ (^jE)}{M\ (^iE)} \cdot \frac{1-\varepsilon_{is}(^iE)}{1-\varepsilon_{is}(^jE)} \cdot \frac{1-\varepsilon_{st}(^iE)}{1-\varepsilon_{st}(^jE)} \cdot \frac{1-\varepsilon_{imp}(^iE)}{1-\varepsilon_{imp}(^jE)} \qquad \text{(eq 5)}$$

Also, this equation only contains ratios (the corresponding uncertainty budget is given in Table 6). The isotope amount ratio then serves to calibrate the measured abundance ratios.

The N_A measurement as a "primary method" for amount ratios

As described above, a completely understood and fully described measurement procedure does result from the isotopic measurements of Si for the determination of N_A. The equations relating "measurement signals" to what is intended to be measured are all in expressed (in ratios of quantities expressed) in SI units and do not contain any empirical term. We think therefore that they qualify as a "primary method of measurement". If so, other amount ratio measurements, using this procedure can also be considered as having been measured by a "primary measurement method" which is subject to the supreme "quality assurance" exerted by the fundamental constants network. Ensuing results thus borrow their credibility and stated uncertainty from that network of fundamental constants.

Consequences for isotope dilution as measurement method

An isotope dilution measurement procedure compares an unknown amount of a representative isotope of an element in a sample X to a known amount ("spike") of a representative but other isotope of the same element in a sample Y (De Bièvre 1990,1993)

through the measurement of an amount ratio R in their isotopic blend B,

$$R_B = \frac{n\ (^iE)_X}{n\ (^jE)_Y} \qquad \text{(eq. 6)}$$

All other isotopes in unknown sample and spike are only correction terms to the above equation (De Bièvre 1990,1993). The full general equation is,

$$\frac{n\ (E)_X}{n\ (E)_Y} = \frac{R_Y - R_B}{R_B - R_X} \cdot \frac{\Sigma R_{iX}}{\Sigma R_{iY}} \qquad \text{(eq. 7)}$$

The connection of the measurement of a (very) small amount or a (very) small concentration can therefore be visibly and traceably made to a pure substance (the isotopically enriched spike material). This in itself can be expressed in mol kg^{-1} through corrections of mass due to impurities, deviation of 100% isotopic purity, a known (deviation of) stoichiometry and known atomic weights. Alternatively, the spike can be measured by comparing it to a pure substance of natural isotopic composition (reverse isotope dilution). Thus traceability to the value in mol kg^{-1} in a pure substance can be established using a measurement method which in itself is controlled by the Avogadro constant and the network of fundamental constants.

When the kilogram itself has been redefined as the mass of so many atoms as there are contained in 0.012 kg of ^{12}C, exclusive traceability to the mole will have been established since the kg will have disappeared from the traceability chain.

Other evidence for a fundamental role of isotope amount ratio measurements

When measuring the abundance ratios of the Si isotopes on SiF$_4$ gas, it is obvious that the inlet of the gas into the ion source of the mass spectrometer must be done through pinholes in a (gold) leaf (Fig 5). This process continuously changes the isotopic composition of the gas (actually enriching the sample in the expansion vessel prior to the inlet, in the heavier isotopic molecules). The size of this effect is derived directly from kinetic gas theory; it is the very well known square-root-of-mass-ratio. Performing measurements over many hours, of exponentially changing values of the isotope amount ratio over time or, better, over the continuously measured ion current of one isotope, enables back-extrapolation of the isotope amount ratio to find its value at time zero, the opening of the valve of the sample container. The gas flow rate into the ion source is,

$$-dN_i(t)\ /dt = \beta \cdot {}^iM^{-\Phi} \cdot N_i(t) \qquad \text{(eq. 8)}$$

where $N_i(t)$ is the number of molecules in the container at $t = 0$, and β is a constant for a given effusion barrier. Integrating from t to t_o yields;

$$N_i(t) = N_i(to) \cdot exp\ (-\beta \cdot {}^iM^{-\Phi} \cdot t) \qquad \text{(eq. 9a)}$$
and
$$N_j(t) = N_j(to) \cdot exp\ (-\beta \cdot {}^jM^{-\Phi} \cdot t) \qquad \text{(eq. 9b)}$$

Thus, for isotopic gas molecules, one establishes that,

$$ln\ \frac{I_{i/j}(t)}{I_{i/j}(t_o)} = -\beta \cdot ({}^iM^{-\Phi} - {}^jM^{-\Phi}) \cdot t \qquad \text{(eq. 10)}$$
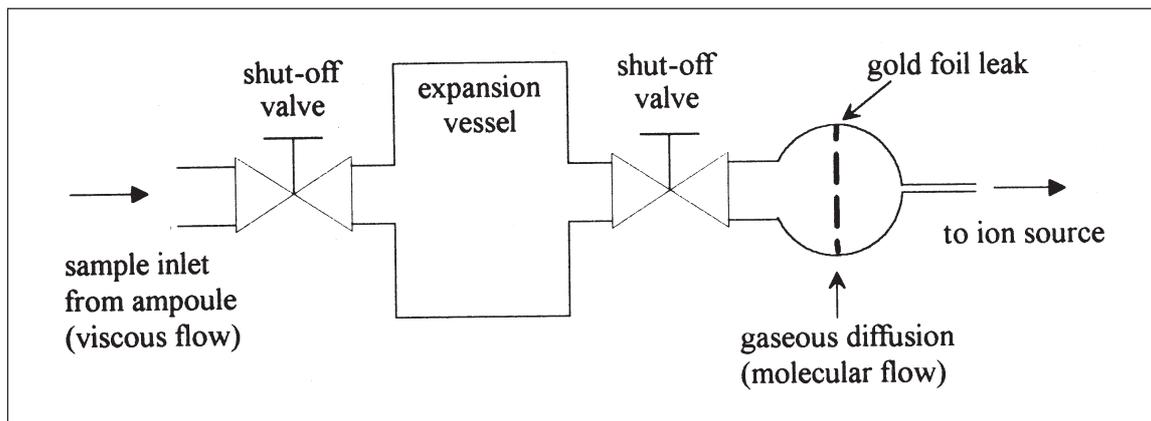
Figure 5. Inlet path of gas into ion source of gas isotope mass spectrometer.

Table 9

Theoretical and experimental values of $M(^{14}N_2)/M(^{14}N^{15}N)$; uncertainties (1$s$) are given below the digits to which they apply.

	predicted by kinetic gas theory	experimentally observed values	difference	relative difference
$[(^{28}SiF_4)/(^{28}SiF_4)]^{0.5}$	1.00000	1.00026 0.00016		
$[(^{29}SiF_4)/(^{28}SiF_4)]^{0.5}$	1.00480	1.00469 20	0.00011 20	$-1.1\ 10^{-4}$
$[(^{30}SiF_4)/(^{28}SiF_4)]^{0.5}$	1.00957	1.00911 31	0.00046 31	$-4.6\ 10^{-4}$

and also that

$$ln\ \frac{I_j(t)}{I_j(t_o)}\ =\ -\beta \cdot (^jM^{-\Phi} \cdot t) \qquad \text{(eq. 11)}$$

Consequently,

$$ln\ I_{i/j}(t)\ =\ \frac{^iM^{-\Phi}}{^jM^{-\Phi}}1\quad ln\ \frac{I_j(t)}{I_j(t_o)} + ln_{i/j}(t_o) \qquad \text{(eq. 12)}$$

and values for $(^iM/^jM)^{-\Phi}$ can be estimated from the slope of $lnI_{i/j}(t)$ against $ln\ I_j(t)$.

From a best fit of these experimental values for the changing ratio, experimental values for Φ can be obtained. Optimizing instrument design, vacuum conditions and measurement procedures, the experimental values from Table 9 have been observed. The gratifying agreement with gas kinetic theory values, gives direct support that the measurement process is in a better than 10^{-3} agreement with this other law of basic physics, kinetic gas theory. The measurement process is monitored for "accuracy" by the kinetic gas theory, which gives it an additional feature for being qualified as "primary method of measurement".

Conclusions

Measurements of ratios of isotope amounts (isotopic measurements) are revealed to be of great fundamental importance not only because of their inherent potential for very small uncertainties but also for their measurement potential directly in SI units. They are fully under-stood and are corroborated by the fundamental constants network at the $3\ 10^{-5}$ combined relative uncertainty level. The measurement process itself seems to conform with kinetic gas theory at the 10^{-3} combined relative uncertainty level or better. When combined with isotope dilution, they offer the potential of opening a new route for establishing traceability of amount measurements to (a realization of) the mole, perhaps one could say, to the Avogadro constant.

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