

The Avogadro experiment and the redefinition of the mole - an SI-unit for chemistry

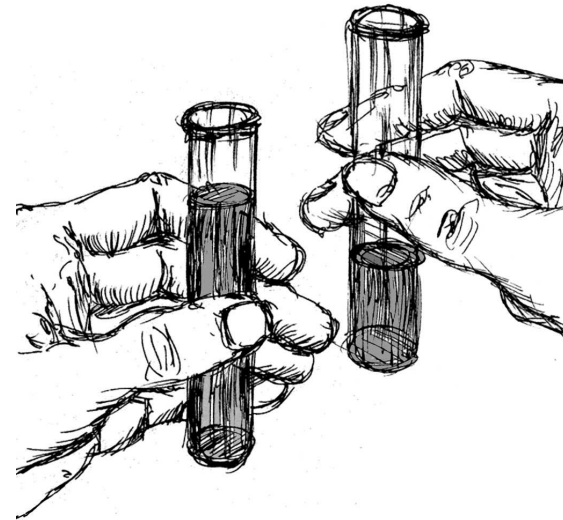
Dr. Bernd Güttler



1. Evolution and definition of the unit
2. The Avogadro-experiment
3. Consequences of a re-definition
4. realization and dissemination

the mole - an SI-unit for chemistry

- The "mole" is an SI-base unit for the base quantity "amount of substance".
- It corresponds to fixed number of defined particles.

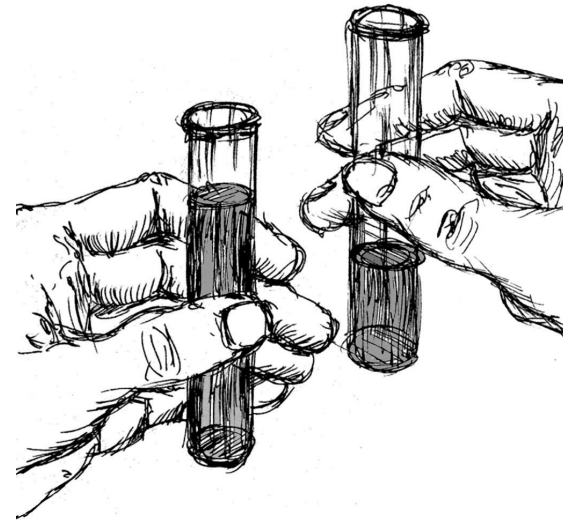


Chemical reactions occur on the basis of multiples of those smallest identifiable entities of substances (atoms or molecules).

The mole allows for a quantitative description of chemical processes in a clear and simple way.

the mole – an SI-unit for chemistry

- The mole creates a link between the SI of the Metre Convention and chemistry.
- The mole allows to make quantitative measurements in chemistry traceable to the SI and internationally comparable.



The unit mole comprises for practical and historical reasons a (large) number of particles such that the unit can be easily related to other SI units such as the kilogram.



John Dalton

Therefore we may conclude that *the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, &c. ...*

... Now it is one great object of this work, to shew the importance and advantage of ascertaining *the relative weights of the ultimate particles ...*

- relation to a discrete, microscopic base quantity: "**ultimate particles**"
- every element consists of characteristic, identical and impartible particles
- the particles cannot be destroyed or created by chemical means
- elements differ with respect to their mass and volume

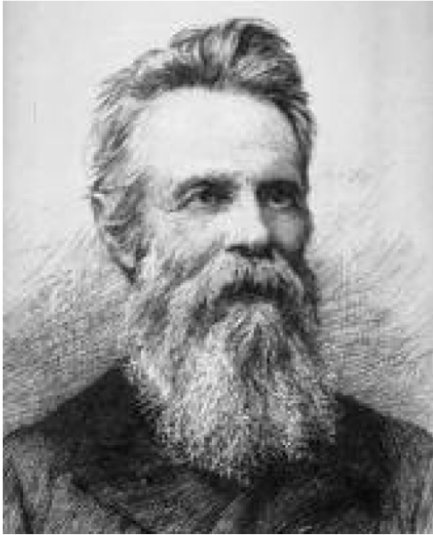
„A New System of Chemical Philosophy“, p. 143, Chpt. 2 „On the constitution of bodies“,
R. Bickerstaff, Strand, London **1808**

"The first hypothesis ... and obviously the only permissible one, is the assumption, that the number of molecules in all gases is the same in the same volume and that this number is always proportional to the volume...."



Amedeo Avogadro

Essay on a Manner of Determining the Relative Masses of the Elementary Molecules of Bodies, and the Proportions in Which They Enter into these Compounds
Journal de Physique, 73, 58-76 (Orig. 1811)



Joseph Loschmidt

$$N_L = \frac{3}{4 \pi \lambda s_0^2}$$

s_0 : Loschmidt's molecular diameter

λ : mean free path

$$N_L = 2,686\,7805\,(24) \cdot 10^{25} \text{ m}^{-3}$$

...and as the most accurate experiments of the mean free path (of those particles) reveal a value of 170 parts of a millionth of a millimeter we finally obtain 1.17 millionth of a millimeter, i.e. the diameter of a molecule of air is about 1 millionth of a millimeter.

Zur Größe der Luftmoleküle, in: Anzeiger der Kaiserlichen Akademie der Wissenschaften Wien, Mathematisch-Naturwissenschaftliche Klasse, 2, S. 162-164, 1865



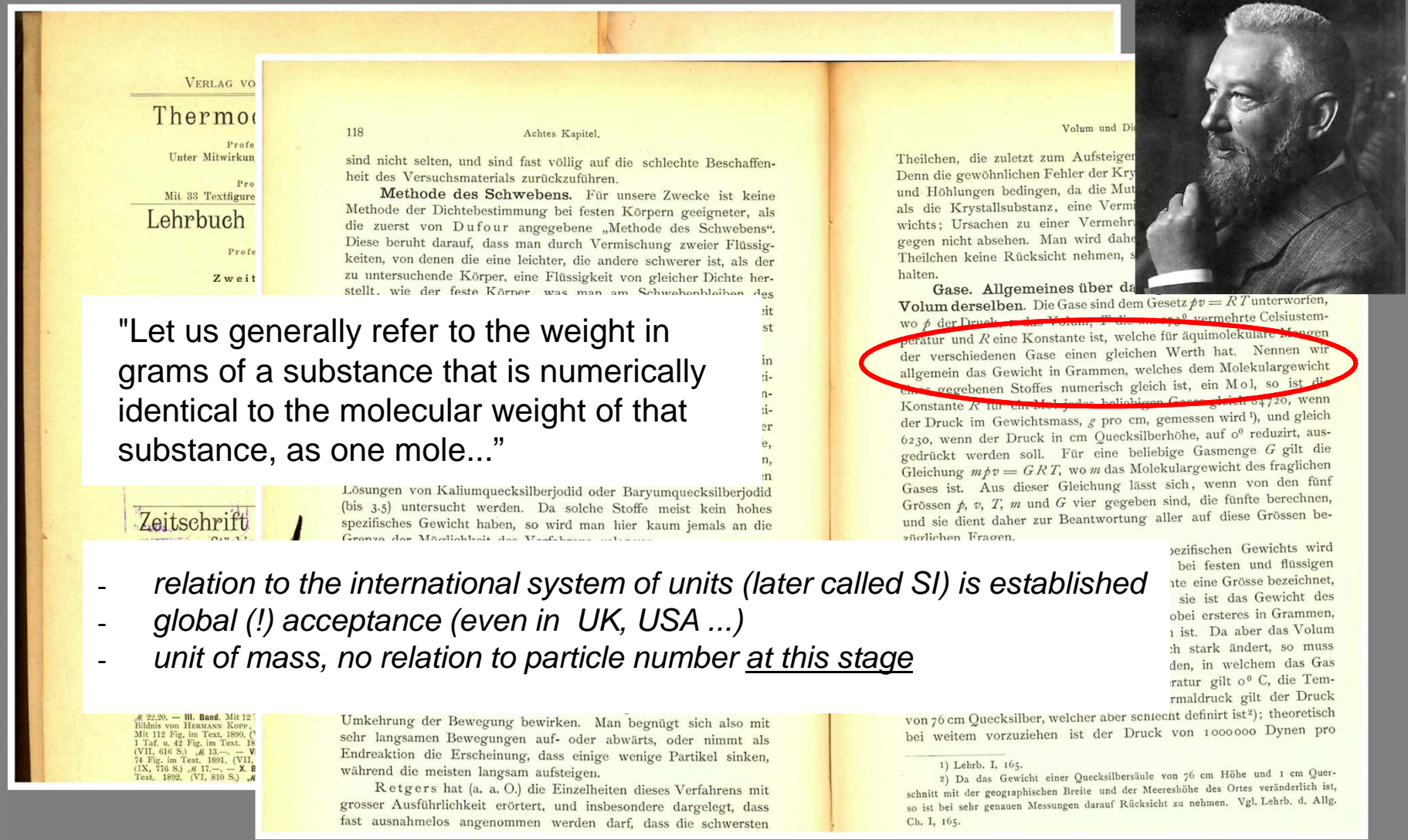
...about Avogadro's hypothesis and Daltons "hypothesis on molecules" ...

Walther Nernst

of course, there is no proof for this hypothesis as there is also no proof for the hypothesis about molecules in general but it seems very likely because it can explain the validity of the third law on gases* in a very simple way. The numerous successes that were observed by its consistent application are all witnesses in its favour;

Nernst, W.: Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik, (1893), S. 31, Stuttgart: Enke Verlag

*law on multiple proportions



"Let us generally refer to the weight in grams of a substance that is numerically identical to the molecular weight of that substance, as one mole..."

- relation to the international system of units (later called SI) is established
- global (!) acceptance (even in UK, USA ...)
- unit of mass, no relation to particle number at this stage



...Theilchen, die zuletzt zum Aufsteigen ... Denn die gewöhnlichen Fehler der Kry ... und Höhlungen bedingen, da die Mut ... als die Krystallsubstanz, eine Verm ... wichts; Ursachen zu einer Vermehr ... gegen nicht absehen. Man wird dah ... Theilchen keine Rücksicht nehmen, s ... halten.

Gase. Allgemeines über da
Volum derselben. Die Gase sind dem Gesetz $p v = R T$ unterworfen, wo p der Druck, v das Volum, T die am 273° vermehrte Celsiusstemperatur und R eine Konstante ist, welche für äquimolekulare Mengen der verschiedenen Gase einen gleichen Werth hat. Nennen wir allgemein das Gewicht in Grammen, welches dem Molekulargewicht eines gegebenen Stoffes numerisch gleich ist, ein Mol, so ist die Konstante R für ein Mol jeder beliebigen Gase gleich 84720 , wenn der Druck im Gewichtsmass, g pro cm, gemessen wird¹⁾, und gleich 6230 , wenn der Druck in cm Quecksilberhöhe, auf 0° reduziert, ausgedrückt werden soll. Für eine beliebige Gasmenge G gilt die Gleichung $m p v = G R T$, wo m das Molekulargewicht des fraglichen Gases ist. Aus dieser Gleichung lässt sich, wenn von den fünf Grössen p, v, T, m und G vier gegeben sind, die fünfte berechnen, und sie dient daher zur Beantwortung aller auf diese Grössen bezüglichen Fragen.

spezifischen Gewichts wird bei festen und flüssigen ... te eine Grösse bezeichnet, sie ist das Gewicht des ... bei ersteres in Grammen, ... ist. Da aber das Volum ... stark ändert, so muss ... den, in welchem das Gas ... ratur gilt 0° C, die Tem ... raldruck gilt der Druck ... von 76 cm Quecksilber, welcher aber schlecht definit ist²⁾; theoretisch bei weitem vorzuziehen ist der Druck von 1000000 Dynen pro

1) Lehrb. I, 165.
 2) Da das Gewicht einer Quecksilbersäule von 76 cm Höhe und 1 cm Querschnitt mit der geographischen Breite und der Meereshöhe des Ortes veränderlich ist, so ist bei sehr genauen Messungen darauf Rücksicht zu nehmen. Vgl. Lehrb. d. Allg. Ch. I, 165.

"Let us generally refer to the weight in grams of a substance that is numerically identical to the molecular weight of that substance, as one mole..."

Ostwald 1893



The mole, mol, is the unit of amount of substance of a specified elementary entity, which may be an atom, molecule, ion, electron, any other particle or a specified group of such particles; its magnitude is set by fixing the numerical value of the Avogadro constant to be equal to exactly $6.022\ 141\ 8 \times 10^{23}$ when it is expressed in the unit mol⁻¹.

proposed definition

"Let us generally refer to the weight in grams of a substance that is numerically identical to the molecular weight of that substance, as one mole..."

$$M(X) = A_r(X) \times M_u$$

$$n(X) = M_x/M(X)$$

$M(X)$	molar mass of X
$A_r(X)$	Σ rel. atomic masses (dimension less) of X
M_u	molar mass constant (10^{-3} kg/mol)
M_x	mass of X

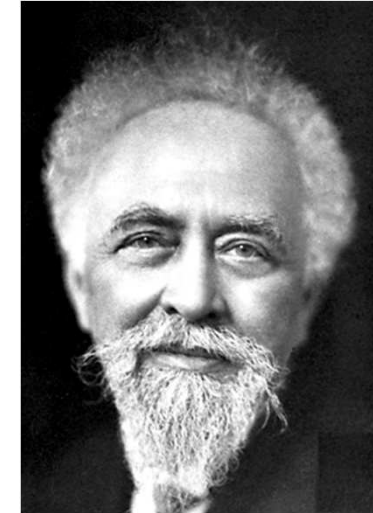
Ostwald 1893



Albert Einstein

$$N_A = (1/\langle x^2 \rangle)(RT/3\pi\eta r)$$

- η viscosity
- r particle radius
- x average displacement



Jean Perrin

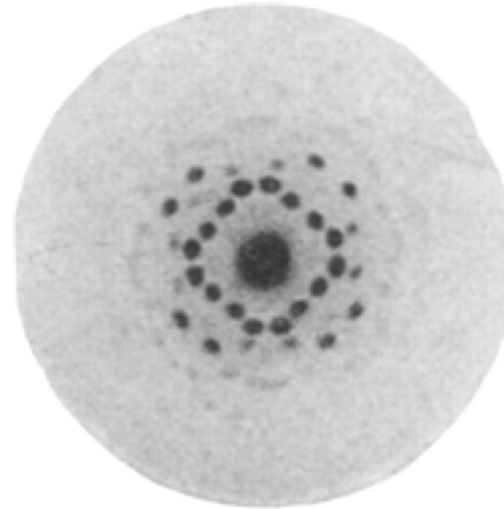
"Any two gram-molecules always contain the same number of molecules. This invariable number N is a universal constant which may appropriately be designated Avogadro's constant."

*Perrin. J.: Brownian Motion and Molecular Reality
aus: Annales de Chimie et de Physique 18, 1-114 (1909)*



Max von Laue

Interferenzerscheinungen mit Röntgenstrahlen
beim Durchgang durch Kristalle
von W. FRIEDRICH, P. KNIPPING und M. LAUE und erläutert die
Bedeutung dieser Versuche für die Klärung unserer Auffassung



Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Klasse der Königl. Bayerischen Akademie der Wissenschaften zu München S. 303 (1912)

8. Mit den Bezeichnungen „Mol“ und „Äquivalent“ verbundene Begriffe und Einheiten



Ulrich Stille

"First of all it (the mole) is understood as a chemical mass unit in accordance with **Ostwald's view of a continuum** and has an individual value for each type of molecule.

The other understanding of the "**Mole**" is that of a **number of atoms or molecules**, that is comprised in a mole. (We will call it mole number.)"

When you intend to find a more precise wording, for example by introducing a base quantity "**Stoffmenge**" (amount of substance) it can be considered as the numerical value of the amount of substance."

Stille U.: Messen und Rechnen in der Physik, Vieweg & Sohn S. 117f. (1955)

"Let us generally refer to the weight in grams of a substance that is numerically identical to the molecular weight of that substance, as one mole..."

quantification

1. The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is "mol".

identification

2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

N_A

Ostwald 1893

current definition (1971)

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current definition (1971)

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current definition (1971)

$$M(X) = A_r(X) \times M_u$$

$$M(X) = m(X) \times N_A$$

$$m(X) \quad A_r(X) m_u$$

$$m_u \quad m(^{12}\text{C})/12$$

$$N_A \quad \text{Avogadro constant}$$

now:

$$u(M_u) = 0$$

$$u(N_A) = 2 \times 10^{-8}$$

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current definition (1971)

- In the new SI all 7 base units will be defined by constants of nature (SI reference constants),
- the respective SI reference constants will have exact numerical values,
- the new SI is expected to be more stable since there are no artefacts involved.

demands for redefinition

1. The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is “mol”.

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proposed definition

The mole, mol, is the unit of amount of substance of a specified elementary entity, which may be an atom, molecule, ion, electron, any other particle or a specified group of such particles; its magnitude is set by fixing the numerical value of the Avogadro constant to be equal to exactly $6.022\,141\,8 \times 10^{23}$ when it is expressed in the unit mol^{-1} .

proposed definition

$$M(X) = A_r(X) \times M_u$$

$$M(X) = m(X) \times N_A$$

$$n(X) = M_x / M(X)$$

$$n(X) = N(X) / N_A$$

$N(X)$ number of particles X

then: $u(M_u) \leq 4 \times 10^{-9}$
 $u(N_A) = 0$

A *mise en pratique* for the definition of a unit is a set of instructions that allows the definition to be realized in practice at the highest level. The *mise en pratique* should describe the primary realizations based on top-level primary methods.

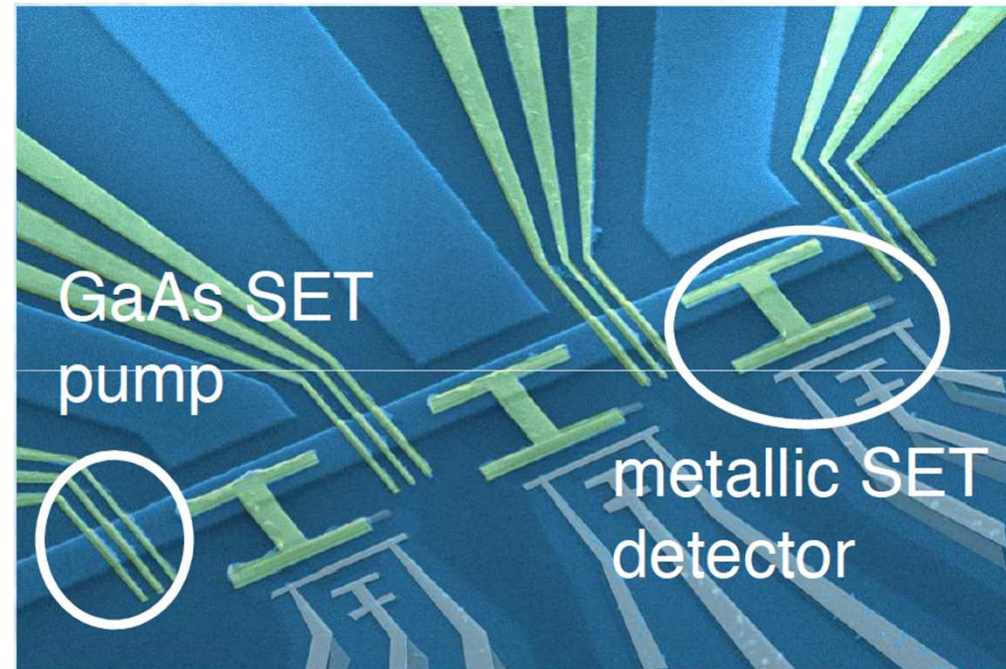
CCU would like to see some homogeneity in their content.

(report of the [97th meeting of the CIPM \(2008\)](#)).

The mole can be realized by counting N_A electrons in a conductor line with a SET device.

$$n_{el} = \langle N_{el} \rangle / N_A$$

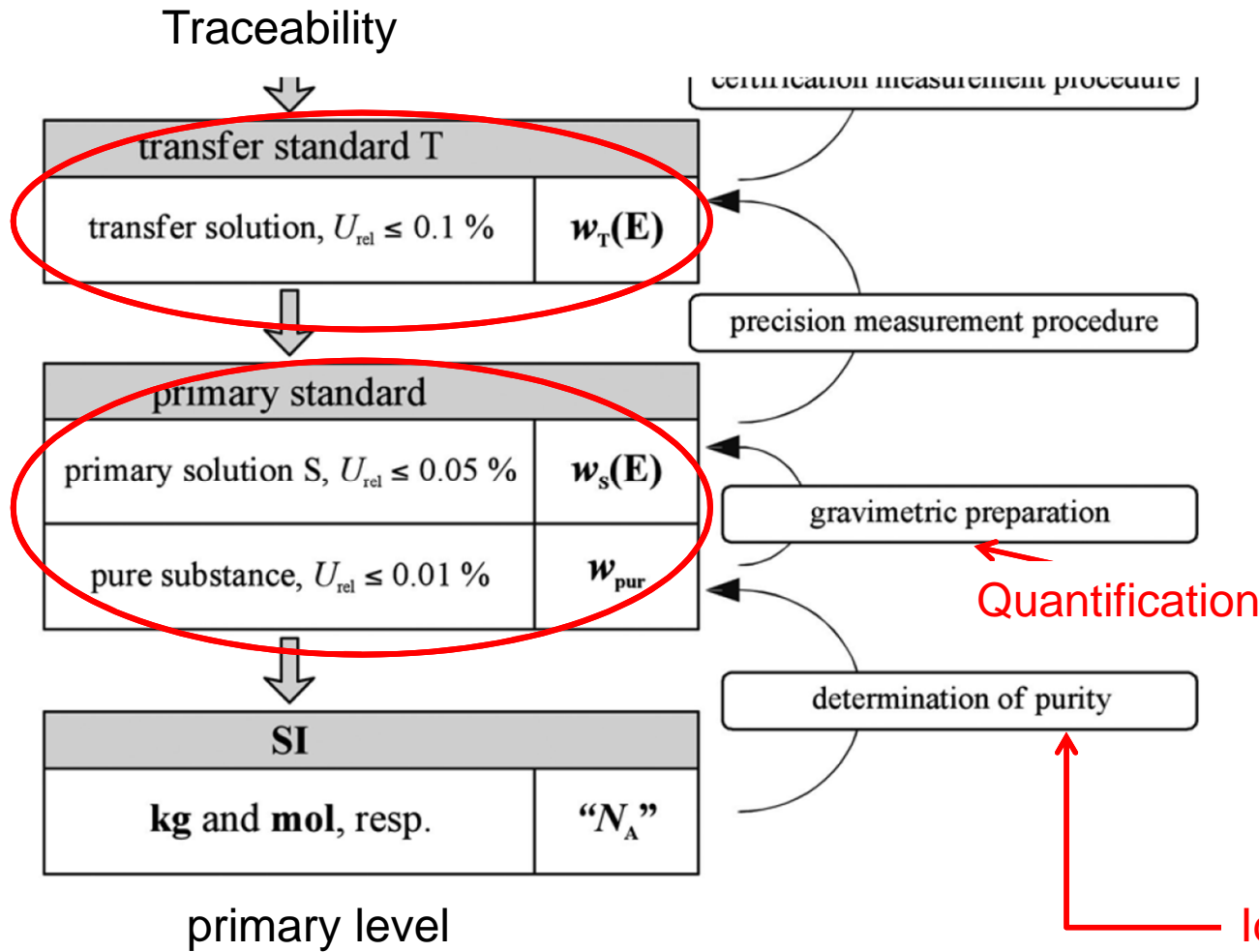
"One Ampere is realized by measuring the current created by the charge of 2.66046×10^{-5} mol_{el}/s passing through a SET turnstile device."



A semiconductor single-electron-tunneling (SET) pump.

$$I = \langle N_{el} \rangle ef$$

S. P. Giblin et al. Nature Communications 3.930
 DOI 10.1038 ncomms 1935
 from: U. Siegner, PTB



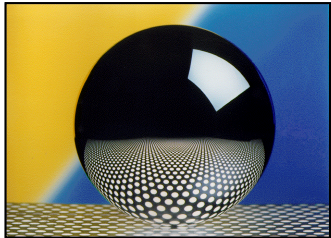
transfer standard

$$c(X) = \frac{n(X)}{V_{sol}}$$

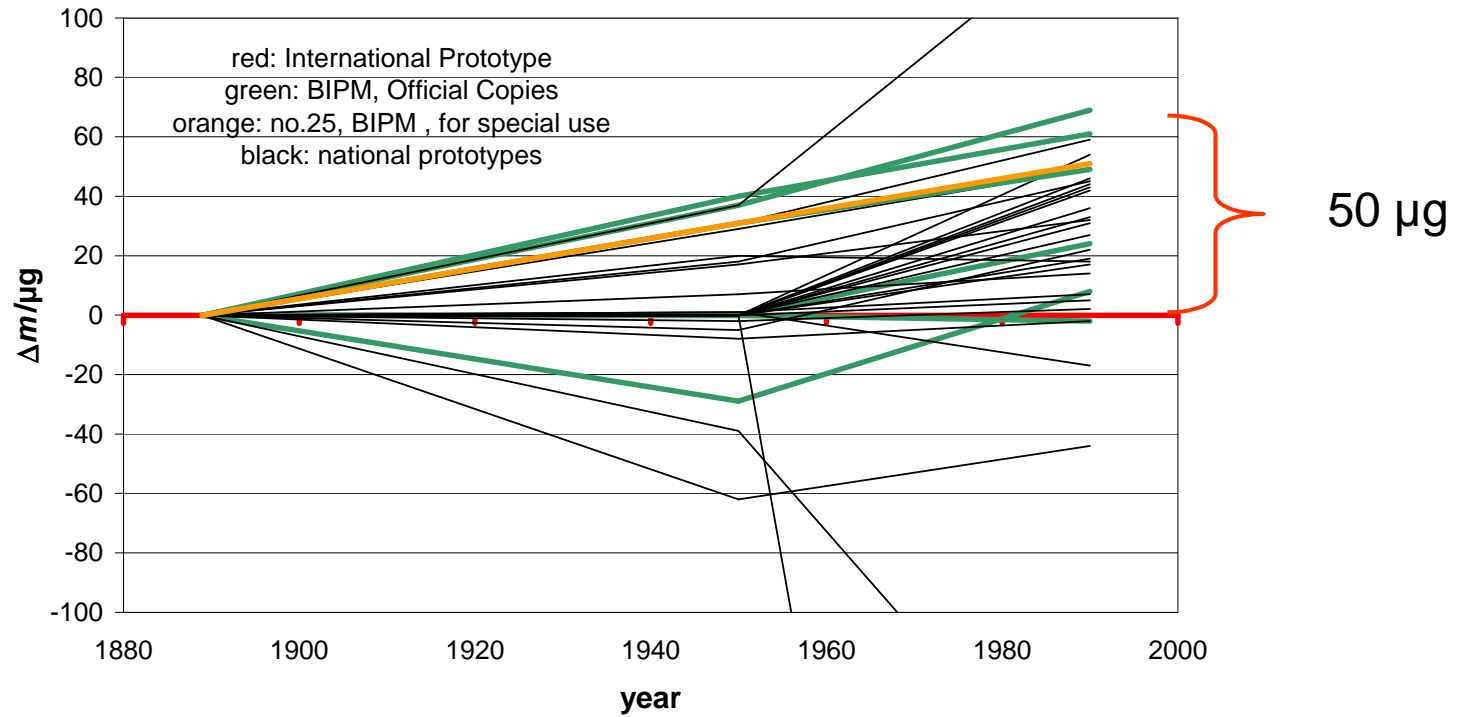
primary standard

$$n(X) = \frac{M_x}{M(X)} R(X)$$

Identification



Mass values of the prototypes in 1889, 1950 and 1990

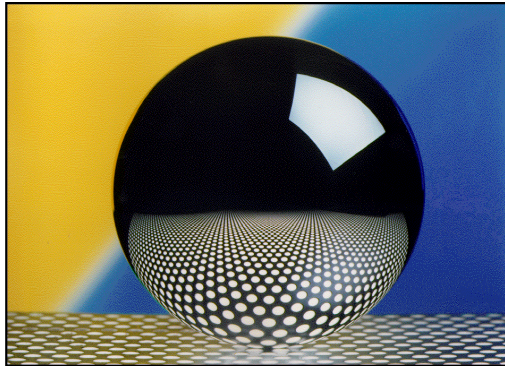


$$N_A = \frac{8 \cdot M \cdot V_{\text{sphere}}}{m \cdot a^3}$$

Measurement challenge:

$u(N_A)$ or $u(h) \leq$ present situation

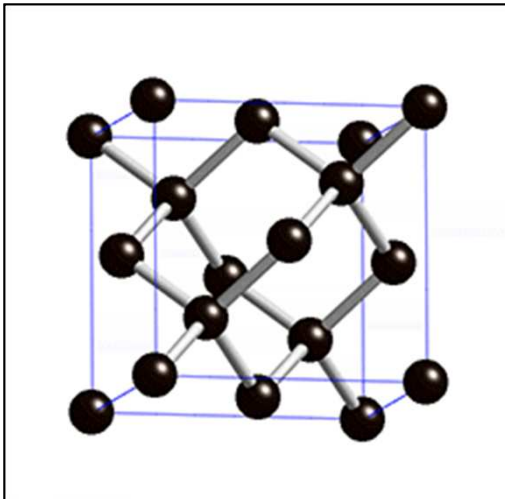
- Three measurement results of N_A or h available
- one of them should have a rel. stand. uncertainty of $2 \cdot 10^{-8}$ and
- two should have a rel. standard uncertainty of $5 \cdot 10^{-8}$



$$N = V_{\text{Sphere}} / V_{\text{Atom}}$$

$$n = N / N_A = m / M$$

$$N_A = (M / m) (V_{\text{Sphere}} / V_{\text{Atom}})$$

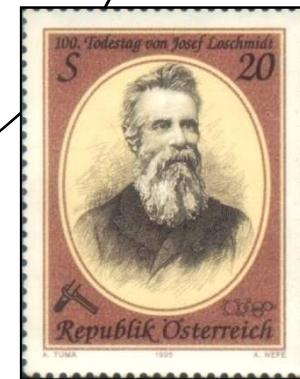


$$N_A = \frac{8 \cdot M \cdot V_{\text{sphere}}}{m \cdot a^3}$$

$$N_A h = \frac{c A_r(e) M_u \alpha^2}{2 R_\infty}$$

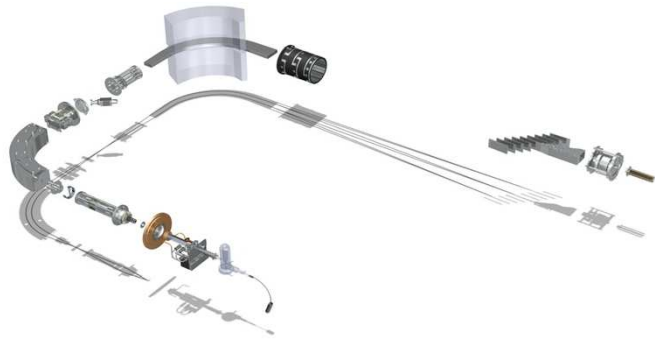
<http://www.msm.cam.ac.uk/phase-trans/2003/MP1.crystals/MP1.crystals.html>

see J. Stenger & E.O. Göbel, Metrologia 49 (2012), L25–L27



2010 Grenoble





Multicollector ICPMS

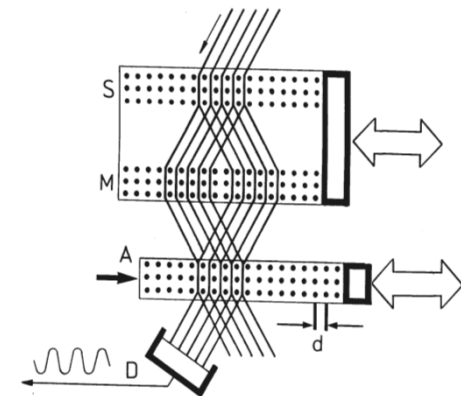
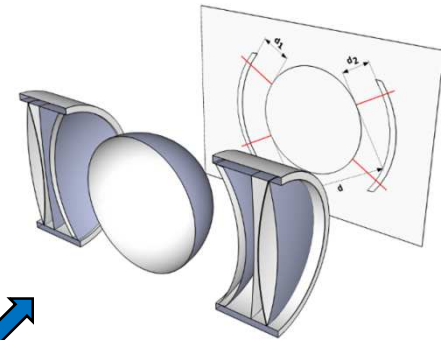


Mass comparator

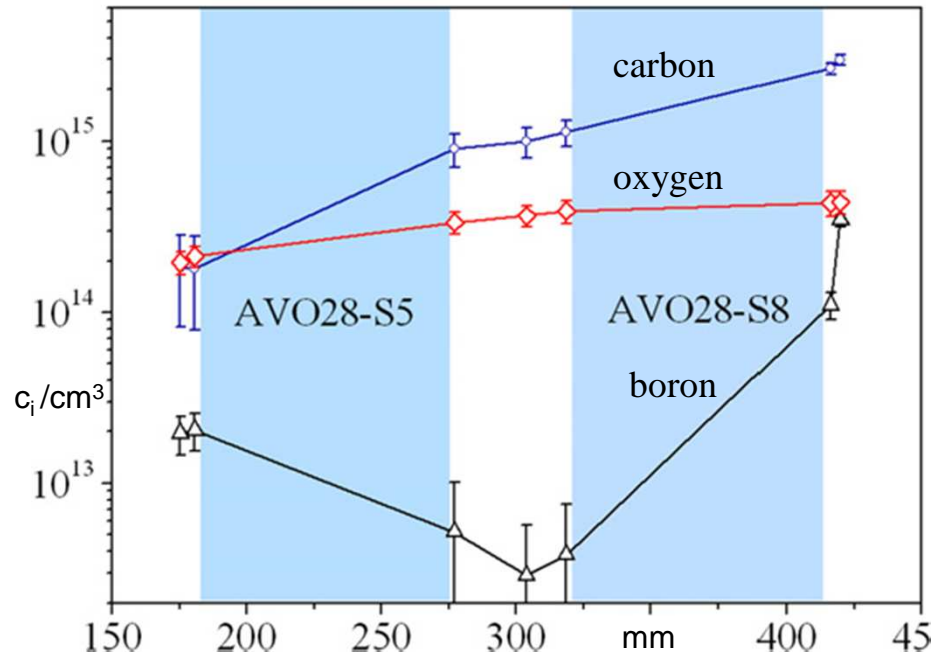
$$N_A = \frac{8 \cdot \underline{M} \cdot \underline{V_{\text{sphere}}}}{\underline{m_{\text{sphere}}} \cdot \underline{a^3}}$$

Surface layer :	XRR, XRF, XPS, opt. ellipsometry
Impurities:	IR, NAA

Optical sphere interferometer

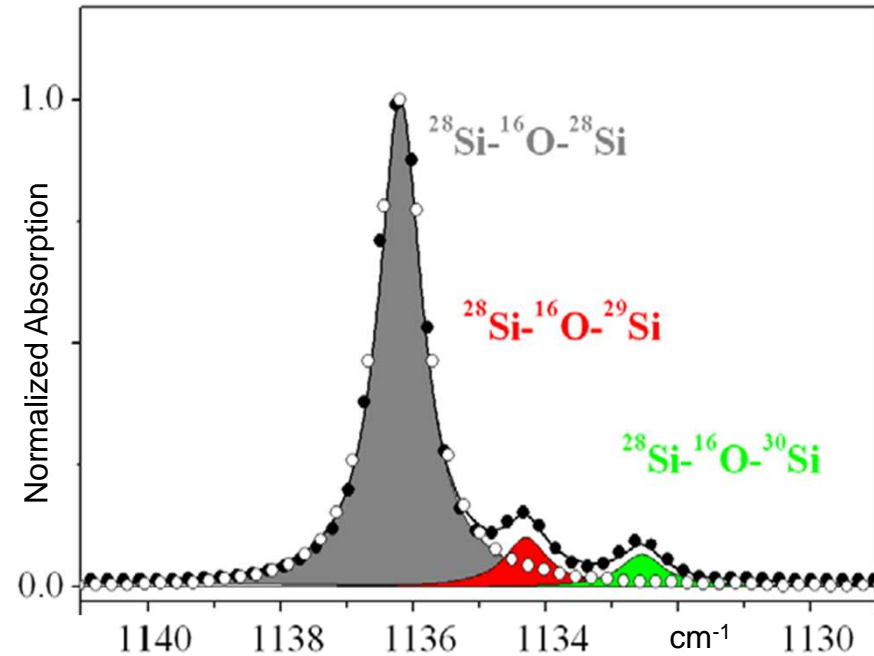


X-Ray Interferometer



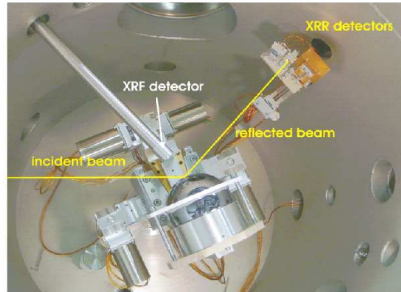
Major impurities by infrared absorption spectroscopy

contribution to $u(N_A)_{\text{rel}}$: $\ll 1 \times 10^{-9}$



Infrared absorption spectra of oxygen in Si at 7K

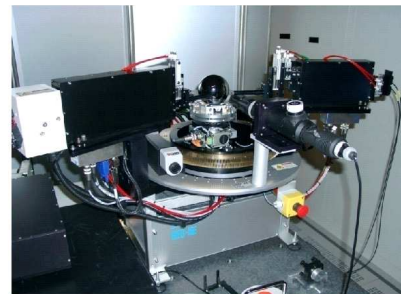
The three dominant vibrational modes of oxygen (coloured) in natural Si (full circles). For comparison the measured spectra of ‘Si28’ (open circles).



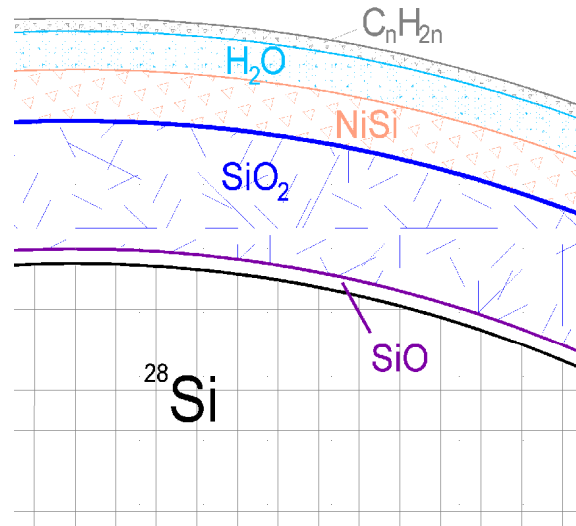
X-ray reflectometry (BESSY)



X-ray spectroscopy (METAS)



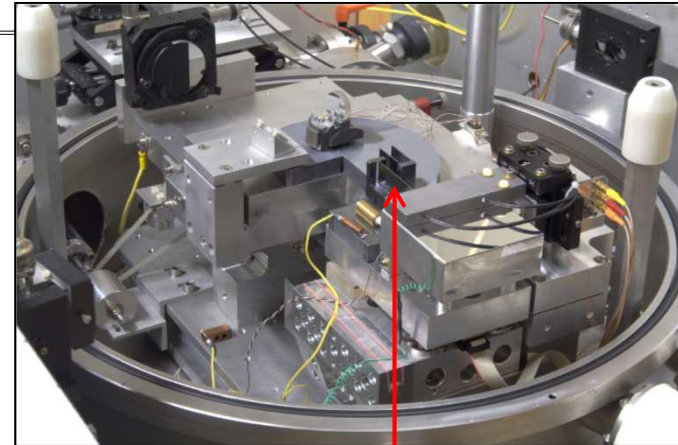
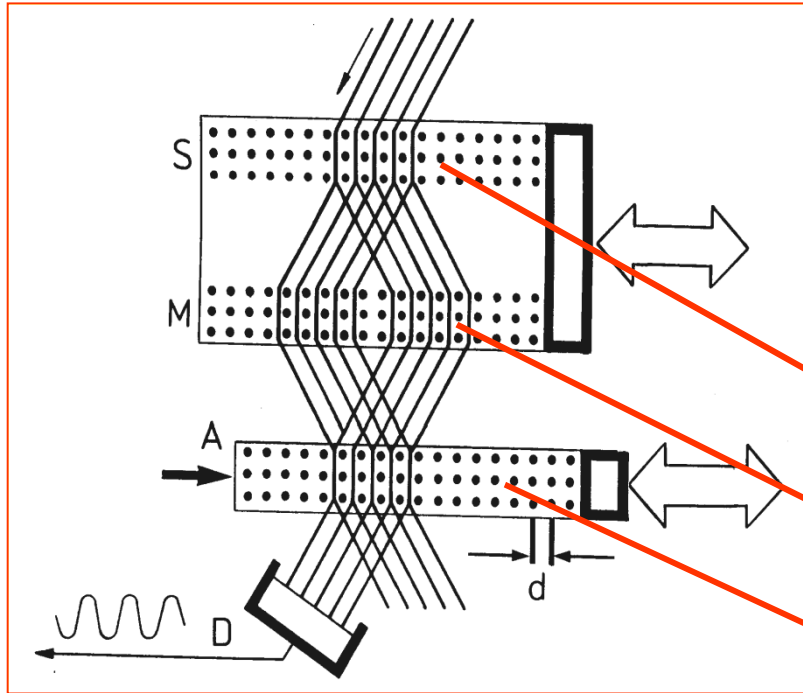
Spectral ellipsometry (PTB, NMIJ)



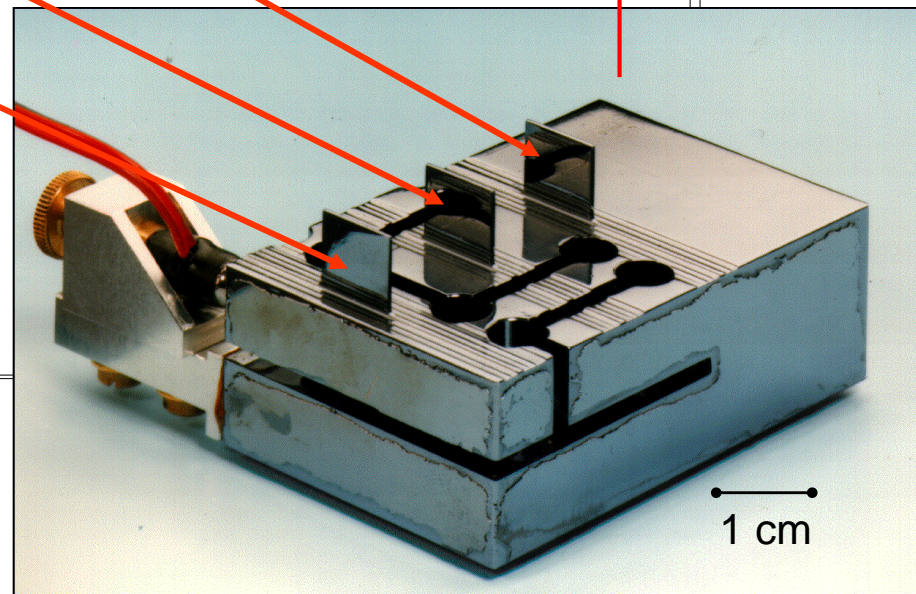
sphere	d_{SL}	m_{SL}
S5	2,88(33) nm	222,1 (14,5) μg
S8	2,69(32) nm	213,6 (14,4) μg

relevant parameters:

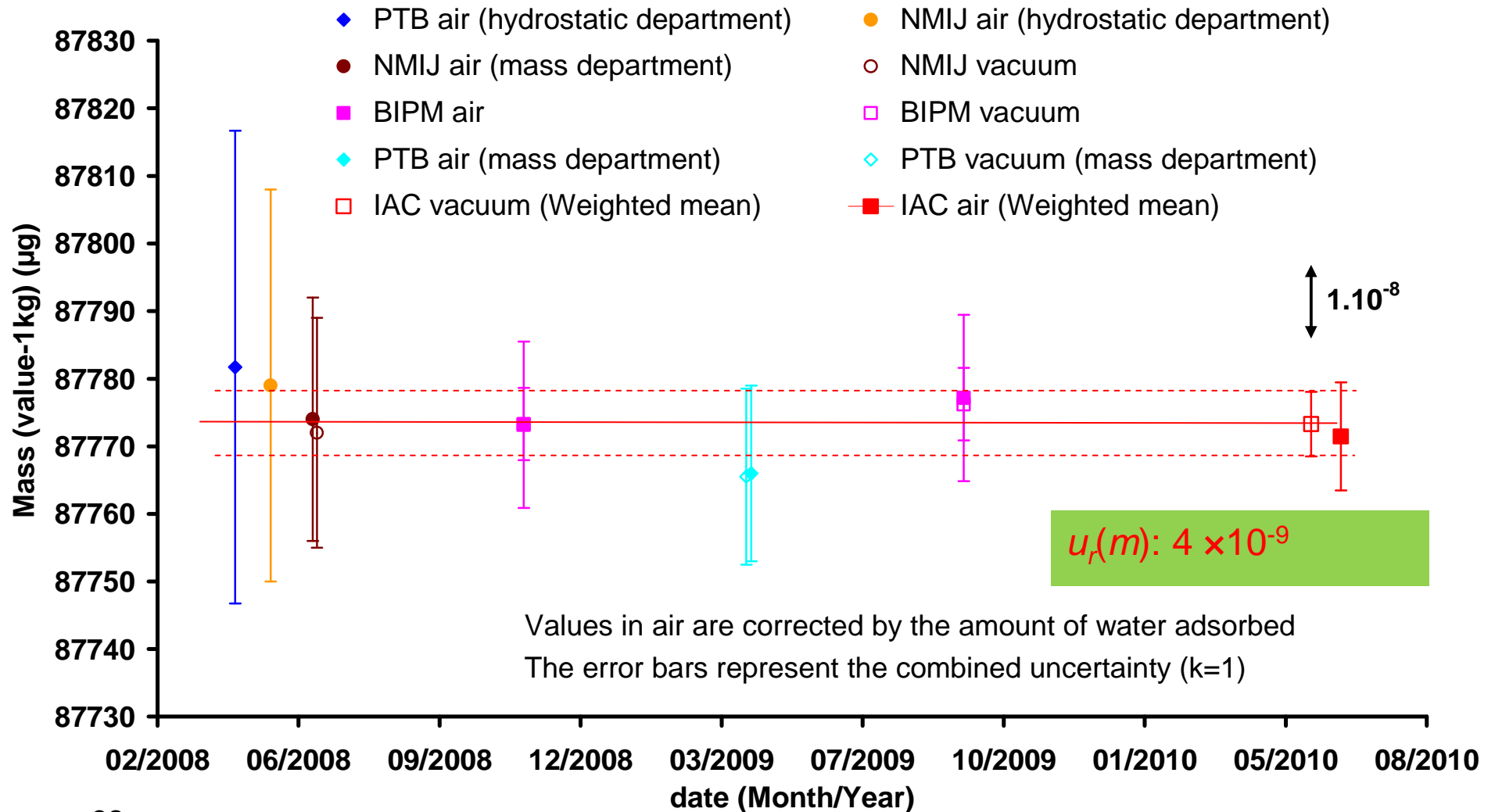
- Optical constants
 - Contamination
 - Surface quality
- Total uncertainty: 0,3 nm
14 μg



Combined optical and x-ray interferometry

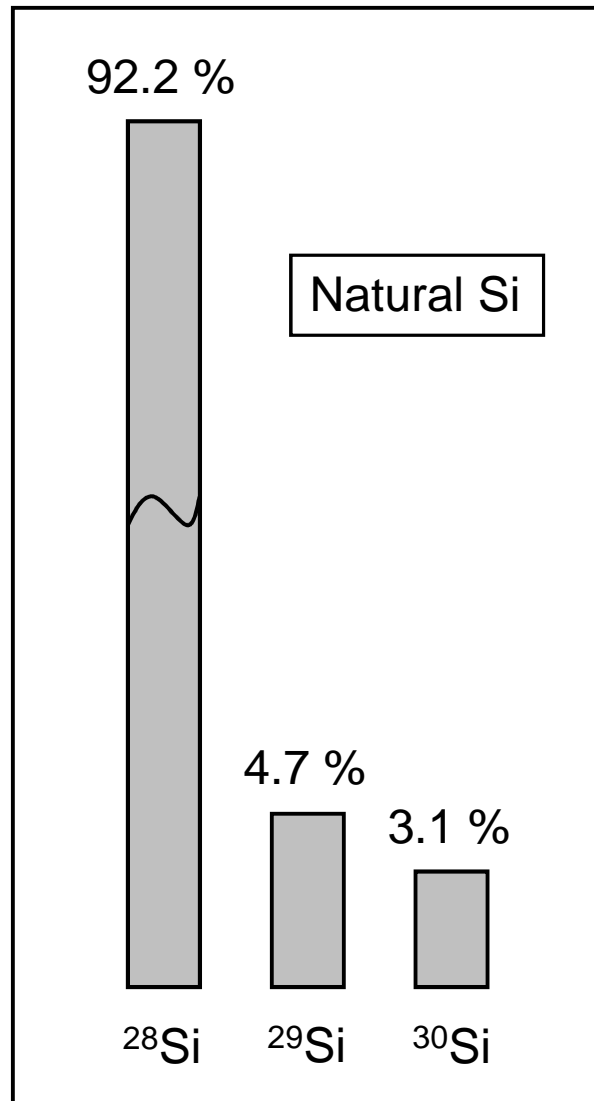


Mass comparison in air and under vacuum on the ^{28}Si sphere **S5**



- three isotopes: ^{28}Si , ^{29}Si , ^{30}Si
- amount fractions $x \leftrightarrow$ isotope ratios R
- Challenge: Target uncertainty of $u_{M,\text{rel}} \leq 1 \cdot 10^{-8}$

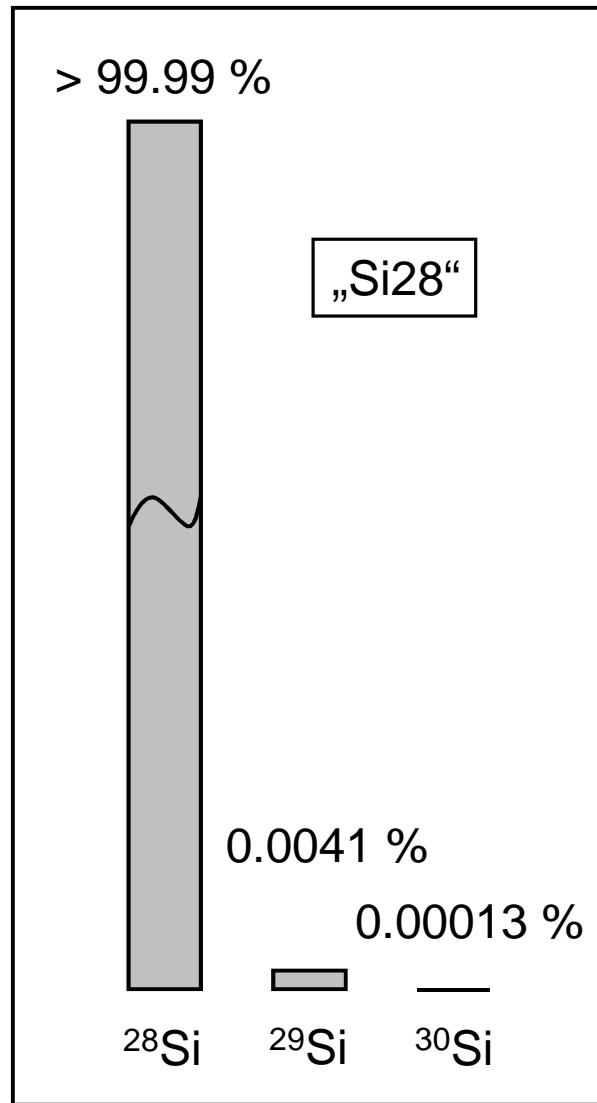
$$M(\text{Si}) = \sum_{i=28}^{30} [x(^i\text{Si}) \cdot M(^i\text{Si})] \quad x(^i\text{Si}) = \frac{R_i}{\sum_{j=28}^{30} R_j}$$



Isotopic ratios

	nat. Si	
$R_{28/28}$	1	
$R_{29/28}$	$5.0 \cdot 10^{-2}$	
$R_{30/28}$	$3.4 \cdot 10^{-2}$	

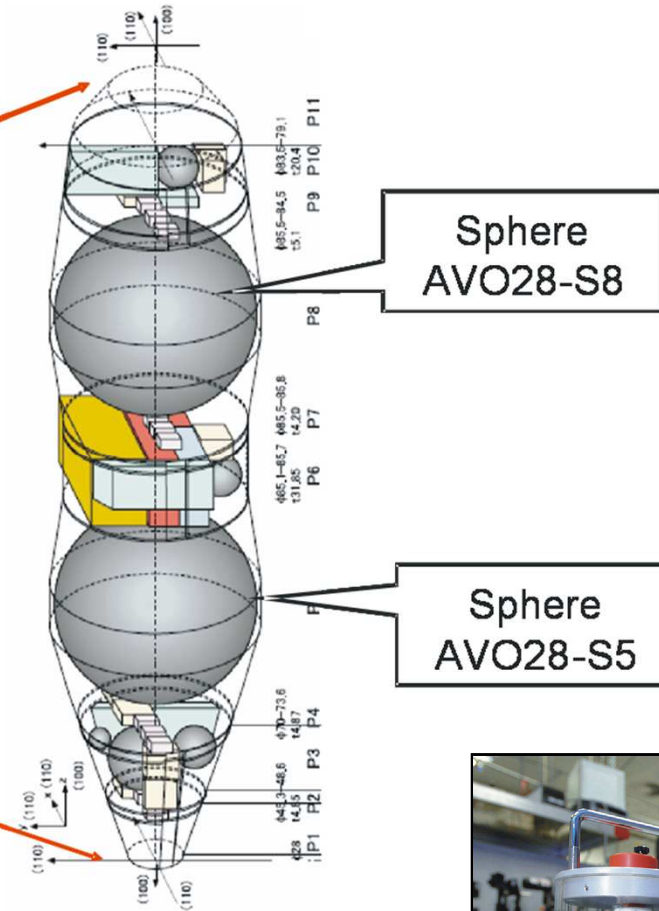
$$U < 10^{-7}$$



Isotopic ratios

	nat. Si	
$R_{28/28}$	1	
$R_{29/28}$	$5.0 \cdot 10^{-2}$	
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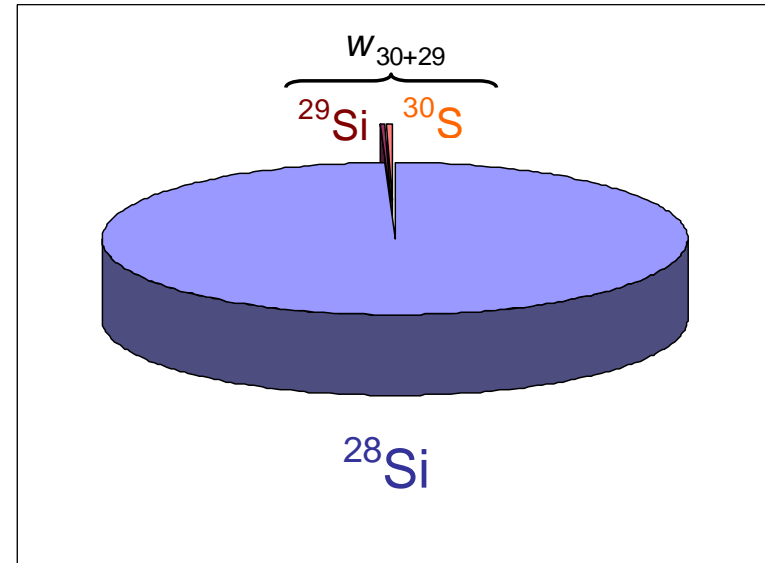
$$U < 10^{-7} \quad U \approx 10^{-3}$$



Isotopically enriched Si(28) material



- ^{29}Si and ^{30}Si treated like a virtual two-isotope-element impurity in the isotopically enriched Si (28) matrix
- Measurement of the mass fraction w_{30+29} by IDMS

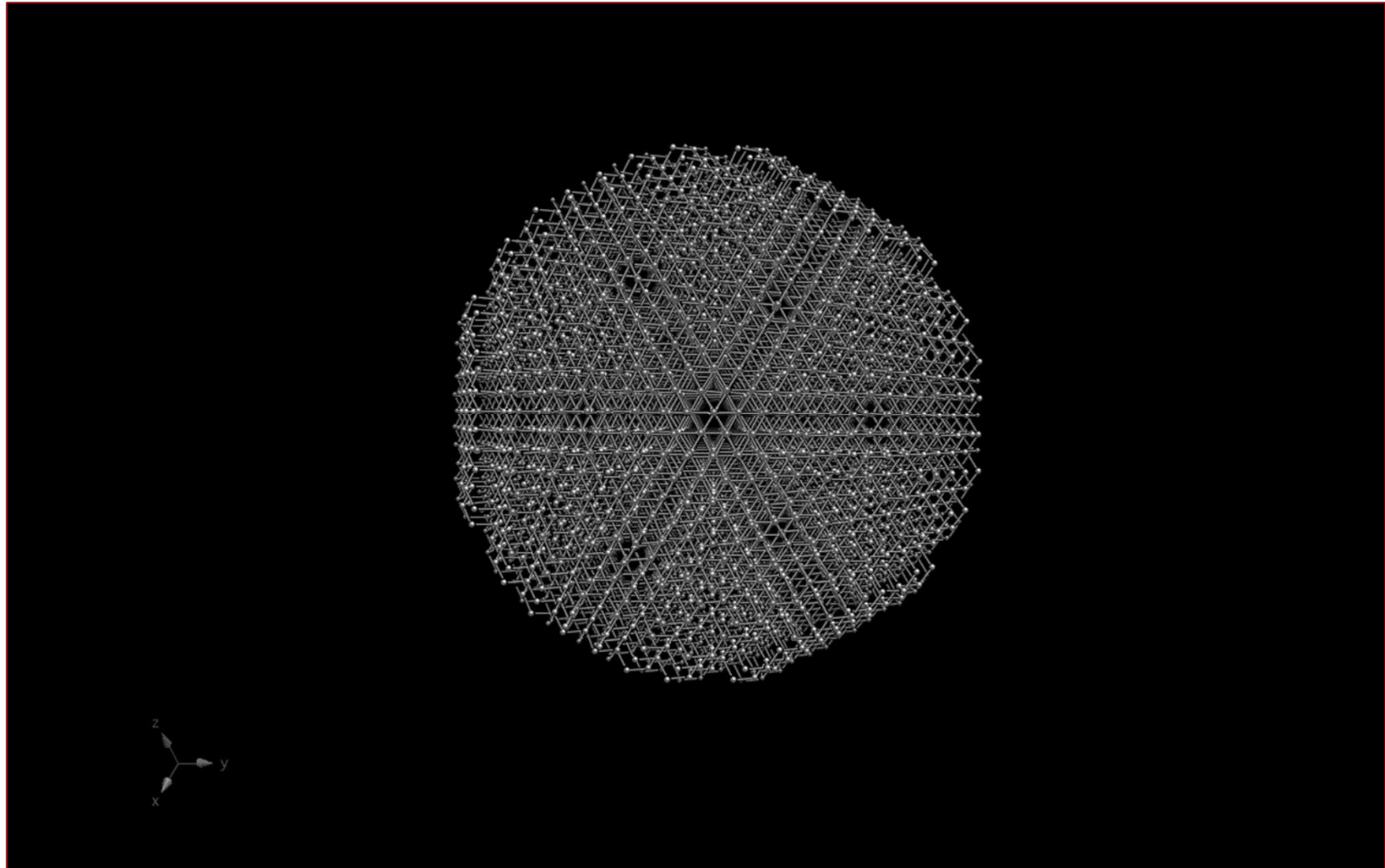


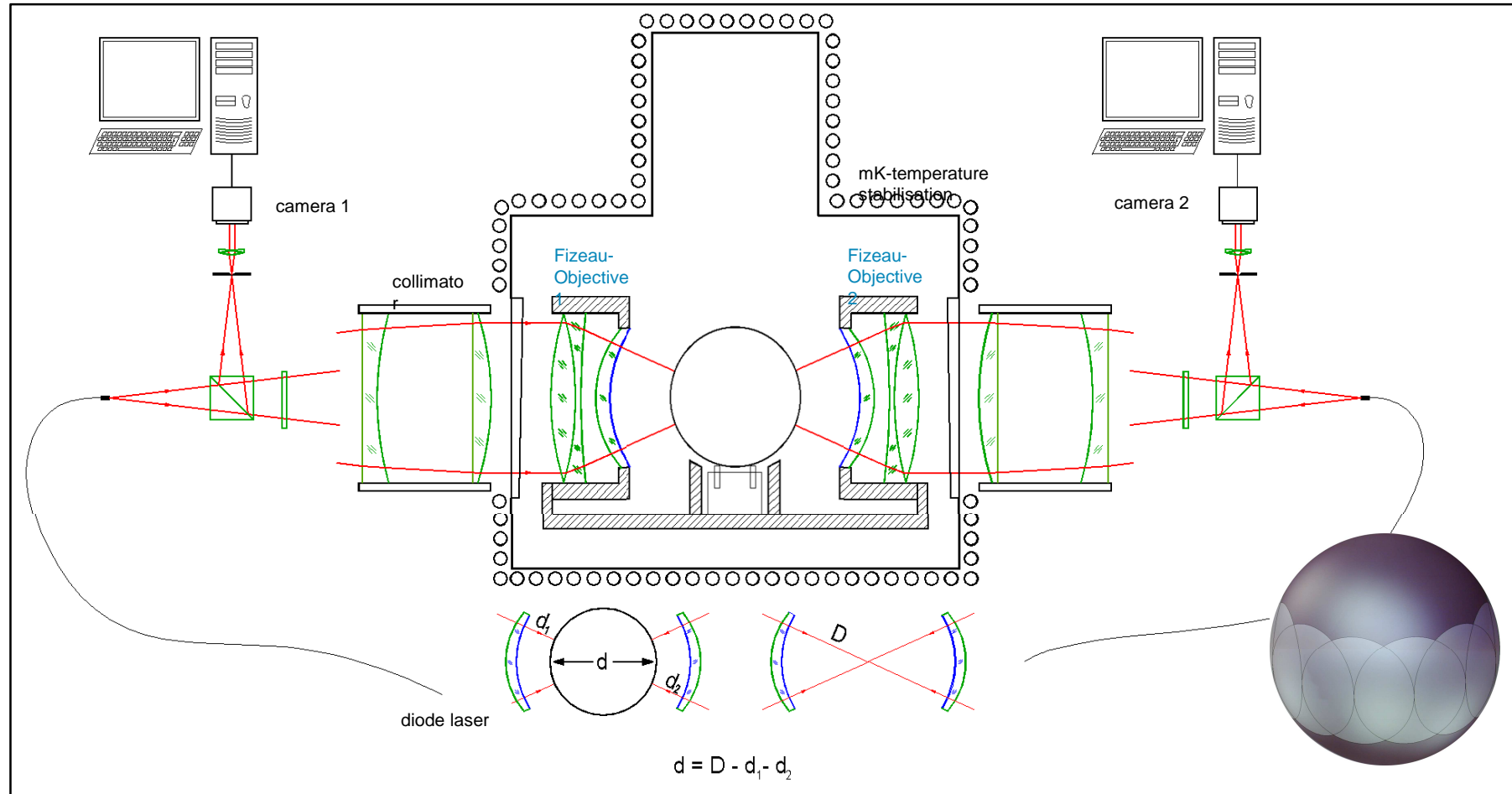
$$w_{30+29} = w_{\text{imp}} = \frac{m_{29} + m_{30}}{m_{28} + m_{29} + m_{30}} = \frac{m_{\text{imp}}}{m_{28} + m_{\text{imp}}}$$

Quantity	Relative uncertainty/ 10^{-9}	100 × Contribution
Molar mass	8	5
Lattice parameter	11	9
Surface	15	18
Sphere volume	29	66
Sphere mass	4	1
Point defects	3	1
Total	36	100

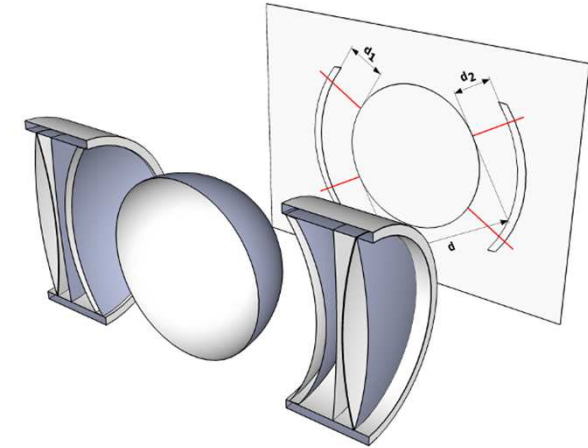
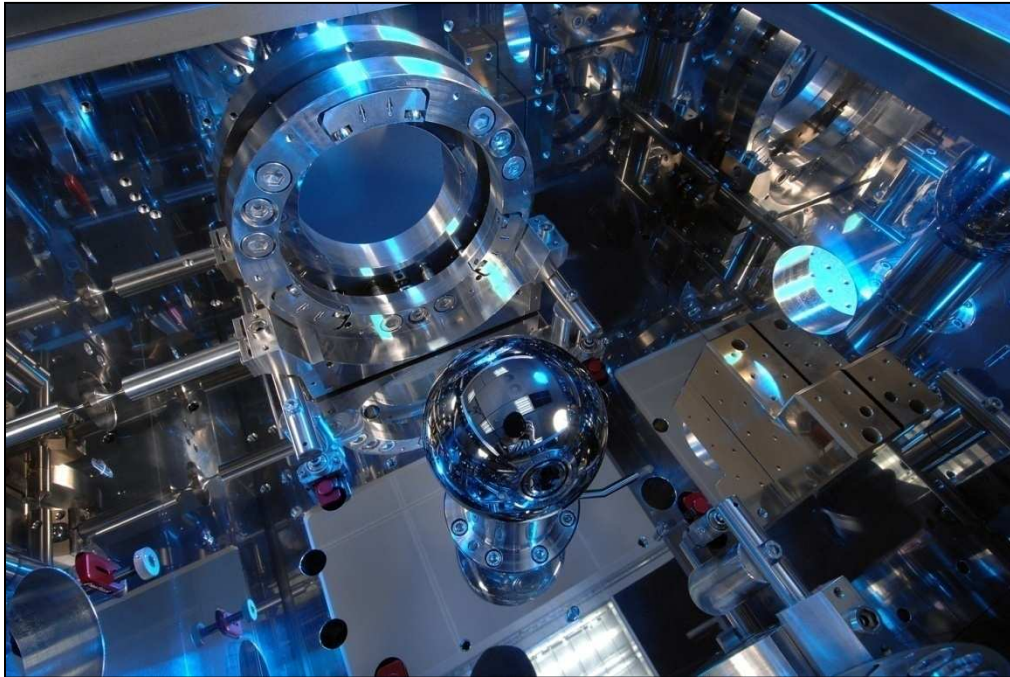
Der prozentuale Anteil der gesamten Messunsicherheit sind die relevanten Varianzanteile an der Gesamtvarianz- Die größten Beiträge zur Messunsicherheit liefern die Oberflächencharakterisierung und die Volumenbestimmung.

aus: B Andreas et al., *Metrologia*, 48 (2011) S1–S13





thousands of diameters are measured simultaneously

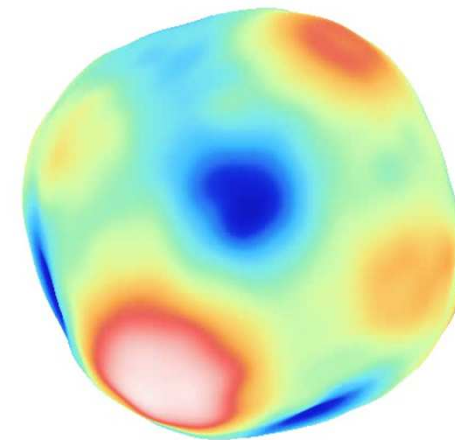


PTB's sphere interferometer with spherical symmetry

PTB's sphere interferometer enables complete topographies of spheres, $n_{\text{diameter}} \approx 600\,000$.

The radius uncertainty is 0.7 nm or 8×10^{-9}

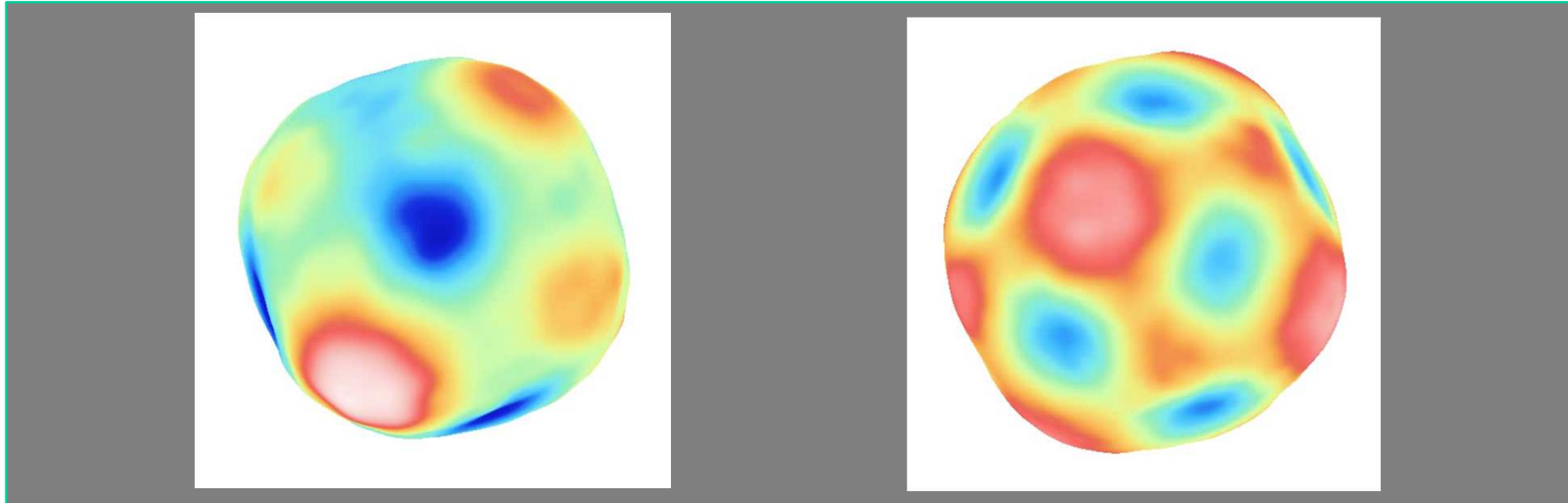
Radius topography of ^{28}Si -sphere S8. Peak to valley deviations from roundness amount to 99 nm.



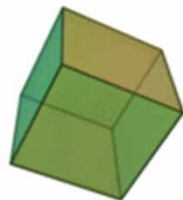
application of 3 marks



in a distance of 90°



Hexaeder (Würfel)



Kuboktaeder

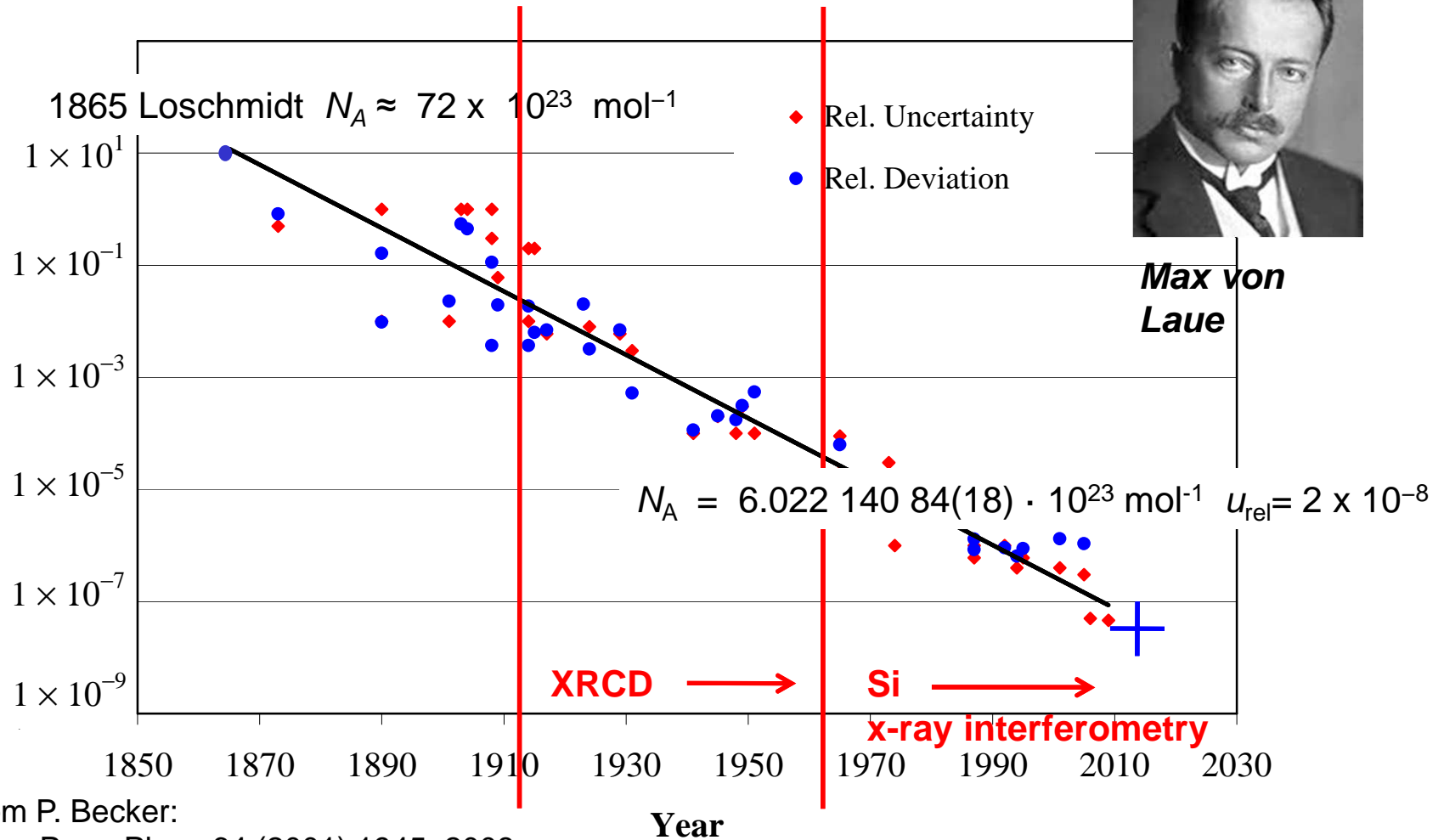


- working group 5.41, Dr. Arnold Nicolaus
- Measurement of ^{28}Si -S5

Avogadro constant: Relative uncertainty and deviation from CODATA



Max von Laue



from P. Becker:
Rep. Prog. Phys. 64 (2001) 1945–2008

The kilogram, kg, is the SI unit of mass; its magnitude is set by fixing the numerical value of the Planck constant to be equal to exactly $6.626\,068\,X \cdot 10^{-34}$ when it is expressed in the unit $\text{s}^{-1} \text{m}^2 \text{kg}$, which is equal to J s

$$N = 8V_{\text{sphere}} / a(^{28}\text{Si})^3$$

2.2 Realization by the X-ray-crystal-density (XRCD) method

To realize the definition of the kilogram, the mass m_s of (a ^{28}Si single crystal) sphere is... expressed in terms of the mass of a single atom

$$m_s = Nm(^{28}\text{Si})$$

and

$$m_s = hN[m(^{28}\text{Si})/h]$$

The XRCD experiment determines N ; $m(^{28}\text{Si})/h$ is a constant of nature whose value is... known to high accuracy and h is now exactly defined.

2. Realization of the definition of the mole

Currently, the most accurate method of realizing the mole is by counting ^{28}Si atoms in a single crystal of Si enriched in ^{28}Si using volumetric and X-ray interferometric measurements

$$N_{\text{A}} = \frac{8 \cdot M \cdot V_{\text{sphere}}}{m \cdot a(^{28}\text{Si})^3} \quad (1)$$

$$N = 8 V_{\text{sphere}} / a(^{28}\text{Si})^3 \quad (2)$$

$$n = N / N_{\text{A}} \quad (3)$$

One mol of ^{28}Si atoms is equivalent to the number of ^{28}Si atoms that is contained in a sample of a ^{28}Si single crystal with a volume of **12.05867069** cm³ at 20 °C and in vacuum. The relative standard uncertainty of this volume would be **2×10^{-8}** . (Hypothetical!)

Identification step:

In case that the specified elementary entity is ^{28}Si and the real crystal is **not** purely ^{28}Si also other elementary entities (elemental impurities, i.e. C, O, B and isotope impurities, i.e. ^{29}Si , ^{30}Si) and the volume of the surface passivation layer must be considered (i.e. excluded). In the ^{28}Si enriched single crystal Si-sphere AVO28-S5 the following statements apply:

One mol of ^{28}Si atoms is equivalent to the number of ^{28}Si atoms that is contained in a sample of the AVO28-S5 single crystal sphere with a volume of **12.05918321** cm³ at 20 °C and in vacuum.

The AVO28-S5 single crystal sphere contains **35.7452948469** mol of ^{28}Si atoms.

$$N_A h = \frac{c A_r(e) M_u \alpha^2}{2 R_\infty}$$

- N_A Avogadro-constant
- h Planck-constant
- c speed of light
- α fine-structure constant
- R_∞ Rydberg constant
- e elementary charge
- M_u molar mass constant = 1×10^{-3} kg/mol

c, h, N_A fixed in the definitionen of metre, kilogram and mole
 α und R_∞ remain independent measurands

$A_r(e), M_u$ dependent variables of those measurands

$A_r(e)$: changes mean deviation from $A_r(^{12}\text{C}) = 12$ - exakt

M_u : changes mean deviation from 1×10^{-3} kg/mol – exakt ($\leq 1,4 \times 10^{-9}$ ($k = 1$))

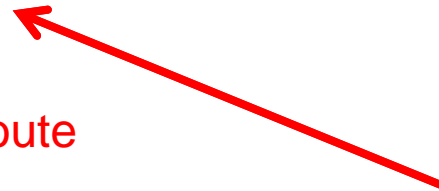
kilogram



Mole



Planck-route



Avogadro-route



$$n(X) = \frac{N_x}{N_A}$$

primary standard



- the most accurate realisation of the mole: the perfect implementation of a mise en pratique of the mole
- possibly the origin of the fixed value of the natural constant that accompanies the unit mole
- the only realisation of the mole that does not require the determination of a mass (i.e. is independant of the mass)
- a description that is closely linked to the mise en pratique of the kilogram so that the interrelation of the units can be made easily transparent
- a perfect tool to explain the mole to the world outside of the chemical community