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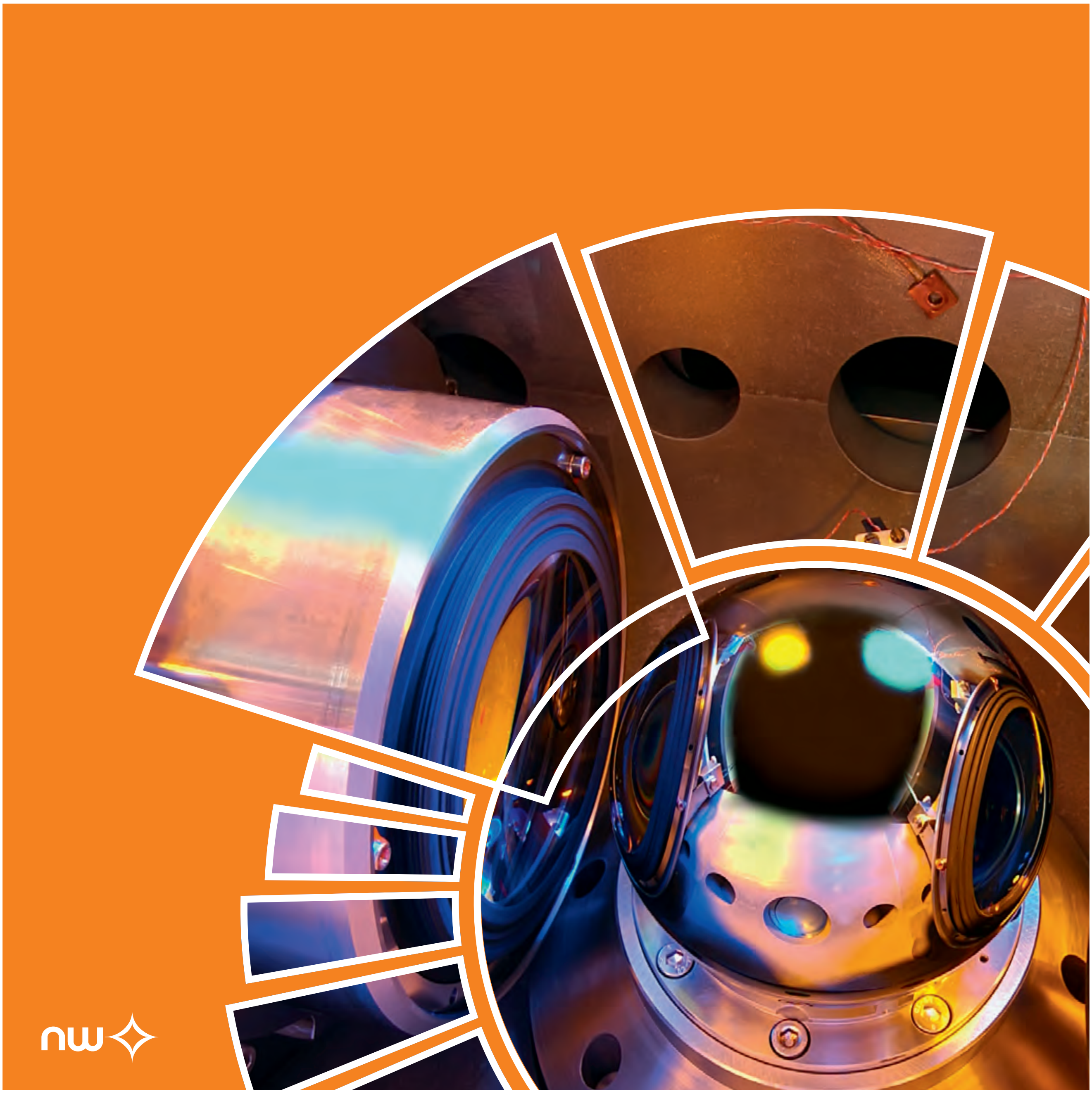
SPECIAL ISSUE

The System of Units



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Contents

The System of Units

Cover picture

The definitions of the base units referring to the SI system are on the brink of a fundamental change. In future, they are to be related to defined fundamental constants – the kilogram, for example, to Planck's constant (in the picture: a SI sphere of the Avogadro Project).

Impressum

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A Short Introduction to the International System of Units

Ernst O. Göbel*

Metrologists are currently facing big scientific challenges: They want to free the base units of their definitional inadequacies – you just have to think of the unit of mass and its embodiment by a certain metal cylinder in a safe near Paris – and place them instead on an unshakable foundation, as has already been done for the metre, whose definition now is based on the speed of light. If metrologists can master this challenge, then in future no longer will the International System of Units rest on seven base units, but in contrast, on a set of fixed fundamental constants.

A brief history of the SI

Since time immemorial, agreed units of measurement for quantities such as length, weight and volume have been needed for fair trade of goods. We know that the great cultures and states of old had a highly developed measurement system. Some impressive examples of this are the Nippur cubit dating from the third millennium BC, which was found in the remains of an ancient Mesopotamian temple and is now kept in the Archaeological Museum in Istanbul; the renowned royal cubit of the Egyptians, which was used as the basic measure for building the Egyptian pyramids; or the oldest sundial in Europe, found in Oropos in Greece and dated to about 350 BC.

With the emerging feudalism of the Middle Ages, however, the high metrological[1] culture was lost, and, thus, in Germany around 300 years ago there were more than 50 different standards for mass and over 30 different length standards. This made trade more difficult and encouraged misuse and fraud, until about 300 years ago, a development was started to put an end to this metrological "Tower of Babel". France led the way, and even at the height of the French Revolution, the French Academy of Sciences was requested to develop stable standards for mass and weight based on rational principles and "for all men and all times". Two options were discussed for the standard of length: the seconds pendulum and the length of a meridian of the Earth. Because of the dependence of the oscillation period of a pendulum on the local acceleration due to gravity, this option was not pursued. Instead, the two astronomers Jean-Baptiste Joseph Delambre and Pierre Méchain were commissioned to determine the length of a meridian of the Earth through triangulation of the distance of the meridian arc between Dunkerque and Barcelona. They were to define the unit of length, the metre, from this as the 40 millionth part of a meridian. As an embodied standard, this original metre was made of platinum and was placed in the Archives de France in 1799 (Mètre des Archives).

The unit of mass was derived from the unit of length as the mass of one cube of 1 dm edge length of pure distilled water at its greatest density (i. e. at 3.98 °C) and was called the kilogram. This event can be described as the birth of the metric system, which, however, was only accepted in Europe – even in France – very hesitantly at first. It, thus, took until 1875 for the metric measurands to be introduced with the foundation of the Metre Convention by a treaty which was signed by 17 nations at that time. Today 55 states have signed the Metre Convention, in addition to a further 33 countries and organizations which are associated members. The first General Conference[2] of the Metre Convention took place in 1889. During the conference, the new prototypes of the metre and the kilogram made of a platinum-iridium alloy were officially sanctioned as the international standards. The copies of these international prototypes – which were produced at the same time – were distributed among the Member States by drawing lots. The German Empire received the prototypes with the numbers 18 (for the metre) and 22 (for the kilogram). Shortly before, in 1887, the *Physikalisch-Technische Reichsanstalt (Imperial Physical Technical Institute – PTR)* had been founded in Berlin through the driving force of Werner von

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[1] Metrology: the science and application of precise measurement

[2] Conférence Générale des Poids et Mesures, CGPM

Siemens and Hermann von Helmholtz. Among other things it was to support industry and science through making measuring standards available and improving them. The *Physikalisch-Technische Bundesanstalt (PTB)*, founded in 1951 as the successor to PTR, has taken on this mandate and is, hence, the National Metrology Institute of the Federal Republic of Germany.

At the early General Conferences, which nowadays take place every four years, the system of the international units of measurement was continuously extended and improved. Some important milestones for the development of the SI system are simultaneously linked to many of the General Conferences. At the 10th CGPM in 1954, the units for length, mass, time, electric current, thermodynamic temperature and luminous intensity were designated and defined as the base units of the so-called practical system of units. At the 11th CGPM (1960), the metre was redefined in terms of the wavelength of light, specifically a yellow-orange spectral line of the noble gas krypton at about 0.6058 µm. The definition of the second by the ephemeris second was confirmed as the unit of time. The six units kilogram, metre, second, ampere, kelvin and candela were then introduced as the base units of the SI (Système International d'Unités). At the same time, rules for the SI prefixes and the derived units were compiled. A new definition of the second was adopted by the 13th CGPM in 1967/68 via the frequency of electromagnetic radiation corresponding to an electronic transition in the Cs isotope 133, and the 14th CGPM completed the SI base units with the mole, the unit for the amount of substance. On the occasion of the 17th CGPM in 1983, the metre was finally defined as the length of the path travelled by light in vacuum during a specific time, and the SI took on the form that is still valid today.

The SI today – and its limitations

Today's SI system, which is based on seven base units and on units derived from these, is a coherent system. In other words, the derived units can be defined as the products of powers of the base units, and the product of the powers only contains "1" as a numerical factor (e.g. $1\ \Omega = 1\ \text{m}^2\ \text{kg}\ \text{s}^{-3}\ \text{A}^{-2}$). The immediate consequence of this is that the numerical value equations have exactly the same form as the corresponding quantity equations.

Since absolute measurements cannot, as a matter of principle, be more precise than the uncertainty of the realisation of the corresponding unit, the realisation of the unit according to its definition and with the smallest possible uncertainty is a constant challenge which is always *per se* on the front line of the scientific and technical state of the art.

Although today's SI system largely fulfils the current requirements of science and technology, it is far from being the ideal "for all men and all times". Hence, tracing back the SI units as far as possible to fundamental constants – as is already the case for the second and the metre – is a task set by the Metre Convention for its member institutions. In the foreseeable future, completing this task for the ampere, the kilogram, the mole and the kelvin seems possible.

The general approach is the same for all measurement units. In order to avoid a scale jump in the envisaged redefinition of a unit on the basis of a fundamental constant, first of all the value of this constant[3] must be determined consistently, with the highest possible accuracy, in the existing system of units. For practical reasons, minimum requirements may be prescribed. In the next step, this value is permanently assigned to the respective fundamental constant, i.e. exactly. The redefinition can then be carried out on this basis. The next challenge is to find a practical path from this fundamental constant to the corresponding unit physically and technically with as few sources of measurement uncertainty as possible.

The new SI

Any modification of the definition of a unit in the SI is decided by the General Conference of the Metre Convention, based on a recommendation of the CIPM[4]. Any possible advantages of a redefinition – such as a lower uncertainty in its realisation or a greater stability – are to be thoroughly weighed up against possible disadvantages such as the difficulty to realise the unit or to explain the concept outside scientific circles, etc. In addition, it must be ensured – for practical and economic reasons – that the redefinition will not bring about a scale jump – either now, or in the foreseeable future. The metrological community is unanimous about the fact that defining a unit on the basis of a fundamental constant is the optimum solution[5] when it comes to stability. It is, however, important to pay attention to the consistency of the system of fundamental constants, since certain individual constants depend on each other due to physical laws.

Since the definition of the **metre** is already based on the speed of light, there is no reason for modifying it. The **second**, too, is already defined by means of a fundamental constant: the quantum-mechanical energy splitting caused by the hyperfine interaction of the ^{133}Cs atom in the ground state. The reason for a possible redefinition can therefore only be the desire to reduce the uncertainty and to improve the stability and, thus, to reduce the measuring times (averaging times). This will soon become reality with the so-called "optical atomic clocks", where the frequency of the

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[3] The accepted best numerical values according to the respective state of the art of research are determined and regularly published by an international commission of experts (CODATA's Task Group on Fundamental Physical Constants).

[4] Comité international des poids et mesures – the governing body of the Metre Convention.

[5] This is related to the hypothesis (which has – to date – not been refuted) that the fundamental constants are locally and – with the uncertainty required for metrological purposes – also temporally stable.

transition used for the definition no longer lies in the microwave range but in the optical spectral range.

To trace the **kilogram** back to a fundamental constant, two alternatives are currently under investigation. These are, however, not fully independent of each other. On the one hand, there is the so-called “watt balance experiment”, which traces the kilogram back to Planck's constant h, and – on the other hand – the Avogadro experiment, which links up the kilogram with the Avogadro constant N_A and the atomic mass unit.

For the envisaged redefinition of the unit of amount of substance, the relation between the **mole** and the kilogram will be abandoned. A possible definition could read: *The mole is the amount of substance in a system consisting of* $\{N_A\}$ *identical elementary entities. These elementary entities may be atoms, molecules or other particles.* As a result, the unit “mole” would be nothing but another name for the numerical value of the Avogadro constant.

The possible redefinition of the **kelvin** will no longer be based on a material property (of water), but on the thermal energy related to temperature. For this purpose, the value of the Boltzmann constant first has to be determined accurately enough at the temperature of the triple point of water.

Contrary to the very complicated definition of the **ampere** in today's SI, the unit of electric current could be defined very simply – at least conceptually – if it were possible to manipulate single charges reliably. If, for example, single charges q (e. g. electrons) were transported with a frequency f, the current would be $I = q \cdot f$. Since the frequency f can, in turn, be derived from an atomic clock, the ampere could thus be traced back to the elementary charge.

Conclusions

The International System of Units (SI) is facing fundamental changes as it is the aim of the metrologists to trace all SI base units back to fundamental constants. This means that fundamental redefinitions are to be expected for the kilogram and the mole, the ampere and the kelvin. And also the definition of the second will be adapted to state-of-the-art measurement capabilities (keyword: “optical clock”). The System of Units would thus be based on a set of defined fundamental constants – among them the speed of light, the Avogadro constant, Planck's constant, the elementary charge and the Boltzmann constant.

The impacts of this on our everyday lives, on industrial production and on the monitoring of environmental parameters will probably be hardly noticeable. The radio-controlled clock that gets us out of bed in the morning will keep on “ticking” at the same pace; the scales in the supermarket will show the same value; the components of a technical device which are produced in a multitude of different sites distributed all over the world will still fit together precisely to the micrometre during the final assembly; doctors will still be able to use their blood pressure monitors, ergometers or ECG devices. These everyday measurements, which, most of the time, do not have to achieve the smallest possible uncertainties, will not be affected by the redefinitions of the units. From a conceptual point of view, however, something fundamental will happen, since the units will be defined via the link-up to fundamental constants, i. e. regardless of space and time. No matter whether a measurement is performed in Japan, the USA, Germany or even on Mars – the result will be the same.

From a physical point of view, however, this aim will not be achieved until all precision measurements in question are realised with sufficiently small uncertainties, so that the realisations of the “new units” will then be just as good as those of the “old units”. As with all experimental work, it is difficult to forecast when this will happen. The current situation seems to indicate, however, that several more years of hard scientific and technical work will be necessary until this occurs. The upcoming General Conference of the Metre Convention (CGPM) in 2011 could therefore take place too early for a redefinition. It seems more likely that it will be the General Conference which will follow after that (the CGPM in 2015) where the “new SI” will be introduced. ■

Length – the SI Base Unit “Metre”

Harald Schnatz*

1 Overview

Each advanced civilization has developed a system of living together which allows the creation of large buildings or the indication of a chronological order of events. Each society is dependent on guaranteeing a fair exchange of goods *(Leviticus 19:35: “Ye shall do no unrighteousness in judgment, in meteyard, in weight, or in measure”)*. Reliable weights and measures (systems of units) are indispensable for this.

As long as these measures are only used within a certain country or society, the absolute size of the measurement unit only plays a subordinate role. Here it is enough for the chosen unit to be produced and disseminated with a sufficient reproducibility. Only with the emergence of trade across a border does the aspect of a generally recognized, precise measurement unit which is constant with time receive increasing importance.

The following article provides a brief overview of the development of the unit of length (Section 2) up to the definition which is valid today and its realization by means of frequency-stabilized lasers (Section 3). Section 4 is dedicated to the dissemination of the unit of length and shows how – with the aid of interferometric methods – a precisely known wavelength can be transferred to embodied measures or be used for determining unknown wavelengths. The last section deals with the question of how the frequencies of optical clocks at different locations can be compared with each other without a loss of precision and discusses several applications for high-precision optical frequencies.

2 Development of the Unit of Length up to the Current Definition

2.1 Historical units of length

In ancient times, lengths of body parts were used. The ell (cubit) and the foot, for example, were common as units of length *(Genesis 6:15: “And this is the fashion which thou shalt make it of: The length of the ark shall be three hundred cubits, the breadth of it fifty cubits, and the height of it thirty cubits”)*.

The oldest measure that we know of, the Nippur cubit, dates from the first half of the 3rd millennium BC (Figure 1). This measure weighs over 40 kg and is kept in the Museum of the Ancient Orient in Istanbul. Different engravings represent the then commonly used units of the ell, the foot and the finger. The length of an ell at 51.8 cm results from these divisions. All the pre-metric units of length can be derived from this ell [1].

In Egypt, at about the same time, the royal cubit was introduced as a measure of length. The primary standard was made of granite. Various wooden copies of this measure of length were produced as working standards and were compared

Figure 1:
Nippur cubit, the oldest known measure of length from the 3rd millennium BC. (Source of photo: http://de.academic.ru/pictures/dewiki/78/Nippur_cubit_.JPG).

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with the primary standard at regular intervals. Even that long ago, the calibration and traceability of a measure were an essential consideration in the introduction of a uniform measuring system. Using counterfeit measures was punished stringently.

Medieval units of length can also be traced back to body measurements. Charlemagne introduced the *foot* as a unit in the whole Kingdom of the Franks. In England, in 1011, the yard was defined by Henry I as the distance from the tip of his nose along his outstretched arm to the end of his thumb.

These measures were derived from the random body size of each particular ruler but they could be reproduced easily and, thus, came into general use (Figure 2). An early approach to defining a measure of length that did not depend on the arbitrary stature of a sovereign and could be derived from nature was found by the mathematician J. Köbel at the end of the 16th century (Figure 3). He suggested a so-called "natural measure" of: "16 men, large and small" who came out of church after mass one after the other and placed their feet in a line. The sixteenth part of this total length was then to be one foot [2].

Figure 2:
Example of a body measure: the Braunschweig cubit.

Figure 3:
J. Köbel's suggestion for defining a "natural measure". (Source of picture: Wolfgang Torge "Geschichte der Geodäsie in Deutschland", Gruyter, Walter de GmbH).

This measure was still basically a body measure, but because of its averaging of "many feet", he hoped that this definition would be more suitable for reproducing a measure of length at different locations.

This idea could not, however, prevail in the age of absolutism and so there were – until the middle of the 18th century – in the area covering the later German Empire alone, more than forty different cubits with lengths between 40 and 80 cm.

2.2 The Metre Convention

At the end of the 18th century, the discussion about a uniform measuring system that was to be based on natural constants began in Europe. The then existing diversity of different measures of length proved to be a decisive barrier to the emerging European trade.

In 1790, the French National Assembly ordered a committee to define a new standard of length. In contrast to the older length measures, which were predominantly derived from body measures, the new unit of length was to be traced back to a natural constant. As a basis, it was decided to use the length of that quadrant of the Earth's meridian which runs through Paris. One ten-millionth of this was to represent the new unit of length, the metre (derived from the Greek "μετρον" for measure).

A segment of the Parisian meridian between Barcelona and Dunkerque was chosen for the measurement (Figure 4). After many difficulties during the French Revolution, the two astronomers, Jean-Baptiste Joseph Delambre and Pierre Méchain, were able to submit their measurements to the National Convention (Figure 5) and the "Mètre des Archives" (the first prototype metre bar) was created. The distance between the end surfaces of a cuboid-shaped block made of platinum was officially recognized as a metre on 10 December 1799 and has been kept in the Archives de la République in Paris since then.

With the introduction of a new, generally valid unit of length, the aim was to have all countries measure with the same unit. It was, however, to take until 1875 before this thought was realized and the Metre Convention – for the establishment of an internationally recognized system of units – was founded as a treaty signed by 17 nations.

Even before the signing of the Metre Convention it emerged, however, that the Earth's diameter did not represent a real constant, and the prototype was no longer a match for the growing demands of developing precision metrology. As the above metre definition was also very complex to repeat, in 1872 it was decided to replace the bar of pure platinum with several copies made of a stable platinum-iridium alloy (90 % platinum and 10 % iridium). A total of 30 copies were produced. One of these new line scales with an X-shaped cross-sectional profile was selected by the General Conference on Weights and Measures (CGPM) in 1889 as the international prototype of the metre and was

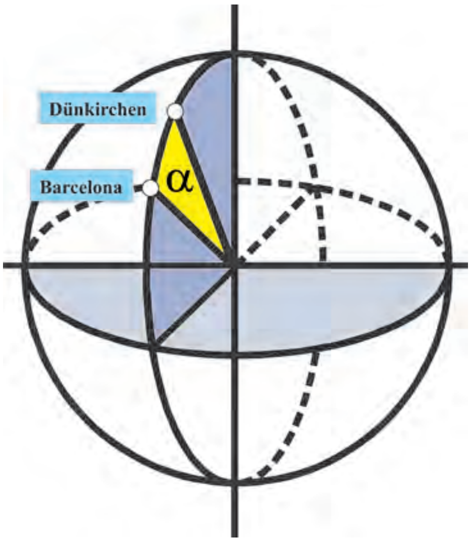

Figure 4:
Comparison of the distance between Dunkerque and Barcelona with the length of the quadrant of the Earth's meridian for the definition of the unit of length (Source of picture: J. Helmcke; PTB Mitteilungen **103**, (2003) p. 26.

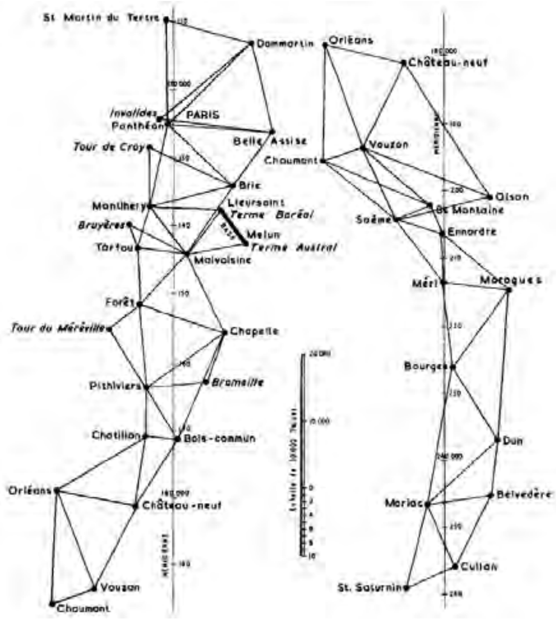

Figure 5:
Part of the network for Delambre's and Méchain's measurement of the quadrant of the Earth's meridian by means of triangulation (copied from the *Base du Système Métrique Décimal,* Tome 3, P1. III.).

used as the basis of the definition of the unit of length [3]. The other copies of the metre prototype were made available to the Member States of the Metre Convention.

The new standard bar was no longer derived from the meridian, but rather directly from the original prototype of the metre. The length of 1 metre was, thus, defined as:

> **"the distance between two lines on a standard bar of an alloy of platinum with ten percent iridium, measured at the melting point of ice."**

The original definition of the unit of length was based on the freezing point of water. Warmed up from 0 °C to 20 °C, the "metre" lengthens by about 0.3 mm. The metre prototype was kept as the valid definition and realization of the unit of length until 1960 (Figure 6). Line scales derived from it are still used today to transfer the unit to embodied measures.

2.3 The krypton lamp: the unit of length from 1960 to 1983

Realizing the metre by the metre prototype has the crucial disadvantage of this material standard being dependent on many external parameters and thus not being stable in time.

Possible ways of defining lengths more exactly than is allowed, in principle, by their definition were discussed very early on. The possibility of defining the unit of length by a light wavelength was, thus, portrayed by J. Babinet as far back as 1827. This idea was taken up in 1887 by A. A. Michelson who suggested using an optical interferometer for the measurement of length [4].

The wavelength of visible light represents a natural scale which offers a considerably higher resolution and which can be transferred to embodied measures with the aid of interferometers. Michelson and J. R. Benoît were, thus, able to determine the length of the metre prototype in units of a red cadmium spectral line at the International Bureau of Weights and Measures (BIPM). This meant that it was possible for the first time to link the unit of length to a natural constant which can be reproduced at any chosen location without a loss of precision.

Significant advances in length measuring techniques were then achieved in the 20s to the 50s of the last century. They are closely connected with the then Head of the Length Laboratory at PTR, Wilhelm Kösters [5], and his colleague and later successor at PTB, Ernst Engelhard.

With the development of an interference comparator (1920) [6], of standard lamps for length measuring techniques (1928) [7], and of a vacuum wavelength comparator – with which the influence of the refractive index of air is eliminated – by Kösters, and the development of a wavelength standard lamp by Engelhard [8], the way was paved for a modern length measuring technique. Interference comparators according to Kösters are still used worldwide for calibrating gauge blocks [9].

The red wavelength of the krypton lamp developed by Engelhard at the Physikalisch-Technische Bundesanstalt (Figure 7) was superior to every embodied measure in terms of stability and reproducibility. The transition $2p_{10} \rightarrow 5d_5$ of the krypton delivers a narrow line in the red spectral range (λ = 606 nm), which was stimulated by an electron impact in a gas discharge lamp. To avoid overlapping by the different krypton isotopes, the lamp was filled with highly enriched ^{86}Kr. The wavelength of the selected red spectral line of the ^{86}Kr isotope amounts to $\lambda_{Kr} = 0.605\,780\,210\,3$ µm. The work of Kösters and Engelhard then led to the redefinition of the metre on the basis of the wavelength of krypton in 1960 [10]. One meter was then:

> **"to be equal to 1 650 763.73 wavelengths in vacuum of the radiation corresponding to the transition between the levels $2p_{10}$ and $5d_5$ of the krypton 86 atom.[1]"**

As a result, an SI unit was traceable, for the first time, to an atomic constant, and a determination that could be reproduced well was found, the accuracy of which was better by a factor of 10 than the realization that had been used previously with the prototype of the metre. By means of the krypton lamp, the metre could be realized with a relative uncertainty of 10^{-8}.

This definition of the metre coincided with the discovery of the laser. Because of the extremely high time-dependent and spatial coherence of the laser radiation, it became clear early on that the laser represented an excellent light source for interferometry. The optical frequency can, however, vary by many 100 MHz, so that the use of a laser as a reference wavelength requires the stabilization of the laser frequency. In the course of time, the development of a great number of stabilized lasers succeeded, whose relative reproducibilities exceeded that of the krypton lamp by many orders of magnitude.

Figure 6:
International prototype of the meter, a line standard with X-shaped cross-sectional profile made of platinum-iridium.

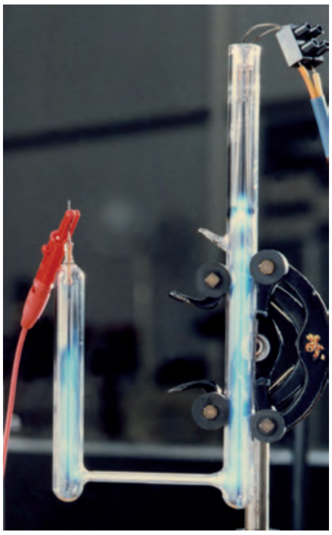

Figure 7:
Krypton lamp according to Engelhard for the realization of the unit of length 1960–1983.

One of the most wide-spread frequency/wavelength standards is the helium-neon laser (He-Ne laser) at a wavelength of 633 nm (see Section 5b). For the stabilization of its output frequency, atomic transitions in an iodine molecule are used. Today's iodine-stabilized He-Ne lasers reach a frequency uncertainty of approx. 10 kHz; at a frequency of 473 612 353 604 kHz this corresponds to a relative uncertainty of $2 \cdot 10^{-11}$ [11].

3 Today's Definition of the Unit of Length and its Realization

3.1 The definition of the metre since 1983

Twenty years after the unit of length had been defined via the radiation of the krypton lamp, the time was ripe again: The invention of the laser had opened up a broad field of application possibilities and allowed wavelengths to be realized with a precision so far unexpected. If one wanted to keep up with this development, it was foreseeable that the definition of the unit of length would have to be adapted to the constantly progressing metrology and that other redefinitions would follow within a few years.

As the frequency and the wavelength of an electromagnetic radiation are interrelated via the speed of light, it seemed obvious to link the definition of the metre to the second by assigning a fixed value to the speed of light in vacuum c. By precision measurements of the wavelength and of the frequency of a methane-stabilized He-Ne laser, the value of the speed of light had been determined with great accuracy [12]. A limiting factor was the wavelength uncertainty of the krypton lamp, which was the realization of the unit of length at that time. A further reduction in the measurement uncertainty – maintaining, at the same time, the then valid definition – was, therefore, ruled out. For that reason, in 1975, the CGPM recommended using the measured value of the speed of light c for the definition of the unit of length [13][2] . In 1983, the 17th General Conference on Weights and Measures, the CGPM, accepted this proposal and determined the following:

> **The metre is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.**

This definition, which defines the value of the speed of light in vacuum as c = 299 792 458 m/s, as a fundamental constant with the uncertainty "zero", is closely connected with the definition of the second.

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[1] The 11th Conférence Générale des Poids et Mesures (CGPM),

considering

- that the international Prototype does not define the metre with an accuracy adequate for the present needs of metrology,
- that it is moreover desirable to adopt a natural and indestructible standard,

decides

1. The metre is the length equal to 1 650 763.73 wavelengths in vacuum of the radiation corresponding to the transition between the levels $2p_{10}$ and $5d_5$ of the krypton 86 atom.
2. The definition of the metre in force since 1889, based on the international Prototype of platinum-iridium, is abrogated.
3. The international Prototype of the metre sanctioned by the 1st CGPM in 1889 shall be kept at the BIPM under the conditions specified in 1889.

Today’s definition of the unit of length via the speed of light is abstract and does not, initially, provide any concrete approach for the realization of the metre. For that reason, the International Committee for Weights and Measures (CIPM) published recommendations for the realization of the metre (“Mise en Pratique”), together with the redefinition. These recommendations are constantly adapted to the progressing technical development and the recommended wavelengths and reference frequencies are updated

3.2 The realization of the metre

For the realization of the unit of length, the CIPM recommends the following three methods:

a. **Time measurement:**
The length of a section *L* results from the measured time *t* which a plane electromagnetic wave in vacuum needs for the section *L*, according to the relation $L = c \cdot t$.

Length measurements via time intervals are excellently suited for large distances, as here the required time resolution can be easily realized with modern clocks. Two examples may be briefly mentioned here:

Measurement of the lunar orbit:
In the case of the so-called Lunar Laser Ranging (LLR), short laser pulses are emitted from stations on Earth, reflected by reflectors on the Moon – which have, for example, been left there by the American Apollo missions between 1969 and 1973 – and received again on Earth by receiver telescopes after the signal travelling time *t* [14]. The distance between the Earth and the Moon then results from half the signal travelling time, multiplied by the speed of light *c*. LLR measurements which are performed today reach accuracies in the range of cm and can thus give information about the Earth-Moon system.

Worldwide navigation satellite system:
The most commonly known **Global Navigation Satellite Systems (GNSS)** are surely the American **Global Positioning System GPS** and the European system Galileo which is under construction. Up to 30 satellites orbit the Earth at a flight altitude of approx. 25 000 km and emit their orbit and time data. To determine the position of a receiver on Earth, at least 4 satellites must be received simultaneously. From the measured time of flight between the receiver and the satellite, the current position (including the altitude) of the receiver can be determined. One’s own position can be determined exact to a few metres even with commercially available mobile pocket receivers.

b. **Frequency measurement:** Realization of the unit of length by laser
The vacuum wavelength λ of a plane electromagnetic wave results from the measured frequency ν in accordance with the relation $\lambda = c / \nu$.

As the speed of light directly interlinks the wavelength and the frequency of an electromagnetic radiation, a strict distinction between the wavelength and the frequency of a laser will, in the following, no longer be made. If the frequency of a laser is stabilized by suitable measures, this is called a “wavelength standard” or “frequency standard”. Both terms are mostly used synonymously.

For applications in which a stable frequency is to the fore, the term “frequency standard” is most frequently used. In length measuring technique, stabilized lasers are mostly referred to as wavelength standards as here, the wavelength of the radiation represents the reference quantity.

For interferometric measurements, light of a known – and as stable as possible – wavelength is required. The required wavelength stability is achieved by suitable measures (stabilization), e. g. by comparison with small atomic absorption lines. The basic principle of a frequency-stabilized laser is shown in Figure 8:

Atoms, ions or molecules have exactly known excitation spectra, whereby the energy difference $\Delta E = E_a - E_b$ between the single levels E_a and E_b corresponds to the frequency ν of an electromagnetic wave. $\Delta E = h\,\nu_{ab}$ is valid, h being Planck’s constant. These transitions represent exactly known reference frequencies. The atomic absorbers may be contained in a vessel, move in an

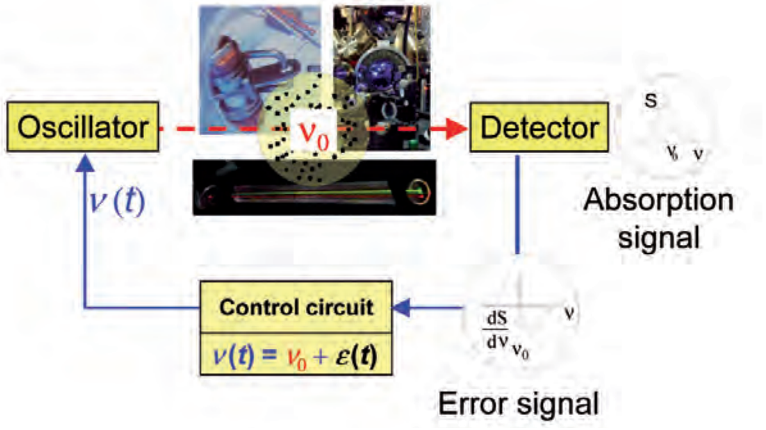

Figure 8:
Scheme of a frequency/wavelength standard. Ions, atoms or molecules serve as absorbers.
ν_0: “Unpertubed” transition frequency
$\varepsilon(t)$: Frequency noise, systematic shifts

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[2] Resolution 2 of the 15th CGPM (1975): Recommended value for the speed of light

The 15th Conférence Générale des Poids et Mesures, considering the excellent agreement among the results of wavelength measurements on the radiations of lasers locked on a molecular absorption line in the visible or infrared region, with an uncertainty estimated at ± $4 \cdot 10^{-9}$ which corresponds to the uncertainty of the realization of the metre, considering also the concordant measurements of the frequencies of several of these radiations, recommends the use of the resulting value for the speed of propagation of electromagnetic waves in vacuum c = 299 792 458 metres per second.

atomic or molecular beam or they may be stored in an electromagnetic trap (ions) or in an optical lattice.

If the radiation of a laser passes through this ensemble, the tuneable radiation of a laser can interact with the atoms if the laser frequency ν_L agrees with the frequency ν_{ab} of the atomic transition. If, for example, the absorption of the laser beam caused by atoms is measured, an error signal can be generated from it (Figure 9) which adjusts the laser frequency with the aid of an electronic control circuit in such a way that $\nu_L = \nu_{ab}$ is valid

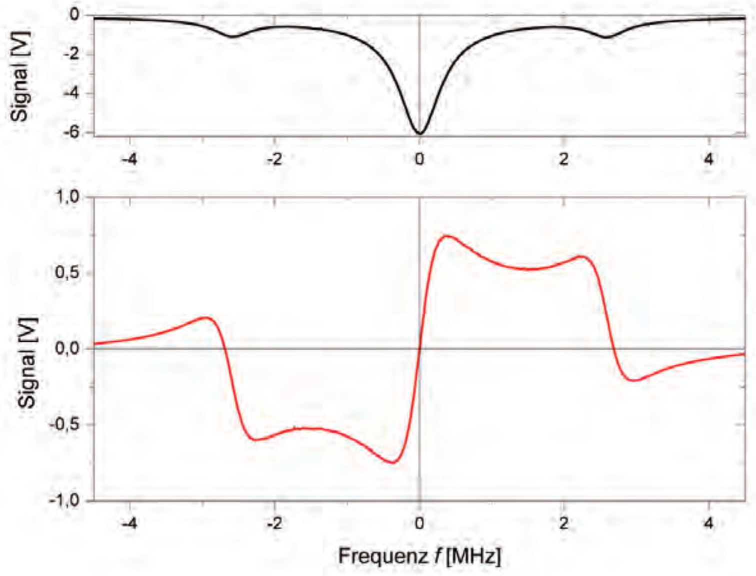

Figure 9:
Signal of the saturated absorption (black) and of the associated dispersion signal for the frequency stabilization of a Nd:YAG laser (red) at a modulation frequency of 5.185 MHz.

For the stabilization, optical transitions with a high quality factor $Q = \nu/\delta\nu$, which can be observed with as large a signal-to-noise ratio (SNR) as possible, are advantageous. If, in addition, transitions are selected which depend only to a small extent on external influences (electromagnetic fields, pressure, temperature), one obtains a laser wavelength standard or a frequency standard of high temporal stability and accuracy. In this way, a wavelength which has been measured once – and thus the unit of length – can be maintained permanently in laser wavelength standards.

For length metrology, iodine-stabilized lasers have proved to be excellently suited. The iodine molecule offers a rich spectrum of small absorption lines which reach from the near infrared to the green wavelength range [15]. These lines belong to the transition between the electronic B state and the X ground state.

In particular helium-neon lasers at a wavelength of $\lambda = 633$ nm are widely used. These lasers reach a relative frequency uncertainty of $2.5 \cdot 10^{-11}$ [11].

In addition to gas lasers, diode-pumped solid lasers have been developed in the past years which – in addition to having a higher optical power – also reach a better short-time stability and a higher accuracy.

In the emission range of a frequency-doubled laser at 532 nm, strong, narrow absorption lines of the iodine molecule are located. They are almost ideal references for the stabilization of frequency-doubled Nd:YAG lasers. Both the frequency spacings of the single hyperfine components [16–18] and the optical transition frequencies [19–22] were exactly determined.

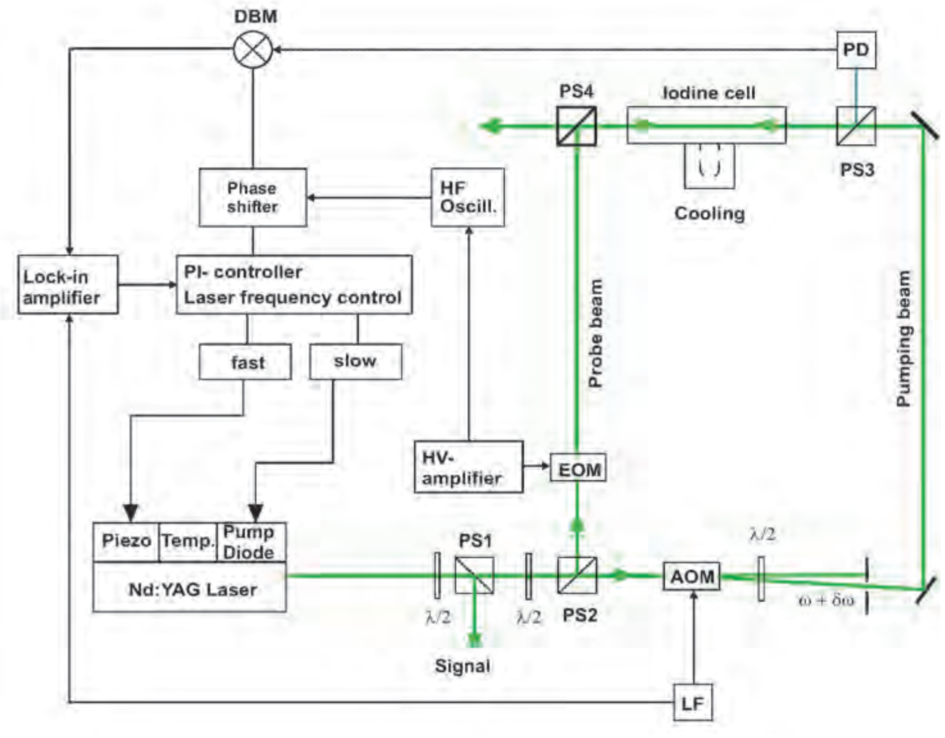

Figure 10:
Experimental set-up for frequency stabilization by means of frequency modulation spectroscopy of an Nd:YAG laser on hyperfine components of the iodine molecule:

AOM:	Acousto-optical Modulator
DBM:	Double-balanced Mixer
EOM:	Electro-optical Modulator
LF:	Frequency generator
PD:	Photodiode
λ/2:	wave plate
PS:	polarizing beam splitter

For the frequency stabilization, different spectroscopic procedures such as, for example, wavelength modulation spectroscopy and frequency modulation spectroscopy, are available [23–25].

The Nd:YAG laser described in the following uses saturated absorption of the hyperfine components of the P(54) 32 – 0 I_2-transition at a wavelength of λ = 532 nm [26]. The I_2-molecules are located in an absorption cell made of glass. The vapour pressure, i. e. the density of the iodine molecules, can be adjusted via the temperature of a so-called cooling finger.

For the generation of the error signal required for frequency stabilization, the laser radiation is split up at a polarizing beam splitter (PBS2) into counter propagating pumping and sampling beams (Figure 10). By means of a wave plate, the power ratio of pump and sample beam can be adapted. The sample beam is displaced in its frequency and amplitude-modulated by means of an acousto-optical modulator. The pumping beam passes through an iodine cell 50 cm in length and periodically saturates the absorption of the molecules, whose Doppler-shifted transition frequency agrees with the frequency of the pumping beam. This saturated absorption is detected by the counter propagating sampling beam. In addition, a phase modulation is impressed to the weak sample beam by means of an electro-optical modulator (EOM) [25]. In the case of resonance, an intensity modulation occurs at the frequency of the phase modulation which is measured with detector PD. This modulation is then demodulated and used to generate the error signal. To suppress frequency shifts by disturbing linear absorption, the demodulated signal is, with the aid of a lock-in amplifier, additionally detected phase-synchronously before it is used for the stabilization of the laser.

Frequency comparisons with further I_2-stabilized Nd:YAG lasers exhibit a relative frequency instability of $< 2 \cdot 10^{-13}$ at an averaging period of 1 second. At an averaging period of 1000 s, it was possible to achieve relative frequency instabilities of $5 \cdot 10^{-15}$ [27]. The deviation of the laser frequency of different systems is usually smaller than 3 kHz. In addition to the reproducibility of the frequency standards, this deviation is caused by smallest impurities of the iodine cells with other gases.

At short averaging periods, I_2-stabilized, frequency-doubled Nd:YAG lasers (see Figure 11) already reach a stability which is larger by approx. 2 orders of magnitude compared to I_2-stabilized He-Ne lasers [28].

Figure 11:
I_2-stabilized, frequency-doubled Nd:YAG laser.

c. Recommended reference wavelengths *λ* or reference frequencies *ν*:

The application of these highly stable frequencies in length measurements requires the exact knowledge of the frequency. If it is known, the wavelength can be calculated via the relation $\lambda = c / \nu$. In the past, the exact determination of the frequency was a difficult problem. By means of frequency chains, selected optical frequencies of a few 100 THz were compared with the frequency of a primary Cs clock [29, 30]. The measurement of optical frequencies was possible only in a few national institutes and required an enormous effort.

For that reason, CIPM published a list of selected radiations whose frequencies have been measured and which can, thus, be used for the realization of the unit of length. In addition to stating the frequency and the vacuum wavelength, this list contains exact data about the required operating parameters.

These radiations are, above all, generated by stabilized lasers. Former radiation sources such as, for example, the krypton lamp, can also still be used for the realization if only a low accuracy is required. In connection with more precise instructions for the operating conditions to be met, these radiations can be used with the stated uncertainty without having to redetermine the frequency *ν* again each time.

Figure 11 shows that I_2-stabilized lasers allow an uncertainty in the range of $1 \cdot 10^{-11}$ to be reached. This is usually absolutely sufficient for length measurements.

3.3 Frequency standards and wavelength standards of the latest generation

In addition to the use as wavelength standards in length metrology, stabilized lasers are also used as frequency standards. Due to the high optical fre-

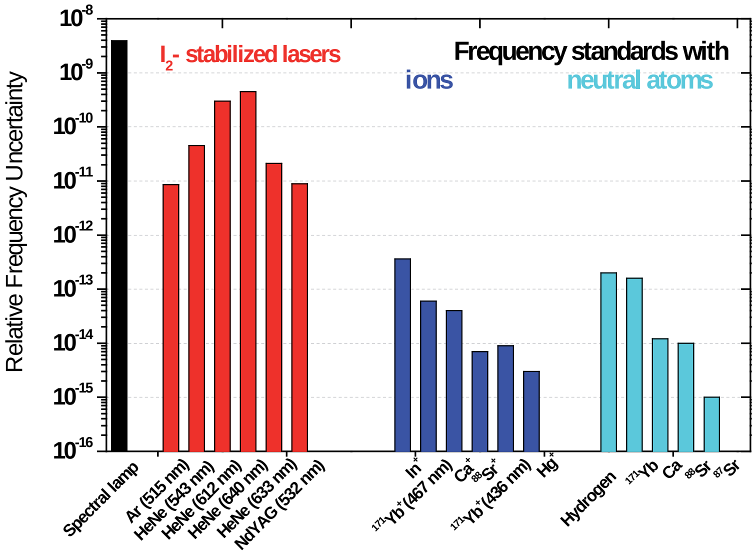

Figure 12:
Relative frequency uncertainty of some of the radiations indicated in the list of recommended wavelengths/frequency standards [34].

quencies (some 100 THz) and due to the extremely narrow transition lines of the atoms used, these lasers reach an instability in the range of $1 \cdot 10^{-15}$ at an averaging time of one second. Today, the smallest uncertainties are reached by lasers which use as a reference a single ion stored in an electromagnetic trap [31], an ensemble of neutral atoms prepared in a magneto-optical trap [32] or atoms stored in an optical lattice [33].

At present, it is being investigated worldwide to what extent optical frequency standards can be used for a future realization of the SI base unit the “second”. Due to its extremely high short-time stability and the obtained small uncertainty, some frequency standards from the list of recommended radiations were already proposed in 2006 as a secondary realization of the unit of time (so-called optical clocks) [34].

Among these frequency standards, there are two optical frequency standards which are investigated at PTB [35, 36].

For the achievable accuracy and instability of an (optical) clock, several factors have to be considered:

- on the one hand, systematic shifts of the undisturbed line centre limit the accuracy due to external disturbances or interactions between the atomic absorbers,
- on the other hand, the linewidth and the signal-to-noise ratio determine the achievable instability when the atomic resonance is interrogated.

A measure of the instability is the Allan standard deviation $\sigma_y(\tau)$ as a function of the averaging period τ. In the ideal case, it is given by

$$\sigma_y(\tau) = \frac{\Delta\nu}{\pi \cdot \nu_0} \sqrt{\frac{T}{N}} \cdot \frac{1}{\sqrt{\tau}} \ ,$$

T describing the cycle time required for the interrogation, N the number of detected atoms or ions, $\Delta\nu$ the Fourier-limited linewidth and ν_0 the frequency of the transition.

In the case of frequency standards with single ions, the instability is limited by the fact that only one particle is interrogated. If many ions are stored simultaneously in a Paul trap, their electric interaction leads to a degradation of the localization and, thus, to a larger uncertainty. Due to the extremely long storage time of the ion in the Paul trap and the small natural linewidth of the transition used, the achievable linewidth is usually limited by the linewidth of the interrogation laser. Today’s interrogation lasers reach linewidths from a few hertz [37] to a few 100 mHz [38] so that relative stabilities of a few 10^{-15} can be reached at an averaging period of 1 second [39, 40].

An alternative to the ion clocks described in the article of A. Bauch [41] are clocks with cold, neutral atoms. In the past, different approaches such as, for example, the use of an atomic beam [42] or the preparation of cold atoms in a magneto-optical trap (MOT) were investigated [43, 44].

Today, optical lattice clocks are favoured which use a $^1S_0 - {}^3P_0$ transition with a very low natural linewidth (for ^{87}Sr, only approx. 1 mHz) and store the atoms in standing light waves [45]. The most simple one-dimensional optical lattice is formed by a laser beam reflected back on itself. The atoms are trapped in the intensity maxima of the standing wave of the optical lattice.

In contrast to the spectroscopy of the clock transition in a MOT, the atoms in a lattice clock are interrogated in the presence of this trapping field. This usually leads to a large AC Stark shift of the involved levels. It was, however, possible to show that – when a “magic wavelength” is irradiated – the displacement of the ground state and of the excited state are of the same magnitude and thus compensate each other [46]. In the case of a magic wavelength of approx. 813 nm, ^{87}Sr atoms can, for example, be stored in the ranges of high field strength in the lattice, without shifting the frequency of the $^1S_0 - {}^3P_0$ reference transition.

By laser cooling and subsequent storage in an optical lattice, the atoms are confined in the Lamb-Dicke regime [47]. A consequence of this localization to ranges clearly smaller than an optical wavelength is that, for example, contributions of the Doppler effect of first and second order can be neglected. In addition, the collisional shifts can be drastically reduced when multi-dimensional lattices are used, because the lattice is, on average, occupied by less than one atom. As up to one million absorbers are interrogated at the same time, clearly higher stabilities can be reached with lattice clocks than with single-ion clocks [48].

At present, magnesium [49], strontium [50], ytterbium [51] and mercury [52] are being investigated for optical lattice clocks. The best of these clocks work with ^{87}Sr and are investigated in Boulder [53, 54], Paris [55, 56], Tokyo [57], and at PTB [58]. Additional Sr lattice clocks are being established, for example, in Florence and London.

At PTB, the frequency of the clock transition in the ^{87}Sr atom has lately been compared directly with the frequency of a primary Cs fountain clock with a relative uncertainty of 10^{-15} [59]. In this comparison, the contribution of the ^{87}Sr frequency standard to the overall uncertainty was estimated to be $2 \cdot 10^{-16}$.

Figure 13 shows that – in spite of different set-ups – the relative frequencies of the Sr lattice clocks of the JILA, of Tokyo University, of SYRTE and of PTB show an agreement with one another of better than $3 \cdot 10^{-15}$. This fact shows the potential of the lattice clocks and confirms ^{87}Sr impressively as a secondary realization of the second [34].

One basic requirement for the inclusion in the list of radiations recommended by the CIPM is that the frequency of these optical transitions has been compared directly with the frequency of a primary time standard. In the following section, this traceability of optical frequencies to the base unit “second” by means of a frequency comb will be briefly described.

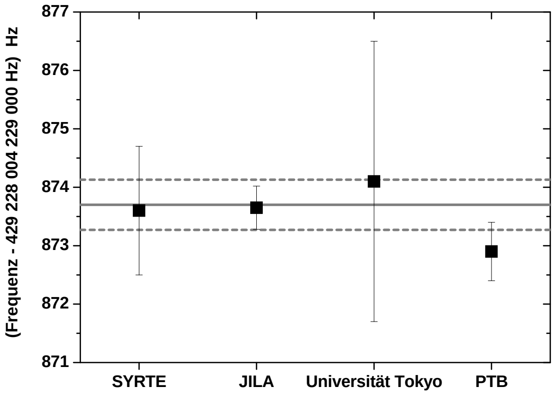

Figure 13:
Frequency of the ^{87}Sr clock transition, measured at different laboratories: SYRTE [55], JILA [54], Tokyo University [57], and PTB [59]. The horizontal lines show the value recommended by the CIPM and the uncertainty (broken line) for ^{87}Sr as a secondary realization of the second [34].

3.4 Traceability of the optical frequency to the unit of time: frequency combs

The first experiments to compare optical frequencies directly with the Cs atomic clock utilized the method of frequency multiplication. Here, a harmonic wave was generated from the known frequency of an oscillator. A further oscillator with an output frequency close to the harmonic wave was then coupled to the harmonic wave by means of a phase control circuit. This procedure was repeated successively over many steps until a microwave frequency was multiplied to the optical range [29].

Such a frequency chain had the disadvantage that a frequency chain of its own had to be established for practically every optical frequency to be measured.

Significant progress in the field of optical frequency measurement was achieved by the invention of the frequency comb generator [60].

The key technology for the measurement of the frequency of optical frequency standards consists in frequency comb generators which allow an optical frequency of a few 100 THz to be imaged without accuracy loss on radiofrequencies which can be easily measured (typically 10 – 100 MHz) and, thus, be compared with the frequency of a primary standard for time and frequency (of the Cs clock).

The frequency comb is a mode-locked laser which emits extremely short pulses separated by a time interval Δt which corresponds to the time of circulation in the laser resonator. The reciprocal value of the time interval is referred to as pulse repetition frequency f_{rep}. This pulse repetition frequency $f_{\text{rep}} = 1/\Delta t$ can be measured easily with a fast photodiode.

Due to non-linear effects in the laser resonator, each laser pulse experiences an additional small phase shift per cycle which causes a shift of the phase of the light relative to the envelope of the pulse. In the frequency range, this phase shift per cycle results in a shift of the whole frequency comb spectrum by a contribution ν_{ceo}. The offset frequency ν_{ceo} corresponds to the absolute position of the comb modes with respect to the zero point of the frequency.

The particularity of this laser is the special frequency spectrum which consists of a great number of equidistant modes which correspond – metaphorically speaking – to the millimetre lines on a ruler (Figure 14). With it, each single mode m of the frequency comb can be completely described in the frequency space by two parameters. The following is valid: $\nu(m) = m \cdot f_{\text{rep}} + \nu_{\text{ceo}}$.

The unknown absolute frequency ν_{Laser} of a laser to be measured is obtained by measuring the beat frequency $\Delta\nu$ with a specific mode, provided that also the mode reference number n is determined (e. g. with a simple wavelength measuring instrument). The frequency of the laser is obtained as $\nu_{\text{Laser}} = \nu \cdot f_{\text{rep}} + \nu_{\text{ceo}} + \Delta\nu$.

A phase-coherent frequency measurement thus means that the optical frequency ν_{Laser} is traced back to three radio frequencies (f_{rep}, ν_{ceo}, $\Delta\nu$) and a multiplier n. Thereby, the attainable accuracy is not

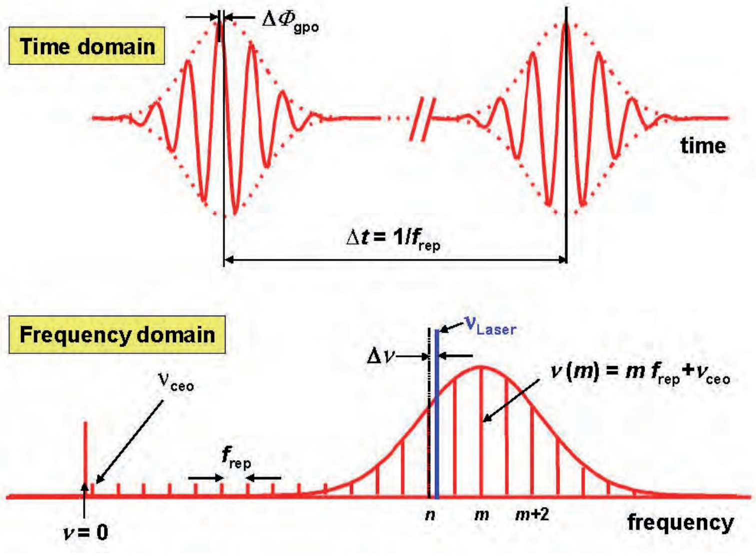

Figure 14:
Principle of an optical comb generator in the time domain or frequency domain. Mode-locked femto-second lasers generate a "comb spectrum" of equidistant lines (frequency marks) which allow an optical frequency to be mapped without any loss of accuracy to three radio frequencies.

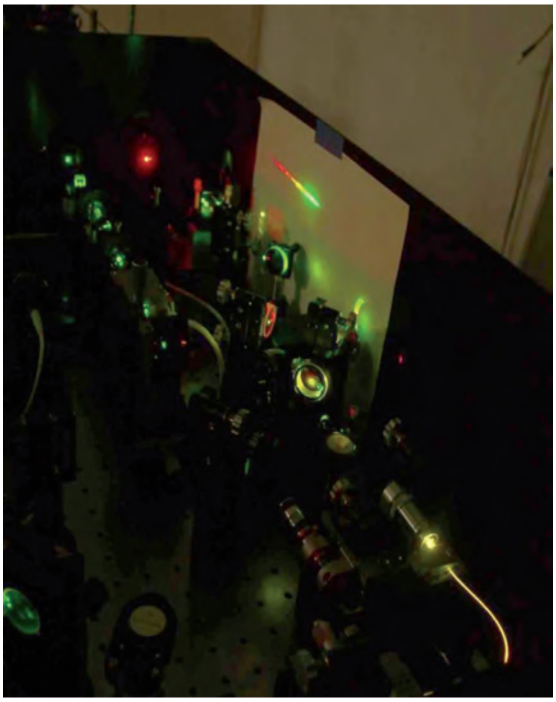

Figure 15:
Spectrally expanded frequency comb spectrum of a titan-sapphire laser for the measurement of optical frequencies.

limited by the measuring process itself, but only by the involved standards.

In contrast to older frequency chains, any laser frequency desired can be measured, provided that it lies within the frequency spectrum of the fs-frequency comb (see Figure 15) and that the beat signal $\Delta\nu$ can be detected with a sufficient signal-to-noise ratio.

In addition to the comparison of optical frequencies with primary Cs clocks, frequency combs are successfully used if, for example, two optical frequencies have to be directly compared with each other at different wavelengths [61], or if the excellent stability of an optical frequency standard is to be transferred to another spectral range [62]. If a frequency comb is used as an optical frequency divider, a microwave signal can be generated from an optical clock, whose phase purity exceeds that of the best microwave oscillators [63].

Today, fiber lasers at $\lambda \approx 1.5$ µm are used to an ever increasing extent as frequency combs [64] – in addition to titan-sapphire lasers [65] at $\lambda \approx 800$ nm.

In addition to a compact construction, the latter exhibit excellent properties in continuous operation. In this way, an essential prerequisite for the future realization of optical clocks has been estabilished.

4 Dissemination of the Unit of Length

4.1 Interferometry for the transmission of the unit of length to embodied measures

In the previous sections, the bases of today's definition of the metre have been described. This section gives a short survey of the interferometric transfer of the wavelength of a stabilized laser to embodied measures (so-called "gauge blocks", Figure 16), as they are still used today in industry and technology.

With the aid of an interferometer, the length of a gauge block can be traced back to the SI base unit "metre". In an interferential length measurement, the length to be determined is compared with an exactly known wavelength. In this connection, the fact is utilized that the overlapping of two light waves of the same wavelength provides a pattern of light and dark fringes (interference pattern). If the interference pattern is, for example, formed by a standing light wave having the wavelength λ, which is formed by the reflection of a light wave on a displaceable mirror, the distance of two successive light fringes corresponds to a displacement by just half a wavelength $\lambda/2$ of the light wave.

(Roughly speaking, the number of wavelengths which fit on the length of the measure is now counted.) The wavelength of green light amounts to approx. 1/2000 mm so that about 4 million fringes in the interference pattern match on a section of 1 m. The counting of the fringes and the exact knowledge of the wavelength then furnish the precise length of the measurement object.

In this method, a modified Michelson interferometer is normally used (Figure 17). In a beam splitter, the radiation of a stabilized laser is distributed to the two arms of the interferometer. The beam which passes through the reference arm is reflected on a reference mirror. The measurement arm contains the gauge block whose length is to be determined. Whereas the front face of the gauge block is directly used as a mirror, an additional

Figure 16:
Gauge block set for calibrations in industry and technology.

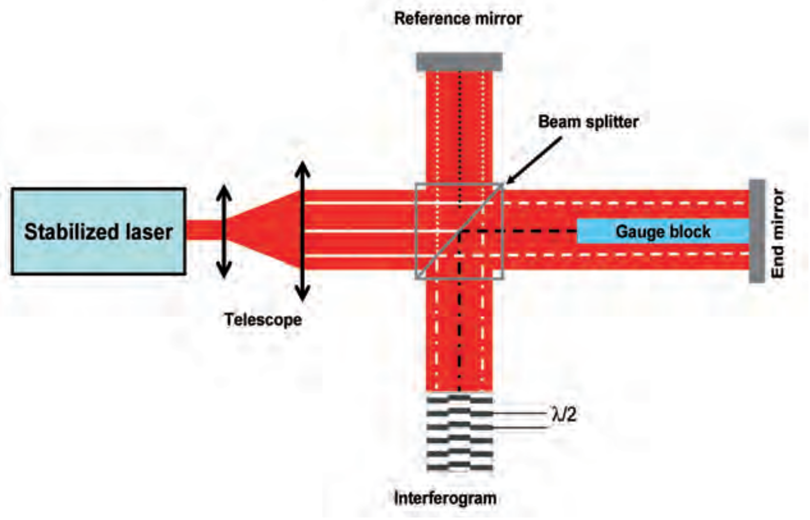

Figure 17:
Principle of a Michelson interferometer for gauge block measurements.

mirror on the end face is contacted, so that the laser beam is reflected on both the front face and the end face. At the beam splitter, these two partial beams overlap with the radiation from the reference arm and generate two fringe systems in the visual field. In each interference pattern, the fringe distance corresponds to a path difference of $\lambda/2$.

If the wavelength λ is known, the length L of a gauge block can be determined from the following equation

$$L = (\mathrm{m} + \varepsilon)\, \mathrm{n} \cdot \lambda/2;\ \mathrm{m} \in \mathrm{N}.$$

Here, m describes the number of the interference order and ε the remaining fraction of an interference order. The fraction ε is determined from the ratio between the displacement of the interference fringes and the fringe distance. The integer m-value is determined from a known stored value which is obtained by comparison with a known length or by the use of several stable and exactly known wavelengths. If, in addition, the refractive index of the air n is taken into account, the length L of the gauge block is obtained from the determination of m, ε and the frequency v of the wavelength standard.

Under the best possible conditions, the lengths of the gauge blocks can be determined with a relative uncertainty of a few 10^{-8} [9]. Normally, these measurements are limited by the surface roughness of the front faces, the reproducibility of the end plate wringing and the determination of the refractive index. A detailed description of the latest interferometric measurement techniques is given in [66].

4.2 Interferential wavelength determination

In addition to the length measurement of gauge blocks, the principle of the Michelson interferometer is excellently suited for the precise comparison of wavelengths in the complete visible and near infrared spectral range. If a defined displacement of a mirror ΔL is measured simultaneously with two different wavelengths λ_1 and λ_2, the following is valid: $\Delta L = m_1\, \lambda_1 = m_2\, \lambda_2$, oder $\lambda_2 = m_1/m_2\, \lambda_1$. This allows an unknown wavelength λ_2 to be calculated from the known wavelength λ_1 and the measured number of interference orders m_1 and m_2.

Figure 18 shows a scanning interferometer for the determination of wavelengths in the visible and in the near infrared spectral range. This interferometer reaches a relative measurement uncertainty of $2.5 \cdot 10^{-9}$ [67].

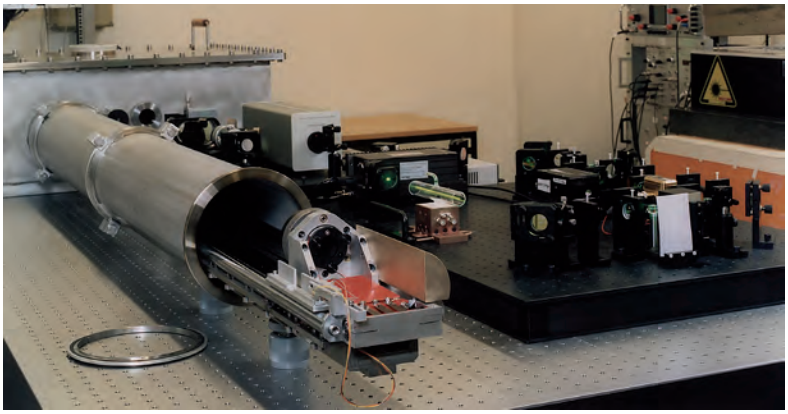

Figure 18:
Interferometer for the determination of wavelengths of stabilized lasers.

5 Dissemination of Optical Reference Frequencies and Wavelengths via Optical Fibers

The methods presented in the preceding sections are based on the exact knowledge of the optical frequency of the wavelength standards/frequency standards. To guarantee this in the long run, it is "good scientific practice" to compare these standards at regular intervals. This purpose serves, for example, key comparisons at the highest level, as those performed at regular intervals by the International Bureau of Weights and Measures, BIPM, or by direct traceability of the optical frequency to the primary time standards (see Section 5).

The optical clocks described in Section 3.3 reach uncertainties which are clearly smaller than the current uncertainty of primary clocks [40], and they are at present not yet transportable.

For a long time, frequency comparisons by means of satellites have been an established procedure for comparisons between primary Cs clocks of the national metrology institutes; under realistic observation times, they do not, however, reach the accuracy required for optical clocks [68]. This is why optical clocks require a new comparison method which allows the instability of the clocks to be reached within a few minutes or, at maximum, within a few hours. As an alternative to frequency comparisons per satellite, the use of optical connections per optical fibers is currently being intensively investigated [69]. The wavelength range around 1.5 µm used in telecommunications is particularly well suited to bridge large distances by means of optical fibers, as here signals can be transferred with a lower loss. A survey of different methods for frequency comparisons by optical fiber connections can be found in [70].

Lately, two methods have established themselves: the transfer of a highly stable high-frequency signal by amplitude modulation of an optical carrier wave [71] and the direct transmission of a highly stable optical carrier frequency [72]. With the first method, a relative frequency instability in the range of 10^{-18} was reached over a section of 86 km at an averaging period of one day [73]. For larger distances, problems are, however, encountered due to signal weakening and dispersion of the optical fiber.

The direct transmission of a highly stable carrier frequency offers the advantage that stability losses due to the conversion of the frequency of the optical clock into the high-frequency range and due to distortions of the transferred modulation are avoided. Optical clocks in laboratories which are far away from each other can be compared by transferring the radiation of a narrowband continuous-wave laser via an optical fiber connection of an already existing 1.5 µm telecommunications network and comparing the frequency of this transfer laser in both laboratories with the local optical clock. With the aid of frequency comb generators, the frequency ratio between the transfer laser and the optical clock can be measured relatively easily [74]. Continuous-operation-proof femtosecond fiber lasers are particularly well suited for this purpose [75, 76]. Within a measuring time of a few hours, such a frequency comparison can reach a relative uncertainty below 10^{-17} [62].

A fundamental problem of all procedures for frequency transmission with optical fibers is the impairment of the stability by fluctuations in the optical length. Phase fluctuations in the transferred optical carrier wave are, for example, caused by slight mechanical stress of the optical fibers and changes in the ambient temperature. In the case of transfers over long distances, the fluctuations which dominate on long time scales are those which are caused by temperature variations in the fiber. Other low-frequency disturbances such as, for example, variations of the polarization mode dispersion or temperature changes in the measuring set-up or in the devices, can also lead to a degradation of the long-term stability. Noise sources playing a role on shorter time scales are, among others, thermal and $1/f$-noise in electronic components, shot noise of photo detection as well as phase jitter occurring in the fiber by the conversion of amplitude noise. To guarantee a highly stable frequency transfer via an optical fiber, the phase jitter of the transmission path must typically be suppressed for all distances longer than 100 m by an active optical wavelength stabilization [77].

In cooperation with the *Deutsches Forschungsnetz (German Science Network – DFN)*, GasLINE (a provider of blank telecommunications fiber cables of German gas suppliers) and EnBs (local supplier for energy supply and telecommunications), a fiber connection approx. 73 km in length was put into operation between PTB and a laboratory of the Institute for Quantum Optics (IQ) at Leibniz University in Hanover (Figure 19). This fiber connection allows highly stable lasers to be directly compared at two different places with a short-time stability of $\sigma_y(\tau) \approx 2 \cdot 10^{-15}\,(\tau s)^{-1}$ [78]. As can be seen from Figure 20, this allows the best optical clocks to be compared within a few minutes with an accuracy which is only limited by the clocks themselves [79].

The networks of long-distance pipelines of gas supply companies and local telecommunications suppliers offer a considerable potential for the development of a comprehensive infrastructure for optical fiber connections. In cooperation with the Max-Planck Institute for Quantum Optics, MPQ, in Garching, PTB has recently put into operation another test section for the first long-term transmission of an optical carrier frequency over a distance of 900 km [80]. In this way, the section length has been extended into an order of magnitude which would allow the highly stable and exact clocks in many European laboratories to be compared, and modern systems for optical frequency distribution to be investigated in real size and under typical environmental conditions.

From the results obtained so far it can be expected that the use of optical fibers for the comparison of optical clocks in Europe is an excellent alternative to satellite-based frequency comparisons, provided that suppliers can be found who grant the national metrology institutes access to a European network and support them in the establishment of national networks.

We expect that this will lead to new applications and significant progress in current research. The transfer of a highly stable frequency to a user who is far away will allow frequencies from the microwave frequency range up to the visible spectral range to be generated on site with a stability which has so far been available only in a few metrology institutes. The applications range from the dissemination of the unit of length to the synchronization of particle accelerators [81], spatially networked astronomic telescope facilities such as, for example, the Atacama Large Millimeter Array [82], the Deep Space Network of NASA [83], or in the range of interferometry with a large base length (VLBI) [84].

An available European optical fiber network for the transfer of highly stable frequencies could contribute to the improvement and validation of satellite-based time and frequency transfer and of worldwide satellite navigation (GPS, Galileo) [85], or to new applications in the field of geodesy and fundamental physics.

Last but not least, the further development of optical clocks will also benefit from a fiber network, as a redefinition of the SI second on the basis of optical clocks seems to be realistic only if adequate comparison possibilities are available.

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Figure 19:
Scheme of a comparison of optical frequency standards via a commercial optical fiber connection (blue and red lines). At PTB, a fiber laser is stabilized to an optical frequency standard at a wavelength of 1.5 µm. Its radiation is transferred by means of optical fibers to Leibniz University in Hanover where it is compared with the frequency of a frequency standard with cold magnesium atoms [79].

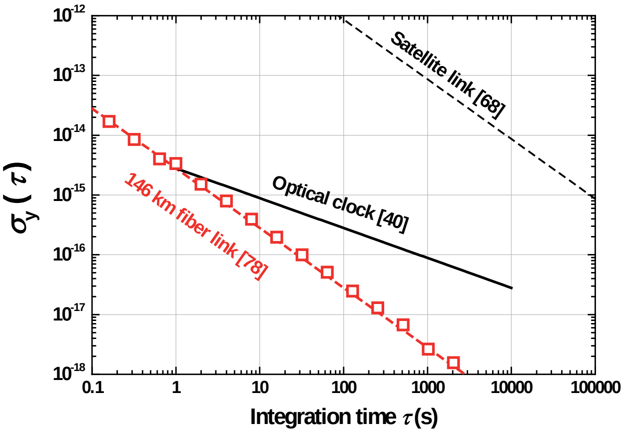

Figure 20:
Relative instability of the transferred optical frequency measured after 146 km (red squares) [78] compared to the instability of an optical single-ion clock [40] (black line) and a clock comparison by satellite (broken line) [68].

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Time – the SI Base Unit “Second”

Andreas Bauch*

Structure

1 Introduction

“Time is a strange thing ...”[1] . In fact, the SI base unit “the second” has a special position among the units: It is the SI unit which has been realized by far with the highest precision – and this is why other base units are defined or realized with reference to it. The metre, for example, has been a derived unit since 1983, defined as the length of the path travelled by light in vacuum during a time interval of 1/ 299 792 458 of a second. The realization of the volt – the unit of the electrical voltage – makes use of the Josephson effect, which links the volt with a frequency via the ratio of two fundamental constants, $h/(2e)$ (e: elementary charge, h: Planck’s constant). All this will be dealt with in the various articles of this publication. But there are other remarkable facts: The only measuring instrument most people have on them in daily life is a watch. Time touches every person every day (at least in our civilization). For decades, indicating the time – an essential task for everyday life – has been the privilege of the authorities in town and in the country, and doing so is associated with prestige and has a direct influence on the life of the people. The transition from astronomic time determination to time determination on the basis of atomic clocks – which will be the subject of Section 2 of this article – has, therefore, been associated with all kinds of disputes in the scientific circles involved. In countries where the legal responsibilities are less clearly regulated than in Germany (in Germany, the regulation is based on the *Units and Time Act*), the rivalry between the interest groups continues to this day. The work which was started at the *Physikalisch-Technische Reichsanstalt* (Imperial Physical Technical Institute – PTR) in the early 1930s and continued at PTB in Braunschweig after 1950 has given an essential impetus to this transition.

In the following, a short survey of earlier definitions of the unit of time will be given, followed by sections dealing with the current definition and, thus, with the caesium atomic clock and international cooperation in the field of time measurement. Section 6 will then deal with the popular services which PTB makes available for the dissemination of legal time in Germany. To this day, research in the field of clock development is undertaken intensively. A research group announcing that it has achieved progress towards an even more exact clock can be sure to find the interest of the media. In Section 7, an answer will be given as to whom this will benefit.

2 The Definitions of the Unit of Time

2.1 The rotation of the Earth as the measure of time

People’s natural measure of time is the day. It is defined by the rotation of the Earth around its axis. Following an old cultural tradition, it is subdivided into 24 hours, each comprising 60 minutes, with each minute comprising again 60 seconds [1, 2]. If one assigns the moment 12 o’clock to the zenithal culmination of the Sun, the true solar day is obtained as the period of time in-between. Due to the inclination of the Earth’s axis relative to the plane of the Earth’s orbit around the Sun, and due to the elliptical Earth’s orbit, its duration changes during one year by up to ± 30 s. Averaging over the length of days of 1 year leads to the mean solar time, whose measure is the mean solar day d_{m}. Until the year 1956, its 86 400th part served as the unit of time, the “second”. It was realized with the aid of high-precision mechanical pendulum clocks and, later on, with quartz clocks, to make – on the one hand – time measures and – on the other hand

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[1] Hugo von Hoffmannsthal, Libretto to the opera “The Rose Cavalier”

– the unit hertz (Hz = 1/s) available for frequency measurements. The mean solar time related to the zero meridian passing through Greenwich is called *Universal Time* (UT).

If time measures and time scales are derived directly from the recordings of the moments of star passages through the local meridian, these are falsified by the changes in the position of the axis of rotation in the Earth's body, the so-called "polar motion". This polar motion occurs, in particular, at a period of approx. 14 months and, in addition, accidentally. In the time scale called UT1, the predictable periodic portions have been eliminated so that UT1 is (almost) proportional to the angle of rotation of the Earth. The recordings of the planets' positions and of the Moon's orbit relative to the starry sky – dated in UT1 – collected over many years – revealed, however, that the duration of the mean solar day, too, is subjected to continuous changes [3]. There is, on the one hand, a gradual deceleration of the Earth's rotation by tide friction. 400 million years ago, for example, the year had 400 days. Mass shifts inside the Earth's body and large-scale changes in the sea currents and in the atmosphere lead, on the other hand, to a change in the moment of inertia of the rotating Earth and, thus, in its period of rotation. These effects which have been – partly – understood and are – partly – unpredictable, conceal the gradual deceleration. And as regards proof of the resulting seasonal variations – this is a topic we will still have to talk about!

2.2 Time and frequency at the PTR and in the early days of PTB

If we compare the quartz clock shown in Figure 1 – which was developed at the PTR in the 30s of the last century – with what we are wearing today as wrist watches, it becomes clear why we speak of a "quartz revolution" [4]. Although the contribution of the PTR – and later that of PTB – to this modern development has been comparably small, the success of the PTR was, however, of essential importance for the abandoning of the astronomic time determination. The motivation for the activities at PTR was the emerging of wireless communication traffic and the necessity of measuring the transmitter frequencies in the kHz and MHz range. For this purpose, E. Giebe and A. Scheibe developed frequency standards in the shape of luminous resonators: small quartz rods equipped with electrodes in glass flasks filled with a neon-helium gas mixture which were excited to a glow discharge as soon as the frequency of an electrical a. c. field at the electrodes agreed with one of the mechanical resonance frequencies of the tuning fork [5]. The relative measurement uncertainty was between 10^{-6} and 10^{-7}. Maintaining the form of the tuning forks, these were later integrated into an electric oscillator circuit, as had been shown before in a similar way by W. G. Cady, G. W. Pierce and W. A. Marrison [6]. Until 1945, a total of 13 quartz clocks had been developed at the PTR. Their rate stability, which was superior to that of pendulum clocks, motivated the *Geodätisches Institut Potsdam* and the *Seewarte Hamburg* to fabricate four of these clocks – or two, respectively – in accordance with the design principle of the PTR.

To link the frequency which had been realized with the quartz clocks up with the astronomically defined unit, the PTR received the signals of the time signal transmitter Nauen, checked by the *Seewarte Hamburg*, and of the transmitters Rugby (UK) and Bordeaux (F) which – in the course of 1 day – all emitted time signals in the frequency band around 16 kHz (wavelength: 18.5 km). In the rate of the quartz clocks, long-term – and obviously deterministic – fluctuations occurred relative to the time signals received and were corrected by the "improvements" of the broadcasting times subsequently published. When these fluctuations occurred on several clocks of sufficiently different construction, A. Scheibe and U. Adelsberger judged this – already in 1936 – as an indication of periodic fluctuations of the period of the Earth's rotation [7]. Meticulously, they tried to improve and to document the quality of their clocks. In doing so, they – first of all – had to convince the protectionists of the superiority of mechanical pendulum clocks, rather than the astronomers, who were very well informed about the irregularity of the Earth's rotation [8]. Figure 2 shows the – probably most frequently published – measurement result obtained with quartz clock III. After

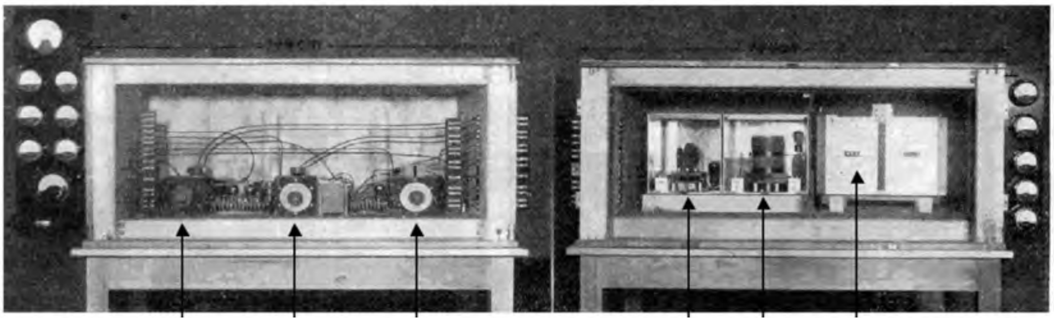


Figure 1:
Quartz clock of the PTR, constructed after 1935; the arrows – from left to right – point to 3 frequency dividers, 3:1, 10:1, 6:1, to amplifiers, control transmitter and, at the far right, to the internal thermostat with the tuning fork.

the war, A. Scheibe and U. Adelsberger described this phase of the PTR's work in detail [9]. Later on, they tried very hard to furnish proof of a regularity of the oscillations of the Earth's rotation period. Meanwhile, it has been shown by means of considerably improved observation methods and clocks that from the Earth's rotation, the time unit cannot be derived better than to a relatively few 10^{-8}: In addition to the periodic changes, there are also non-predictable changes in the Earth's moment of inertia.

After the war, the development of quartz clocks was resumed at PTB and continued until the 1960s in the quartz clock cellars of the Giebe Building [10]. The aim was to minimize the dependence of the clock frequency on temperature, air pressure, electric operating parameters, and on the typical aging of the quartz resonator which leads to a drift of the clock frequency. Until mid-year 1970, the generation of standard frequency and time signals for emission with the long-wave transmitter DCF77 (see Section 6) was based on quartz clocks, before rubidium atomic clocks were installed at the Mainflingen transmitter [11].

2.3 The course of the year as a measure of time – the ephemeris second

The Earth apparently revolves uniformly around the Sun. For this reason, it was suggested to use the period of the Earth's revolution to determine the unit of time and, in 1956, the second was redefined as a fraction of the so-called "tropical year" – called the *ephemeris second*. The tropical year is the period between two successive spring equinoxes. As this period is alterable in a known, regular way due to the precession and nutation of the Earth's axis, the 31st of December 1899, 12 o'clock Universal Time of the differential tropical year, was referred to as the centre point [12, 13]. The defined number of the Universal Time seconds in this tropical year is based on a calculation by Simon Newcomb from 1895; he had evaluated astronomic observations from the years 1750 – 1892 and had determined the mean ratio of the periods of Earth rotation and Earth revolution.

From the Earth's revolution, however, points in time cannot be read so exactly that a more precise unit of time could actually ever be derived for practical use. Here, only the "atomic" definition of the unit of time led to real progress. One could shrug this off as an episode in history, but the effects have lasted up to the present day. As – during the period of time observed by Newcomb – the Earth had rotated faster than it does today, both atomic seconds as well as ephemeris seconds are, by definition, shorter than Universal Time seconds nowadays. This has brought us – to this day – the leap seconds [13].

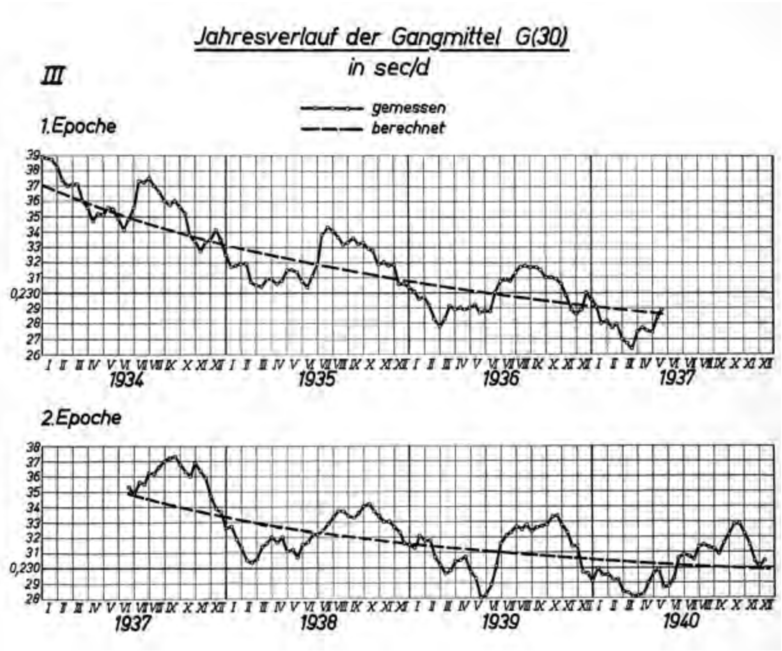


Figure 2:
Rate of quartz clock III of PTR, related to a pilot clock connected to the astronomic time scale; the seasonal oscillations superimpose the systematic rate change due to aging (broken curve); the vertical scale corresponds to the length of day minus 86 400 s, given in seconds.

2.4 The "atomic" definition of the second

The interaction between the positively charged nucleus and the shell of negatively charged electrons of the atoms causes the formation of stable configurations of the electron shell, whose regularities are indicated by quantum mechanics. This theory predicts, among other things, how the binding energy of these configurations – also called *eigenstates* of the atom – depends on fundamental constants such as, for example, the electron-to-proton mass ratio, the elementary charge, the speed of light and the so-called fine-structure constant α. One of the basic assumptions of most of the physical theories is that the designation "constants" is justified and that the energy distance between eigenstates is, therefore, also constant. Already in 1870, the English physicist James Clerk Maxwell had proposed using such fundamental constants – as a matter of principle – for the determination of the physical units, and not to refer to measures furnished by the Earth – such as the length of day for the second, or the circumference of the Earth for the metre.

A transition between two atomic eigenstates with an energy difference ΔE is associated with the absorption or emission of electromagnetic radiation of the frequency $f = \Delta E/h$. Accordingly, the frequency f or the period $1/f$, respectively, of such a radiation is basically constant – in contrast to the period of the Earth's rotation and, even more, the oscillation period of a pendulum. A specific multiple of $1/f$ could be defined as a new unit of time – this had already been proposed by the Englishman Louis Essen in 1955 – using the transition between the hyperfine structure level of the basic state of the caesium-133 atom. But the time for such a radical change in the concept for the definition of the second was not yet mature then. Shortly before, Essen and his colleagues had put the first caesium atomic clock (abbreviation: Cs clock) into operation at the English National Physical Laboratory, Teddington [14]. From 1955 to 1958, the duration of the unit of time valid at that time – that of the ephemeris second – was determined in cooperation with the United States Naval Observatory, Washington, to be 9 192 631 770 periods of the Cs transition frequency [15]. A discussion of the measurement uncertainty for this numerical value furnished the value 20 – although nobody seriously believes that it was possible to indicate the duration of the ephemeris second to relatively $2 \cdot 10^{-9}$. Nevertheless, this measurement result provided the basis for the definition of the unit of time in the International System of Units (SI) which was decided in 1967 by the 13th General Conference of Weights and Measures (CGPM) and which is still valid today:

"The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium 133 atom."

In the middle of the 1950s, PTB started to work on atomic frequency standards. In addition to initial tentative work on caesium, the 23.8 GHz inversion oscillation in the NH_3 molecule was excited in the so-called ammonium maser and later, the 1.4 GHz transition in atomic hydrogen was used for the construction of a hydrogen maser. However, in the end, only the development of the caesium atomic clock in the "Unit of Time" laboratory, directed by Gerhard Becker, was successful and will be described in further detail below.

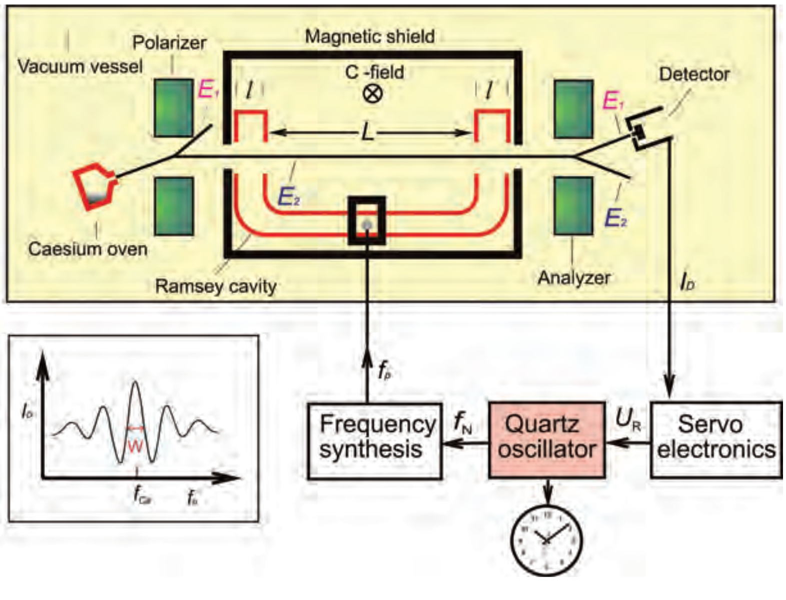


Figure 3:
Cs-clock, schematic representation; f_N: standard frequency, f_p: frequency for irradiation of the atoms, I_D: detector signal, U_R: signal for regulation of the quartz oscillator; Insert on the left: detector signal I_D as a function of the frequency of the microwave field f_p if it is tuned across the resonance point at f_{Cs}; the linewidth W is indicated.

3 Realization of the SI Second

3.1 The caesium atomic clock

Any clock can be imagined to consist of 3 parts: an internal clock generator (pendulum, balance, oscillation of a quartz); a counting mechanism, which counts the clock rate events and indicates their number; and an energy source (weights, spring, electric energy from battery or electrical connection). The special feature of an *atomic clock*, however, is that the clock rate is derived from single, free atoms, which is basically possible with different elements. The isotope caesium-133 has proved to be particularly suited for this because it allows a high-precision, infallible and compact clock to be constructed with comparably simple means.

Figure 3 illustrates the functional principle of a Cs clock as it has been built since the middle of the 1950s and is still used today: Based on a quartz oscillator, a microwave field of the frequency f_p is generated by means of a frequency generator and coupled into the resonance apparatus (see the large rectangle shaded in yellow). f_p already suits the transition frequency of the caesium atoms f_{Cs} quite well. In the apparatus, a Cs atomic beam is produced in vacuum by heating caesium to approx. 100 °C in the oven. The beam passes a first magnet – called the "polarizer" – which diverts only atoms in the energy state E_2 into the desired direction. These atoms fly through the Ramsey cavity (named after Norman F. Ramsey, who won the Nobel Prize in 1989). In the two end sections of the length l of the resonator, the atoms are irradiated with the microwave field. In this way, the transition between the two energy levels is excited with a certain probability. This maximum probability and, thus, the maximum number of atoms in the state E_1 behind the resonator are achieved when the resonance condition is complied with, i. e. when f_p and f_{Cs} exactly agree. The analyzer magnet now deflects especially E_1-atoms onto the detector where Cs atoms become Cs^+ ions, and from the ionic current an electrical signal I_D is obtained. If f_p is tuned over the resonance point, a so-called "resonance line" (see Figure 3) appears when the signal I_D is recorded. Its linewidth W is given by $W \approx 1/T$, with T being the time-of-flight of the atoms through the resonator having the length L. Now: How can the resonance point be found? For this purpose, f_p is modulated around f_{Cs}, and the resulting modulation is detected in the detector signal I_D. From this, the voltage bias U_R is obtained by means of which the quartz oscillator is tuned in such a way that f_p gets, on average, into agreement with f_{Cs}. In this way, the natural oscillations of the quartz frequency are suppressed in accordance with the adjusted control time constant. The atomic resonance then determines the quality of the emitted standard frequency f_N (usually 5 MHz). However, if a short electrical impulse is generated after each 5 million periods of f_N, the successive impulses have the temporal distance of 1 second – with atomic accuracy.

3.2 Systematic frequency uncertainty and frequency instability

Much ado is made of the accuracy of the atomic clocks, and the question is posed what this accuracy is good for (see Section 7). In the following, we will, therefore, briefly describe what is to be understood – in the narrow sense – by "atomic accuracy". When the transition between atomic energy levels is excited, the maximum transition probability – i. e. the middle of the resonance line – is recorded at a value of the excitation frequency which never agrees exactly with the resonance frequency f_0 (here: 9 192 631 770 Hz) for undisturbed atoms at rest. As the term "accuracy" is used in English, we use the composite term *frequency accuracy* in German to describe the agreement between the actual value and the desired value of the output frequency (1 Hz, 5 MHz, etc.) of a clock. Metrologically correct is the following procedure: A detailed list of all possible "disturbing" effects is laid down in the so-called uncertainty budget of a (primary) clock. This uncertainty budget contains the quantitative assessment of all effects which lead to a deviation of the realized transition frequency from that which is to be expected in undisturbed atoms at rest. As the relevant physical parameters as well as the theoretical relations are known to a limited extent only, such an assessment is affected by an uncertainty. As the final result, a combined uncertainty value is determined, and this quantity will be mentioned several times in the following. The practical consequence of this – not really exact – knowledge is: Not even an atomic clock is perfect: two clocks will always exhibit slightly different rates. *Rate* refers to the change in the *reading* of a clock relative to a reference clock: If yesterday, the difference of the reading was ΔT_1 and it is ΔT_2 today, the rate of the clock is calculated to be $(\Delta T_2 - \Delta T_1)/1$ day. Typical of atomic clocks is a rate of a few nanoseconds per day. If this is written as a relative frequency difference, one obtains multiples of 10^{-14}.

The uncertainty budget of Cs clocks contains contributions which depend on the velocity of the atoms (Doppler effect), but also on electric and magnetic fields along the trajectory of the atoms. This is why the magnetic shielding shown in Figure 3 is used.

The output frequency of atomic clocks – and generally of electric oscillators – is, as has already been said, subject to systematic – but also statistical – influences. The oscillations of the output frequency of a Cs clock are, for example, associated with the statistically varying number of atoms arriving at the detector, and these variations – quite clearly – become smaller, the larger the number of atoms and the larger the processed signal. In literature, a great number of representations of the respective characteristics, of their calculation and of their interpretation can be found [16] which are indispensable for both the understanding of the properties of the clocks and the selection in special applications. In the following, some terms will be briefly presented.

The quasi-sinusoidal output voltage of a frequency standard is described by

$$V(t) = V_0\,(1 + \varepsilon(t)) \cdot \sin\{2\pi\nu_0 t + \Phi(t)\}, \qquad (1)$$

V_0, ν_0 being the nominal amplitude and frequency, and $\varepsilon(t)$ and $\Phi(t)$ the momentary amplitude or phase variations. As additional quantities, we introduce the relative frequency deviations $y(t) = \mathrm{d}\Phi/\mathrm{d}t\,/\,(2\pi\nu_0)$. The statistical parameter most widely used for the relative frequency instability is the Allan variance

$$\sigma_y^2(\tau) = \left\langle (\bar{y}_{k+1}(\tau) - \bar{y}_k(\tau)) \right\rangle^2 , \qquad (2)$$

which links successive frequency differences with each other which, then in turn, present mean values over time τ. The usual case is a double-logarithmic plotting of $\sigma_y(\tau)$ as a function of τ. In this representation, different instability contributions can, in many cases, be identified by means of the slope of the $\sigma_y(\tau)$ graph. Figure 4 (on the right) and Figure 5 represent such "sigma tau diagrams". They show the duration of the observation times needed to achieve a desired measurement uncertainty – and they also show whether the frequency standard is possibly not at all suited for the measurement task.

3.3 Commercial atomic clocks

Since the end of the 1950s, Cs-clocks have been offered commercially, and today approximately 200 of them are produced annually worldwide. Already in the early 1960s, PTB made use of a commercial atomic clock – called the "atomichron" [17] – to monitor the rates of the quartz clocks in Braunschweig and Mainflingen. Over the course of years, we have come to understand the interfer-

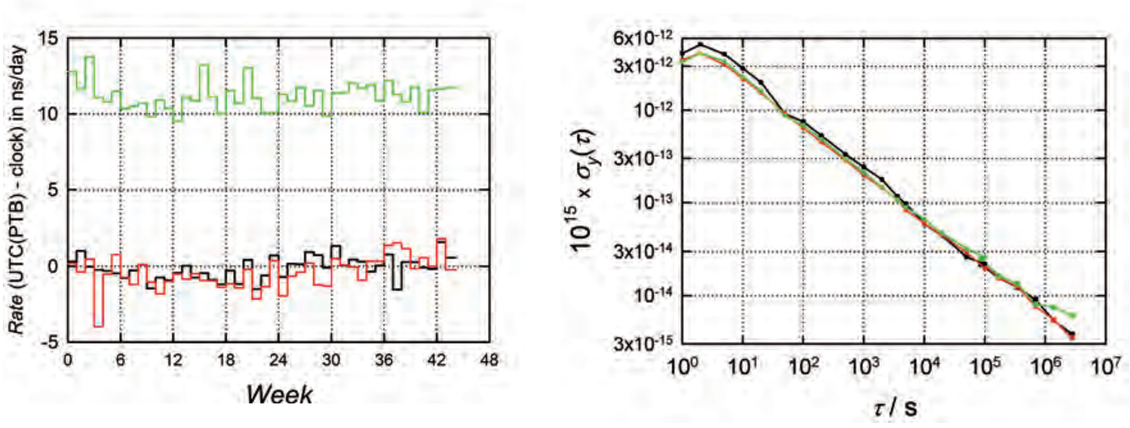


Figure 4:
Rates (on the left) and relative frequency instability (on the right) of the three commercial caesium clocks of PTB during 43 weeks of the year 2010. The week referred to with "0" starts with 28 January. UTC(PTB) serves as a reference for the investigations.

ing parameters and the regularities of its effect better and better and to reduce the uncertainty. At present, the best models realize the SI second with a relative uncertainty of a few 10^{-13} and a relative frequency instability of a few 10^{-14} averaged over a period of 1 day. They are used in the following fields of work: Navigation, geodesy, space science, telecommunications and in the time-keeping institutes (such as PTB). At present, PTB operates, for example, 6 of these clocks – three in Braunschweig and three at the DCF77 transmitter (see Section 6). Figure 4 shows the rates of the clocks in Braunschweig, recorded in 2010, and their relative frequency instability.

The principle of the atomic clock can also be realized with elements other than caesium. In most atomic clocks produced worldwide, the respective hyperfine-structure transition in the atom rubidium-87 is used. The number of these clocks produced per year probably amounts to some ten thousands, and they can be found in telecommunications facilities, in the fixed network and in base stations of the mobile services. The hydrogen maser is based on the hyperfine structure transition in the ground state of the atomic hydrogen at 1.4 GHz and is – due to its particularly stable output frequency – used for averaging periods of up to a few hours, in particular as a frequency reference in radioastronomy. Figure 5 shows the stability properties of commercial frequency standards that are presently available, along with values of primary clocks. These will be discussed below.

3.4 The primary clocks CS1 – CS4 of PTB

In the mid 1960s, PTB started to make efforts to develop a caesium atomic clock of its own and these efforts were – eventually – successful. Holloway and Lacey had proposed improving essential details of the construction principles selected originally by Essen and Parry [18] and, in the next few years, the new ideas were implemented by PTB in CS1. The following points were regarded as essential advantages [19]:

- Reduced instability due to a two-dimensional focussing of the atoms with magnetic lenses (instead of the dipole magnets sketched in Figure 3);
- Axial-symmetric geometry of the atomic beam with small radial extension;
- Improvement of the inhomogeneity of the magnetic field by use of a long cylindrical coil and cylindrical shielding – instead of a magnetic field transverse to the beam direction.

In 1969, CS1 was used for the first time [20]. In the years thereafter, a gradual reduction in the frequency uncertainty was achieved so that PTB took a leading position in the development of primary clocks. As early as in 1974, work on CS2 started on the basis of CS1. It would, however, take several years – until 1985 – for the clock to be put into operation [21] (but then all good things are worth waiting for!). In addition to a small frequency uncertainty, it was their robustness as well as the simplicity of everyday operation which was characteristic of the two clocks and, therefore, they were operated continuously in the next decades and became – deservedly – the showpiece of the laboratory. They were updated in several steps, and since 1999, their relative frequency uncer-

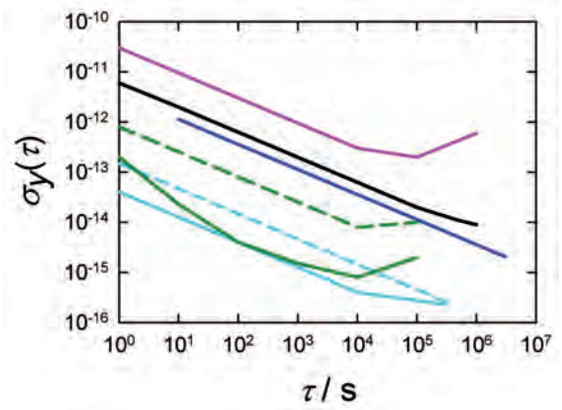


Figure 5:
Relative frequency instability $\sigma_y(\tau)$ of different atomic frequency standards. Magenta: rubidium standard, standard values; black: caesium atomic clock Symmetricom 5071A (see Figure 4) broken green line: passive hydrogen maser; green line: active hydrogen maser, standard values; cyan: measured instability of the fountain clocks FO-2 of the LNE-SYRTE and CSF1 of PTB (broken line); blue: measured instability of the primary caesium clocks CS1 and CS2 of PTB compared over 8 years.

tainty has been assessed to be $8 \cdot 10^{-15}$ (CS1) and $12 \cdot 10^{-15}$ (CS2) [22]. Their role in the realization of the International Atomic Time is acknowledged in Section 4, whereas a detailed description of their development and properties can be found in [23]. Figure 6 shows a current photo of the two clocks.

Less successful was the development of other clocks on the basis of the same construction principle, CS3 and CS4, which began as early as in 1980. The idea to select slower atoms by constructing the magnetic lenses correspondingly and, thus, achieve a smaller linewidth was – basically – correct, and the objective to reach also a smaller frequency uncertainty was also almost reached. But – in spite of the great commitment of the staff – the desired operational reliability was never achieved. Finally after completion of the – much more exact – caesium fountain CSF1, this effort did not make sense any more, and the clocks were dismounted.

Figure 6:
PTB's primary clocks CS1 and CS2.

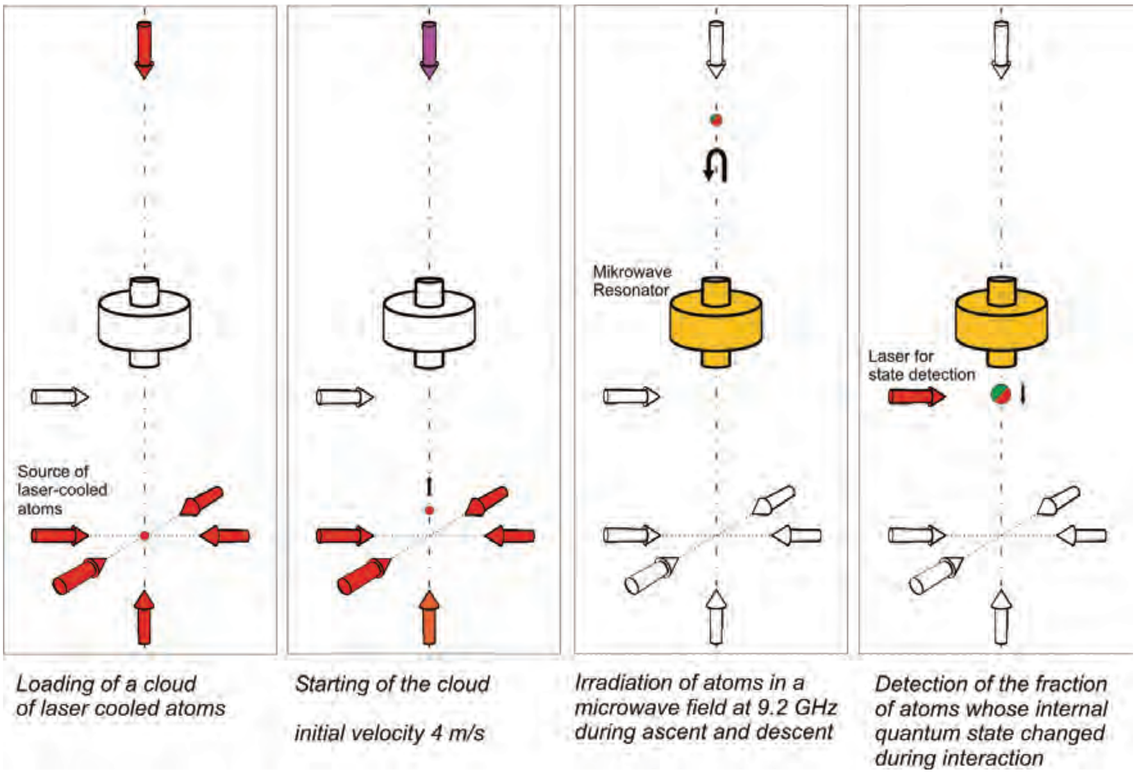
3.5 The caesium fountains CSF1 and CSF2

One of the main objectives in the further development of atomic clocks has always been to extend the time in which the atoms interact with the microwave field and – thus – reduce the linewidth. This promised, at the same time, a smaller frequency instability and a smaller frequency uncertainty. When laser cooling was discovered and understood in the middle of the 1980s [24], its importance for clock development was recognized immediately. At PTB, the new atomic clocks CSF1 [25] and, later on, CSF2 were developed, which are shown in Figure 7 [26]. Although the principle shown in Figure 3 is still applied, the new – and very important – feature is that it is laser radiation which is used to influence the state of energy and the movement of the atoms [27]. Laser cooling in a magneto-optical trap or in optical molasses furnishes “cold” atoms with a thermal velocity of approx. 1 cm/s. Expressed in the temperature unit, this corresponds to a few millionths of kelvin – compared to the 300 kelvin of the environment. These cold atoms are placed on trajectories, as outlined in Figure 8. The time-of-flight T of the atoms above the microwave resonator is 50 times longer than the respective time-of-flight T in CS2. The resonance line, to the centre of which the microwave oscillator is stabilized, is correspondingly narrower. With a relative uncertainty of only approx. $1 \cdot 10^{-15}$, CSF1 and CSF2 already come quite close to an ideal clock. Comparisons with CS1 and CS2 allow their frequency uncertainty – which previously could only be estimated – to be verified now. According to these revisions, CS2 agrees well with CSF1 within the uncertainty of 1 σ. In the case of CS1, a deviation of approx. $9 \cdot 10^{-15}$ is found. Since the beginning of 2010, CSF1 has been used as a frequency reference for the realization of the time scale at PTB. Unlike conventional clocks, CSF1 does not furnish any second pulses which directly represent a time scale. In fact, the output frequency of CSF1 is compared with that of a hydrogen maser. From that comparison, a correction of the maser frequency is calculated, and the time scale is derived from the maser corrected with it.

Figure 7:
The two caesium fountains CSF1 and CSF2, with Dr. Stefan Weyers, Head of the “Time Standards” Working Group.

4 Atomic Time Scales: TAI and UTC

A time scale is defined by a sequence of second marks which starts from a defined beginning. *International Atomic Time* TAI (Temps Atomique International) – and especially *Coordinated Universal Time* (UTC) – allow events in science and technology to be dated. At the same time,



Loading of a cloud of laser cooled atoms

Starting of the cloud

initial velocity 4 m/s

Irradiation of atoms in a microwave field at 9.2 GHz during ascent and descent

Detection of the fraction of atoms whose internal quantum state changed during interaction

Figure 8:
Function of a fountain frequency standard, represented in four time-dependent steps from the left to the right; laser beams are illustrated by arrows (white, if blocked).
1) Loading of an atomic cloud;
2) Throwing the cloud up by detuning the frequency of the vertical lasers;
3) Dilatation of the initially compact cloud due to the thermal energy which remains in spite of the cooling. The atoms fly upwards and downwards through the microwave resonator, and a specific population of the two hyperfine structures is reached;
4) After the second passage of the microwave resonator, the population of the state is measured by laser irradiation and fluorescence detection.

UTC provides the basis of the "time" that is in use in everyday life. Since 1988, the *Time Department* of the BIPM (Bureau International des Poids et Mesures) has been charged with its calculation and propagation. For its calculation, approx. 350 clocks from approx. 70 time-keeping institutes, distributed all over the world, are used. From PTB, the measurement values of the primary clocks CS1 and CS2, of the three commercial caesium clocks and, since around 1990, of the hydrogen maser have been transmitted. The algorithm used to combine all data is designed in such a way that it reliably produces an optimized, stable time scale over an averaging period of 30 days. For this purpose, statistic weights – which follow from the rate behaviour of the clocks during the past 12 months – are assigned to the contributing clocks when their rates are averaged. The more stable the rate of a clock, the higher its statistic weight. The mean obtained in this way is called EAL (Echelle Atomique Libre, free atomic time scale). In a second step, TAI is obtained, whose scale unit is to agree with the SI second as it would be realized at sea level, i. e. it shall be as long as indicated in the definition of the second (see Section 2.4). For this purpose, the TAI second is adapted to seconds realized with primary standards. In 2009 and 2010, 14 standards were involved. With its clocks CS1 and CS2 and the two caesium fountains CSF1 and CSF2, PTB has, for many years, taken a prominent position worldwide. No other standard worldwide has transmitted so many measurement values as CS1 and CS2: From CS2, for example, values for 288 months in succession (including August 2010) were transmitted.[2] For a number of years, only these two clocks have been available worldwide for this purpose. Figure 9 shows current measurement values of all fountain clocks relative to the – already controlled – time scale TAI. Accordingly, the TAI second agrees very well with the SI second, the deviation is exactly known. A discussion of the mean offset and of the scattering of the single values would go beyond the scope of this essay.

The beginning of TAI was defined in such a way that the 1st of January 1958, 0 o'clock TAI, agreed with the respective moment in UT1 (see Section 2.1). From TAI one obtains UTC, which is the basis of today's universal time system with 24 time zones. UTC results from proposals of the CCIR (Comité Consultatif International des Radiocommunications) of the ITU (International Telecommunication Union). According to these proposals, the emission of time signals should be "coordinated" worldwide, i. e. it should be related to a common time scale. If TAI had been used for it, the time signals would have been shifted gradually with respect to the indication of a universal time clock, i. e. the moment 12:00 o'clock would have been shifted with respect to the highest position of the Sun at the zero meridian. The latter follows from the adaptation of the duration of the atomic second to the ephemeris second described above.

For navigation according to the position of celestial bodies, knowledge of UT1 is necessary, and time signals have been emitted since the early 20th century, in particular due to the requirements of navigation. Since in the 1960s, astronomic naviga-

[2] Then the whole thing stopped – the caesium filled in in 1989 had been used up. Since December 2010, CS2 has been ticking again!

tion was still important, it was decided to introduce the following rule [13]: UTC and TAI have the same scale unit, the difference between UTC and UT1 is, however, limited by leap seconds in UTC to less than 0.9 seconds. From this, the stair curve shown in Figure 10 follows for UTC–TAI (beginning with January 1, 1972) which closely follows the monotonous curve of UT1–TAI. The leap seconds are inserted at the turn of the year or in the middle of the year as the last second of December 31 or of June 30 in UTC. This is determined by the International Earth Rotation and Reference Systems Service (IERS, http://www.iers.org) as a function of the observed period of the Earth's rotation. Averaged over the decade 1999 – 2009, the mean solar day was 0.604 ms longer than 86 400 SI seconds. In the previous decade, the deviation amounted to approx. 1.962 ms.[3]

In practically all countries, UTC has become the basis for the “civil”, “official” or “legal” time used in the respective time zone. UTC is published in the form of calculated time differences with reference to the time scales UTC(k) realized in the individual time-keeping institutes (k). The UTC(k) scales shall agree as well as possible with UTC – and thus also mutually. At the end of 2010, 46 time scales with a deviation UTC–UTC(k) of less than 100 ns were available worldwide, among them that of PTB. Figure 11 shows the difference between UTC and the realizations UTC(k) in four European time-keeping institutes during one year.

5 Clock Comparisons

Albert Einstein once said that time could be replaced by the position of the little hand of his clock [28]. By this, he aptly expressed that the time furnished by a clock is independent of its state of motion and of the gravitational potential in which it is located – but only for an observer in the same reference system. The definition of the second relates to this *proper time* (Section 2.1). Therefore, it is not necessary to point to the theory of relativity in the text of the definition. Today, this seems quite natural; in the 1960s it was, however, the subject of serious discussions [29]. Only if one intends to compare two clocks which move relative to each other, or in which atoms with different velocities are used, or which are subject to different gravitation – or, if it is intended, as described below – to combine the atomic clocks of all time-keeping institutes operating worldwide – only then must the rules of the theory of relativity be known and applied. Here it applies, however, that the velocity-dependent time dilatation due to the movement of the atoms in the atomic beam and the effect of the field of gravity of the Earth are by far larger than the frequency uncertainty of the best clocks achieved today. An interpretation is possible from two different perspectives: If the rates of atomic clocks are compared with each other to learn something about their quality – and thus about our understanding of the different physical effects which are effective in the clocks – the relativistic effects must be taken into account correctly. On the other hand, no objects on Earth are better suited to detect and quantitatively analyze relativistic effects than atomic clocks [30].

Now, how is it possible to establish a common time scale from 350 clocks that are distributed all over the world? This requires, first of all, local time

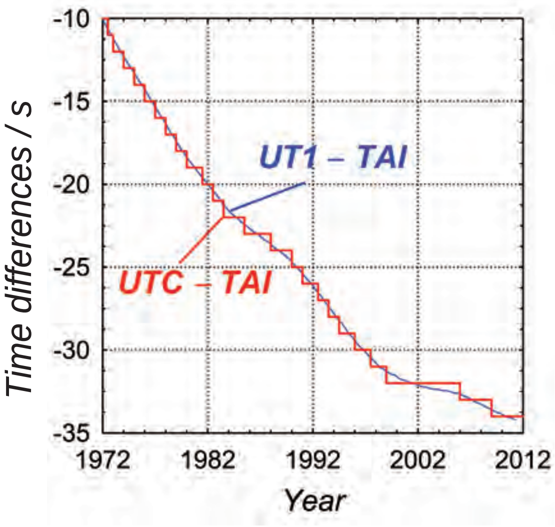


Figure 10:
Comparison of (astronomical) Universal Time UT1 and Universal Coordinated Time UTC with International Atomic Time TAI since 1971.

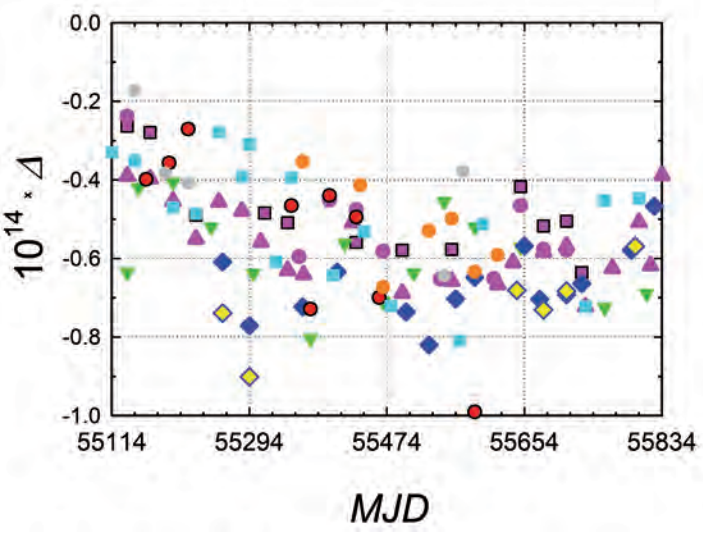


Figure 9:
Comparison of fountain frequency standards with TAI during two years, ending with MJD 55834, on September 30, 2011: The quantity Δ is the relative deviation of the second as it is realized with individual standards, from the scale unit of TAI during the respective operating time of the standards, typically 20 to 30 days. The uncertainty of the single measurement values varies between 0.05 and 0.4, depending on the standard and on the measurement period. Symbols: blue: PTB CSF1, yellow-blue: PTB CSF2, cyan: NPL CsF2, orange: NMIJ-F1 (Japan), green: NIST-F1 (USA), grey: NICT-CsF1 (Japan), red: IT-CSF1 (INRIM, Italy), magenta: LNE SYRTE/Observatoire de Paris, squares: FO1, triangles: FO2, points: FOM.

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[3] Volume 48(3) of *Metrologia* deals with the history and significance of time scales and the leap second issue

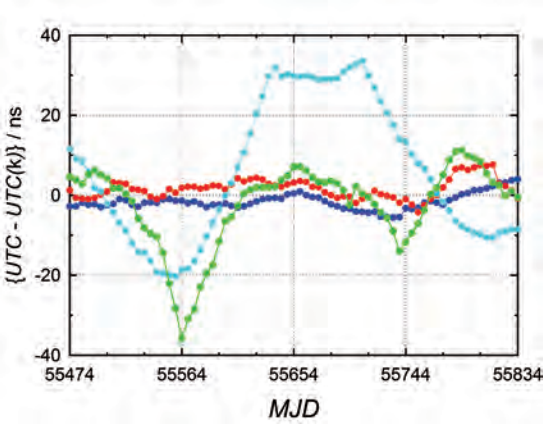

Figure 11:
Comparison of Universal Coordinated Time UTC with atomic time scales UTC(k) realized in four European time-keeping institutes (k) during one year; MJD 55834 refers to September 30, 2011;
red: Istituto Nazionale di Richerca di Metrologia, INRiM, Turin;
cyan: NPL, Teddington, UK;
green: METAS, Swizerland;
blue: PTB.

comparisons between the clocks and the respective time scales UTC(k) of the institutes k operating the clocks, and then comparisons of UTC(k) among each other. The former is quasi trivial. For the latter, a standard procedure exists which uses the signals emitted by the satellites of the American Satellite Navigation Systems GPS and of the Russian GLONASS. Special time receivers determine the arrival times of the signals of all satellites which are simultaneously visible above the horizon with respect to the local reference time scale and furnish original data of the kind {local time scale minus GPS time T(GPS)} (or GLONASS time). To compare the time scales of two institutes (i) and (k) with each other, the time differences are determined, the measurement data are exchanged and (e. g.) the differences [*UTC(i)-T(GPS)]–[UTC(k)-T(GPS)*] formed. By averaging typically 500 daily observations with a duration of approx. 15 minutes, the time scales of two time-keeping institutes can be compared worldwide with a statistic uncertainty of approx. 2 – 4 ns (1 σ).

Not only the clocks themselves, but also the methods of the intercontinental comparisons were – and still are – continuously further developed. By a combination of all methods available, the comparison of caesium fountains could – in an international collaboration – be realized with a statistic uncertainty of $1 \cdot 10^{-15}$. The values were averaged over 1 day each [31]. PTB intensively pursues the use of geostationary telecommunication satellites for time comparisons – called “Two-Way Satellite Time and Frequency Transfer (TWSTFT)” – and operates ground stations for the traffic with Europe/USA and Asia. Figure 12 shows a mobile station for the calibration of signal transit times [32] located next to the permanent installations on the Laue Building.

The time comparison data collected worldwide can largely be retrieved on servers which are publicly available. A time and frequency comparison of the highest accuracy can, thus, be performed with respect to UTC(PTB), with respect to many other realizations UTC(k), or to UTC and TAI und – thus – to the SI second – and this with the accuracy suited for almost every application.

6 Dissemination of Time for Society

The dating of events and the coordination of the various activities in a modern society have been recognized as being so important that in many countries how legal time is to be indicated is regulated by law. This is also the case in Germany. International traffic and communications make it necessary for the times of the countries which are fixed in this way to be coordinated with each other. The basics for this were laid down in October 1884 by the Washington Standard Time Conference [1, 2]. Thereby, the position of the zero meridian and the system of the 24 time zones – each one having a geographic longitude of 15° – were determined.

After the second had been redefined on the basis of quantities of atomic physics in 1967, the regulation for the legal time valid in Germany also had to be adapted. This was realized by the *Time Act* of 1978 in which PTB was entrusted with the realization and dissemination of the time which is decisive for public life in Germany. Central European Time (CET) or – if introduced – Central European Summer Time (CEST) were determined as the legal time. CET and CEST are derived from UTC, adding one or two hours:

$$\begin{aligned} \mathrm{CET(D)} &= \mathrm{UTC(PTB)} + 1\mathrm{h}, \\ \mathrm{CEST(D)} &= \mathrm{UTC(PTB)} + 2\mathrm{h}. \end{aligned}$$

Figure 12:
Establishment of a transportable satellite terminal for calibration of the time comparisons via TWSTFT with the stationary facility (background).

In addition, the *Time Act* also authorizes the German Federal Government to introduce, by way of a statutory ordinance, Summer Time between 1 March and 31 October of each year. The dates for the beginning and the end of CEST are determined by the Federal Government in accordance with the currently valid directive of the European Parliament and of the Council of the European Union and are announced in the Federal Law Gazette. The *Time Act* of 1978 and the *Units in Metrology* Act of 1985 were combined to a new, joint act, i. e. the *Units and Time Act*, which was adopted in 2008 and in which all regulations concerning the determination of time have been taken over without changes.

During the past few decades, PTB has used different procedures to disseminate time and frequency information to the general public and to use it for scientific and technical purposes. The long-wave transmitter DCF77 of Media Broadcast GmbH is the most important medium for this because the number of receivers in operation is estimated to be more than 100 million. It is often the case that PTB is known to many Germans and to many people in Europe only due to one service: the control of radio-controlled clocks. The carrier oscillation 77.5 kHz of this emission is used for the calibration of standard frequency generators. Before the war, PTR had already offered a comparable service, using the "Deutschlandsender". With DCF77, the time and date of legal time are transmitted in an encoded form via the second marks. In 2009, in memory of 50 years of DCF77 broadcasting, topics such as the current state of the broadcasting programme, the receiver characteristics, radio-controlled clocks and the history of time dissemination in Germany were intensively addressed in publications [33]. Corresponding services on long-wave also exist in England, Japan and the USA [34].

Since the mid 1990s, PTB has been offering time information via the public telephone network. Computers and data acquisition facilities can retrieve the exact time from PTB with the aid of telephone modems, calling the number 0531 512038. The major part of the calls (presently approx. 1700 calls per day) comes from the measuring stations of different energy suppliers who need this information for the fiscal measurement of natural gas.

With the advent of the Internet, a new medium for time dissemination came into being which has meanwhile become extraordinarily popular. Publicly available servers with the addresses *ptbtimeX.ptb.de (X = 1, 2, 3)* serve to synchronize computer clocks in the Internet with UTC(PTB). Figure 13 shows the number of current accesses to the three servers in the course of one week. During the past few years, the number of accesses has increased to approx. 3000 per second (as shown in the diagram).

7 Further Developments and Applications

For a great number of technical, military and – last but not least – scientific applications, exact and stable clocks and frequency references are indispensable. In the previous sections, the – seemingly – constant improvement of the accuracy of time measurement has been outlined. This – and also PTB's role – is impressive, but inevitably, the question arises: What is the use of all this? Where will the development take us?

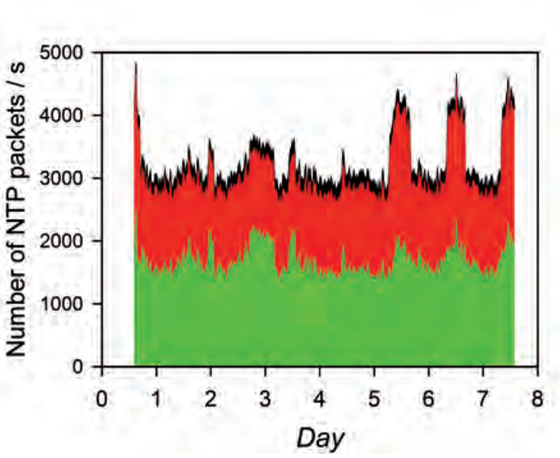

Figure 13:
Number of the NTP packages received during one week from the three externally accessible NTP servers ptbtimeX: 0 corresponds to 15.12.2010, 0:00 UTC; green: X = 1, red: X = 2, black: X = 3.

Let's deal with the second question first: All atoms and ions have states of energy. Between these, transitions occur – at frequencies that are up to 10^5 times higher than those we have discussed up to now (i. e.: in the range of the visible or ultraviolet radiation). In that case, schoolbook physics teaches us that the transitions from the higher to the lower state of energy run rapidly and spontaneously. In special cases, the transition probabilities are, however, strongly suppressed and, at the same time, the transition frequencies depend only to a small extent on external parameters. If the frequency of a laser is stabilized to such a transition line, it represents a very good standard for the frequency and the wavelength [35, 36]. In the case of the selected "clock transitions", linewidths W in the Hz area are obtained which furnish – with a transition frequency from 10^{14} to 10^{15} Hz – a correspondingly high line quality and, thus, a small frequency instability. The quality gained with the transition from low to higher clock frequencies (mechanical clock: 1 Hz, quartz clock: 10 kHz, atomic clock, so far: 10 GHz) is continued and, consequently, also leads to a reduction in the frequency uncertainty.

In the past few years, the development of optical frequency standards has been rapid. At the end of 2010, the smallest value of the frequency uncertainty published lay at $9 \cdot 10^{-18}$ [37]. From this, the perspective for a possible redefinition of the second results, and the question arises as to how the atomic transition best suited for it can be found. The category "secondary representation of the second" was created [38]. The categories which have been recognized so far are based on a microwave transition in rubidium and on optical transitions in the ions $^{88}Sr^+$ (strontium), $^{199}Hg^+$ (mercury) and $^{171}Yb^+$ (ytterbium) and in the neutral atom ^{87}Sr [36, 38]. Due to the development of frequency comb technology, the comparison of optical frequency standards with each other can be made with a smaller uncertainty than the realization of the SI second itself [39]. These comparisons can show whether the reproducibility of the optical standards – which so far have been operated only intermittently – confirms the assessed small uncertainty.

Already early in the 80s, work on the calcium frequency standard was started in the "Length" Group of the former "Mechanics" Division of PTB. In the past few years, work on strontium was started. (See also the article of H. Schnatz in this publication) [40]. For many years, work in the "Time and Frequency" Department has been concentrated on transitions in the ion of the isotope ytterbium-171. The core piece is a so-called "ion trap", in which a single ion (a positively single-charged atom) can be retained for weeks and months. Figure 14 shows the ytterbium ion traps presently used at PTB. The relative measurement uncertainty for the transition frequency of the selected clock transition of $1.1 \cdot 10^{-15}$ is – as can be seen by a comparison with the information given on CSF1 – determined decisively by the uncertainty of the realization of the time unit [41].

A completely new concept investigated at PTB is that of an optical clock which shall be based on a gamma radiation transition in the atomic nucleus (not – as is usual – in the electron shell) of the isotope thorium-229 [42]. The special feature of this transition is the energy which, for a nuclear transition, is extremely low, so that it can be excited with the radiation of a laser.

Where can this concept be used? In everyday life, time and frequency measurements are of extraordinary importance. Without atomic clocks or without the dissemination of exact time information, our telecommunications system, the quality of energy supplies across frontiers, and navigation with GPS – to give just a few examples – would not function the way we are used to. The integration of better (optical) clocks into these established technical systems cannot be achieved in a trivial way; in the long term, it can, however, lead to an improvement of these systems and also allow new applications in everyday life.

Less common and less obvious is the use of time measurement in Earth observation. Everyone uses the key words "climate change" and "tsunami", but only a very detailed understanding of our Earth and the measurement of a great number of quantities in SI units, with a correspondingly long-term comparability of measurements, allow reliable statements and forecasts to be made and behaviour guidelines to be given for politics and for society. To achieve this, the establishment of the "Global Geodetic Observation System" (GGOS) has been agreed upon [43]. With the equipment commonly used today in observation stations, various research aims can be reached to a limited extent only. Here, access to better clocks would help – be it that improved clocks are operated in the observation stations, be it that these stations are interlinked with time-keeping institutes via modern procedures [40, 44].

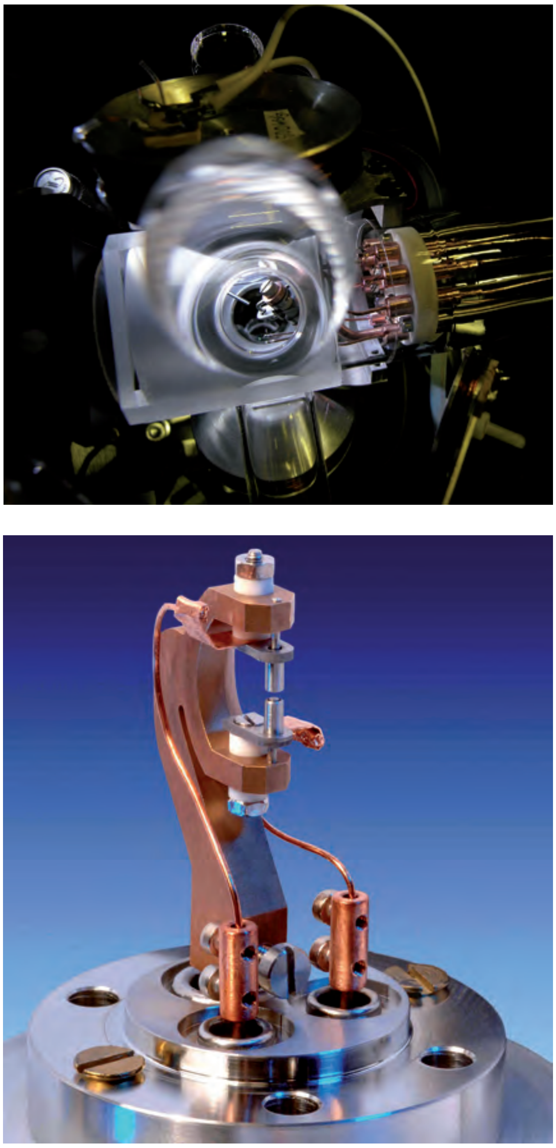

Figure 14:
On the left: Vacuum recipient with ion trap (in the centre) for the spectroscopy of single ytterbium ions [41]; on the right: Detail of the latest trap arrangement, a so-called end cap trap which has been used since the beginning of 2010.

Where do time and frequency measurements play a role when it comes to answering fundamental questions of physics? Let us mention the development of quantum mechanics as an example from the past: This development progressed when the theoretical explanation of subtle characteristics of atomic spectra succeeded. In most cases, the experimental data were the result of frequency or wavelength measurements. Quantitative tests of the general and special theory of relativity are based on time and frequency comparisons [30, 45, 46]. The – although indirect – proof of the radiation of gravitational waves in a rotating double-star system was provided by the analysis of the arrival time of the pulse signals with respect to atomic time scales [47]. Many of the approaches searching for "new physics" concentrate on possible deviations from Einstein's Principle of Equivalence [30]. An experiment in this connection which can be easily carried out is the comparison of two atomic clocks with different atomic references (e. g. caesium clock versus hydrogen maser) in the time-dependent gravitational potential of the Sun – during the annual rotation of the Earth on its elliptical orbit [48]. In the past 20 years, hypothetical infractions of the Principle of Equivalence have – to an ever increasing extent – been gradually ruled out. The availability of more exact clocks and improved possibilities for the comparison of clocks were the prerequisite [49]. In future, this type of time measurement will continue to offer a wide field of activities for PTB which will excellently complement PTB's tasks of everyday routine.

8 Closing Remarks

"Sometimes I get up in the middle of the night and stop all the clocks. However, we should not fear time – it, too, is a creature of the Father who created all of us".(1) ■

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Mass and Amount of Substance – the SI Base Units “Kilogram” and “Mole”

Peter Becker*[1], Michael Borys*[2], Michael Gläser*[3], Bernd Güttler*[4], Detlef Schiel*[5]

Contents

1 Introduction

The physical quantities *mass* and *amount of substance* are measured in the units *kilogram* and *mole*. They are two out of a total of seven units of the International System of Units (SI). Although the kilogram and the mole are defined as independent base units, they are closely related to each other. One mole of the carbon isotope ^{12}C has, for example, a mass of exactly 12 grams. Usually, the instrument used to determine the mass of an object is the balance; it is, however, also used to determine the amount of substance. The mass divided by the known molar mass furnishes the amount of substance in the unit mole. Colloquially, the word “weight” is mostly used instead of “mass”. In science, the weight is, however, a synonym of the weight force which not only depends on the mass, but also on the gravitational acceleration. The unit of mass is the kilogram, that of the force the newton. Analogically, the word “molecular weight” is often used in chemistry instead of the term “molar mass” which is the correct designation. The molar mass has the unit *gram/mole*. The amount of substance differs from the mass in particular by the fact that identical amounts of different substances contain the same number of atoms, molecules or other atomic particles, but do not usually have the same mass.

The number of atoms, molecules or other atomic particles in a mole is indicated by the *Avogadro constant*. When $m_A(X)$ is the mass of an atom, a molecule or of another atomic particle X, and $M(X)$ is the molar mass of this particle, the Avogadro constant N_A is obtained as follows:

$$N_A = \frac{M(X)}{m_A(X)} \qquad (1.1)$$

In future, the units *kilogram* and *mole* – but also *ampere* and *kelvin* – are to be redefined. The kilogram is the only one of the seven SI base units which is still defined by a material embodiment, i. e. by the international prototype of the kilogram. As such a body is subject to changes, it is planned – through redefinitions – to trace the kilogram as well as the mole, the ampere and the kelvin back to invariable fundamental constants. The experiment for the determination of the Avogadro constant with the aid of a silicon single crystal can make a contribution to the redefinition of the kilogram – but also of the mole – as in the definition of the mole, *mass* and *amount of substance* are interlinked (see equation (3.1) below).

After a brief historical survey, Section 2 describes the realization of the kilogram according to its definition and its dissemination [1]. In Section 3, the same is done for the mole. In Section 4, an outlook is given of the planned redefinitions.

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2 Kilogram

2.1 History

Mass – together with *length* and *time* – is one of the oldest measurands of humankind. The previous designation *weight* did not yet make a distinction between the *weight force* and the physical quantity *mass*. It was only Newton who introduced the term "mass" and postulated that the force by which a body changes its state of motion is proportional to its mass and its change of motion. He also showed that this so-called inert mass is also proportional to the gravitational mass of the body. The gravitational mass is the mass which is proportional to the weight force. The concept "weight" therefore is today synonymous with "weight force" [2]. Only colloquially, weight is often still used in the meaning of mass.

For a few thousand years, measuring instruments such as, for example, beam balances and suitable weights have been used in trade and in the general exchange of goods to determine the quantity of goods. Findings of scales and weights of old civilizations in Mesopotamia, on the river Nile and in the Indus valley date back as far as 3000 B.C. The weights were frequently provided with a sovereign's emblem as evidence of their correctness. Standard measures of the state were also stored in temples or in other sanctuaries. In the Roman Empire, the *exagia* were, for example, stored in the Capitol in Rome. After the Migration Period, Charlemagne tried to introduce uniform measures and weights in his empire by an ordinance. During the ensuing period, however, a large number of units of measurements and weights came into existence. Most cities defined their own units which, in addition, differed according to the goods traded. This situation changed only at the beginning of the industrial era. During the French Revolution, the change in the political situation was utilized to change and unify the weights and measures as well. The era of enlightenment led – among the intelligentsia of the 18th century – to a universal, transnational way of thinking which promoted the ideal of worldwide uniform weights and measures. Still in 1791 – under Louis XVI – a law on the introduction of natural and invariable units of measurements was decreed [3, 4]. Other nations were to be included. The length of a quarter of the meridian should serve as the basis. The Frenchmen Delambre and Méchain measured the distance from Dunkerque to Barcelona and determined the length of the meridian. In 1793, the ten millionth part of the quarter of the meridian was defined as the new unit of length *"metre"* and the mass of a cubic decimetre of water as the mass unit *"grave"*. Later on, the gram was chosen and only in 1799 was the kilogram given its name and was then defined as the mass of a platinum cylinder representing the mass of a cubic decimetre of water at 4 °C. At that time, the metre was also defined as the distance between two division marks on a platinum rod. The platinum cylinder is known as the "kilogram of the archive" and is today stored in the Musée des Arts et Métiers in Paris. After a return to the old system of units, from 1840 on, only the metre and the kilogram were used for measuring and weighing in France. Other countries also adopted the new French units and in 1875, 17 countries joined together to sign a treaty on the introduction of the metric units which is referred to as the *Metre Convention*. New prototypes, which were – within the scope of the measurement accuracy achieved at that time – in compliance with the French prototypes of 1799, were manufactured for the metre and the kilogram from a platinum-iridium alloy. In 1889, these standards, which were called the "international prototypes for the metre and the kilogram", were confirmed by the first General Conference on Weights and Measures[5].

Since 1901, the definition of the kilogram has been [2]:
The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.

2.2 Realization and dissemination

Since its sanctioning by the first General Conference on Weights and Measures in 1889, the international prototype of the kilogram has embodied the unit of mass [6] (Figure 1). The definition and the realization of the unit of mass are thus linked to this cylindrical platinum-iridium artefact.

The dissemination is performed via an uninterrupted chain of mass comparisons, with the international prototype of the kilogram being at the top of the hierarchy (Figure 2). At the highest level, these comparisons are carried out with copies of the international prototype of the kilogram. The copies consist of the same platinum-iridium alloy (PtIr 10) and have the same cylindrical shape and the same dimensions.

Since 1889, more than 80 copies have been distributed to the Member States of the Metre Convention and to the BIPM. To distinguish them, they are marked with a number. The national prototype of the kilogram of the Federal Republic of Germany is prototype No. 52 which was acquired in 1954. The dissemination of the unit of mass from the international prototype of the kilogram to the national prototypes is usually performed via the kilogram prototypes which are used by the BIPM as working standards. For this purpose, the national prototypes are recalibrated approximately every ten years at the BIPM. Comparisons with the international prototype of the kilogram are carried

Figure 1:
International prototype of the kilogram (kept under three bell jars at the Bureau International des Poids et Mesures (BIPM) in Sèvres near Paris).

out at considerably larger intervals within the scope of so-called periodic verifications. After the first comparison measurements in the years from 1883 to 1888, the national prototypes of the kilogram have been called in for only three periodic verifications: 1899 to 1911 (at the first periodic verification, not the international prototype of the kilogram, but kilogram prototype No. 1 was used as a reference), 1939/46 to 1953 (interrupted by the Second World War) and 1988 to 1992 [7]. The uncertainty with which the mass of the national prototypes of the kilogram is determined by the BIPM depends on the time passed since the last link-up of the working standards of the BIPM with the international prototype of the kilogram. In the past, the mass of the national prototypes was determined with typical standard uncertainties in a range between 2 µg and 8 µg (relative $2 \cdot 10^{-9}$ to $8 \cdot 10^{-9}$, cf. Figure 2).

Based on the national prototypes of the kilogram, the unit of mass is disseminated in the metrology institutes to their secondary standards which usually consist of non-corrosive, non-magnetic steel. Due to the required transition from a density of 21,500 kg/m³ (Pt-Ir) to a density of 8,000 kg/m³ (steel) and the correspondingly

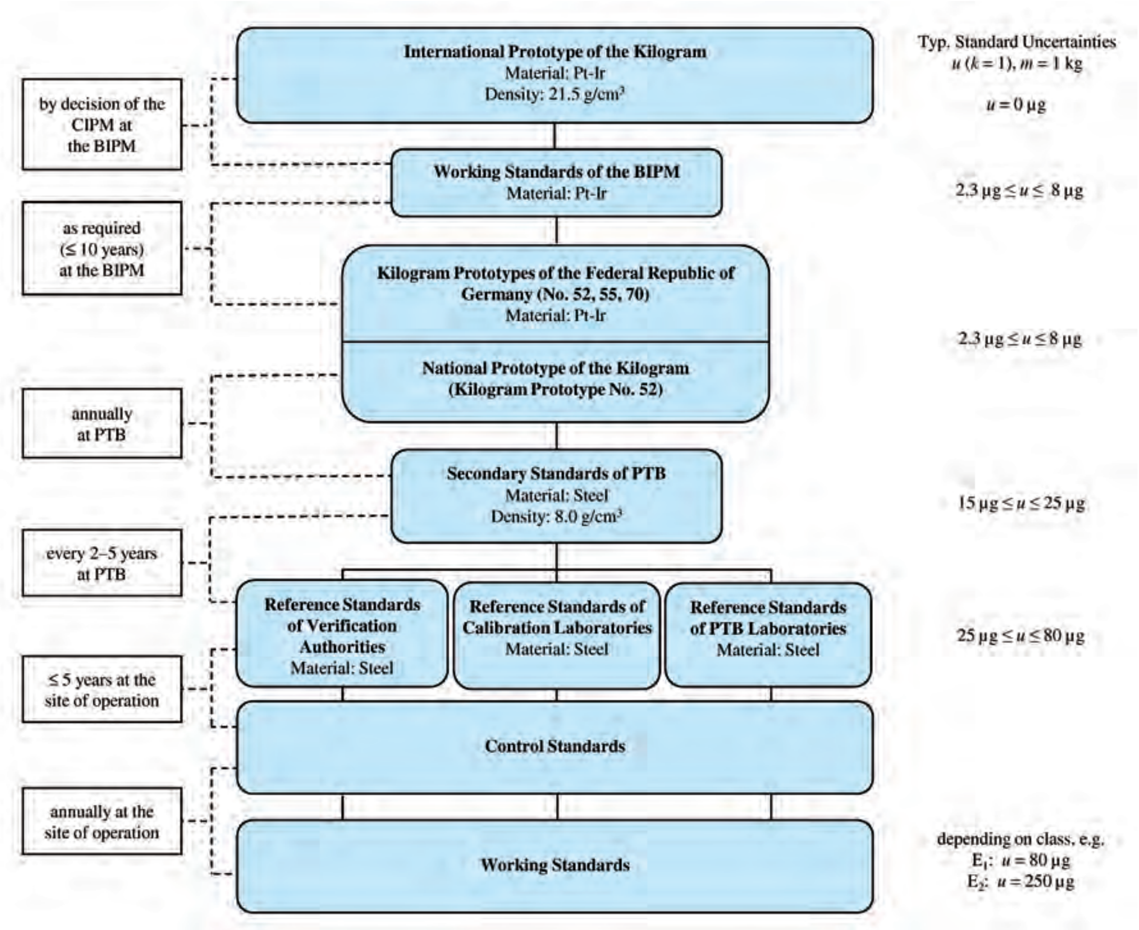

Figure 2:
Traceability of mass standards in the Federal Republic of Germany (Pt-Ir: alloy made of 90 % platinum and 10 % iridium, BIPM: Bureau International des Poids et Mesures, CIPM: Comité International des Poids et Mesures).

different air buoyancy, special demands on the air density determination have to be considered. If a mass comparison between a kilogram prototype with a mass m_{Pt} and a volume V_{Pt} and a mass standard made of steel with an unknown mass m_{St} and a volume V_{St} is performed in the form of a substitution weighing in air with a density ρ_{a}, and if a weighing difference (already corrected for buoyancy) $\Delta m'_{\mathrm{W,St-Pt}}$ is determined, the following weighing equation is obtained [8]:

$$m_{\mathrm{St}} = m_{\mathrm{Pt}} + \rho_{\mathrm{a}}\left(V_{\mathrm{St}} - V_{\mathrm{Pt}}\right) + \Delta m'_{\mathrm{W,St\text{-}Pt}} \,. \tag{2.1}$$

The uncertainty with which the mass of the unknown standard can be determined thus depends on the uncertainty components of the mass of the kilogram prototype, of the air density, of the volume difference and of the weighing process. The term ρ_{a} ($V_{\mathrm{St}} - V_{\mathrm{Pt}}$) describes the buoyancy difference between the two bodies and is referred to as “buoyancy correction”. When a steel mass standard of 1 kg is linked up with a kilogram prototype made of platinum-iridium, the volume difference of approx. 80 cm^3 leads – under normal ambient conditions – to a buoyancy difference of approx. 100 mg. To correct this buoyancy difference with sufficient accuracy, the air density is determined during the weighing process by measuring the air density parameters (temperature, pressure, humidity and, where required, CO_2 content) with the aid of the air density formula (also called the “CIPM equation”) recommended by the Comité International des Poids et Mesures (CIPM) [9]. This can be achieved with a relative standard uncertainty of approx. $6 \cdot 10^{-5}$ if the air density parameters are measured with the utmost effort. For a mass comparison between a platinum-iridium standard and a steel standard, an uncertainty contribution of approx. 6 µg results. Hence, the uncertainty of the air buoyancy correction is often significantly larger than the uncertainty contributions of the weighing and of other influence quantities [8]. Even smaller uncertainties can be achieved by the weighing of special buoyancy artefacts [10]. With this method, air density determinations with relative standard uncertainties of approx. $2 \cdot 10^{-5}$ are possible [11–13].

The mass link-up of 1 kg secondary standards with national prototypes of the kilogram is carried out on special 1 kg mass comparators, i. e. on so-called “prototype balances” (Figure 3). Compared to their maximum capacity, they have only a small weighing range which, however, allows a very high resolution with small linearity deviations. The mass comparator shown in Figure 3b has, for example, an electric weighing range of 2 g which can be resolved with 0.1 µg, i. e. in steps of $2 \cdot 10^7$ and with a maximum linearity deviation of approx. one microgram. To reduce the remaining uncertainty contributions of the linearity and the adjustment of the weighing range, suitable mass standards are used as auxiliary weights which limit the weighing difference to approx. 10 % of the weighing range. Today, prototype balances are kept almost exclusively in pressure-tight enclosures which can, in most cases, also be evacuated. Under conditions with stable pressure and temperature variations of a few millikelvins, relative stand-

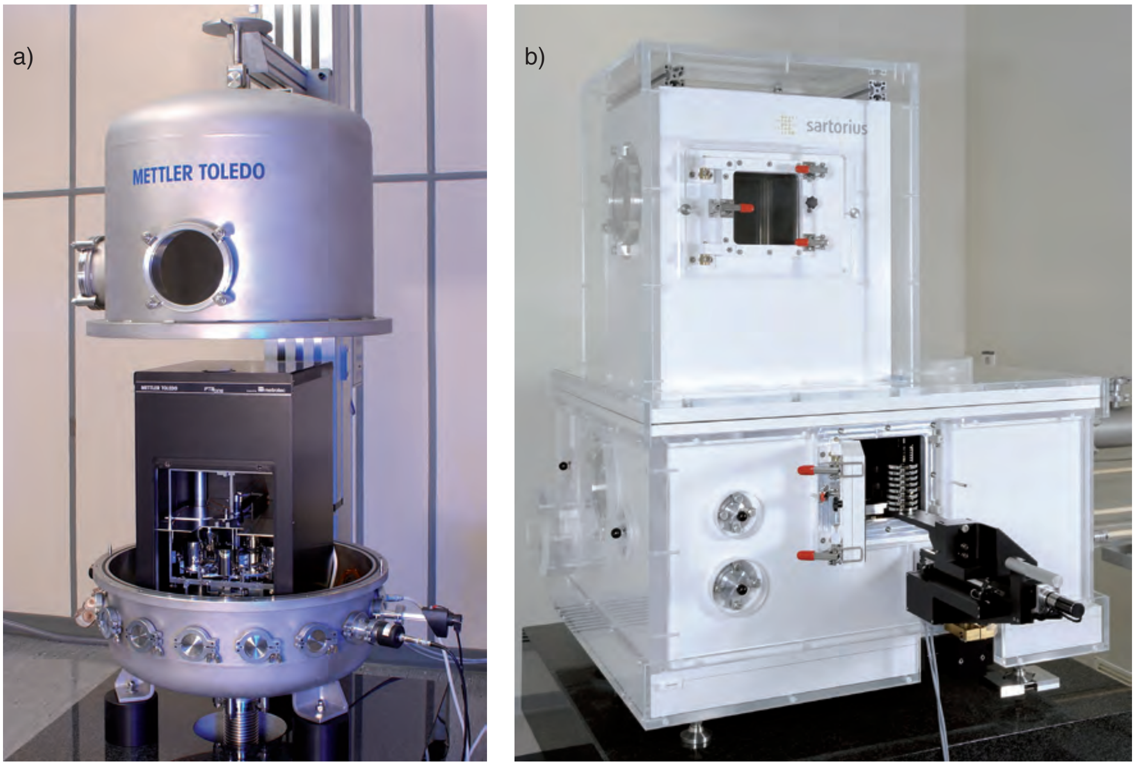

Figure 3:

PTB’s prototype balances (1 kg vacuum mass comparators, installed in vacuum-resistant chambers).

a) Mettler-Toledo M_one: automatic weight exchange facility with 6 positions, resolution 0.1 µg, standard deviation ≤ 0.3 µg;

b) Sartorius CCL1007: automatic weight exchange facility with 8 positions, resolution 0.1 µg, standard deviation ≤ 0.2 µg ard deviations of $\leq 2 \cdot 10^{-10}$ can be achieved with modern prototype balances.

The quality of the mass standards used must be such that – within the recalibration intervals – a mass stability is guaranteed which is sufficient in relation to the uncertainty of their mass. Language differentiates between “mass standards” and “weights” which are admissible for verification (in the latter case, the words “admissible for verification” are often omitted). For weights (admissible for verification), international directives and recommendations as well as national regulations are valid which define the maximum permissible errors, the materials, the shape, the magnetic properties, the surface quality, etc. [14–17]. Mass standards should at least meet the requirements which have been established for the surface quality and the magnetic properties of weights of comparable uncertainty.

The determination of the masses of any test pieces requires the realization and dissemination of multiples and submultiples of the unit “kilogram”. In the national metrology institutes, multiples and submultiples of the unit are derived from the national prototypes as a so-called mass scale [8, 18]. The derivation is performed with the aid of weight sets of a suitable sequence in accordance with a weighing scheme which defines the respective combinations of mass standards with identical and different nominal values for the mass comparisons to be carried out. The weighing scheme is designed in such a way that an over-determined system of weighing equations is obtained. The masses of the standards to be determined as well as their variances and covariances are calculated using a least-squares adjustment carried out with this system of equations. As a result of the derivation, secondary standards are available which have been traced back to the national prototype of the kilogram and which embody multiples and submultiples of the unit. They allow the unit of mass to be disseminated to the reference standards of institutions and authorities in legal metrology, of calibration laboratories in the field of industrial metrology and of other institutions of research, industry and metrology. The mass scale is derived for the nominal values which are required regularly and for which particularly high requirements must be met. The range in which the mass scale is derived – for example at PTB – comprises the nominal values from 1 mg to 5 t, i. e. more than nine orders of magnitude. For the derivation of the mass scale and the dissemination of multiples and submultiples over several orders of magnitude, mass comparators and weighing instruments must be used which have been optimized for the respective range of the nominal load. Table 1 shows a selection of the systems used for this purpose at PTB, including their most important characteristics.

Figure 4 gives a survey of the smallest uncertainties with which mass standards can be calibrated at PTB in accordance with the entries in the CMC[1] tables of the BIPM [http://kcdb.bipm.org/appendixC/]. The relative uncertainties, expanded by the factor $k = 2$, lie in a range from $2.8 \cdot 10^{-8}$ (for 1 kg) to $4 \cdot 10^{-4}$ (for 1 mg). The uncertainties stated in the CMC tables of the BIPM have been confirmed

Table 1:
Data of the balances and mass comparators used at PTB for the realization of the mass scale and for high-precision mass determinations [18],
(Max: maximum capacity, d: scale division value, s: standard deviation, s_{rel}: relative standard deviation related to the usable maximum capacity, EMFC: electromagnetic force compensation)

Range of nominal values	**Max / *d***	**Weighing principle**	***s***	***s***
1 mg to 5 g	5 g / 0.1 µg	Electronic comparator balance with complete EMFC	0.3 µg	$6 \cdot 10^{-8}$
10 g to 100 g	111 g / 1 µg	Mass comparator with automatic weight exchange facility, 4 positions	1.2 µg	$1.1 \cdot 10^{-8}$
100 g to 1 kg	1 kg / 0.1 µg	Vacuum mass comparators with automatic weight exchange facility, 6 and 8 positions (prototype balances)	0.3 µg	$3 \cdot 10^{-10}$
2 kg to 10 kg	10 kg / 10 µg	Mass comparator with automatic weight exchange facility, 4 positions	20 µg	$2 \cdot 10^{-9}$
20 kg to 50 kg	64 kg / 0.1 mg	Mass comparator with automatic weight exchange facility, 4 positions	0.4 mg	$6.3 \cdot 10^{-9}$
100 kg to 500 kg	600 kg / 0.1 g	Electronic comparator balance with complete EMFC and automatic weight exchange facility, 2 positions	0.2 g	$3.3 \cdot 10^{-7}$
500 kg to 5000 kg	5000 kg / 0.02 g	Mechanical, equal-armed beam balance with automated acquisition of measured data	0.6 g	$1.2 \cdot 10^{-7}$

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[1] Calibration and measurement capabilities (CMC)

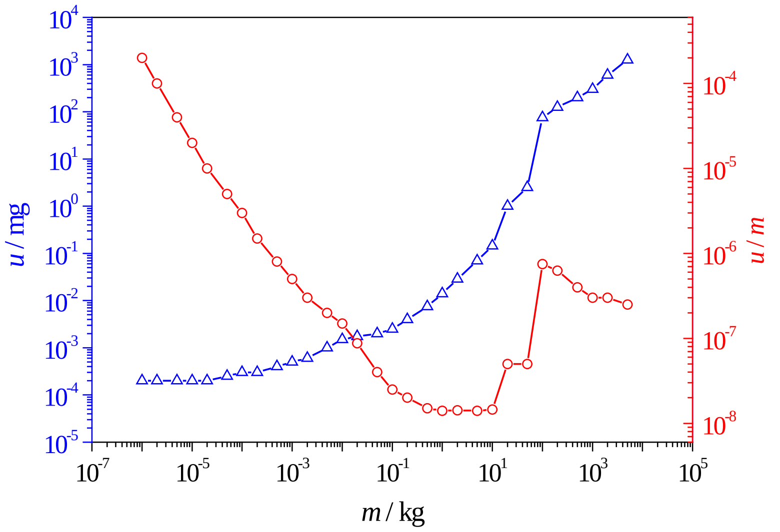


Figure 4:
Smallest standard uncertainties ($k = 1$) with which mass standards can be calibrated at PTB in agreement with the entries in the CMC[2] tables of the BIPM [6] (triangles: absolute values u in mg, circles: relative values u/m).

within the scope of international comparison measurements (key comparisons) and are mutually recognized by all metrology institutes involved, in accordance with Annex C of the mutual agreement (MRA) of the International Committee for Weights and Measures (CIPM) [http://www.bipm.org/en/cipm-mra/].

3 Mole

The mole is the SI base unit for the base quantity "amount of substance" and corresponds to a number of identical, defined elementary entities. Chemical reactions take place on the basis of multiples of these smallest, identifiable components of a substance, e. g. their atoms or molecules. This is why the mole is the natural unit for measuring the amount of substance.

3.1 History

The concepts "mole" and "Avogadro constant" are based on the interpretation of chemical processes as interactions between atoms and molecules. In 1808, John Dalton (1766–1844) declared that atoms of an element do not differ from one another and that they have a defined atomic mass. In 1811, Avogadro (1776–1856) published his hypothesis that the same volumes of all gases contain – at the same temperature and the same pressure – the same number of molecules. Initially, his observation was forgotten until Stanislao Cannizarro revived it again and published, in 1858, a consistent system of chemical formulas and "atomic weights" (relative atomic masses, see below) of all elements. Subsequently, terms such as atomic and molecular weight as well as other terms based on atomic theory developed in chemistry [19].

The origin of the concept "mole" is attributed to Wilhelm Ostwald (see, e. g., [20]). In his *"Hand- und Hilfsbuch zur Ausführung Physiko-Chemischer Messungen"* of 1893, he writes: "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..." [21]. Similar terms such as, for example, "g-Molekel" or "g-Mol" with a comparable meaning were, however, at the same time also used by others (see, e. g., [23]). According to this definition, the unit "mole" was, therefore, closely connected with the mass and for a long time it was interpreted as "chemical mass unit". Although the atomic perception – which links the mole up with a particle number and, therefore, requires the introduction of an additional base quantity, the "amount of substance" – had existed since Dalton and Avogadro there was, first of all, a lack of experimental results which could confirm these models [22]. The experimental confirmation of the atomic theory and the determination of the Avogadro constant (particle number per mole) finally led to two different perceptions of the mole, which Stille [23] differentiated by the concepts "mole" (as chemical mass unit) and "mole number" (as a unit related to a particle number which is defined by the Avogadro constant).

The integration of the unit "mole" into the SI system of units resolved this contradiction and made a differentiation of the concepts superfluous. It took place at a very much later date, in October 1971, after the 14th General Conference of the Metre Convention had decided to introduce the "amount of substance" as the 7th base quantity. The English term "amount of substance" was derived from the German term "Stoffmenge", introduced by Stille [24, 25]. The decision had been preceded by a corresponding recommendation of the International Union of Pure and Applied Physics (IUPAP), of the International Union of Pure and Applied Chemistry (IUPAC) and of the International Organization for Standardization (ISO), together with the note to select the carbon isotope ^{12}C as the reference point [6]. A committee of the BIPM (previously: Metre Convention) that deals with issues related to the base quantity "amount of substance" (Comité Consultatif pour la Quantité de Matière – CCQM) was again established much later, i. e. in 1993 [26].

3.2 The mole as an SI unit in chemistry

The mole establishes a connection between the SI of the Metre Convention and chemistry. With the aid of the mole, quantitative relations in chemistry can be traced back to SI units and internationally compared. Based on the mole, a large number of national standards for important measurands in chemistry have been introduced in recent years so that they are now traceable to the SI.

In daily practice (e. g. in the performance of chemical reactions in the laboratory or in the chemical industry), a very large number of atoms and molecules is involved in any reaction. The unit "mole" therefore combines – for practical and historical reasons – so many particles that reference to other units (the kilogram) can be made relatively easily.

The definition of the SI unit "mole" is [6] :

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".
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.

In this definition, it is understood that unbound atoms of carbon 12, at rest and in their ground state, are referred to [6].

Unlike Ostwald, whose definition related only to the mass, reference is now made to a particle number. The number of particles corresponds to the numerical value of the Avogadro constant which is today determined with maximum accuracy within the scope of the Avogadro project.

In practice, traceability to the mole is, however, in most cases realized via a weighing process and reference to the relative atomic mass. The connection between the amount of substance n_A of an analyte A and its mass m (measured in grams) is performed via its molar mass $M(\mathrm{A})$ (measured in g/mol):

$$n_\mathrm{A} = \frac{m}{M(\mathrm{A})} \qquad (3.1)$$

whereby the molar mass of ^{12}C, $M(^{12}\mathrm{C}) = 12$ g/mol, serves as a reference basis for $M(\mathrm{A})$. The molar mass of a substance can be calculated from the mean, relative atomic masses A_r of the elements involved, which are usually well known. These also have ^{12}C as the reference point; $A_\mathrm{r}(^{12}\mathrm{C}) = 12$ (dimensionless) by definition. The mean relative atomic masses take the relative atomic masses of all isotopes of an element and their abundance on earth into account [6, 27]. The molar mass $M(\mathrm{A})$ of the substance A is the sum of the mean relative atomic masses A_r of all elements of a molecule of the substance A in accordance with its stoichiometric composition $A_\mathrm{r}(\mathrm{A})$ multiplied by the molar mass constant M_u. From the definition of the mole it follows that M_u is exactly 1 g/mol:

$$M(\mathrm{A}) = A_\mathrm{r}(\mathrm{A}) \times M_\mathrm{u} \qquad (3.2)$$

Traceability to the mole without reference to the mass via a determination of the particle number is, however, also conceivable, provided that the Avogadro constant is known. Concepts for measurements of the number of elementary entities have been available for a long time, although this had been limited to special cases (see Section 4.2.1). The measurement can, for example, be performed by determining the amount of substance of a crystalline solid with the aid of its microscopic, crystallographic lattice parameter and its macroscopic volume. In principle, this is also done within the scope of the Avogadro project where a high-purity ^{28}Si single crystal sphere and its crystal lattice parameters are measured. Similar – albeit simpler – experiments have been carried out since the discovery of X-ray diffraction. There are also experiments for the (direct or indirect) counting of elementary entities, e. g. of ions [28] and electrons (single-electron-tunnelling – SET circuits) which could become relevant, for example, within the scope of a quantum-metrological redefinition of the SI base unit *ampere* (for further details, see the article *The SI Base Unit "Ampere"* by *F. J. Ahlers* in this brochure, as well as [29, 30, 31]). Counting rates of several GHZ have been achieved with this approach [31].

In addition, there are numerous procedures for the observation of single atoms (scanning probe microscopy) and also chemical-analytical procedures for the identification and detection of single molecules [32]. None of these procedures is currently suited to quantify macroscopic sample quantities in the order of 1 mol. But this may also not be necessary in some application fields (e. g. in nanotechnology).

Unlike the other base units the mole is, thus, defined by two sentences. The first one defines a particle number. The second one requires the identification of the elementary entities and establishes – beyond the field of physics – the connection to analytical chemistry. The complete description of a measuring operation for the determination of the amount of substance of a measurand in the unit mole thus requires the **identification** and **quantification** of a specified entity (analyte). The amount of substance 1 mol always contains the same number of specified entities. This number is identical to the numerical value of the Avogadro constant which is currently being redetermined within the scope of the Avogadro project.

As regards the identification of the entities, the additional notes in the SI-defining publication also explain: "It is important to always give a precise specification of the entity involved (as emphasized in the second sentence of the definition of the mole); this should preferably be done by giving the empirical chemical formula of the material involved." [6]. This implies that – in addition to the chemical formula – other information may be required for their complete description such as, for example, information about their structure.

3.3 Realization and dissemination

3.3.1 Primary standards as reference points

Traceability to an SI unit can be achieved via the practical realization of the unit in the form of primary standards with a specified quantity value and an associated measurement uncertainty [33]. Primary standards are measurement standards established using a primary reference measurement procedure [33]. This is a reference measurement procedure used to obtain a measurement result without relation to a measurement standard for a quantity of the same kind [33]. Primary measurement procedures are, therefore, at the same time the first step in the dissemination chain from the SI to the end user [34].

In the case of the amount of substance and the unit mole, a primary standard requires a measurement procedure that can be used to identify and quantify the measurand. In practice, information is usually required on measurands, such as the substance concentration c_A of an analyte A in a matrix

$$c_\mathrm{A} = \frac{n_\mathrm{A}}{V}\text{, indicated in mol/m}^3, \tag{3.3}$$

or of its amount fraction x_A

$$x_\mathrm{A} = \frac{n_\mathrm{A}}{n_\mathrm{Matrix}}, \tag{3.4}$$

indicated as dimensionless quantity or in mol/mol.

The identification requires a measurement procedure which recognizes a molecule as a whole (counting of the atomic components is not sufficient). In the case of mass spectrometry, this is, for example, done on the basis of the mass of the molecule. Other ways of achieving an identification are the observation of the characteristic intramolecular vibrational frequencies with the aid of infrared and Raman spectrometry ("fingerprint" method) or with the aid of characteristic chemical shifts of resonance frequencies in the case of nuclear magnetic resonance spectroscopy.

In practical applications, the quantification of a measurand by measuring the number of elementary entities is, in most cases, unrealistic. This is why it is performed by comparison with a pure substance of analyte A, whose amount of substance n_A is known from the known mass m of the pure substance and its purity $R(\mathrm{A})$:

$$n_\mathrm{A} = \frac{m}{M(\mathrm{A})} R(A) \tag{3.5}$$

Example: National standards for the determination of element concentrations in solutions

Safeguarding the correctness of measurements of the element concentration in solutions is one of the most frequently performed metrological tasks in chemistry. For this purpose, PTB provides – in cooperation with the *BAM Bundesanstalt für Materialforschung und -prüfung (Federal Institute for Materials Research and Testing)* – national standards in the form of monoelement solutions in water as reference points. Here, the practical link-up of the element content with the mole is realized with the aid of "pure materials" (metals and salts). The purity of these materials specifies the fraction of the main component (A) of the material, e. g. the fraction of Cu in a Cu material. On the basis of its mass $m_\mathrm{A} = m \cdot R(\mathrm{A})$ (m = total mass of the material) and the molar mass M_A, an amount of substance can be assigned to this fraction in accordance with equation 3.5 and the SI link-up can, thus, be realized. The uncertainty of the link-up, i. e. the uncertainty of the amount of substance n_A, is determined by the uncertainty of the purity, by the uncertainty of the mass measurement and by the uncertainty of the molar mass. In contrast to that, the absolute amount of the purity is, in principle, irrelevant to the link-up, although smaller uncertainties for the purity may be achieved for high-purity materials.

The pure substances are investigated with regard to their impurity contents caused by all other conceivable elements to obtain an uncertainty of the purity $U_\mathrm{rel}(R)$ which should preferably be smaller than $5 \cdot 10^{-5}$ g/g. This makes it, for example, necessary to measure – in addition to metals – also such non-metals which are difficult to measure – such as carbon, oxygen and nitrogen – up to relative contents of 10^{-6} g/g. This is a well-known problem of many commercial pure substances which are offered with a nominally high purity, but have been investigated only with respect to the elements which are analytically easy to access. [35]

For dissemination, the national standards for element analysis maintained by the BAM must be transferred into solution. At PTB, this is done gravimetrically, i. e. the element content is determined only on the basis of the measured masses of the pure substances and of the chemical products used for dissolving and diluting. In addition, secondary solutions (transfer solutions) are linked up with the primary solutions with the aid of preci-

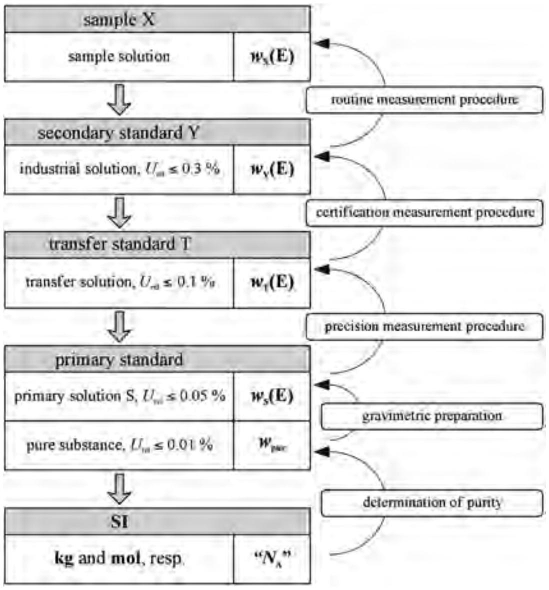


Figure 5:
Traceability system for monoelement calibration solutions.

sion measurement procedures and disseminated to calibration laboratories. The relative uncertainty of the element content of the primary solutions is U_{rel} (primary solution) $\leq 10^{-4}$ g/g, whereas the relative uncertainty of the transfer solution U_{rel} (transfer solution) amounts to $\leq 2 \cdot 10^{-3}$ g/g. This system, which is based on the dissemination of reference materials (in most cases: monoelement calibration solutions) is shown in Figure 5. It allows the test laboratories to obtain traceable and – thus – also comparable measurement results. In particular in the EU, comparability is a quality characteristic which is demanded for measurement results to an ever increasing extent.

When real samples (e. g. waste water, food) are measured using non-primary methods in test laboratories, matrix effects may occur. They cause measurement value deviations although traceability has been established on the basis of monoelement calibration solutions. This makes a validation of the measurement methods with the aid of traceable matrix reference materials indispensable. Unfortunately, only a few of them are currently available, among other things, due to the large variety of substances in chemistry. A possibility of overcoming this bottleneck is by comparison measurements. In this case, metrology institutes or calibration laboratories assign traceable values to the materials used. This allows the test laboratories to validate their measurement procedures during each comparison measurement (mandatorily or voluntarily). This concept is applied by PTB in almost all traceability and dissemination systems and guarantees a rational, comprehensive and sustainable dissemination.

Examples of primary measurement procedures

Different primary measurement procedures for establishing traceability to the mole have been discussed [34, 36]. We concentrate here on procedures with a particularly high relevance to practice. In most cases, these procedures are used to establish traceability to the mole.

In most cases, traceability is realized with the aid of so-called “ratio primary reference measurement procedures” [33, 34] such as, for example, isotope dilution mass spectrometry. Here, an exactly known quantity of the analyte is added to the sample in a synthetic, isotope-modified form as an internal, chemically identical standard. Then, signals of the synthetic and of the natural form of the analyte can be distinguished in the mass spectrum. The concentration of the analyte can be determined by comparing the signal intensities of the natural and of the added, isotopically labelled analyte (isotopologue). This procedure allows measurement results to be determined with measurement uncertainties which are not influenced by recovery rates and analytical preparation steps. A particularly high accuracy is achieved when the measuring operation is related to an exactly known, gravimetrically prepared reference mixture of the analyte in the same matrix and in a similar concentration. The same quantity of the isotopically labelled standard is added to this reference mixture, and the results are compared (“exact matching”) [37]. In this case, the measurement accuracy is no longer influenced by the isotopically labelled standard. An equivalent procedure can also be applied in the case of the vibration-spectroscopic procedures mentioned above which are based on other physical principles, but are also mass-sensitive and, therefore, allow isotopologues to be observed separately and to be used as internal standards [38].

Primary measurement procedures based on this principle allow measurement uncertainties in the range from 1 % to 3 % ($k = 2$) to be achieved, e. g. in trace analysis in environmental protection (e. g. Hg in drinking water) or in clinical chemistry (e. g. creatinine in blood serum).

Gravimetry and coulometry allow a substance to be directly quantified by weighing or by measuring the electric charge [34, 36]. With the aid of gravimetry it is, for example, possible to prepare – as described above – reference solution by weighing a substance to be solved or by preparing a gas mixture. In the case of coulometry, the amount of substance of a solved, ionic substance is determined in an electro-chemical process via the charge z. The electric conductivity is proportional to the amount of substance n_{A} of the analyte A:

$$n_{\mathrm{A}} = \frac{1}{z\,F} \int I \mathrm{d}t \, . \qquad (3.6)$$

F is the Faraday constant, *I* the electric current and *t* the time.

These measurements initially furnish, however, in both cases only the quantity of an unidentified substance of unknown purity as a result. For traceability to the mole, the measurement result (mass or electric charge) must be complemented by an identification and by a purity determination of the substance investigated with the aid of additional measurement procedures.

3.3.2 Establishment of international comparability

Beyond a realization of the mole, the international comparability of measurement results also requires suitable, internationally accepted reference points. In addition, the exact and documented knowledge of the correctness of these reference points and their measurement uncertainty shall also allow comparability of measurement results over long periods of time. Measurement results which can be compared over many decades are, for example, required in environmental protection and in climate control.

In the case of the SI unit "mole", complete traceability would require primary standards for all distinguishable chemical compounds, i.e. ultimately for the whole variety of natural and synthetic substances. These substances may be concentrations of pollutants in air or water or clinical markers in blood serum, but also – as described above – high-precision solutions of elements in water which have been prepared gravimetrically and which are required for calibration in element analysis. The definition of the analyte and the matrix is, thus, an indispensable part of every standard used for traceability to the SI unit "mole".

Considering the enormous variety of chemical compounds, it is evident that primary standards cannot be made available for all chemical measurands. It was not least due to this complexity of chemistry that the integration of chemical measurands into the International System of Units was delayed and that the work of the Metre Convention in the field of chemistry started only a long time after the foundation of the Metre Convention. The provision of chemical measurement results which are comparable at the international level is, however, indispensable in view of the constantly increasing importance of such measurements in all fields of daily life. The measurands to be traced back are to be selected on the basis of a strategic decision that comprises technical, national and international considerations. Important criteria are the international comparability of chemical measurement results in topics which are particularly important for people's life or well-being, e.g. in clinical diagnosis, in environmental protection or in the field of food safety. The establishment of international comparability requires worldwide coordination with respect to these measurands. This is part of the work of the CCQM. In many fields of application of chemical measurands – and also in the topics mentioned – comparability and traceability are, therefore, also preferentially required for particularly important measurands (so-called "priority substances"). These are often specified in international directives (e.g. in the *Air Quality Framework Directive* or in the *Water Framework Directive* of the EU) or by recognized professional organizations (e.g. in the directive of the *German Medical Association*) and provided with practically relevant quality objectives with regard to the required measurement ranges and the measurement accuracy. The realization, maintenance and dissemination of internationally recognized standards for just these measurands are priority objectives of metrology in chemistry.

The foundation of the CCQM by the CIPM in 1993 initiated the establishment of international traceability structures in chemistry [39]. Other organizations, such as Eurachem (European network of organizations having the objective of establishing traceability in chemical analysis) and CITAC (Cooperation on International Traceability in Clinical Chemistry) and the regional metrology organizations such as EURAMET (European Association of National Metrology Institutes) are involved in this lasting process.

With the MRA of 1999 for the mutual recognition of national standards and certificates [http://www.bipm.org/en/cipm-mra/], a global reference system has been established which is, for the first time, also valid for chemical measurements. In chemistry, this international recognition is based on the international key comparisons of the CCQM, with the aid of which the degree of comparability of the standards can be quantified. As in other fields of metrology, the national standards which have been assessed and examined in this way enter into the CMC database which is made available by the BIPM and is accessible to the public [http://kcdb.bipm.org/appendixC/]. At present, approx. 5000 national standards for chemical measurands are recorded there. Focal points are measurands from the topics "health", "food safety" and "environmental protection". As has been mentioned before, the strategic orientation is of special importance for the work of the CCQM.

The results of the work of the CCQM are of increasing importance for international organizations which depend on chemical-analytical measurement results. These are, for example, the International Atomic Energy Agency (IAEA), the International Federation of Clinical Chemistry and Laboratory Medicine (IFCC), the Committee on

Reference Materials of the International Organization for Standardization (ISO REMCO), the International Union of Pure and Applied Chemistry (IUPAC), the World Health Organization (WHO), the World Meteorological Organization (WMO) and the International Laboratory Accreditation Cooperation (ILAC). The cooperation of CCQM with all these organizations is regulated by cooperation agreements. IAEA, IFCC, ISO REMCO and IUPAC are members of the CCQM. In addition, close contacts exist with other institutions and organizations such as, for example, the World Anti-Doping Agency (WADA).

3.3.3 Dissemination and traceability to the mole

Traceability of measurement results of the test laboratory to the national standards

It is the objective of all traceability structures to allow the test laboratories to relate their measurement results to an internationally recognized national standard. In the test laboratory, traceability of a measurement result is realized with the aid of comparison measurements and calibration materials. These are used for the validation of the (non-primary) measurement procedures in the test laboratory. In this way, a traceability chain is established which allows measurement results of test laboratories, e. g. in environmental protection or in clinical chemistry, to be made traceable to the SI.

As in other fields of metrology, a tripartite traceability system has been established in Germany in many fields of chemistry. Due to the large number of test laboratories, a direct connection between the national level and the test laboratories can usually not be established. To allow the test laboratories to furnish the required proof of traceability for their results in spite of that, a connection via calibration laboratories at an intermediate level has been facilitated. They act as multipliers and are in direct contact with the test laboratories.

A national network for the traceability of chemical-analytical measurements

In almost all sub-fields of metrology, the national standards are made available by the Physikalisch-Technische Bundesanstalt (PTB). Due to the above-mentioned complexity and the large number of analytes in chemistry, the role of PTB in the field of chemistry is changing at the highest level. Although PTB is the institution responsible by law, it now no longer acts alone, but as a coordinating partner in a network of institutions. All partners assume responsibility in defined sub-fields of chemistry. The tasks of the network partners are regulated in bilateral agreements with PTB. The bilateral character reveals the role of PTB as a contracting partner. The network partners must furnish proof of their competence in their field of activity in a suitable way. At present, participants of this network are, in addition to PTB as the coordinator, the *Federal Institute for Materials Research and Testing* (BAM), the *Federal Environment Agency* (UBA), the *Deutsche Vereinte Gesellschaft für Klinische Chemie und Laboratoriumsmedizin* (DGKL) and the *Federal Office for Consumer Protection and Food Safety* (BVL). These institutes form the national reference framework (of the national standards) which allows traceability to the SI for chemical-analytical measurement results. PTB has its own competences and maintains national standards in the working fields.

The traceability of the standards of the calibration laboratories to the national standards is realized, for example, by comparison measurements within the scope of an accreditation by the *Deutsche Akkreditierungsstelle* (DAkkS). The dissemination to the laboratories at the working levels is achieved by the provision of different calibration possibilities (e. g. reference measurements, interlaboratory comparisons or reference materials).

The infrastructure established in this way has proved its worth for traceability. There are, however, different variants of the system in the different fields of activity. In many fields of activity, it is also possible and common practice to disseminate reference materials directly to the test laboratories at the level of the national standards (e. g. for metals and alloys).

Example: Traceability and quality assurance in clinical chemistry

Reliable and trustworthy measurements in medicine are not only important for the life and well-being of every patient involved, but they are also a considerable cost factor in health care in general. As a result, binding arrangements for ensuring the correctness of medical measurements have been made in Germany. Their implementation has been regulated in the “Directive of the Federal Medical Association for Quality Assurance of Quantitative Investigations in Medical Laboratories” [40]. The directive is based on the *2*nd *Law for Amending the Medical Devices Act*. The directive which was implemented at the same time has been elaborated in agreement with the Physikalisch-Technische Bundesanstalt and in cooperation with the competent medical associations, with the verification authorities and with the competent industrial association. In this directive, minimum requirements for quality assurance – in particular for the measurement accuracy of quantitative analyses of medical laboratories – are laid down. The aim is to improve the reliability and the mutual acceptance of clinical-chemical measurement results which are determined for diagnostic or therapeutic purposes in the large number of laboratories of the German health care system. Confidence in the correctness of the measurement results is achieved by furnishing proof of the traceability of the measurement results to recognized standards, based, as far as possible, on SI units. For that purpose, a structured system has been implemented which supports the quality system for the clinical laboratories described in the directive [40]. As in other fields of metrology, an arrangement in three levels also exists in clinical chemistry:

1. Primary standards are made available as national standards by PTB as the national metrology institute (NMI) and by its partner, the Reference Institute for Bioanalysis (RfB) of the DGKL.
2. These reference points are disseminated to the reference laboratories appointed by the Federal Medical Association by comparison measurements.
3. The large number of clinical-chemical laboratories furnishes proof of their measuring capability to the reference laboratories within the scope of the so-called "external quality control".

Due to the special requirements of the directive of the Federal Medical Association, the internal structure of the three levels and the sequence are especially tailored to clinical chemistry. The mean level has the already mentioned multiplier function for the dissemination of the reference points to the large number of clinical laboratories and does – in this respect – not differ very much from the level of the DAkkS calibration laboratories in other fields of metrology. In addition, there is the harmonization with the rules of the Federal Medical Association and of the Medical Devices Act. At this level, reference laboratories are appointed by the Federal Medical Association. The appointment is realized in accordance with the Directive. It is based on the nomination by a reference institution, in cooperation with the technically competent scientific medical associations for a duration of four years each time. The qualification of a reference laboratory is determined by accreditation as a calibration laboratory according to ISO 17025 and as a reference measurement laboratory according to ISO 15195. Within the scope of these accreditations, these laboratories must furnish proof of the traceability of their measurement results to the SI, which is done, among other things, by comparison measurements with the competent network partner at the primary level. These calibration and reference laboratories are – according to the directive – responsible for the so-called "external quality assurance" of the large number of clinical laboratories. This serves the objective surveillance of the quality of results of quantitative investigations of medical laboratories and, thus, supplements the so-called "internal quality assurance" which is performed at short intervals (several times a day) and which is to establish the stability of the measuring devices with time with the aid of control sample measurements.

The external quality assurance in the medical laboratory is performed by the regular participation in intercomparisons (4 times a year). Due to the large number of clinically relevant molecules, external quality control is carried out only for a selection of the most important measurands under clinical aspects (priority substances, see above).

Beyond the national framework, the question of traceability has also found its way into European directives (98/79/EC, *in vitro* Diagnostica (IVD) Directive). There, it says: "The traceability of values assigned to calibrators and/or to control materials must be assured through available reference measurement procedures and/or available reference materials of a higher order" [41]. To define the contents of this directive has been a motivation for the establishment of the "Joint Committee on Traceability in Laboratory Medicine (JCTLM)" within the scope of a meeting at the BIPM in June 2002 [http://www.bipm.org/en/committees/jc/jctlm/]. At the quality level of reference/calibration laboratories, laboratories, measurement procedures and reference materials are certified here and recommended, for example, to the European Commission, as a reference laboratory, as a reference procedure and as reference materials of a "higher order".

3.4 Future developments

Due to the described complexity of the topic, the international traceability structures in metrology in chemistry can never be complete. However, compared to the conventional fields of metrology, metrology in chemistry is still in the development phase. An expansion of existing fields and the inclusion of new fields is urgently required. Clinical chemistry and environmental analysis will remain important fields of work also in the future; additional activities are required, for example, for food analysis or forensics. The CCQM supports this development by joint workshops with the international technical organizations.

As it is a relatively new sub-section of metrology, a considerable need for scientific research exists in almost all fields of metrology in chemistry. As an example, the development of reference procedures for highly complex molecules (proteins) can be mentioned which are particularly important as clinical biomarkers. Immunochemical measurement procedures often furnish measurement results which are barely comparable for such analytes. Here, structural differences must be characterized in addition to the stoichiometry of an analyte. A long-term objective is measurement procedures which can measure as many measurands as possible at the same time and with as high an accuracy as possible, e. g. for the continuous surveillance of the health status of a patient. Comparable measurement results are required for climate research and environmental protection which allow worldwide changes to be followed up with high accuracy and also over very long periods of time (decades). Together with the World Meteorological Organization (WMO), the metrological reliability of the global climate control networks is to be improved. A higher accuracy in ultra-trace analysis is, in particular, of great importance for environmental protection. Greater importance could, in future, also be attached to chemical analysis in the nanoscale range (nanotechnology, nanoparticles).

4 Redefinitions

4.1 General

The kilogram is the only one of the seven base units of the SI that is defined by a material embodiment as the mass of the international prototype of the kilogram. The other base units are defined by reference to a fundamental constant of physics and/or by an experimental procedure [6]. Some units also depend on other base units. The metre, which is defined as the path travelled by light in vacuum in a specific fraction of a second is, for example, defined by a specified value of the speed of light. In that definition, the second is referred to as a unit of the time. The definition of the ampere describes an idealized arrangement of two electrical conductors and states for it the values of measurands in the units *kilogram, metre* and *second*. These values in addition define the magnetic constant. According to the present state of knowledge, it is assumed for such definitions that the unit is invariable although its practical realization is always affected by a particular uncertainty. Also, definitions of this kind enable the unit to be realized at any location and at any time.

It has also been found that the masses of the national prototypes of the kilogram have significantly drifted during the last hundred years with respect to that of the international prototype [7, 42]. On average, they have put on about 0.05 mg. As the international prototype does not basically differ from the other prototypes as regards its physical properties, it is rather probable that it has lost weight compared, for example, to an atomic mass. Also, all prototypes might be subject to an additional drift which is still unknown.

Therefore, for more than 30 years the attempt has been made to define also the kilogram via an atomic constant or a fundamental constant of physics. Under discussion are Planck's constant and the Avogadro constant or the atomic mass unit. Two types of such experiments have meanwhile progressed to such an extent that a redefinition of the kilogram in the years to come is probable. These types are the watt balance for the determination of Planck's constant and the Avogadro project for the determination of the Avogadro constant.

At present, the differences between the results provided by the watt balances of NIST and NRC (previously at NPL), but also between the results of the watt balance of NIST and the results of the Avogadro project are statistically not yet compatible with the respective uncertainties stated. According to the state of the art, the masses of the primary standards of the watt balances mentioned would – after a redefinition of the kilogram – differ by approx. 300 µg and that of the most exact watt balance and of the Avogadro project by approx. 170 µg. Mass differences between the best realizations of a redefinition in this order would, however, not be acceptable for mass metrology [43]. Against this background, the Comité International des Poids et Mesures (CIPM), different advisory committees (CC) and international standardization bodies are at present dealing with the subject of the redefinition of the kilogram, with practical realizations and foreseeable consequences resulting from the dissemination of the redefined unit for mass metrology. The Comité consultatif pour la masse et les grandeurs apparentées (CCM) has, for example, summarized minimum requirements in its recommendations G 1 (2005) [44] and G 1 (2010) [45] which must be met before a redefinition of the kilogram can be realized in order to avoid negative effects on the realization and dissemination of the mass unit. The CCM considers it necessary that a redefinition can be realized by at least three independent experiments with relative standard uncertainties $\leq 5 \cdot 10^{-8}$. Here, the relative standard uncertainty of the best realization should not be larger than $2 \cdot 10^{-8}$ and the results of the experiments should agree within a confidence range of 95 %. The other bodies also agree that a relative uncertainty of a few 10^{-8} and a corresponding agreement of the current experiments are a precondition for a redefinition. The question as to whether the redefinition of the kilogram is to relate to the atomic mass unit or to Planck's constant is still under discussion [46, 47].

In addition to a redefinition of the kilogram, it is planned to redefine also the ampere, the kelvin and the mole. Whereas sufficiently exact results are also still awaited for the redefinition of the kelvin for which the Boltzmann constant is to be determined, known devices, which are already used for practical standards and which are based on the Josephson effect for the volt and on the quantum Hall effect for the ohm, are to be used for the ampere. The constants are to be selected in such a way that $h/(2e)$ and h/e^2 will in future have fixed values (h Planck's constant, e elementary charge). For the mole, the definition valid so far shall be reworded in such a way that it is based on a fixed value of the Avogadro constant N_A without relating to the unit "kilogram" as is the case in the current definition [48].

4.2 The experiments

The first experiments for a redefinition of the kilogram started in the 1970s: the Avogadro experiment with a silicon single crystal at different research institutes according to proposals of Bonse and Hart, [49] and the so-called watt balance experiment of B. Kibble at the National Physical Laboratory (NPL, Great Britain) [50, 51]. Shortly after the first publications, the two experiments were undertaken and further developed worldwide to achieve as low a measurement uncertainty as possible. Ultimately, a relative uncertainty of $2 \cdot 10^{-8}$ is internationally required to end the era of the prototype kilogram. Meanwhile, the two experiments have the potential of winning the kilogram race.

Another approach was pursued with the voltage balance which – at CSIRO and PTB – furnished results with relative uncertainties of approx. $3 \cdot 10^{-7}$ [52, 53] and which was not continued, as an improvement with a reasonable effort and outlay was not to be expected. The experiment "Superconducting Magnetic Levitation" of NMIJ/AIST was also interrupted after a reproducibility of 10^{-6} [54] had been achieved. The Russian *All Russia D I Medeleyev Scientific and Research Institute for Metrology* (VNIIM) and the Finnish *Centre for Metrology and Accreditation* (MIKES) are planning to establish a new Magnetic Levitation Experiment [55]. The experiment "Ion Accumulation" of PTB was started in 1990. Although the principle of the ion accumulation could be demonstrated [28, 56] and although its concept via the mass of a specified number of atoms can be regarded as an experiment which suggests itself for a redefinition of the kilogram, it seems improbable that it will achieve the required uncertainty within the period of time provided.

4.2.1 Silicon single crystal and the Avogadro constant

The Avogadro project has its origins in the 1970s, when German researchers succeeded for the first time in determining the lattice distances in a silicon crystal by X-ray interferometry. This allowed the kilogram to be linked up with the atomic mass unit. The Avogadro constant which indicates the number of atoms in a mole acts as a connecting link between a macroscopic mass and the mass of an atom.

The Avogadro constant is named after the Italian count and lawyer Amedeo Avogadro who – at the beginning of the 19th century – dealt with atomism which had been explained by Dalton and who brought in line all observations connected with it. Dalton had demonstrated that all gases expand in the same way when they are heated. This, concluded Avogadro, could be explained only by the fact that the number of gas particles involved is also always the same: Identical volumes of all gases had to contain – in the case of identical external conditions – the same number of the smallest particles. But it seems that Avogadro did not really know how to determine this number.

Only in 1865 did Josef Loschmidt calculate the particle number per volume with the aid of the mean free path of gas molecules which was determined by Oskar Meyer and, later, by James Maxwell. At that time, this value deviated by only 20 % from the value recognized today. Forty years later, Albert Einstein tried to indicate the Avogadro constant more precisely: In his doctoral thesis of 1905, in which he determined the number of molecules per mole on the basis of a novel diffusion equation from measurements carried out on a sugar solution, his values deviated – due to a calculation error – by a factor of three.

In 1917, Robert Millikan reduced the error to less than one percent by clearly improving his famous oil droplet test for the determination of the elementary charge. Today, this accuracy is no longer sufficient. Under the direction of PTB, scientists from several metrology institutes have joined forces to determine – with the aid of a nearly perfect silicon crystal – the Avogadro constant as exactly as never before.

The achievement of this objective required, however, many years of development work. At the beginning, silicon crystals of natural isotope composition were used for the determination of the Avogadro constant. At several metrology institutes such as, for example, PTB, the National Institute of Standards and Technology (NIST, formerly: NBS, USA), the National Physical Laboratory (NPL, Great Britain), the National Metrology Institute of Japan (NMIJ) and the Istituto Nazionale di Ricerca (INRIM, formerly: IMGC, Italy), measurements of the Avogadro constant were started at the end of the 1970s with the establishment of an X-ray interferometer for measuring the lattice parameters in the silicon single crystal. The Institute for Reference Materials and Measurements (IRMM, Belgium) participated with the measurement of the relative fractions of the three isotopes ^{28}Si, ^{29}Si and ^{30}Si in natural silicon. Initial success was achieved at NIST [57], where a value with a relative measurement uncertainty in the range of 10^{-6} was published. Despite the increased efforts made at all institutes involved, it has – in the following years – been impossible to achieve a measurement uncertainty of less than $3 \cdot 10^{-7}$. Success was reached only when some years ago, the newly established International Avogadro Project (IAC) and other institutions and companies repeated the measurements with highly enriched ^{28}Si.

For the determination of the Avogadro constant, the volume *V* and the mass *m* are determined on a silicon sphere (Figure 6):

$$N_A = \frac{nMV}{mv_0} \tag{4.1}$$

The molar mass *M* and the volume v_0 of an atom are determined using samples of the same crystal. *n* is the number of atoms in the unit cell. When the number of atoms per mole is known, it is easy to draw conclusions regarding the number of atoms in one kilogram of the same substance. All quantities measured must, of course, be traced back to the SI base units. This is why the volume of the silicon sphere is determined by interferometric measurements of the sphere diameter. This provides a complete surface topography of the sphere. At the Australian Centre for Precision Optics (ACPO), the spheres are polished and exhibit a deviation from a perfect shape of less than 100 nanometres. The silicon sphere is coated with a thin "disturbing" oxide skin, some nm in thickness, whose geometry and density must be characterized. The mass of the silicon sphere is linked up with the kilogram prototype by weighing. Due to the large density differences between silicon and platinum-iridium, the accuracy requirements for the mass determination can, at present, be achieved only under vacuum conditions, i. e. without air buoyancy correction. Volume and mass determinations must then – in addition – be corrected with respect to the oxide layer. The atomic volume is determined from the lattice plane spacing of the crystal lattice with the aid of an X-ray scanning interferometer. Sufficient knowledge of the impurities and of the crystal defects is an indispensable prerequisite for this. The molar mass is determined by mass spectrometry from the atomic masses of the three isotopes ^{28}Si, ^{29}Si and ^{30}Si which occur in natural silicon and from their relative frequencies. The atomic masses are linked up with the mass of the carbon isotope ^{12}C by means of Penning traps. For natural silicon, the measurement uncertainty in the determination of the molar has – under mass-spectrometric aspects – reached its limits. This is why the investigations for the determination of the Avogadro constant were stopped some years ago when a measurement uncertainty of approx. $3 \cdot 10^{-7}$ was reached [58].

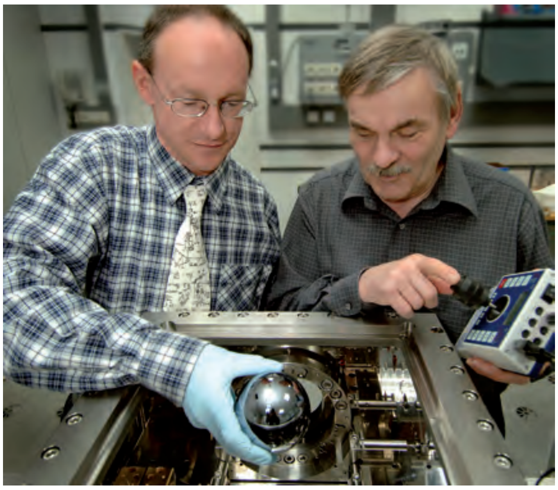
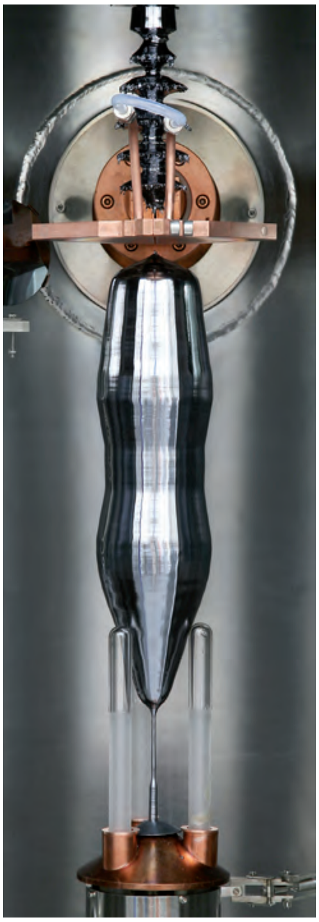


Figure 6:
The sphere of a silicon single-crystal is being positioned in the sphere interferometer.

In addition to insufficient accuracy for the redefinition of the kilogram, the observed deviation of the measurement value of approx. $1 \cdot 10^{-6}$ relative to results of other experiments, also caused quite a headache for the researchers. Was the deviation due to miscounting or were there unrecognized inconsistencies in the system of the physical constants? The possibility of using enriched silicon-28 on a large scale for sample preparation gave new impetus to the Avogadro project. Estimates showed that the uncertainties for the measurement of the isotope composition would be considerably reduced, but the researchers were forced to repeat also all other investigations on this material. In 2003, in a cooperation with research institutes in Russia, several national and international metrology institutes therefore launched the ambitious plan to prepare approx. 5 kg of highly enriched ^{28}Si (99.99 %) as a single crystal and to reach a measurement uncertainty of approx. $2 \cdot 10^{-8}$ by the year 2010.

And they almost succeeded: In 2008, the material was successfully prepared with the growing of a perfect single crystal at the Institute for Crystal Growth (IKZ) in Berlin (Figure 7) and two 1 kg ^{28}Si spheres were then polished at the Australian ACPO.

The first results obtained on the enriched material have shown that it was possible to reach a more exact determination of the Avogadro constant and that it was possible to detect the cause of the observed deviation with respect to other fundamental constants. At present, the achieved measurement uncertainty is $3 \cdot 10^{-8}$ [59]. The relative deviation from the CODATA 2006 value amounts to approx. $-1.7 \cdot 10^{-7}$ (Figure 8). Although the IAC



project has meanwhile been completed, PTB and other metrology institutes are keeping their projects for the redefinition of the unit of mass and its realization in the running.

4.2.2 Watt balance and Planck's constant

With the watt balance, Planck's constant is determined in two modes (Figure 9).

In the first mode, the balance is used to compare the weight force of a mass standard with the electromagnetic force (static mode). Thereby, the current is measured in a coil situated in the radial field of a magnet. In the second mode, the coil is moved in the same magnetic field in the vertical direction (moved mode). The velocity and the voltage induced in the coil are measured. The equations for the current and the induced voltage are then combined by eliminating the gradient of the magnetic flux. In this way, the following is obtained:

Figure 7:
^{28}Si single-crystal, degree of enrichment 99.995 %.

$$UI = 4\,mgv \qquad (4.2)$$

Here, U is the induced voltage, I the current in the coil, m the mass of the mass standard, g the gravitational acceleration and v the velocity. Equation (4.2) is valid for measurements in vacuum. In this equation, an electric power is equated with a mechanical one – hence the name "watt balance". If I and U are measured via the quantum Hall resistance and the Josephson voltage, Planck's constant is obtained:

$$h = \frac{4mgv}{\nu_m \nu_g} \qquad (4.3)$$

where ν_m and ν_g are frequencies of a microwave radiation which is measured for the Josephson voltages in the first or in the second mode.

After the first success at NPL, a watt balance was also installed at NIST [60, 61] with the aid of

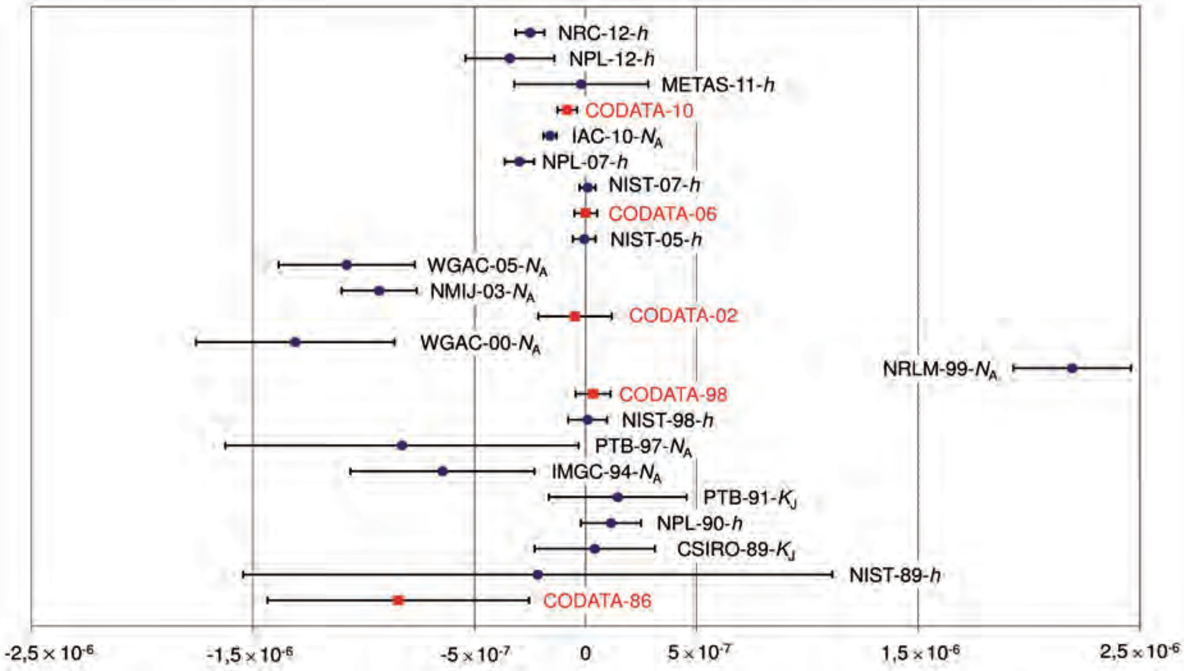


Figure 8:
Measurement results for the Avogadro constant N_A with uncertainties, represented as relative deviations from the CODATA 2006 value ($N_A = 6.02214179(30) \cdot 10^{23}$ mol^{-1}). The results for Planck's constant, h, (watt balance) and for K_J (voltage balance) have been converted by means of the CODATA 2006 constants. Explanation: "NPL-07-h", for example, means: NPL's result in 2007 for a measurement of h. WGAC: Working Group Avogadro Constant, IAC: International Avogadro Coordination

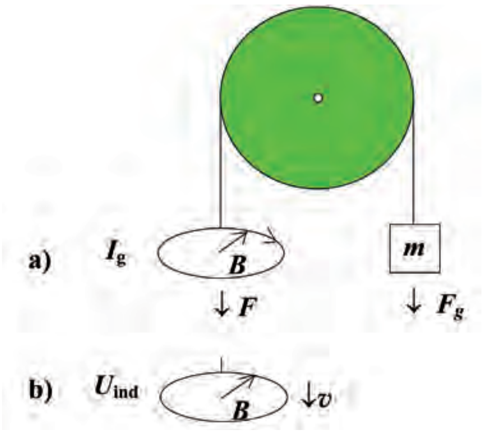


Figure 9:
Principle of the watt balance.
a) static mode,
b) moved; *B* radial magnetic field, I_g current of the coil, F_g weight force of the mass *m*, *F* electromagnetic force, U_{ind} voltage induced in the coil, *v* velocity of the moved coil

which the most exact value of Planck's constant so far was measured in 2007 (relative uncertainty with $3.6 \cdot 10^{-8}$) [62]. After having examined its recent measurements, the NPL has come to the conclusion that an error could not be ruled out. The relative uncertainty has, therefore, been increased from 0.66 to $2 \cdot 10^{-7}$ [63]. Meanwhile, the NPL watt balance has been delivered to NRC (Canada) and has been put into operation there. In 2012, a first result with a relative uncertainty of $6.5 \cdot 10^{-8}$ was published [64].Additional watt balance experiments have been established or are in the test phase [65]: at the Federal Office of Metrology (METAS, Switzerland) since 1997, at the Laboratoire National de Metrologie (LNE, France) since 2000 and at the BIPM since 2002. The metrology institutes in China and New Zealand are also working on watt balances.

The watt balances in the different institutes [65] do not differ in their principle, but in their practical design. At NPL and NIST, masses of 1 kg are used, at METAS a mass of 100 g. NIST uses a superconducting magnet and a cable pulley as a balance beam, NPL, METAS and BIPM use cobalt-samarium magnets, NPL an equal-armed beam balance, METAS and BIPM a modified commercial mass comparator. For velocity measurement, NPL and NIST use Michelson interferometers, whereas a Fabry-Perot interferometer is used at METAS. The BIPM is developing a watt balance where the static and the moved mode are realized in a single experiment. The LNE is developing a watt balance of its own manufacture for which a mass standard of 500 g is suited and which will work with a cobalt-samarium magnet. For the measurement of the acceleration due to gravity, the institutes use an absolute gravimeter. The LNE uses a cold atom gravimeter.

The currently most exact results of the two methods do not yet agree in the range of their measurement uncertainties. The CODATA adjustment calculus of 2010 furnishes for N_A and *h* values whose relative deviations from the previous values (2006) amount to approximately $9 \cdot 10^{-8}$.

4.3 Realization and dissemination in accordance with the redefinitions

4.3.1 Kilogram

The future dissemination of the unit of mass is based on the possible realizations of the redefinition (described in the future so-called *mise en pratique*). Independent of the decision to which one of the two favoured constants the future definition of the kilogram will relate, it will be possible to use both the Avogadro and the watt balance experiments for independent realizations of the redefinition. The basis for this is provided by the product referred to as "molar Planck constant"

$$N_A h = \frac{c A_r(e) M_u \alpha^2}{2 R_\infty} \tag{4.4}$$

(*c* speed of light, A_r(e) relative mass of the electron, $M_u = 10^{-3}$ kg mol^{-1}, *α* fine structure constant, R_∞ Rydberg constant, *e* elementary charge). With the aid of equation (4.4), *h* and N_A can be converted into each other with a relative standard uncertainty ($k = 1$) of $1.4 \cdot 10^{-9}$ [66]. This uncertainty is by more than one order of magnitude smaller than that of the currently most accurate experiments conducted for the determination of *h* and $N_{A.}$

In the most precise watt balances, mass standards from different materials such as, for example, gold, gold-plated copper and gold-platinum alloys are used for the determination of *h*, where the uncertainty of their mass contributes to the overall uncertainty with a fraction of less than 10 %. After a redefinition, the mass of these standards could be determined experimentally from Planck‘s constant with the aid of equation (4.3) and could be used to realize the definition. Hereby, all uncertainty components which are independent of the mass would contribute to the uncertainty of the mass determination of the primary standards. In the case of the most precise watt balance, the uncertainty contribution of the mass standards to the standard uncertainty of Planck's constant amounts, for example, to 10 µg [62]. If the same mass standards were used as primary standards for the realization of a redefinition, a standard uncertainty of approx. 35 µg would be obtained for their mass. In a comparable way, it would be possible to realize a redefined kilogram with the aid of a silicon single crystal, using equation (4.1). At present, the mass of the ^{28}Si spheres used for the Avogadro project contributes to the determination of the Avogadro constant with a standard uncertainty of approx. 5 µg [59]. As a realization of a redefined kilogram, a ^{28}Si sphere would, however, have an increased mass uncertainty of approx. 30 µg.

Even if the CCM recommendations [44, 45] are complied with, it is foreseeable that the uncertainties for the dissemination of the SI unit "kilogram" to the national standards of the metrology institutes and to the most accurate reference standards of authorities and calibration laboratories will increase, compared to the values obtained so far [43]. An increase within the scope of these recommendations would not, however, jeopardize the compliance with the uncertainty requirements for the calibration of weights and mass standards in accordance with the most accurate OIML class E_1 (relative standard uncertainty $8 \cdot 10^{-8}$) by authorities and calibration laboratories.

After a redefinition of the kilogram, a national metrology institute could receive traceability for its national mass standard directly from an institute which realizes the redefinition. To limit negative impacts of larger differences between different realizations, it was proposed to use the weighted mean from several realizations for the dissemination of a redefined kilogram [45]. This more reliable reference value could, in principle, be determined via a comparison measurement (key comparison) between the metrology institutes which realize the redefinition or by comparison measurements with all available realizations in one reference laboratory. CCM, for example, recommended as such a reference laboratory the BIPM, where a group of secondary standards (ensemble of reference mass standards) is to be used for the dissemination of the kilogram after a redefinition. For this purpose, mass standards made of different materials are to be used (as they are also used by the leading experiments for the preparation of the redefinition), linked up with the available primary standards and kept under different conditions (air, vacuum, inert gas). Based on the masses of the primary standards involved, the masses of the secondary standards are determined by a least-squares adjustment. Then, the BIPM could use a selection from the group of the secondary standards to disseminate the unit of mass to the national mass standards. As the mass standards for the realization of the redefinition of the kilogram via the Avogadro constant and via Planck's constant are used in vacuum, a vacuum/air transfer is required at least at one step in the dissemination chain, taking sorption corrections into account. If the vacuum/air transfer is performed with the inclusion of sorption artefacts, the uncertainty contribution of the sorption correction can be limited to a few micrograms [67, 68]. In addition to the realizations on the basis of the Avogadro and watt balance experiments, the international prototype of the kilogram will probably also be part of the *mise en pratique*. With its mass of exactly one kilogram and an uncertainty which is derived from the experiments for the determination of Planck's constant and the Avogadro constant, it still embodies – at the moment of the redefinition – a realization of the definition. Accordingly, the uncertainties of all mass standards derived from the international prototype of the kilogram will increase.

If the redefinition is subsequently realized in accordance with the procedures of the *mise en pratique* and if the mass of the international prototype of the kilogram is redetermined experimentally with the aid of corresponding primary standards, it can no longer be regarded as a realization of the definition. As a secondary standard, however, it will have an exceptional status for future observations of the long-term stability of the previous kilogram definition, its realization and maintenance by platinum-iridium prototypes.

In the past 120 years, the hierarchic system of the dissemination of the unit of mass, based on kilogram prototypes, has proved to be extremely appropriate and has contributed decisively to the high degree of uniformity of mass determination worldwide. It can, therefore, be assumed that also after a redefinition, kilogram prototypes will play an important role in the dissemination chain of the unit of mass.

4.3.2 Mole

Also after the planned redefinition of the mole by the determination of N_A, the amount of substance will only in rare cases be determined by the counting of atoms or molecules. This means that ratios of amounts of substances will also in future be measured with mass spectrometers. Weighing of the reference material will remain the method for the determination of the quantitative reference point. Here, the question arises of whether – or how – the molar masses will change after a redefinition.

If the mole will in future be defined by a fixed value of the Avogadro constant N_A, and the kilogram by a value of Planck's constant h – as is currently being planned – this will lead to a redundant dimensioning as N_A and h depend on each other via other constants. Then, in equation (4.4), c, h and N_A are defined in the definitions of the metre, the kilogram and the mole, whereas α and R_∞ remain independent measurands. This means that only $A_r(e)$ or M_u come into consideration as variables which are dependent on these measurands. If the value of $A_r(e)$ changed as a result of new measurement results of α and R_∞ and a corresponding adjustment calculus, all relative atomic masses would change as well. In particular $A_r(^{12}C) = 12$ would no longer be exactly valid as a reference. As the relative atomic masses are measured with uncertainties which are comparable to that of α, future changes would be significant and require the preparation of new tables of the relative atomic masses. This is why the proposal to introduce M_u as a variable [69] seems to be more practicable and would, in addition, have negligible impacts. As the molar mass of an atomic particle X is calculated according to $M(X) = A_r(X)\ M_u$, the molar masses would change with M_u.

From the moment of the redefinition until the availability of new values of α or R_∞, $M_u = 10^{-3}$ kg mol^{-1} will still continue to be valid. After the redefinition, the relative uncertainty of M_u and, correspondingly, that of the molar mass of ^{12}C, will depend predominantly on the measurement uncertainty of α^2 which lies at present in the order of 10^{-9}; future relative changes will probably not exceed this value. In view of the smallest relative uncertainties which are achieved in the realization of the mole and the molar masses (approx. 10^{-5}), no changes will result in practical applications.

5 Summary

For the determination of the two quantities – i. e. “mass” and “amount of substance” – weighing plays a central role. Whereas mass is independent of the kind of substance, the amount of substance always relates to a specific, uniform substance. It is proportional to the number of exactly specified atoms or molecules, which are contained in a specific amount of substance. After short historical surveys, the realizations of the SI units “kilogram” and “mole” were explained in accordance with their definitions. The international prototype of the kilogram conserved at the BIPM is, at the same time, the realization of the unit “kilogram”. The mole, in contrast, is realized for different substances in different institutions by primary standards. After the explanations regarding their realization, the dissemination of the kilogram and the mole via secondary standards in calibration or test laboratories all the way to the user of these units is described. Finally, a survey was given of the planned redefinitions of these units, of the relevant experiments and of the possible consequences for realization and dissemination. Moreover, problems which remain to be solved were highlighted. ■

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Electric Current – the SI Base Unit “Ampere”

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Structure

1 Definition of the Ampere in the SI System of Units

The ampere, the unit of electric current, is the SI base unit for electricity and magnetism. Until the middle of the 20th century, the ampere was defined on the basis of electrolytic processes. This so-called “international ampere” was defined as the current at which 1.118 mg of silver per second precipitate out of a silver nitrate solution. The currently valid definition, which is based on electrodynamics, was adopted at the 9th General Conference of the Metre Convention in 1948. It reads: *The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to* $2 \cdot 10^{-7}$ *newton per metre of length.* Figure 1 illustrates the definition of the base unit “ampere”.

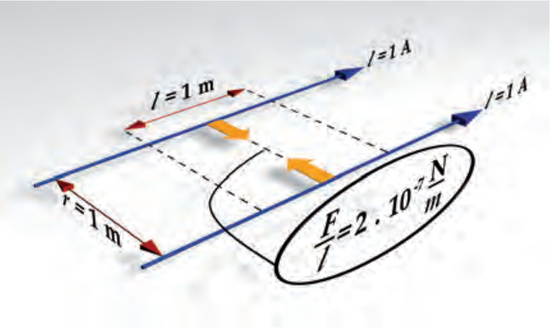

Figure 1: Schematic representation of the ampere definition.

This definition exploits the fact that, in the described arrangement, the electrodynamic force F per conductor length l between two straight parallel conductors which are placed at the distance r and through which a current I flows, is

$$\frac{F}{l} = \mu_0 \frac{I^2}{2\pi r}$$

in vacuum. In this equation, μ_0 is the magnetic constant. The numerical value of the magnetic constant is fixed through the definition of the ampere:

$$\mu_0 = 2\pi \frac{F}{l}\frac{r}{I^2} = 4\pi \cdot 10^{-7} \ \frac{\mathrm{N}}{\mathrm{A}^2}$$

Since the numerical value of the speed of light c has been fixed through the definition of the metre, also the numerical value of the electric constant ε_0 is fixed according to the Maxwell relation $\mu_0 \cdot \varepsilon_0 \cdot c^2 = 1$.

The definition of the ampere describes an ideal arrangement which has the advantage of providing an exact indication of the relation between the current and the mechanical and dimensional quantities. The practical implementation of this definition – which, in metrology, is called *realisation* – must be performed with the aid of measuring arrangements that can be realised experimentally. The realisation of the ampere is dealt with in Section 2. Thereby, one distinguishes between *direct realisation* – in which, as in the definition, the current is related to a mechanical force – and *indirect realisation*. The latter is based on Ohm’s law $I = U/R$ and the ampere is realised through the realisation of the electric voltage U and the electric resistance R. Section 2 describes in what way the fixing of the numerical value of the electric constant ε_0, which follows from the definition of

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the ampere, ensures the link between the indirect realisation of the ampere and its definition.

The – still valid – definition of the ampere is based on mechanical quantities. A completely different approach to define the ampere and the electric units is the use of quantum effects in solids which provide a relation between the electric quantities and the fundamental constants of physics. With the aid of the Josephson effect [1], the voltage U, and with the aid of the quantum Hall effect [2], the resistance R can be traced back to the elementary charge e and Planck's constant h. Thanks to these effects, the volt, the ohm and, using Ohm's law, also the ampere can be reproduced with highest accuracy. The use of quantum effects has great practical advantages, but it cannot be derived from the definitions of the units in the SI system. One therefore speaks of a "reproduction" of the electric units – and not of their "realisation". The reproduction of the volt, the ohm and the ampere is dealt with in Section 3.

The new definition of the ampere – which has been suggested by the bodies of the Metre Convention – is based on the elementary charge e. In this way, the path taken for the reproduction of the electric units – i. e. away from the link-up to mechanical units and towards the utilisation of quantum effects and fundamental constants which are universal according to our current knowledge – is consistently pursued. The new definition of the "quantum ampere" and the state of the art of research on its practical implementation are described in Section 4. Section 5 deals with consistency tests aiming to ensure the implementation of the new ampere definition. The article closes with an outlook.

2 Realisation of the Ampere in the SI System of Units

2.1 Direct realisation

The direct realisation of the ampere – which is only of historical interest today – is based on a realisable implementation of the ampere definition. In this way, it directly uses the fixed value μ_0. The "conductors of infinite length" are replaced by conductors of finite length that are arranged as a coil system. The difference between these two geometries can be exactly calculated. The force between the coils through which a current I flows is measured by balancing it with a gravitational force, using the so-called "current balance". The fundamental problem of such an experiment is that the current flows through wires of finite diameter, but that the current density in the wires is not necessarily constant over their total cross-section. This applies especially when it comes to warped wires which, for example, are wound into coils. In this case, the distance between the current paths which enters into the defining equation of the ampere is not identical to the geometrically determined distance. With such an experiment, therefore, only relative uncertainties in the range of a few 10^{-6} were achieved [3].

2.2 Indirect realisation

The indirect realisation of the ampere can be performed with a lower uncertainty than the direct realisation. One starts from the electric constant ε_0 whose numerical value is also indirectly fixed due to the relation $\mu_0 \cdot \varepsilon_0 \cdot c^2 = 1$ via μ_0 and c. As mentioned above, the defining equation of an electric resistance, $R = U/I$, is used to realise the ampere via the unit "ohm" of the electric resistance R and the unit "volt" of the electric voltage U. In what way the numerical value of ε_0, which ensures the equivalence of the indirect realisation and the direct realisation, enters into this definition is described below.

The crucial element making it possible to use ε_0 with a low uncertainty is an electrostatic theorem which was discovered by *A. M. Thompson* and *D. G. Lampard* in 1956 [4]. According to the theorem, the capacitance C – between two pairs of parallel metal cylinders arranged symmetrically and diagonally (the electrodes) – can be calculated and depends solely on the length l of the cylinders and on ε_0. To avoid boundary effects, one determines in an experiment only the change ΔC of capacitance for a change Δl of the electrically active length of the capacitor (which can be determined very accurately by means of an interferometer):

$$\Delta C = \varepsilon_0 \frac{\ln 2}{\pi} \Delta l$$

With such a "calculable cross capacitor" (which is also called *Thompson-Lampard capacitor*) it is, therefore, possible to realise the unit farad directly. At alternating current of frequency ω, a capacitance C represents a reactance having the value $1/\omega C$ which can be compared with an effective resistance in a special AC bridge – a so-called quadrature bridge. It is, thus, possible to derive the unit of resistance. In practice, a whole series of high-precision measurements is required. These measurements are, however, very well mastered, so that the relative uncertainty of the ohm's realisation is in the order of 10^{-7} and even better.

For the indirect realisation of the ampere, besides the unit ohm, also the realisation of the unit volt is needed. Similar to the comparison of electrodynamic forces with gravitational forces in the "current balance," a "voltage balance" is used to compare an electrostatic force between energised capacitor electrodes with a gravitational force. As

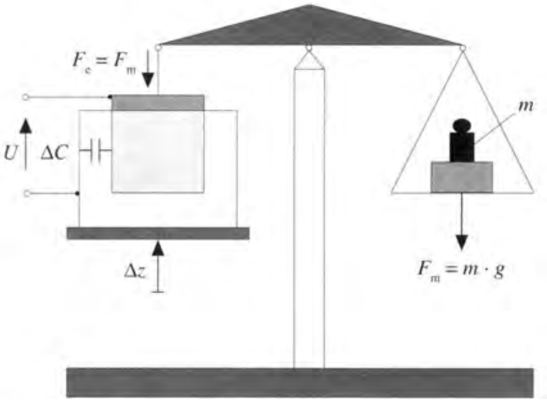

Figure 2:
Principle of PTB‘s voltage balance for the realisation of the volt.

shown in Figure 2 in a strongly simplified way, the electrodes used until 1988 in the arrangement of PTB are two concentric cylinders, the inner one being suspended from a balance. The electrostatic force F_e is compensated by the gravitational force F_m acting on the weight m (g gravitational acceleration at the place of installation of the weighing instrument). If the external cylinder is displaced vertically by a distance Δz, the total energy of the system must remain constant. From this, the relation between the capacitance change ΔC caused by the displacement Δz and the voltage U can be derived:

$$U = \sqrt{\frac{2mg \cdot \Delta z}{\Delta C}}$$

Also in this case, the capacitance realised by means of a calculable capacitor enters into the result. For forces of about 20 mN – corresponding to the weight of a mass of 2 g – voltages of about 10 kV are needed. Special dividers have to be used to step down the voltage to 1 V. This balance achieved a relative overall uncertainty of $3 \cdot 10^{-7}$ for the realisation of the volt [5]. With the indirect method, the ampere can be realised with a similar uncertainty.

Although the indirect realisation of the ampere is the most accurate within the SI, it has, in practice, not played a role any more for more than 20 years. Responsible for this is the possibility – described below – of tracing electric units to fundamental constants which enable the reproduction of the ampere with significantly lower uncertainties than those achievable with the realisation.

3 Reproduction of Electric Units

In all sectors of metrology, efforts have, for a long time, been focused on tracing back the units to fundamental constants, because these are – according to the current knowledge – invariable both temporally and spatially. For this, quantum effects are needed which ensure that physical quantities – unlike their usual behaviour – take on only certain discrete values. A precondition for the use of quantum effects in the field of electricity are sophisticated special devices, low temperatures, and sometimes also extremely strong magnetic fields. The effects which are relevant for the electric units relate the units volt (via the Josephson effect) and ohm (via the quantum Hall effect) to combinations of the elementary charge e and Planck’s constant h.

As in the indirect *realisation* described above, which uses the units ohm and volt, the ampere can also be reproduced indirectly by tracing it back to the h- and e-based units ohm and volt by measuring the resistance and the voltage.

3.1 The Josephson effect and the unit “volt”

In 1962, *Brian D. Josephson* predicted an effect between weakly coupled superconductors which later was named after him [1]. The weak coupling occurs in a so-called Josephson junction made, e. g., by connecting two superconductors via a very thin insulator. If a DC current of the intensity I flows through such an arrangement, and if a microwave of frequency f is applied at the same time, steps of constant voltage will occur in the voltage-current characteristic whose values are proportional to the frequency:

$$U_n = n \cdot K_J^{-1} \cdot f$$
where (n = 1, 2, ...)

The quantity K_J is called the *Josephson constant*. Within the underlying theory, it is given by $K_J = 2e/h$. Its value is approx. $5 \cdot 10^{14}$ Hz/V.

At the low temperatures which are necessary for superconductivity to occur and with frequencies in the range from approx. 10 to 70 GHz, voltages of a few 100 µV can be generated with a Josephson junction. Using series arrays of many Josephson junctions, the voltage can be considerably increased, the required production technology is, however, very elaborate.

The development of this technology was decisively advanced by PTB. As one of very few national metrology institutes worldwide, PTB is able to manufacture Josephson series arrays which allow reproducing voltages of up to 15 volt with a relative uncertainty of approx. 10^{-9} [6].

The latest generation of Josephson junctions developed at PTB (Fig. 3) uses elements whose “insulating layer” is partly or fully made of normal-conducting material. With these elements, the voltage on an individual element can be adjusted at 0 or ± U_1 using an external control. A series array

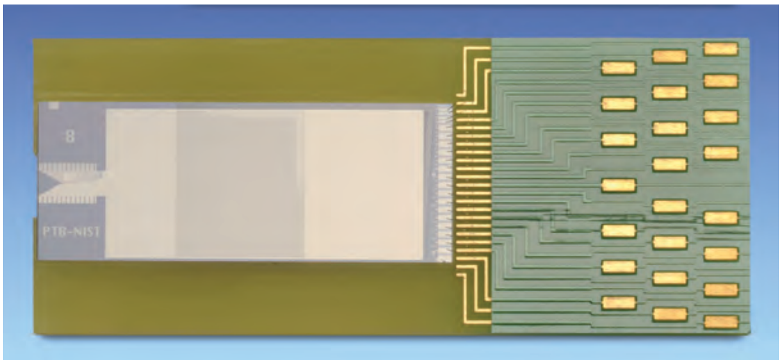

Figure 3:
Programmable 10 volt Josephson array.

of such elements, comprising segments of binary stepped lengths 1, 2, 4, 8, etc., makes it possible to reproduce nearly arbitrary, precise DC voltages in the range from – 10 V to + 10 V [7] with high resolution.

Josephson arrays manufactured with PTB's technology are now being used at numerous national metrology institutes as well as at the BIPM, the Bureau International des Poids et Mesures.

3.2 The quantum Hall effect and the unit "ohm"

Using two-dimensional, i. e. extremely thin conductive layers, *Klaus v. Klitzing* [2] in 1980 discovered a new effect which can be used to realise quantised resistance values. As early as in the year of the discovery, PTB and other national metrology institutes started precision measurements of this new effect. The discovery, for which von Klitzing was awarded the Nobel Prize in physics in 1985, was made on MOSFETs (metal oxide semiconductor field effect transistors). Today, GaAs-GaAlAs layer crystals are used for metrological purposes. They can be manufactured using, e. g., a molecular beam epitaxy facility. PTB is the only national metrology institute having such a facility at its disposal (see Fig. 4).

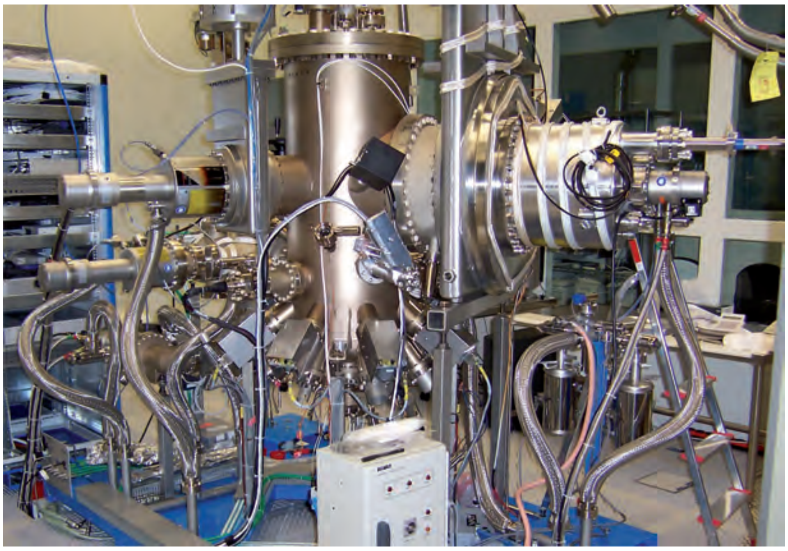

Figure 4:
PTB's Molecular Beam Epitaxy (MBE) facility for the production of GaAs layer crystals for quantum Hall resistors.

At very low temperatures (using liquid helium), a current I is applied to the quantum Hall devices (Fig. 5) and, at the same time, a very strong magnetic field is established vertically to the conductor layer (magnetic flux density about 10 tesla, corresponding to more than 200,000 times the Earth's magnetic field). For the Hall resistance R_H, which is the quotient of Hall voltage and current in the device, steps of constant resistance are then obtained in the resistance-magnetic-field characteristic with the values

$$R_H = \frac{1}{i} R_K$$

where (i = 1, 2, ...)

The quantity R_K is called the *von Klitzing constant*. In the context of the underlying theory, it is given by $R_K = h/e^2$. Its value is approx. 26 kΩ. The steps at $i = 2$ – approx. 13 kΩ – and at $i = 4$ – approx. 6.5 kΩ – are especially well pronounced. The corresponding resistance values can be reproduced with a relative uncertainty of a few parts in 10^{-9} [8].

3.3 International conventions

To achieve international uniformity in the dissemination of the electric units *volt* and *ohm* (and, thus, also of the base unit *ampere*) within the small uncertainties made possible by the Josephson effect and the quantum Hall effect, the International Committee for Weights and Measures fixed exact values for the *Josephson constant* K_J and for the *von Klitzing constant* R_K in October 1988 and recommended them for the maintenance and dissemination of the units [9]. To distinguish the fixed values from the fundamental constants which are not exactly known, they are referred to as $K_{J\text{-}90}$ and $R_{K\text{-}90}$. These recommended values are:

$K_{J\text{-}90} = 483\,597.9 \cdot 10^9\ \mathrm{V^{-1}s^{-1}}$

$R_{K\text{-}90} = 25\,812.807\ \Omega$

These values were defined in such a way that – according to the most precise measurement results valid at that time – they corresponded to the SI numerical values. At that time, the relative uncertainty for $K_{J\text{-}90}$ was $4 \cdot 10^{-7}$ and the uncertainty for $R_{K\text{-}90}$ was $2 \cdot 10^{-7}$.

Since 1 January 1990, $K_{J\text{-}90}$ and $R_{K\text{-}90}$ have been used worldwide for the dissemination of the units volt and ohm. The quantum effects thereby ensure excellent reproducibility.

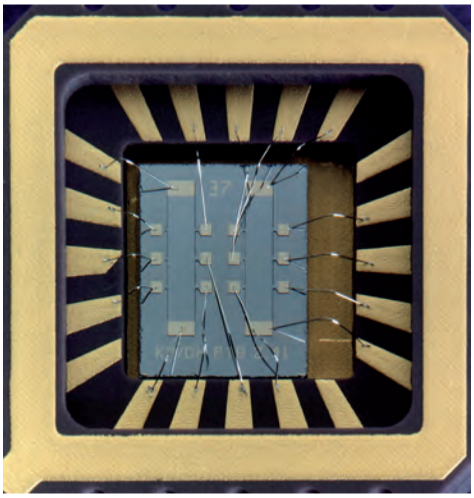

Figure 5:
Quantum Hall resistor in a chip carrier.

Strictly speaking, since 1990, the electric units have no longer been SI units but units in a special system based on fundamental constants. The envisaged redefinition of the whole system of units will solve this rather unsatisfactory situation.

4 Redefinition of the Ampere

The – more than a century old – finding that electric charge is quantised in the form of electrons strongly suggests that a definition of the ampere should take this into account. Correspondingly, the committees of the Metre Convention advocate a new definition of the ampere, in which the elementary charge *e* is attributed a fixed numerical value in the unit "ampere times second". This definition purposely does not refer to the experimental realisation.

This endorsement is made in a recommendation of the Consultative Committee for Electricity and Magnetism (CCEM) [10], in which also different ways for the realisation (*"mise en pratique"*) are presented. One possibility of realising the ampere according to the new definition is based on a quantum current source which generates a current corresponding to the relation $I = e \cdot f$. As an alternative, it is possible to realise a quantum *amperemeter* which exploits the Josephson and the quantum Hall effects to measure a current I.

The technical fundamentals for the practical implementation of the new definition of the ampere are detailed in the sections below.

4.1 Single-electron current sources

Since the end of the 1980s, it has been possible to manipulate single electrons in small electrical circuits. This was especially due to the progress made in microelectronics. The basis for this progress is single-electron tunnelling (SET): tiny metallic or semiconducting islands, less than a µm in size, which are separated by thin insulating barriers, have a very low electric capacitance C. At temperatures in the millikelvin range, the finite energy e^2/C, required to bring one electron onto the island, can no longer be supplied by the thermal energy reservoir. Quantum-mechanical tunnelling through the barriers between the islands is, thus, suppressed. This effect is called "coulomb blockade". If, however, the potential energy of the islands is lowered using control electrodes (gates), tunnelling – and thus the transport of the electrons across the island – becomes possible again. In a chain of such islands, by sequentially triggering the islands with voltage pulses repeated at the frequency f, it is possible to generate a constant current having the value $I = e \cdot f$ [11]. In an array composed of 7 barriers, under ideal conditions single electrons could be transported with an error rate of only $1.5 \cdot 10^{-8}$ [12]. In principle, such a single-electron pump is precisely that component by means of which the new definition of the ampere can be implemented.

In a version of this pump, developed at PTB (Fig. 6), five barriers ("tunnel contacts") suffice since two integrated series resistors improve the error rate of the pump by restraining uncontrolled tunnelling events. With this easier-to-operate pump, an error rate of $2 \cdot 10^{-7}$ is achieved [13].

Despite the low error rates of the single-electron pumps described above, their use is limited to special cases, since only currents of a few pA can be realised with high accuracy. To generate higher currents in the nA range with small error rates, alternative approaches have been developed worldwide – and especially at PTB – to control the transport of single charges. Figure 7 shows a structure which is still quite similar to the structure depicted in Figure 6, but which is less complex. This is made possible by the fact that not only normal-conducting (N), but also superconducting (S) metal is used. The superconducting energy gap ensures that in spite of the simplified arrangement, single electrons are transported with a very low error rate [14, 15].

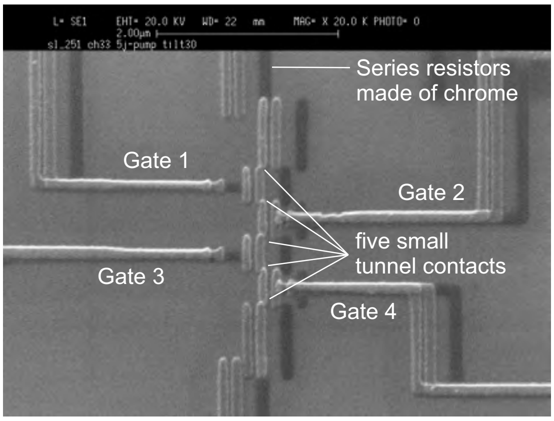

Figure 6:
SEM image of a metallic SET pump with series resistors ("R pump"). The arrows indicate the tunnel barriers.

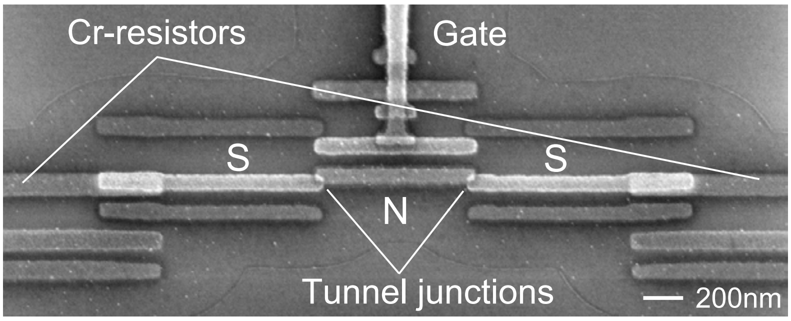

Figure 7:
SEM image of an SNS-SET device.

The most promising approach at the moment for a single-electron component providing currents in the nA range is, however, based on semiconductors. With semiconductors, it is possible to adjust the height of the barriers – and, thus, the tunnelling rates – electrically if they are controlled like in a field effect transistor [16–19]. Figure 8 shows such a device. A narrow conducting channel (coloured in green) is crossed by electrodes which can be biased to form a barrier for the electrons. For operation, only two of the three electrodes are needed, e. g. one of the violet ones and the yellow one. With suitably chosen DC voltages at the electrodes, and by means of an additional AC voltage of frequency f at the front electrode, a current $e \cdot f$ is generated also in this type of pump. The frequency f and, thus, the generated current can be considerably higher than in the case of the metallic structures with the invariable oxide tunnel barriers described above. At a pump frequency of 1 GHz, a current of 0.16 nA was achieved whose uncertainty was estimated by theoretical modelling to 1 part in 10^{-7} [19]. The analysis of experiments carried out at a pump frequency of 0.3 GHz with the model described in [17] yielded an uncertainty of 10^{-9}.

For the SNS devices and the semiconductor pumps, the parallelising of several transport channels has already been successfully demonstrated [20, 21]. Therefore this option is also available, even if the currents generated by the best and most modern single-electron-transport components turn out to be still too small in practical applications.

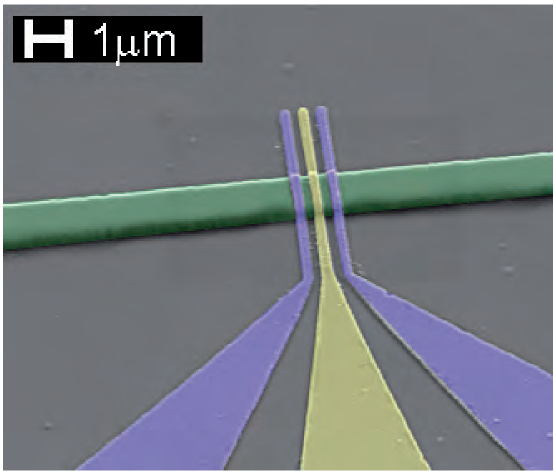

Figure 8:
SEM image of a semiconducting SET pump. Control electrodes (violet, yellow) cross a narrow conductor made of semiconducting material (green).

In order to ensure that single-electron current sources achieve a reproducibility which is comparable to that of Josephson and quantum Hall elements, a new concept will be employed. This concept implies that in suitable – but clearly more complex – circuits, the error rate of the component is monitored during operation at the level of single electrons and corrected, if necessary [22]. The technical possibility for this is also provided by the single-electron tunnelling effect: just as the transport of an electron onto an island can be controlled by applying an electric voltage, the presence of an electron on an island causes a measurable change in the transport properties of the device. Such a device is called a single-electron detector. The concept of such a self-referencing single-electron pump was elaborated at PTB [22], where it is presently being implemented.

4.2 The quantum amperemeter

According to one of the suggested *mise-en-pratique* variants, the ampere can be determined in the future SI system also in such a way that – by comparison with the Josephson effect – the voltage drop U along a well-known resistance R carrying a current is measured. If for R, e. g., a quantum Hall resistor operated at the level $i = 2$ is chosen, then the following applies (for the Josephson voltage level $n = 1$):

$$I = \frac{U}{R} = \frac{K_J^{-1} \cdot f}{R_K/2} = 2 \cdot \left(K_J R_K\right)^{-1} \cdot f$$

If the relations $K_J = 2e/h$ and $R_K = h/e^2$ are exactly valid, this results in the same relation $I = e \cdot f$ as in the case of the quantum current source.

For currents in the microampere range and greater, such a measurement can be performed either directly or via a resistor which has a low uncertainty and was calibrated against the quantum Hall effect. For numerous technical applications, but also for the reasons which will be outlined in the following section, it is, however, important to be able to measure also small currents with low uncertainty. The high resistance values required for this purpose, however, lead to an increased measurement uncertainty, so that another method must be used.

The low current is, in a first step, amplified very precisely by means of a so-called cryogenic current comparator (CCC). In the case of a CCC, a small current generates a magnetic flux in a coil with a high number of turns N. This magnetic flux is compensated by a current which is exactly N-times as high and flows in a second coil having only one turn. A superconducting quantum interferometer (SQUID) is used as a sensitive flux detector and controls a feedback loop which exactly adjusts the higher current.

Such a quantum amperemeter is composed of a current-amplifying CCC, a thermostated resistor which has been precisely calibrated against a quantum Hall resistor, and a Josephson voltmeter by which the voltage to be measured is compared directly with a Josephson voltage. At the LNE, the national metrology institute of France, such a system has been in the setting-up process for several years now [23]. In this set-up, a single-electron current source and a CCC are integrated close to each other in a low-temperature system. So far, this system has achieved a measurement uncertainty of approx. $4 \cdot 10^{-6}$ at currents of a few pA. At present, a quantum amperemeter is being set up at PTB according to the scheme shown in Fig. 9, by which small currents from arbitrary sources can be measured.

5 The Quantum Metrology Triangle

The uncertainty with which a quantum amperemeter measures the current – according to the new definition and traceably to the elementary charge – depends on the accuracy of the relations $K_J = 2e/h$ and $R_K = h/e^2$. This is a fundamental issue for the realisation and dissemination of the electric units in a new, quantum-based, international system of units. The excellent reproducibility of the Josephson [24] and of the quantum Hall effect [8] in various solid-state systems only contributes in a limited way to clarifying this issue, since this still does not rule out that all experimental realisations could suffer from the same deviation from $K_J = 2e/h$ or $R_K = h/e^2$. A direct experimental check is necessary. In order to substantially improve the present state of knowledge, the uncertainty has to be in the order of 10^{-8} [25]. In the SI as it is now, such an uncertainty cannot be achieved by measuring Josephson voltages or the quantum Hall resistances and by comparison with the SI values of e and h. Therefore, an experimental consistency test was suggested already back in 1985 [26]. It is known as the "quantum metrology triangle".

Figure 10 is a schematic representation of the so-called "quantum metrology triangle". In the experiment, the voltage drop which is caused by a single-electron current when passing through a quantum Hall resistor is compared with the Josephson voltage which is expected when the relations $K_J = 2e/h$ and $R_K = h/e^2$ are absolutely correct. From this comparison, upper limits can be determined for possible deviations of K_J from $2e/h$, and of R_K from h/e^2 as well as of the quantised charge transported by the single-electron current source from the elementary charge e.

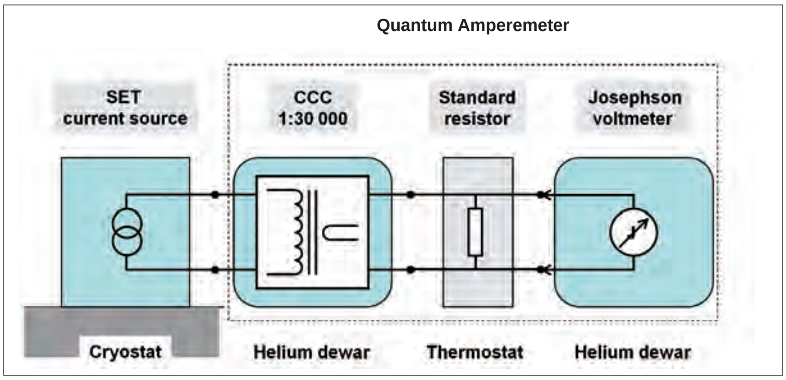

Figure 9:
Scheme of a quantum amperemeter which is represented in the dashed frame. In the sketch, it is connected to a single-electron current source.

To achieve a relative uncertainty in the order of 10^{-8}, the single-electron current source must supply currents in the order of 1 nA. Furthermore, a CCC must be used – as in the case of the quantum amperemeter. Both set-ups – the direct quantum metrology triangle and the quantum amperemeter – look rather similar at first sight. There is, however, a fundamental difference between the two: in the case of the quantum amperemeter set-up, the current source is the measurement object whose unknown current is determined, whereas in the case of the direct quantum metrology triangle, the properties of the single-electron current source must be exactly known. Especially the error rate of the single-electron current source must be determined prior to the experiment by means of independent methods – such as the single-electron detection method described in Section 4.1. At present, the national metrology institutes of France (LNE), Finland (MIKES) and Germany (PTB) are involved in the setting up of the technically highly demanding experiment *"Direct Quantum Metrology Triangle"* or in developing key components for the experi-

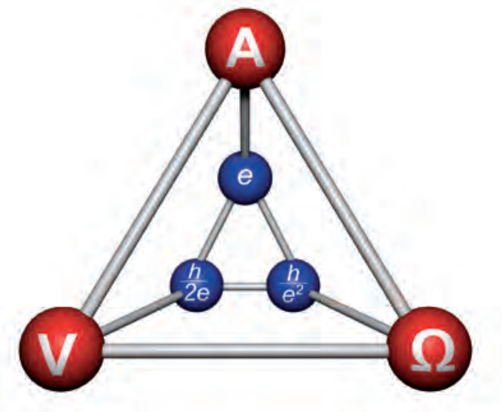

Figure 10:
Schematic representation
of the quantum metrology triangle.

ment. It is expected that PTB – with its technology of semiconducting single-electron pumps – will contribute significantly to this experiment.

An alternative to this experiment is the so-called *"Indirect Quantum Metrology Triangle"*. For this experiment, single-electron current sources can be used which generate currents in the pA range – such as, e. g., metallic *R* pumps. Using these sources, a capacitor of capacitance *C* of approx. 1 pF is charged with a defined charge *Q* of *n* electrons. As described in Section 2.2, the capacitance is traceable to the von Klitzing constant R_K by means of a quadrature bridge. The voltage *U*, which is generated by the *n* electrons and drops across the capacitor, is measured by means of a Josephson voltage standard. In accordance with the relation $Q = C \cdot U$, the elementary charge *e*, $K_J = 2e/h$ and $R_K = h/e^2$ can be related to each other. The experiment was performed at NIST, the national metrology institute of the USA [27]. It was possible to determine the upper limit for a possible deviation of K_J, R_K and *e* from the expected values to be $9 \cdot 10^{-7}$ [28]. PTB is working on the verification and improvement of this result [29].

6 Summary and Outlook

The history of the ampere spans a wide range of disciplines, from electrochemistry to electrodynamics, and further on to modern solid-state physics. This will eventually lead to the abandonment of the derivation of the ampere from the kilogram. In the new definition, the ampere will be defined on the basis of the elementary charge. This has been made possible by the discovery of macroscopic quantum effects in solids which create a bridge between the electric quantities and the fundamental constants of physics. The development also has an impact on other fields of metrology. The planned redefinition of the kilogram by defining the numerical value of Planck's constant *h* is motivated by the watt balance [30], an advancement of the ampere balance described in Section 2.1, which is based on the Josephson effect and the quantum Hall effect. The Josephson effect and the quantum Hall effect have become an integral part of metrology.

The use of the single-electron transport to realise the quantum ampere has not been established yet, but it is a highly topical research subject in the field of electric quantum metrology. The scientific issues in this field are closely related to those of quantum dynamics und quantum data processing in solids, as well as to nano- and superconductor electronics. It is expected that metrological research on the quantum ampere will not only contribute significantly to the new international system of units, but also to the other above-mentioned fields. ■

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Temperature – the SI Base Unit "Kelvin"

Joachim Fischer[1] and Jörg Hollandt[2]

Structure

1 Temperature

Temperature plays an important role - not only in everyday life, but also as an important parameter for climate change, in medical diagnostics and medical therapy, and for the transformation of energy in motors and power plants. Furthermore, it determines the course of vital processes or acts as a control factor in chemistry. For this reason, temperature is one of the most frequently measured physical quantities.

For these applied measurements, a direct realisation of the quantity of state "temperature" T according to the fundamental laws of *thermodynamics* by implementing so-called primary thermometers is not really suited. Although it is possible to measure thermodynamic temperatures by means of primary thermometers with uncertainties which would be absolutely sufficient for almost all practical applications, they are so difficult, sophisticated, and – frequently – so time-consuming to use that they are not suited for practice, for example for the monitoring and control of industrial manufacturing processes. For this reason, one has approximated the thermodynamic temperature scale in a widest possible range by means of an International *Temperature Scale* which has been permanently advanced and improved and which prescribes a system of measuring devices and measuring procedures which is easier to handle than the primary thermometers and ensures uniform temperature measurements worldwide.

2 The History of Temperature Measurement

Although temperature could always be experienced by human perception and everyday observations, it took until the 16th century until Galileo Galilei manufactured the first thermometer. He used the thermal expansion of air in a closed vitreous body filled with a liquid column. However, his thermometer did not have a scale or even numbers at the scale lines. It was not until 1724 that Fahrenheit and 1742 that Celsius introduced the first practicable temperature scales – by using two reproducible fixed points and by subdividing the temperature range in uniform intervals. At about the same time, Guillaume Amontons perfected the ideas of Galilei and developed the gas thermometer with a constant volume whose pressure increase of the gas permits reading the temperature change. From this, he drew the conclusion that the lowest achievable temperature prevails when the gas pressure is disappearing.

The first task of the International Bureau of Weights and Measures (BIPM) was the dissemination of prototypes of the metre to the member states of the Metre Convention of 1875. To be able to accurately take into account the thermal expansion of the metre copies, they were given mercury thermometers which had been calibrated on a precise primary gas thermometer filled with hydrogen. Thus, the standard hydrogen scale of 1887 is the first internationally agreed temperature scale. To this day, the underlying principle has not

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changed: a practical temperature scale with exactly reproducible fixed points based on primary thermometers – which again are based on thermodynamic principles for the determination of the fixed points' temperatures. The hydrogen scale of 1887 was only defined in the range between – 25 °C and 100 °C and it was not until 1927 that the International Temperature Scale of 1927 (ITS-27) became available – being the first scale for vast fields of application in science and technology valid in an extended temperature range from – 193 °C to far beyond 1000 °C. This scale already has all the characteristics of today's International Temperature Scale of 1990 (ITS-90): by contact measuring, electrical resistance thermometers for the range of lower temperatures and optical measuring radiation thermometers above.

The existence of a universal thermodynamic temperature scale which does not depend on the characteristics of special thermometers had already been recognised in 1848 by William Thomson, the later Lord Kelvin. In 1854, William Thomson suggested that the unit of temperature should be determined with the aid of the temperature interval between the absolute zero point and only one appropriate temperature fixed point. However, it lasted exactly one hundred years until the 10th General Conference on Weights and Measures took this proposal into account. Therefore, the unit of temperature is called kelvin today. As the fixed point, the triple point of water was selected and its temperature determined to be 273.16 K [1]. The numerical value was chosen in such a way that the kelvin agrees as precisely as possible with the previously used degree Celsius which – as is generally known – was one hundredth of the temperature difference between the boiling point and the melting point of water at normal pressure. Today, the degree Celsius – with the unit symbol °C – is no more than a special name for kelvin when indicating Celsius temperatures t:

$$t\,/\,°\mathrm{C} = T\,/\,\mathrm{K} - 273.15,$$

if t and T describe the same temperature. The melting temperature of water at standard pressure lies slightly below the triple point temperature.

3 The International Temperature Scale of 1990 (ITS-90)

The currently valid International Temperature Scale ITS-90 [1, 2, 3], which was adopted in 1989 by the International Committee for Weights and Measures (CIPM), superseded the former IPTS-68 and its supplement for use at low temperatures, EPT-76, on January 1, 1990. The IPTS-68 replaced the IPTS-48 scale, which followed the above-mentioned ITS-27 [3]. Temperatures measured according to the regulations of the ITS-90 are marked with the subscript "90", i. e. they are designated T_{90} or t_{90}. (Correspondingly, temperatures measured in conformity with older scales are denoted by the relevant subscripts, e. g. T_{68}.) A detailed overview of the development of the temperature scales from 1887 until today can be found in [4].

The ITS-90 extends from 0.65 K up to the highest temperatures which can practically be measured by means of Planck's radiation law. It is based on 17 thermodynamic equilibrium states which can be well reproduced, the defining *fixed points*, to which particular temperature values are assigned (Table 1). These are mean values of the thermodynamic temperatures which were determined at various national metrology institutes and were considered to be the best values available at the time of the scale definition.

3.1 Fixed points of the ITS-90

The defining fixed points are thermodynamic states of equilibrium between the phases of pure substances. At the melting point of gallium and at the freezing points of the metals, the indicated temperature values are valid for normal atmospheric pressure $p_{\mathrm{atm}} = 101.325$ kPa; however, they depend only weakly on pressure ($|\mathrm{d}T/\,\mathrm{d}p| < 1$ µK/ Pa). Figure 1 schematically shows the pressure-temperature diagram of water with the regions of state of the solid (ice), the liquid and the gas. They are separated by the *melting pressure curve*, the *vapour pressure curve* and the *sublimation pressure curve*. These three curves meet in the *triple point*. This point corresponds to the only state at which the three phases *gas*, *liquid* and *solid* are in a thermodynamic equilibrium. The vapour pressure curve ends in the *critical point*; for higher pressures or temperatures, there no longer is a well-defined boundary between the gas and the liquid phase, and both are subsumed under the designation "fluid phase."

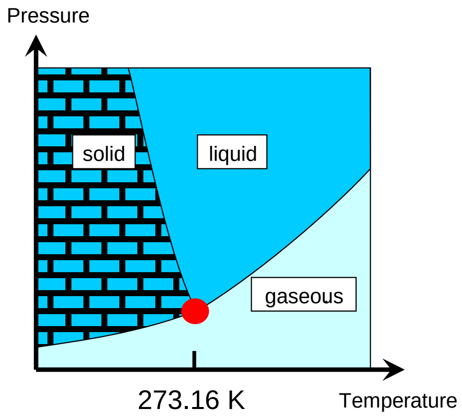

Figure 1:
Schematic (p, T) diagram of pure water.

Table 1: Defining fixed points of the ITS-90

State or quantity of equilibrium	T_{90} in K	t_{90} in °C	Standard uncertainty $u(T)$ of thermodynamic temperature T in mK	Best achievable standard uncertainty of PTB’s fixed point realisation, in mK
Vapour pressure of helium	3 to 5	−270.15 to −268.15	0.3	0.2
Triple point of equilibrium hydrogen	13.8033	−259.3467	0.4	0.1
Vapour pressure of equilibrium hydrogen	17.025 to 17.045 and 20.26 to 20.28	−256.125 to −256.105 and −252.89 to −252.87	0.5	0.3
Triple point of neon	24.5561	−248.5939	0.5	0.15
Triple point of oxygen	54.3584	−218.7916	1	0.1
Triple point of argon	83.8058	−189.3442	2	0.1
Triple point of mercury	234.3156	−38.8344	2	0.13
Triple point of water (TPW)	**273.16**	**0.01**	**0 (Definition of the kelvin)**	**0.06**
Melting point of gallium	302.9146	29.7646	1	0.12
Freezing point of indium	429.7485	156.5985	3	0.4
Freezing point of tin	505.078	231.928	5	0.4
Freezing point of zinc	692.677	419.527	13	0.65
Freezing point of aluminium	933.473	660.323	25	1.0
Freezing point of silver	1234.93	961.78	40	1.5
Freezing point of gold	1337.33	1064.18	50	10
Freezing point of copper	1357.77	1084.62	60	15

3.2 Interpolation between the fixed points

In the ITS-90, different interpolation procedures are prescribed for several temperature ranges and sub-ranges, so as to give the user as much choice in the realisation of the scale as is consistent with the requirements placed on a scale of high reproducibility. With only one exception, T_{90} is defined in all sub-ranges in such a way that no calibrations of the interpolating standard thermometers at external fixed points are necessary. The exception is that platinum resistance thermometers to be used above the neon triple point at 24.5 K have to be calibrated also at the hydrogen triple point at 13.8 K. The sub-ranges cannot, however, be freely selected: a high-temperature resistance thermometer, for example, must be calibrated in the entire range from 273.16 K to 1235 K even if it is to be used only between 933 K and 1235 K. Figure 2 gives a schematic overview of the temperature ranges and sub-ranges and the appropriate interpolation instruments of the ITS-90.

The price to be paid for this flexibility is a certain amount of non-uniqueness: On the one hand, different interpolation methods or instruments can be used in some temperature ranges, or individual specimens of a specified interpolation instrument (e. g. a platinum resistance thermometer) may have dissimilar properties which are not allowed for by the calibration procedure prescribed. On the other hand, different values of the same temperature can be determined with one and the same standard thermometer according to whether it has been calibrated for use in a narrower or in a wider sub-range at few or many fixed points. The associated standard measurement uncertainties are accepted, since for platinum resistance thermometers typical values are of the order of approximately 0.5 mK at most and are thus smaller than the uncertainty in the realisation of the ITS-90 which is contingent

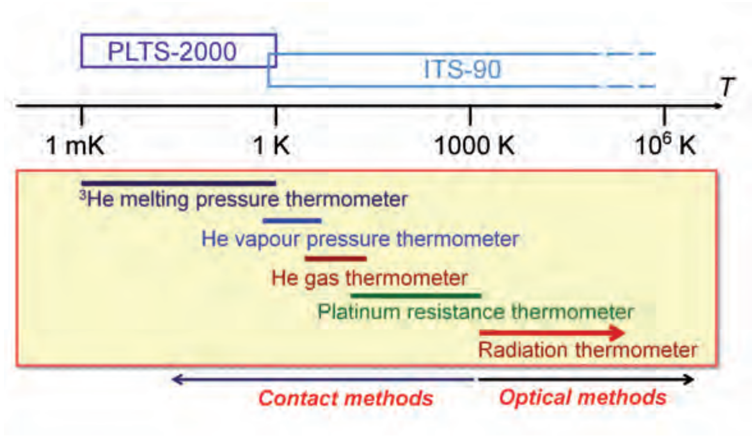

Figure 2:
Temperature ranges of the ITS-90 and the PLTS-2000 as well as interpolation instruments.

on the measuring stability of the interpolation instruments and on the reproducibility of the realisations of the defining fixed points. In the temperature range of the resistance thermometer, typical values for the uncertainty in the realisation of the ITS-90 are approximately 0.5 mK at 13.8 K, 5 mK at 933 K (660 °C) and 10 mK at 1235 K (962 °C), and in measurements using the spectral radiation pyrometer, they are about 0.07 K at 1235 K, 0.45 K at 2500 K and 0.7 K at 3200 K.

3.2.1 Temperature range from 0.65 K to 24.5561 K

Between 0.65 K and 5 K, T_{90} is determined from the vapour pressure of ^{3}He (0.65 K to 3.2 K) or ^{4}He (1.25 K to 5 K) using a *vapour pressure thermometer*. The temperatures are calculated from three vapour pressure equations specified in the ITS-90 whose coefficients are specified according to the gas and the temperature range.

In the temperature range from 3.0 K to 24.5561 K, a *special gas thermometer* with ^{3}He or ^{4}He serves for interpolation. The temperatures are calculated from specified equations whose constants are determined by calibration at three fixed point temperatures (hydrogen and neon triple point as well as a temperature between 3 K and 5 K determined from the vapour pressure of helium).

Above 13.8033 K, it is also possible to employ the *platinum resistance thermometer*.

3.2.2 Temperature range from 13.8 K to 1234.93 K (961.78 °C)

In this temperature range, a special type of *platinum resistance* thermometer serves for interpolation. The temperature is calculated from the *resistance ratio*

$$W(T_{90}) = R(T_{90})/R(273.16\ \text{K})$$

whereas $R(T_{90})$ and $R(273.16\ \text{K})$ are the measured electric resistances at the temperature T_{90} or at the triple point of water. For the realisation of the ITS-90, only thermometers with a measuring resistor of very pure platinum free from mechanical strain are suited. Platinum resistance thermometers suitable for the entire temperature range from 13 K to 1235 K are not available. Today, three different types are in use:

- Capsule thermometers with a protective tube of only approx. 60 mm in length made of platinum, stainless steel or glass, are mainly used at low temperatures as they can be easily incorporated into cryostats. Owing to the need for a metal-glass bushing, they can be used up to approx. 200 °C; their resistance at the triple point of water is, as a rule, about 25 Ω.
- Thermometers for the temperature range from 83 K to 800 K have a protective tube made of quartz glass or Inconel about 600 mm long and about 7 mm in diameter. The measuring resistor is usually designed as in the capsule-type thermometer, the resistance at the triple point of water also being 25 Ω. These thermometers can be easily incorporated into baths without the thermometer head including the connecting leads being heated or cooled.
- Thermometers for high temperatures were specifically developed for the temperature range from 500 °C to 962 °C. Today's protective tubes are made exclusively from quartz glass. The wire for the measuring resistor is selected much thicker than in the other two thermometer types in order to provide greater stability at high temperatures. This leads to a comparably low resistance (in most cases about 0.25 Ω at the triple point of water).

From the measured resistance ratios $W(T_{90})$ the temperature is determined as follows: For each of the temperature ranges 13.8033 K to 273.15 K and 0 °C to 961.78 °C, one reference function is defined describing the temperature dependence of the resistance ratio $W_r(T_{90})$ of a particular platinum resistance thermometer selected as reference thermometer. For each thermometer, a deviation function $W(T_{90}) - W_r(T_{90})$ must be determined by calibration. According to the temperature range, three different deviation functions are used whose coefficients are determined from the values measured for the resistance at the defining fixed points. Temperatures between the fixed points can be easily calculated with the deviation function and the reference function. According to the particular properties of the thermometers, the values obtained differ within certain limits (so-called type 3 of "non-uniqueness").

3.2.3 Temperature range above the freezing point of silver 961.78 °C

Temperatures above the freezing point of silver are measured with the spectral radiation thermometer on the basis of Planck's radiation law by comparing – ideally at a (vacuum) wavelength λ – the spectral radiances $L_\lambda(\lambda, T_{90})$ and $L_\lambda(\lambda, T_{90,\mathrm{ref}})$ of a blackbody radiator of temperature T_{90} and of a fixed-point blackbody radiator with the known, specified temperature $T_{90,\mathrm{ref}}$ and calculating T_{90} from the measured radiance ratio according to

$$\frac{L_\lambda\left(\lambda, T_{90}\right)}{L_\lambda\left(\lambda, T_{90,ref}\right)} = \frac{\exp\left(c_2/\left[\lambda T_{90,ref}\right]\right)-1}{\exp\left(c_2/\left[\lambda T_{90}\right]\right)-1} .$$

For Planck's second constant $c_2 = hc/k$, the value of 0.014388 m · K is used. The fixed-point blackbody radiator can optionally be operated at the temperature of the freezing point of silver ($T_{90,\mathrm{ref}}$ = 1234.93 K), gold ($T_{90,\mathrm{ref}}$ = 1337.33 K) or copper ($T_{90,\mathrm{ref}}$ = 1357.77 K). Here, the cavity radiator represents the blackbody radiator described in Planck's radiation law in very good approximation.

4 Dissemination of the ITS-90

Compared with primary thermometers for the determination of thermodynamic temperatures, the interpolation instruments of the ITS-90 are much easier to use but they, too, are not very well suited for practical use, e. g. for industrial applications. It is true that the ITS-90 can be disseminated in the temperature range from 13.8 K (hydrogen triple point) to 933 K (660 °C, freezing point of aluminium) using robust platinum resistance thermometers which have been calibrated at fixed points. However, the other standard thermometers defined in the ITS-90 - such as the helium vapour pressure thermometer, the interpolating gas thermometer and also the platinum resistance thermometer for high temperatures – are not suitable as practical measuring instruments. This is why in the measurement ranges affected, *secondary thermometers* must be calibrated [5].

As secondary thermometers in the temperature range from 0.65 K to about 30 K, *rhodium-iron resistance thermometers* are frequently used which are among the best precision measuring instruments for this range. If the requirements to be met by the measurement uncertainty are somewhat less demanding, *resistance thermometers* with sensor elements made from materials with a negative temperature coefficient (germanium, Cernox, etc.) or *semiconductor diodes* are also suited.

In the temperature range from 600 °C to 1560 °C, the *platinum-rhodium/platinum thermocouple* is used despite its comparatively high measurement uncertainty of 0.3 K to 1.0 K. In the last few years, a new thermocouple has been developed in the course of the refinement of voltage measuring technology: the *platinum/palladium thermocouple* which can be used excellently up to 1200 °C (standard uncertainty smaller than 0.2 K) and which is well suited for the dissemination of the temperature scale.

Investigations on so-called *industrial resistance thermometers* have shown that several types furnish well-reproducible results up to 800 °C and are thus eligible for the dissemination of the scale if the uncertainty called for is not too small.

For temperatures above 962 °C, the ITS-90 is disseminated by means of calibrated *tungsten strip lamps* and *spectral radiation thermometers*.

5 The Provisional Low Temperature Scale PLTS-2000 from 0.9 mK to 1 K

Just as for the IPTS-68, the predecessor of the ITS-90 – which had been extended towards low temperatures by the provisional temperature scale EPT-76 – the International Committee on Weights and Measures adopted an extension of the ITS-90, the *Provisional Low Temperature Scale from 0.9 mK to 1 K, PLTS-2000*, in October 2000 [6]. The new scale, to the development of which the PTB has made important contributions and which is mainly applied in low-temperature fundamental research and at the manufacturers of ultra low temperature cryostats, overlaps with the lower part of the ITS-90 which extends down to 0.65 K (Figure 2). Here, it should be noted that precise measurements of the temperature dependence of the ^{3}He vapour pressure at temperatures around 1 K and below allowed the deviations of the ITS-90 from the thermodynamic temperature scale and the PLTS-2000 in this temperature range to be analysed. As a result of these investigations, the new ^{3}He vapour pressure scale PTB 2006 [7] for the temperature range from 0.65 K to 3.2 K was set up which solves the problems of the ITS-90 at its lower end and which is consistent with the PLTS-2000.

The PLTS-2000 follows the same principle as the ITS - i. e. imaging the complex measurements of thermodynamic temperatures to phase transitions of pure substances, which can be more easily realised in the laboratory. The new scale is based on the realisation of the phase equilibrium between the fluid and the solid phase of a test sample of the lighter helium isotope ^{3}He. The internationally agreed relation $p(T_{2000})$ between the temperature T_{2000} and the ^{3}He melting pressure p is specified by a polynomial with 13 coefficients, in order to be able to describe the melting pressure in the whole range covering three decades with sufficient precision. The relative standard measurement uncertainty of the PLTS-2000 in respect of the thermodynamic temperature is 0.05 % at 1 K, increases to 0.2 % at 0.1 K and 0.3 % at 0.025 K when the temperature is decreasing and then reaches 2 % at the lowest temperature of 0.9 mK. At T_{2000} = 315.24 mK, the melting pressure has a minimum p_{min} = 2.93113 MPa as well as three further fixed points in the range around 1 mK for pressure and temperature, which are also specified by definition [6] (Table 2): the transition from the normal fluid to the suprafluid "A" phase at the temperature T_A, the "A–B" transition in the suprafluid at $T_{A\text{-}B}$ and the Néel transition in the solid phase at $T_{\text{Néel}}$. Figure 3 shows the characteristics of the ^{3}He melting pressure with the temperature as well as the position of the fixed points over the logarithmic temperature axis. Although the sensitivity of the melting pressure tends towards zero when approaching the minimum and no melting pressure thermometry is possible in its direct environment, the minimum has the great advantage of providing an incorporated fixed point for pressure calibration.

Table 2: Fixed points of PLTS-2000

Fixed point	p in MPa	T_{2000} in mK
Minimum of the ^{3}He melting pressure curve	2.931 13	315.24
Transition from the normal-fluid to the superfluid A phase	3.434 07	2.444
Transition between the superfluid A and B phase	3.436 09	1.896
Néel transition in the solid ^{3}He	3.439 34	0.902

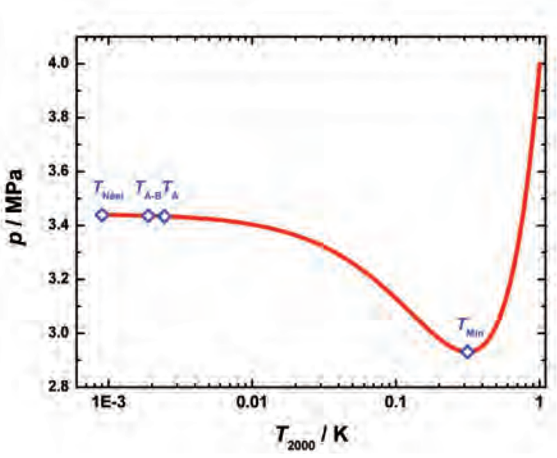

Figure 3:
Melting pressure p of ^{3}He as a function of the temperature T_{2000}. The blue rhombuses mark the fixed points of the PLTS-2000.

Hence, the PLTS-2000 can be realised with a ^{3}He melting pressure thermometer in any laboratory that can generate the respective low temperatures. At the heart of every melting pressure thermometer is the melting pressure sensor in which pressure measuring is carried out capacitively via the deflection of a sensor membrane. For the *in-situ* pressure calibration of the melting pressure sensor, the fixed points of the PLTS-2000 can be used. Due to mechanical nonlinearities of the pressure sensor, the use of a minimum of two fixed points is required for the pressure calibration. For low-temperature facilities which can only attain the minimum but not the three fixed points below 0.0025 K, direct calibration against a pressure standard can be considered which, however, is very complex and expensive. An effective and inexpensive alternative is the calibration of the melting pressure sensor by means of calibrated superconducting reference devices which ultimately, however, lead to a moderately increased uncertainty. Further detailed information about the establishment of a ^{3}He melting pressure thermometer and for the realisation of the PLTS-2000 can be found in [8].

The polynomial established for $p(T_{2000})$ takes measurements by the US-American National Institute of Standards and Technology (NIST), the University of Florida and PTB into account. As there were still differences between the measurement results, in particular for the lowest temperatures below 7 mK, averaging was carried out. This is why the CIPM declared the scale "provisional" for the time being and requested to perform further measurements so that the definition of the scale might be finalized. PTB is currently the only national metrology institute in the world to realise the PLTS-2000 in the whole definition range and disseminates it to the customer by means of calibrations. The dissemination is carried out by calibrating resistance thermometers (germanium, Cernox, ruthenium oxide, amongst others) and superconducting reference devices (W, Be, $Ir_{1-x}Rh_x$, Ir, $AuAl_2$, $AuIn_2$, Cd, Zn, Mo), the latter offering the lowest calibration uncertainties.

6 Further Development of Temperature Measurement

Although the ITS-90 is a very good approximation of the thermodynamic temperature scale and should ensure adequate global comparability of temperature measurements for a foreseeable period of time, many institutions – above all the national metrology institutes – are working on improving temperature measurement, on the reliable determination, analysis and minimization of uncertainty contributions as well as also on improving and simplifying dissemination. The following current PTB activities are examples of this:

- Development of easily manageable primary thermometers for the range of ultra-low temperatures [9]
- Investigation of the influence of impurities and of the isotopic composition on fixed-point temperatures; a more precise definition of the triple point of hydrogen in the ITS-90 as regards the isotopic composition (deuterium component) has already been concluded [10]. The investigations of the metal freezing points of the ITS-90 concerning impurities with the aim of their characterisation which is traceable to the SI system of units are being continued [11, 12].
- Clarification of the discrepancies between ITS-90 and thermodynamic temperatures in the temperature range between the neon point (24.556 K) and the triple point of water [13]
- Radiometric determination of ever lower thermodynamic temperatures with small uncertainties (at present, e. g., 15 mK at 460 °C) [14]
- Calibration of radiation thermometers and thermography cameras for temperatures down to –150 °C, amongst others, for the traceability of satellite-based measurements to the SI system of units [15]
- Investigation and characterization of high-temperature thermocouples [16]
- Determination of the thermodynamic temperatures of novel high-temperature fixed points above 1100 °C (melting and freezing points of metal or metal carbide carbon eutectics) with uncertainties of currently e.g. 200 mK for the Ru-C fixed point at approximately 1950 °C [17].

7 New Definition of the Kelvin

The temperature unit kelvin is the 273.16th part of the thermodynamic temperature of the triple point of water [1]. This definition derives the unit from a rather randomly selected material property. Thus, influences of the isotope composition and the purity of the used water are of essential importance for their practical realisation. Thereby, the stability of the realisation over space and time is jeopardised.

In 2005, the *Comité International des Poids et Mesures (CIPM)* recommended the national metrology institutes to submit adequate proposals for the kelvin – in the same way as for the kilogram, the ampere and the mole – to make sure that these four base units can be newly defined [18]. The aim is to define, in future, the base units via fundamental constants and to make them thus independent of embodied standards, so-called artefacts, or special measurement instructions. As the thermodynamic temperature T always occurs in the combination kT as “thermal energy” in all fundamental laws, the Boltzmann constant k is the natural constant to be fixed. By determining its value, the kelvin is directly derived from the unit of energy “the joule” (similar to the unit of length *metre* by determining the value of the speed of light of the unit of time “second” since 1983).

At present, it is not necessary to modify the structure of the International System of Units and to select other base units [19]. The kelvin should therefore not disappear from this system. A new definition should be of use both for daily application in development and production and for basic research. To avoid recalibrations and conversions, no verifiable discontinuity should occur in the quantity of the unit. The uncertainty of the value of the relevant fundamental constant should thus be comparable to the uncertainty of the realisation pursued so far.

The current internationally accepted value [20] of $1.3806504 \cdot 10^{-23}$ J/K for the Boltzmann constant has a relative standard uncertainty of $1.7 \cdot 10^{-6}$. This value and its uncertainty are mainly based on a single measurement by means of acoustic gas thermometry at NIST in the year 1988. However, one single measurement is not considered to be a sufficient base for a determination of the numerical value. Therefore, a concept was discussed at two workshops at PTB in Berlin with the experts of all important metrology institutes and a time schedule was elaborated in order to achieve a value of k which is based on several different methods [21]. In the following, the customary primary thermometer methods are represented, together with the achieved uncertainties and the uncertainties to be expected.

7.1 Methods for the determination of the Boltzmann constant

As the mean microscopic thermal energy kT is not directly experimentally accessible, macroscopic quantities, which are clearly correlated with the thermal energy [22], must be measured for the determination of k at the triple point of water. Table 3 gives an overview over such dependencies in which T is only related to other *measurable* quantities and known constants. For ideal gases, the thermal energy is proportional to the mean kinetic energy of the gas particles. In a closed volume, this energy is measurable via the gas pressure and the number of particles. The pressure p is described for a negligible interaction between the particles by means of the equation of state of the ideal gas. The thermometer based on this law is the traditional gas thermometer whose uncertainty, however, is too large for absolute measurements. On the other hand, the density, which changes with the temperature at a constant pressure, can be determined via the dielectric constant or the refractive index. Also the velocity of sound in a gas serves as a temperature indicator (acoustic gas thermometer). Laser spectroscopy provides the kinetic energy of the absorbing atoms from the Doppler broadening of absorption lines. If you use the conducting electrons of a metallic resistance as a "measuring substance", the electrical Johnson noise according to the Nyquist formula is suited for thermometry. Finally, an isothermal cavity, in which the light quanta are at thermal equilibrium with the walls, emits radiation, which has been specified according to Planck's radiation law only by means of temperature and which is measured by means of the spectral radiation thermometer. Table 3 also lists the uncertainties to be expected for the determination of k. A compact description of all current methods can be found in the overview article [22].

7.1.1 Acoustic gas thermometer

In a gas, a number of measurands depend on temperature. As the describing equations are generally derived for ideal gases and the interaction between the gas particles for the determination of k is not sufficiently known, the measurements are carried out by means of extrapolation to zero pressure in such a way that the approximation of the ideal gas is sufficient. For the determination of k at NIST, the sound velocity u_0 of the noble gas argon was determined by means of a spherical resonator (Figure 4) at the temperature of the triple point of water and k was calculated from the respective formula in Table 3, whereby R is replaced by kN_A (N_A Avogadro constant).

Table 3:
Overview of the primary thermometers which are suitable for the determination of the Boltzmann constant k, with the relative uncertainties to be expected (T Temperature, u_0 sound velocity in the limiting case of disappearing pressure and of very low frequency, $\gamma_0 = c_p/c_V$ relation of the specific heat, M molar mass of the gas, R molar gas constant, p pressure, ε dielectric constant, ε_0 electric constant, α_0 static electrical polarizibility, c_0 speed of light in the vacuum, h Planck's constant, L_λ spectral radiance, λ wavelength, ν frequency, $\langle U^2\rangle$ mean square noise voltage, R_{el} electric resistance, n refractive index, $\Delta\nu_D$ Doppler width of a spectral line of the frequency ν_0, m atomic mass).

Primary thermometric method	**Law of physics**	**Achievable relative standard uncertainty**
Acoustic gas thermometer	$u_0 = \sqrt{\frac{\gamma_0 RT}{M}}$	$1 \cdot 10^{-6}$
Dielectric constant gas thermometer	$p = kT\frac{(\varepsilon - \varepsilon_0)}{\alpha_0}$	$2 \cdot 10^{-6}$
Spectral radiation thermometer	$L_\lambda = \frac{2hc_0^{\ 2}}{\lambda^5}\left[\exp\left(\frac{hc_0}{\lambda kT}\right) - 1\right]^{-1}$	$50 \cdot 10^{-6}$
Johnson noise thermometer	$\langle U^2 \rangle = 4kTR_{\mathrm{el}}\Delta\nu$	$5 \cdot 10^{-6}$
Refractive index gas thermometer	$p = kT\frac{(n^2 - 1)\varepsilon_0}{\alpha_0}$	$10 \cdot 10^{-6}$
Doppler broadening thermometer	$\Delta\nu_D = \sqrt{\frac{2kT}{mc_0^{\ 2}}}\nu_0$	$10 \cdot 10^{-6}$

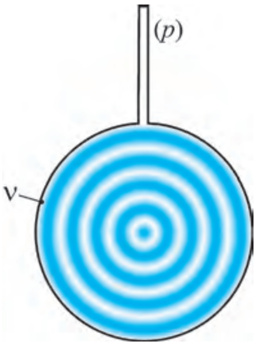

Figure 4:
Acoustic gas thermometer with spherical resonator. The sound velocity u_0 is derived from the resonance frequencies ν and the volume.

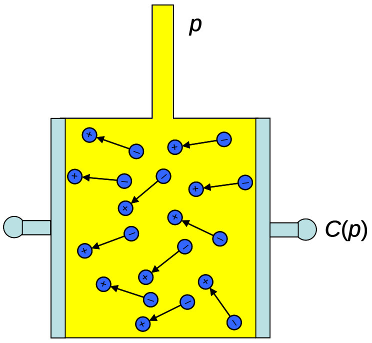

Figure 5:
The central element of the dielectric constant gas thermometer is the measuring capacitor, which here is filled with helium gas with the pressure p, and whose relative capacitance change $(C(p) - C(0))/C(0)$ is measured.

Spherical resonators are also used at other institutes now [22]. The resonator dimensions were determined at NIST by a mercury filling of known density. Today, the resonator is measured by means of microwave resonances. Besides the determination of the dimensions and the connection to the triple point temperature, essential uncertainty contributions result from the dependency of the molar mass on the isotope composition, the purity of the measuring gas, the extrapolation to zero pressure and the position of the acoustic transducers. With the current measuring technique, an uncertainty of $1 \cdot 10^{-6}$ should be attainable when using this method.

7.1.2 Dielectric constant gas thermometer

The determination of the dielectric constant of helium has been in use for a long time in thermometry for low temperatures and is – compared to the measurement of the refractive index – the more advanced and more promising procedure which offers far smaller attainable uncertainties.

For an ideal gas, the dielectric constant is given by $\varepsilon = \varepsilon_0 + \alpha_0 \cdot N/V$ (α_0 for static electrical polarizibility of the gas particles, N/V for the density of their number of particles). By combining it with the equation of state, the relation between p and ε indicated in Table 3 is obtained. Considerable progress made with the ab-initio calculation of the polarizibility of helium, whose uncertainty could be reduced to less than $1 \cdot 10^{-6}$ in the past few years, has made this method competitive. To measure ε, the measuring gas is filled into suitable capacitors. Due to the very low polarizibility of helium, absolute measurements are not possible. Therefore, the measuring capacitor is alternately filled with helium and evacuated, and ε is derived from the relative change in capacitance (Figure 5).

From the linear component of the function of $\varepsilon(p)$, k is finally determined. A considerable source of error when using this method results from the deformation of the measuring capacitor due to the gas pressure. The pressure and capacitance measurements must also be improved to the best possible extent. The estimation of all contributions allows an overall uncertainty comparable to acoustic gas thermometry of about $2 \cdot 10^{-6}$ to be expected. This estimation is supported by the results which have recently been achieved in measurements in the low-temperature range from 2.4 K to 36 K and at the triple point of water [34].

7.1.3 Radiation thermometer

Radiation thermometry is based on the emitted blackbody radiant power which – independent of material and form – only depends on temperature and on fundamental constants. Primary thermometry assumes an absolute determination of the radiant power (Figure 6). Planck's radiation law (Table 3) is then used to determine the temperature.

Radiant power measurements with a relative standard measurement uncertainty of $1 \cdot 10^{-4}$ are based on the electrical substitution radiometer as the primary standard for optical power measurement. In the case of an electrical substitution radiometer, the radiation absorbed in a receiver cavity increases its temperature. In a second measurement, the same temperature increase is generated – with the input aperture closed – by means of electrical heating power, which can be determined very precisely. To attain the required detection sensitivity, the thermal capacity of the cavity must be as small as possible. This can be achieved by cooling down to temperatures near the boiling point of liquid helium (4.2 K). These absolute detectors are therefore called "cryogenic radiometers".

The advantage of the spectral radiation thermometer is that a spectral range can be chosen with a filter in which the absorption and the other optical characteristics can be determined very precisely. However, as only part of the emitted spectrum is measured, the intensity at the detector is low. Besides, the selectivity curve of the filter must be measured with extreme precision. Therefore, it is not expected that it will be possible to reduce the uncertainty further down than to some 10^{-5}, not even by bestowing great care on the experiment. However, after the new definition of the kelvin,

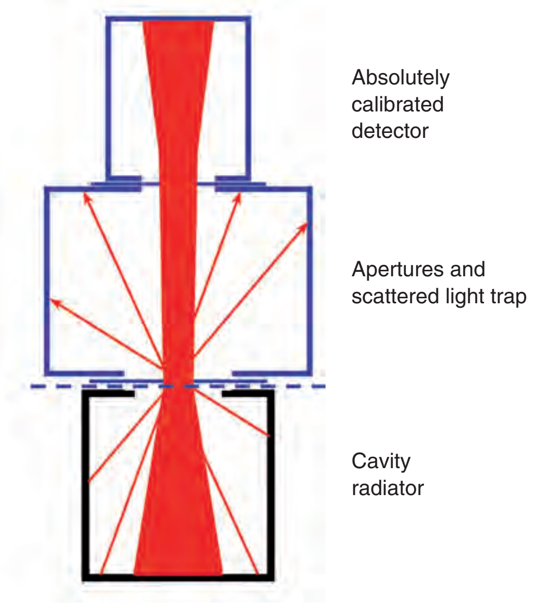

Figure 6:
The radiation thermometer is based on the relation between the emitted radiation power of a blackbody (cavity radiator) and its temperature. The areas of the apertures and their distance as well as the emissivity of the blackbody must be determined independently.

absolute radiation thermometry will play an important role for temperature measurement.

7.1.4 Noise thermometer

The temperature of an object can also be determined by observing statistical or quantum effects. For many years, noise thermometry has been used in thermometry. Noise thermometry determines temperature – by means of the Nyquist formula (Table 3) – from the mean square of the noise voltage which drops at an electrical resistance. The electric resistance value of the test sample at the triple point of water as well as the amplification and bandwidth of the electronic measuring system have to be determined precisely as parameters.

So far, noise thermometry has been well-established at very low and very high temperatures. At high temperatures, it uses the larger measurement signals and is thus less sensitive to disturbances. At low temperatures, highly sensitive, superconducting detectors can be used and the small signals can be evidenced by adequate dynamics. In the area around the triple point of water, particular electronic circuits, e. g. alternately switching digital correlators, have to be used and comparisons with known reference noise sources must be made in order to keep the amplification and the bandwidth stable and to eliminate the influence of drifts and detector and circuit noise. A corresponding project is currently pursued by NIST and the Measurement Standards Laboratory in New Zealand. The main problem is the long measuring time that is required for low uncertainties. To achieve an uncertainty in the range of $1 \cdot 10^{-5}$ for a bandwidth of 20 kHz, a measuring time of about five weeks is necessary. Here, the determination of the Boltzmann constant clearly reaches its bounds.

7.1.5 Doppler broadening thermometer

A further method to determine *k* by means of laser spectroscopy has been proposed only recently [22]. It is based on the measurement of the Doppler broadening of an absorption line by the movement of gas particles in a cell at a homogeneous temperature. Information on the temperature (Table 3) is gained from the width of the absorption profile which is scanned by means of tuneable laser radiation. The advantage of this method is that no absolute radiometry is required as the radiation power does not influence the half-value width, except by means of heating-up effects.

At the Université Paris Nord, experiments have so far been carried out with a CO_2 laser at an ammonia line at 30 THz. By evaluating 2000 individual absorption profiles, a relative standard uncertainty of *k* approximately $3.8 \cdot 10^{-5}$ could be estimated. In a second project, the Second University of Naples and the Polytechnic of Milan cooperate with each other. They use high-resolution spectroscopy at a CO_2 line with a diode laser in the near infrared range. At present, the relative uncertainty is $1.6 \cdot 10^{-4}$. A third experiment is being developed at the Dansk Fundamental Metrology Institute. Due to enormous difficulties with the differentiation of the Doppler broadening of other line shape modifications, which are caused by interaction of the particles, a reduction of the uncertainty to below $1 \cdot 10^{-5}$ is unlikely.

7.2 Consequences of the new definition

The formulation of the new definition of the kelvin could be as follows [19]: The kelvin, K, is the unit of thermodynamic temperature; its magnitude is set by fixing the numerical value of the Bolzmann constant to be equal to exactly $1.3806X \cdot 10^{-23}$ J/K. Thus, the kelvin is the change of the thermodynamic temperature T which corresponds to a change of the thermal energy kT of exactly $1.3806X \cdot 10^{-23}$ joule. This formulation is in analogy to the definition of the metre selected in 1983. Both formulations are practically equivalent.

What are the consequences of such a new definition? First of all, as has already been mentioned, the practical effects will not be spectacular, they should not even be felt, so that international metrology as has been applied so far can continue to function undisturbed and the development of the worldwide division of labour and production continues unaffected. Anything else would create enormous costs. To achieve this, the CIPM Consultative Committee for Thermometry is already working on a "mise en pratique" – a recommendation for implementation – containing not only recommendations for the direct measurement of the thermodynamic temperature T as well as the defining texts of the still valid International Temperature Scales ITS-90 and PLTS-2000 [23, 24], but also a discussion of the differences $T - T_{90}$ and $T - T_{2000}$ with their uncertainties. T_{90} and T_{2000} are temperature values which are determined according to the individual scale specifications. This procedure permits direct thermodynamic temperature measurements far from the triple point of water, e. g. at high temperatures where the radiation thermometer can be used both as an interpolation instrument of the ITS-90 and as a primary thermometer. In future, this will help to substantially reduce the uncertainties which, e. g. at the highest fixed points of the ITS-90 at 1358 K, are almost one thousand times larger than the reproducibility of the triple point of water.

In the temperature range around the triple point of water, which is important in practice, the ITS-90 will still keep its right to exist. However, the triple point of water, which is currently – by definition – provided with an exact temperature, will lose its outstanding position. It will then be a temperature fixed point like any other, which has exactly the same uncertainty as the Boltzmann constant at the time of its definition. The above-mentioned relative uncertainty of $1 \cdot 10^{-6}$ corresponds to 0.27 mK.

8 Summary and Outlook

Figure 7 shows a summary of the published measurements of the Boltzmann constant since 1988. The determination by means of acoustic gas thermometry (AGT), which had been set up by NIST, provides the basis of the currently accepted value. Motivated by the recommendation of the CIPM in 2005, numerous new experiments have subsequently been set up. In 2007, refractive index-gas thermometry (RIGT) at NIST [25] provided a numerical value with a relative standard uncertainty of $9 \cdot 10^{-6}$. From measurements with a non-adapted low-temperature version of the dielectric constant gas thermometer (DCGT) of PTB, a preliminary value of the Boltzmann constant can be derived with a relative uncertainty of $3.0 \cdot 10^{-5}$. As has been mentioned before, initial Doppler broadening measurements (DBT, UniNa) of the Italian group achieved uncertainties of $1.6 \cdot 10^{-4}$ [26]. The Doppler absorption curves (DBT, LPL) at the Université Paris Nord were successively analysed with two different line profiles and published in 2009 and 2010. The relative difference in the value of the Boltzmann constant of $3.7 \cdot 10^{-5}$ illustrates the considerable problems of understanding the line shape for the same input data. A complete uncertainty budget has not been published, it can, however, be estimated at approximately $3.8 \cdot 10^{-5}$ [27]. The most accurate newer values of the Boltzmann constant, which were published in 2009 and 2010, were achieved by the similarly set up acoustic gas thermometers (AGT) at the French national institute LNE [28, 29], at the Italian INRiM [30] and at the British NPL [31]. The relative standard uncertainties amount to $2.7 \cdot 10^{-6}$ and $1.2 \cdot 10^{-6}$, respectively, $7.5 \cdot 10^{-6}$ and $3.1 \cdot 10^{-6}$ respectively. First determinations have been achieved by the noise thermometry experiment at NIST [32], the acoustic gas thermometry experiment at the Chinese state institute NIM [33], which has been launched only recently, and by the new dielectric constant gas thermometry experiment at PTB [34]. The relative uncertainties are $12.1 \cdot 10^{-6}$, $7.9 \cdot 10^{-6}$ and $7.9 \cdot 10^{-6}$, respectively.

The graph shows that so far, no independent method has been able to confirm the AGT measurements of NIST at the required level of uncertainty. Therefore, the international Consultative Committee for Thermometry (CCT) recommended CIPM in 2010 to wait for at least two further results – which will have been achieved by means of independent methods – before re-defining the kelvin. The CIPM followed this recommendation, also due to the discrepancies which occurred with the determination of Planck's constant for the re-definition of the kilogram, and has only the units *kilogram, ampere, mole* and *kelvin* in principle. However, it cannot be implemented until enough consistent measurements are available.

For 2013, the CCT is now expecting an averaged value for *k* with a relative standard uncertainty of $1 \cdot 10^{-6}$ which is based on various experiments with at least two different methods (acoustic gas thermometer and dielectric constant gas thermometer). Besides, the noise thermometer and perhaps also the Doppler broadening thermometer should be able to provide an additional confirmation, though with larger uncertainties. Thus,

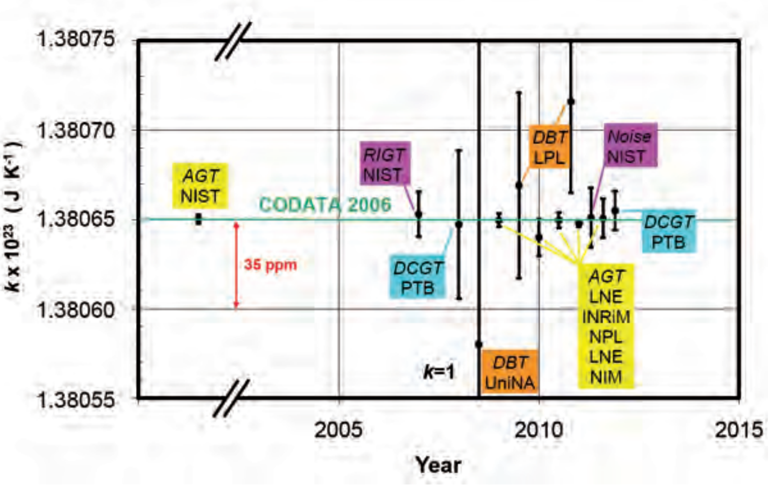

Figure 7:
Overview of the determinations of the Boltzmann constant *k* or the universal gas constant $R = k \cdot N_A$ since 1988. Explanations of the abbreviations can be found in the text. The bars describe the standard uncertainties. The green line indicates the numerical value of *k* which has been internationally recommended by CODATA.

there is enough time to make use of the promising potentials of the different measurement methods.

Due to the significant progress achieved with the development of the described primary thermometers, the Boltzmann constant can be determined with such precision that the new definition of the kelvin will be possible by means of a single fixing of its numerical value. The essential consequences of the new definition of the kelvin are of a long-term nature because a fundamental constant – instead of a material property – is now taken as scale. The system of units would thus be indefinitely stable. This objective is worth the effort made world-wide. ■

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Luminous Intensity – the SI Base Unit “Candela”

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Structure

1 Generation and Measurement of Light Throughout History
2 Spectral Sensitivity and Other Visual Evaluation Functions
3 Realisation of the SI Base Unit “Candela” Today
4 Requirements Placed on the Dissemination of Photometric Units

1 Generation and Measurement of Light Throughout History

We call “light” the small selected part of the electromagnetic spectrum which is perceived as brightness and colour by the human eye. Although light is absolutely vital for humans, they started comparatively late to measure it – and this, although they actually had a valuable tool to perceive and assess all things surrounding themselves, namely: their own eyes! One of the reasons for this, Johann Heinrich Lambert (1728–1777), the founder of photometry (“the technique of measuring light”), mentioned already back in 1760, in his significant work *“Photometria, sive de mesura et gradibus luminis colorum et umbrae”*, namely as he realised, much to his distress, that – contrary to temperature – there were no measuring instruments capable of measuring light absolutely. Until the mid-20th century, “quantities of light” – as one said unspecifically – could only be assessed through the direct comparison with a “reference light source”.

The first to use a device for such a task was Bouguer (1698–1758), in France, in November 1725. This first “photometer” was based on this comparative principle and made it possible to assess the brightness of a test lamp by comparing it with that of a reference lamp; it exploited the direct, simultaneous visual comparison of the impression of luminosity. The two lamps were positioned next to each other, and each one illuminated – from a small distance – one of two holes which were also positioned adjacently and were covered with semitransparent paper. A baffle between the holes towards the lamps prevented light from the other lamp being incident on the other hole. The apertures of the holes define, together with the distance from the lamp, a solid angle under which the light of the lamp can be observed. Today, the “quantity” for this arrangement is called “luminous intensity” [1].

With Lambert’s *Photometria*, but of course also with Newton’s (1642–1726) basic findings on the physics of light, both the theoretical and the practical fundamentals of light measuring technique were now given. However, the quantity of light was significant only for scientific purposes, e. g. in astronomy. In everyday life, the mere existence of light was already more than enough. This did not change until technically more demanding – artificial – light sources were developed which had to be compared with each other.

The beginnings of industrialisation in the mid-18th century saw the appearance of increasingly efficient light sources – from pinewood spill and wax candles to various realisations of oil lamps and even coal gas lamps. At the beginning of the 19th century, gas lamps were used for the first time for lighting streets and factory halls. Their photometric efficiency was improved by means of constant development, especially after the introduction of the Welsbach mantle by the Austrian Carl Freiherr Auer von Welsbach in 1885. From the mid-19th century, the first electrical light sources (metallic filament lamps with platinum filaments and carbon pin or carbon filament lamp) appeared. Due to their efficiency, lifetime and price, they were, however, far from being competitive. This changed in 1879 with Thomas Alva Edison’s (1847–1931) invention. Until the end of the 19th century, he progressively improved the highly resistive carbon filament lamp he had invented himself on the basis of a carbonised bamboo fibre and obtained several patents for this. In Europe, Carl Auer von Welsbach had the first practicable metallic thread lamps patented with filaments made of osmium in 1890 and with tungsten in 1898. Due to the Welsbach mantle and thanks

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to its excellent luminous efficiency, gas lighting could still prevail for general purposes for many years vis-à-vis electric lighting. Electric lighting, however, could not be stopped in its triumphal progression. At the beginning of the 20th century, arc lamps were mostly used for public lighting purposes (e. g. street lighting). With the development of the low-pressure gas-discharge lamps – especially with the fluorescent lamp in 1930 – however, efficient and easy-to-handle light sources became available. High-performance light sources followed with high-pressure mercury-vapour lamps in 1931 and later especially with halogen metal-vapour lamps. Developments went on until well into the last century with the appearance of light-emitting diodes (LEDs), based on semiconductors and even on organic semiconductors.

Already oil lamps often worked with the aid of reflectors which guided the light emitted by the flame in the desired direction, and all-around glazed lanterns protected the flame from external influences – and also reduced fire hazard. For all later types of lamps, luminaires – comparable to lanterns – still serve as the mechanical support with a lamp socket for the luminous source. Furthermore, luminaires always include devices which are necessary for supplying light, as well as devices with optical functions (e. g. reflector, lens, diffuser) with which the directional distribution of the luminous intensity for a luminaire can be optimally adapted to the application in question. The lifetime of a luminaire is also much longer than that of a lamp. The change was, thus, made very easy.

Thus, not only the light, but also the distribution of the luminous intensities in all directions, and especially their integral over the full solid angle, were – and are – of particular economic and technical importance. The quantity corresponding to the integral is called “luminous flux”. Back in 1900 already, F. R. Ulbricht (1849–1923) described a “sphere photometer” which performs exactly this integration. Until now, this photometer in various designs has been supplying the quantity “luminous flux” and is called “Ulbricht sphere” in German (“integrating sphere” in English). It consists of a hollow sphere which has a matt white inside coating and which contains the lamp to be characterised in the middle. Its light is reflected diffusely and manifoldly by the sphere‘s wall and is, thus, distributed so homogeneously that the indirect illuminance measured on any spot of the sphere’s wall is proportional to the luminous flux. Due to this proportionality, the Ulbricht sphere is best suited for fast luminous flux measurements. Fundamentally, the distribution of the luminous intensities is measured successively in all directions using a goniophotometer and is then integrated numerically to the luminous flux – a method which is preferred today when small measurement uncertainties have to be achieved.

Due to its paramount importance, it would have made sense to use the luminous flux unit “lumen” as an SI base unit for photometry. This was even the consideration when the definition of the SI base unit of luminous intensity which is still valid today was laid down. However, the integration over the full solid angle would have caused additional contributions to the measurement uncertainty of the base unit, which are avoided by using the unit of luminous intensity as the SI base unit.

Parallel to this development of the different technologies of light generation, also light metrology became increasingly important. Starting in the last two decades of the 19th century, the technical associations and the associations of gas experts were the motor of the development of light metrology, in Europe as well as in the former German Empire. The main problem thereby was to develop a suitable reference lamp which was able to produce light uniformly enough and was sufficiently reproducible to be used as a standard and realisation of a unit of light. The different nations used different concepts in this respect.

The first standards were wax candles. In the 18th century, they were best suited with regard to stability and reproducibility. The unit they realised was therefore simply called “candle”. In the 19th century, various oil lamps were used. Before kerosene was discovered, animal or vegetal oils (such as rape oil) were burned. Such a standard lamp with a round wick was developed in Paris by Guillaume Carcel (1750–1812) around 1800 and used in France. The luminous intensity of the “Carcel lamp” was approx. 10 candles. Although the dimensions of the lamp were strictly defined, the realisation of the unit depended strongly on the quality of the summer rape oil used, of which a well-defined quantity had to be burned in a certain amount of time; the lamp was fed by means of a clock-driven pump. In 1877, the Englishman A. G. Vernon Harcourt (1834–1919) developed the “pentane lamp”, which was used as the photometric standard in England. In its original design, the pentane lamp had a luminous intensity of roughly one candle. Also in the case of this wickless flame standard, the design, the geometry and the material to be used were strictly defined. Another path was chosen in the USA, England and France when the carbon filament lamp was introduced around 1909. By means of several sets of carbon filament lamps which were compared with each other, a common unit, the “International Candle”, was established. It was suggested for general use by the “International Commission on Illumination”, CIE, in 1921 [2].

In Germany in 1884, Friedrich von Hefner-Alteneck, one of Werner von Siemens’ employees, suggested a flame standard (see Fig. 1) which outperformed all other standards ever used at the time with regard to reliability and manageability.

This light standard, which was later simply called „Hefner lamp", was used in Germany, but also in Austria and the Scandinavian countries. It was operated under very specific conditions, which were defined as follows:

"The luminous intensity (emitted horizontally) of one flame burning free in a still and pure atmosphere serves as the unit of light. This flame raises from the cross-section of a wick saturated with amyl acetate which fully fills a round wick tube made of nickel silver and having an inner diameter of 8 mm and an external diameter of 8.3 mm and a free-standing length of 25 mm, and is measured when the flame is 40 mm high, measured from the edge of the wick tube and at least 10 minutes after lighting."

Figure 1:
Hefner lamp.

The – then – still young *Physikalisch-Technische Reichsanstalt (Imperial Physical Technical Institute – PTR)* played a significant role in the progress of light measurement technology. Already in 1888, a year after its creation, it was charged by the *Deutscher Verein für Gas- und Wasserfachmänner (German Association for Gas and Water Experts)* to participate in the calculation of the generally accepted light measure and to establish an internationally recognised light primary standard. Otto Lummer (1860–1925), Eugen Brodhun (1860–1938) and Emil Liebenthal (born in 1859) accepted the challenge. Lummer and Brodhun furthered the development of clearly more efficient visual photometers for the determination of the luminous intensity of lamps (see Fig. 2), whereas Liebenthal dedicated himself to the testing and certification of the Hefner lamp. In 1893, he laid down that the Hefner lamp had to burn at 760 mm barometric pressure and ambient humidity of 8.8 litres to 1 cbm of dry, carbon-dioxide-free air to obtain a full definition of the luminous intensity unit [3, 4].

The Hefner lamp was, thus, a pure primary standard with constant properties. It represented the unit of luminous intensity, which was generally called "Hefner candle" [HK], with a relative uncertainty of 1.5 % and was valid in Germany from 1896 to 1941 [5].

J. L. G. Violle (1841–1923) furthered a different development in France. This development brought about the Violle unit and directly used the surface of melted platinum as a source of light. This unit was suggested by the 2nd International Electrical Congress as "decimal candle" in 1889, but was replaced a few years later by the Hefner candle, since the reflection properties of the surface turned out to be not stable enough. The basic idea of exploiting the high temperature of melted platinum was taken on in the USA, where the freezing point of melted platinum was used to stabilise the temperature of a cavity radiator whose radiation could be used as unit of luminous intensity.

Figure 2:
Lummer-Brodhun contrast photometer.

This proposal was submitted by the *International Commission on Illumination (CIE) to the Comité International des Poids et Mesures* (CIPM), which supported the recommendation by founding a specific laboratory for photometry at the BIPM (Bureau International des Poids et Mesures) and finally adopted it in 1937 as the luminous intensity unit "new candela" to be implemented in 1941 [6].

Due to WWII, the worldwide implementation of this decision was delayed until 1948; it laid down the first and only internationally valid definition for the realisation of the unit of luminous intensity as a "primary standard" and called it "candela". The 1948 candela definition was slightly modified in 1967 to read:

The candela is the luminous intensity, in the perpendicular direction, of a surface of 1/600 000 square metre of a black body at the temperature of freezing platinum under a pressure of 101 325 newtons per square metre.

As the International System of Units (SI) was introduced in 1960, this definition of the SI base unit "candela" was adopted for luminous intensity; it defines the Planck radiator (a black body) at the temperature of freezing platinum as the "primary standard" for luminous intensity. For its realisation, however, such a radiator really has to be set up and operated in practice (Fig. 3). Only very few national metrology institutes (NMIs) were able to go to such lengths.

Soon, the call for a less complex procedure to realise the unit of luminous intensity became louder. The definition does not state the value of the temperature of freezing platinum, but only the effect at such a temperature. However, if the temperature is known, it is possible, using the Planck function, to calculate the spectral distribution of the black-body radiation and to realise the unit by means of radiometric methods. For a long time, the value of the temperature seemed to be known well enough, since the International Practical Temperature Scale (IPTS68) provided $T_{\mathrm{Pt}} = 2045$ K. Investigations carried out in 1972, however, provided the value $T_{\mathrm{Pt}} = 2040.75$ K, which caused the radiometry-based realisation of the unit of luminous intensity to lead to values of luminous intensity larger by 2.2 % [7].

Due to the great economic importance of the photometric units, such a discrepancy was unacceptable, so that the definition of the candela was finally modified after intense investigations and long discussions. The aims of this modification were: firstly, not to change the unit itself and, secondly, to enable various ways of realising it. In this context, the General Conference at the CIPM decided the following in 1979:

The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540 \cdot 10^{12}$ hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

At first sight, this definition may sometimes be interpreted as the definition of a "primary standard" – but now with monochromatic radiation – which it definitely is not! In the "Principles governing Photometry" [8], recommended by the Comité Consultatif de Photométrie et Radiométrie (CCPR) and published by the CIPM in 1983, the handling of this definition is explained as follows: It exclusively lays down the conversion factor $K_{\mathrm{Def}} = 683$ cd sr/W between photometric and radiometric quantities at the exact location of a wavelength $\lambda_{\mathrm{Def}} = 555.016$ nm corresponding to the frequency of $540 \cdot 10^{12}$ Hz. The most important consequence is that the SI base unit is no longer independent, but that it has to be traced back – e. g. to the watt – to be realised.

For this reason, it is sometimes suggested to delete this SI base unit. This, however, would lead to a modification of all values of photometric and illumination-related quantities, since in the coherent SI system of units, the factor 1/683 can only be implemented via an own base unit.

Another reason which is sometimes stated is that the photometric units are physiologically influenced by the spectral sensitivity of the human eye. This, however, is obviously invalidated by the summary of historical developments: all definitions of the realisation of the luminous intensity unit until today have been indicated without even mentioning visual spectral sensitivity of the human eye $V(\lambda)$. The definition of the unit would therefore still be valid for creatures or things whose spectral sensitivity differs from that of humans – provided their spectral sensors exhibited a measurable sensitivity at $\lambda_{\mathrm{Def}} \cong 555$ nm. The weighting function $V(\lambda)$ and others only become significant when the quantity "luminous intensity" is to be assessed or when the values of photometric quantities are to be calculated from spectroradiometric distributions – which is one possibility, but certainly not the only one.

The relation of units of luminous intensity used in the past can occasionally be of interest. It is,

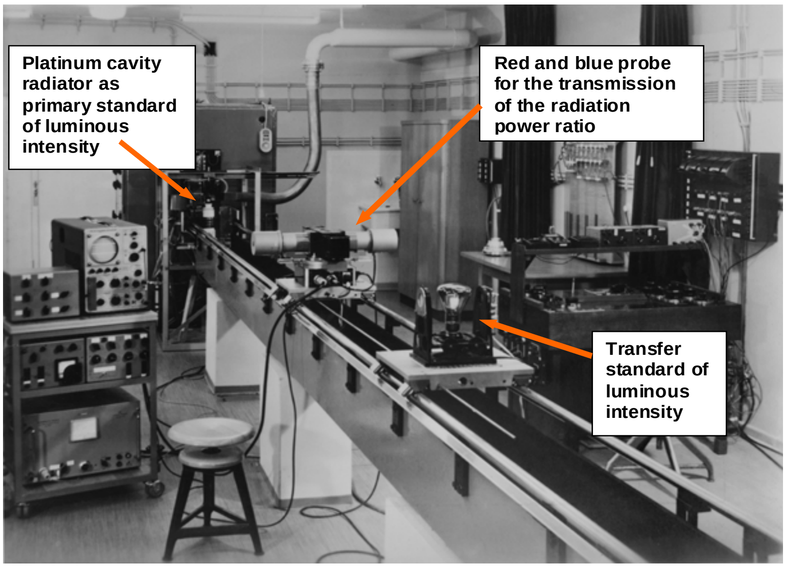

Figure 3:
Measuring arrangement at PTB for the realisation and dissemination of the unit candela by means of the platinum primary standard (around 1967).

however, somewhat difficult to indicate as the defined sources had different colours, which had an influence on the value of the ratio. The colour of thermal radiators can be characterised by the temperature distribution T_V, and for the range $2000\ \mathrm{K} \le T_V \le 2600\ \mathrm{K}$ and the definitions "international candle" [IK], "Hefner candle" [HK] and "candela" [cd], the following ratios apply [9]:

$$\frac{\mathrm{IK}}{\mathrm{HK}} = 1.11......1.17 \quad \text{and}$$

$$\frac{\mathrm{cd}}{\mathrm{HK}} = 1.107.......1.166 \quad \text{and}$$

$$\frac{\mathrm{cd}}{\mathrm{IK}} = 0.981$$

2 Spectral Sensitivity and Other Visual Evaluation Functions

Until the mid-20th century, light was measured exclusively by means of visual photometry, i. e. as a comparison between a test lamp and a reference lamp, using the human eye as the detector. The quality of the light was automatically assessed with the only available detector, the human eye, and its spectral sensitivity. Meanwhile, physical detectors are available which can measure optical radiation, and today they are the only detectors used in photometry and light-measuring technique. In order to adapt their function to the spectral sensitivity of the human eye, it became important to determine the relative spectral sensitivity of the eye $V(\lambda)$.

First investigations into spectral sensitivity involving only a few test persons were published by the CIE in 1924; they showed a bell-shaped line for wavelengths between 360 nm and 830 nm with a peak at 555 nm. In more accurate investigations it soon became clear that at least two criteria had to be distinguished: the size of the field of vision considered and the luminance range. This is closely linked to the set-up of the human eye and the vision process. Furthermore, a clear scattering was observed between different test persons, e. g. also between younger and older persons.

In order to still be able to indicate a mean spectral sensitivity, so-called "observers" were differentiated: the 2° observer $K(\lambda) = K_m \cdot V(\lambda)$ for vision of small objects, and the 10° observer $V_{10}(\lambda)$ for extensive scenarios. Furthermore, vision in the photopic range $V(\lambda)$, i. e. in daylight, is distinguished from vision at extremely low luminance values, the scotopic range $K'(\lambda) = K'_m \cdot V'(\lambda)$. The range in-between those is called "mesopic"; however, no internationally binding observer has been defined to date for this range. The scotopic weighting function $V'(\lambda)$, again, has a bell-shaped curve in the spectral range between 380 nm and 780 nm with a peak at 508 nm. Due to the considerably higher sensitivity, the two weighting functions $K(\lambda_{\mathrm{Def}}) = K'(\lambda_{\mathrm{Def}})$cross each other close to the peak of the $V(\lambda)$ function, i. e. at the wavelength $\lambda_{\mathrm{Def}} \cong 555.016$ nm indicated in the definition of the candela. This is the main reason why the definition of the candela is valid for both assessments and is, thus, independent of the weighting function (Fig. 4).

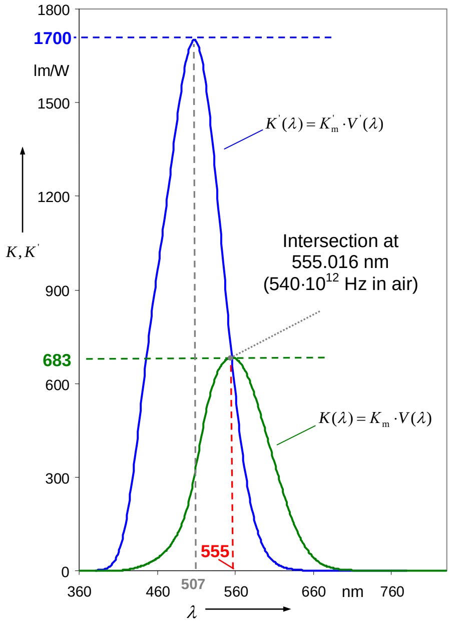

Figure 4:
Spectral luminous efficacy for photopic and scotopic spectral sensitivity.

In the photopic range of luminances, colours can be detected which are described by sensitivities corresponding to the spectral tristimulus functions $\bar{x}(\lambda), \bar{y}(\lambda), \bar{z}(\lambda)$, with the side condition $\bar{y}(\lambda) \equiv V(\lambda)$. Contrary to the colour vision, only shades of grey are detected in the scotopic range, but this with an approx. 2.5-fold better sensitivity.

The investigations and determinations of weighting functions are incumbent on the CIE, whereas all definitions of the units and the application of the weighting functions are the responsibility of the CIPM and are prescribed via the "Principles governing Photometry". The photopic luminous intensity I_v ("v" for "visual") with the unit "cd" for the 2° observer of a source of light with a spectral distribution of the radiant intensity $I_{e,\lambda}(\lambda)$ ("e" for "energetic") can be calculated from the weighting with $V(\lambda)$ and the factor $K_{\mathrm{Def}} = 683$ cd sr/W taken from the definition of the candela for the wavelength $\lambda_{\mathrm{Def}} \cong 555.016$ nm.

$$I_v = K_m \cdot \int_0^\infty I_{e,\lambda}(\lambda) \cdot V(\lambda) \cdot \mathrm{d}\lambda \quad \text{with}$$

$$K_m = \frac{K_{\mathrm{Def}}}{V(\lambda_{\mathrm{Def}})} \approx 683 \frac{\mathrm{cd\ sr}}{\mathrm{W}}$$

In the same way, the scotopic luminous intensity I'_v can be calculated with the same unit "cd".

$$I'_{\mathrm{v}} = K'_{\mathrm{m}} \cdot \int_0^\infty I_{\mathrm{e},\lambda}(\lambda) \cdot V'(\lambda) \cdot \mathrm{d}\lambda \quad \text{with}$$

$$K'_{\mathrm{m}} = \frac{K_{\mathrm{Def}}}{V'(\lambda_{\mathrm{Def}})} \approx 1700 \frac{\mathrm{cd\ sr}}{\mathrm{W}}$$

It is important to point out that the unit does not distinguish between the different weightings. Since a clear attribution of the luminous intensity for scotopic and photopic illumination situations is given due to the different range of values it is, in principle, not necessary to characterise the luminous intensity in particular. Formulations such as "scotopic candela" are therefore definitely wrong. It is permitted to talk about the value of the scotopic luminous intensity with the unit "candela" to emphasize the use of the weighting function $V'(\lambda)$ which is currently not common.

3 Realisation of the SI Base Unit "Candela" Today

Often, the unit of luminous intensity is given a particular position among the seven SI base units, since it depends "mainly on a physiological component, the spectral sensitivity of the human eye". This is due to the lack of differentiation between "quantity" and "unit" – an important fact which was explained in the previous paragraph. It is essential to point out that, of course, all SI base units contain a "physiological component", since they are intended to make the environment metrologically and coherently describable for humans with their own perspective and their interconnection with the processes relating to natural sciences and technique, namely by means of units which are adapted to these human dimensions.

The definition of the candela had been established in such a way that the unit of luminous intensity was not modified. Therefore, the corresponding luminous intensity can be practically realised using the black-body radiator in the bath of freezing platinum, also with the new definition of the candela. Now, also cavity radiators with any random temperature can be used, or even radiators whose spectral radiant intensity was measured traceably to radiometric standards.

At present, PTB is following another path which may seem more complex, but which will considerably reduce the contributions to measurement uncertainty. A laser arrangement which emits very constant radiation in selected wavelength ranges with exactly determinable wavelengths, irradiates alternately a so-called "trap detector" and a cryogenic radiometer. The cryogenic radiometer can compare the optical radiant power of a laser directly by means of electrical power. The electrical power which is determined via the cryogenic radiometer is then compared with the measured photocurrent of the trap detector to obtain the responsivity of the trap detector for the wavelength of the laser as the quotient of its photocurrent and of the previously determined radiant power of the laser radiation. This process is repeated for laser radiation up to a sufficient number of wavelengths to finally obtain the spectral responsivity function of the trap detector using a physical model of the trap detector used. In a next step, the spectral responsivity $s(\lambda)$ of photometric detectors is determined for the photometric quantity "illuminance" (with the derived unit lux = cd sr/m²) in the homogeneous radiation field of, e. g., tuneable lasers, by means of another comparison with this radiometric detector – which can now serve as a transfer standard. Thanks to appropriate glass filters, the relative spectral responsivity function of such photometers is very well adapted to $V(\lambda)$. From the illuminance, which is generated by a special standard lamp on the entrance window of a photometer calibrated in the described way, the luminous intensity of the standard lamp for suitable geometries is determined for exactly defined operating conditions, and this with the smallest possible measurement uncertainty of the values (Fig. 5). The transformation – contained in the definition of the candela – from a power-related quantity to a quantity for luminous intensity which is defined via a solid angle element takes place in the last two steps.

At PTB, a unit of luminous intensity realised in this way, via a network of photometers, is compared once a year with the unit maintained by means of a network of many (currently 22) standard lamps to check the quality and reliability of both the realisation and the maintained unit. The data of the *nationally* realised and maintained unit are traceable over several decades and represent the basis of the entries on photometry in BIPM's so-called CMC (Calibration and Measurement Capabilities) lists. Parallel to this, the *international* reference value of the unit of luminous intensity is maintained by means of further photometers and standard lamps; this reference value was found by means of a worldwide comparison within the framework of a so-called "CCPR key comparison" for which PTB acted as the pilot laboratory. Finally, various types of calibrated photometers and light sources are disseminated to industry and research as transfer standards for the SI base unit candela and further derived photometric SI units; particularly small measurement uncertainties can be achieved thanks to substitution procedures.

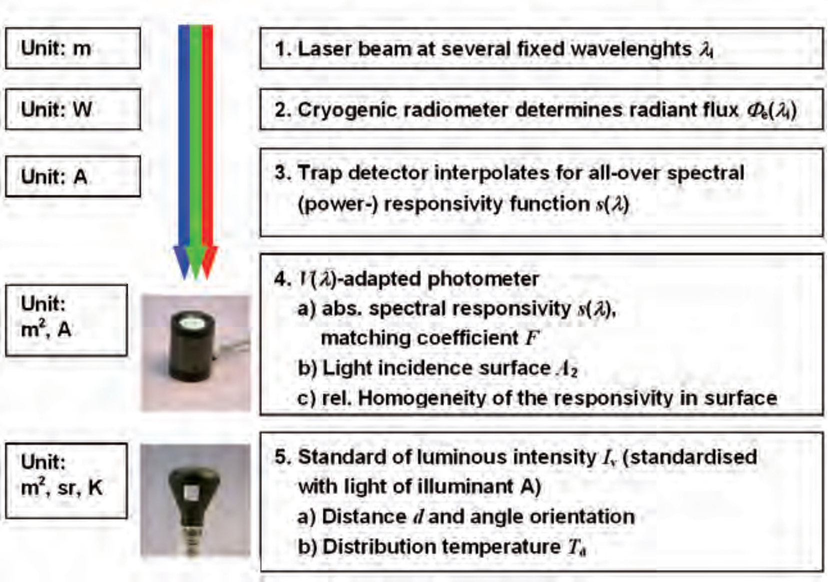

Figure 5:
Traceability chain at PTB.

4 Future Developments and Requirements for the Dissemination of Photometric Units

Photometry was in search of an adequate realisation of the unit of luminous intensity and the most suitable definition for it until 1979. Today, the main issues in photometry revolve around traceability and more specific photometric “observers” to describe human vision even more accurately.

Modern lighting systems are characterised not only by the fact that light sources with high luminous efficiency (e. g. LEDs, energy-saving light bulbs, tungsten halogen lamps) are used, but also by optimised light distribution by means of calculated reflector optics. For this, it is absolutely necessary to know the angle-dependent luminous intensity distribution of the light sources and to characterise or to specify its photometric quantities very accurately. This requires measurement values with very low uncertainties, which brings up the issue of the correct traceability of the units used due to the standardisation provisions in the field of lighting techniques – i. e. traceability within the framework of an unbroken calibration chain with the assigned measurement uncertainties. This is particularly true for the newly introduced measurement procedures based on digital cameras which provide the user with locally resolved information on the photometric quantities. To make matters worse, the measuring instruments used in classic photometry are generally calibrated for *CIE standard illuminant A* – corresponding to the “yellowish” light of a light bulb, or rather: like the light of a cavity radiator with a temperature of 2856 K. This can lead to great measurement errors, especially when measuring the light of energy-saving light bulbs or LEDs which contains only certain distinctive spectral segments (e. g. red, green and blue). To correct such errors, spectrally resolved measurements of the light spectrum are necessary. Spectral measurements are indispensable when, besides the chromaticity coordinates and correlated colour temperature, also the colour rendering index of a light source is to be determined. Due to technological developments, this is essential for lighting systems based on LEDs. The measurement uncertainty of spectrally resolved measurements is, however, often underestimated; for absolute measurements, a correct traceability is still problematic, since certain contributions to the measurement uncertainty are difficult to access due to the influence of correlations.

In industry, these cases are increasingly solved by defining “test procedures” which, under exactly defined test conditions, achieve a measurement value whose “unit” is realised with a certain accuracy within a tolerance range due to the test condition. Examples from the past are the *ANSI-LUMEN*, which is a measure for the directed luminous flux of a projector, or the mean luminous intensity $I_{\mathrm{LED,A}}$ or $I_{\mathrm{LED,B}}$, which represents a certain measure for the luminous intensity of one single LED under defined measurement conditions. Such “characteristics” are not traced back to the units derived from the SI base unit *candela* for luminous flux and luminous intensity, etc., and the values of these parameters cannot be converted into values of another of these parameters. These parameters are exclusively suited to compare similar products of different manufacturers with each other under given conditions. It is owed to the multidimensional properties of light, however, that such test procedures in photometry and colorimetry are only of limited benefit for the users, since the boundary condition of their application generally does not correlate with the test conditions in all metrological dimensions.

Formerly, it was sufficient to determine the total flux of a light source, whereas now, lamp and luminaire designers more often have to measure the so-called ray files of light sources. These ray files reflect the locally resolved and angle-dependent luminance distribution of the radiation which is emitted by the source (Fig. 6).

Ray files can be used directly in computer simulations for the absolute calculation of the luminous flux distribution of a new luminaire, i.e. to optimise the light source + reflector/optic + housing for the planned application. Building complex prototypes thus becomes obsolete. Both at PTB and at other national metrology institutes and international committees, much effort is made today to clarify normative edge conditions and still unsolved metrological questions concerning the traceability and the calculation of the measurement uncertainty of ray files.

Besides these metrological requirements for the traceability to the SI base unit *candela*, also future modifications and extensions to the formulation of the candela definition and its implementation (French: *mise en pratique*) are discussed in international committees.

With a planned reformulation of the definitions of the SI base units, it could become possible to achieve the goal of having the base units (which are currently often formulated as an implementation) be described exclusively in reference to fundamental constants. In the future, there would be a stricter differentiation between the definition of the unit and its realisation. The definition of the candela, for example, would then simply require the photometric spectral luminous efficacy at the frequency $540 \cdot 10^{12}$ Hz to be equivalent to 1/683 lumen per watt. In the definition of the candela, the photometric spectral luminous efficacy as fixed conversion factor would, thus, represent a quasi fundamental constant. There would be no reference to a source in the definition of the units – which is, strictly speaking, no different now. The edge conditions for realisation would then be detailed entirely in the implementations.

In this context, also current efforts are worth mentioning which aim to trace back the value of the photometric spectral luminous efficacy to a number of photons per second whose energy ($h\nu$) corresponds to the frequency $\nu = 540 \cdot 10^{12}$ Hz, instead of tracing it back to the watt – the derived SI unit of power. Such a modification, which is called *"quantum candela"* by its supporters, would, however, not change anything of the nature of the spectral luminous efficacy as a quasi fundamental constant. The sense of such a realisation is, however, at least questionable if one takes into account how confusing it would be in photometry to express the efficiency of a light source as a function of the photons instead of power. In addition, a large number of photon supporters work in that field of radiometry where the focus does not lie on the visual spectral range – for which the spectral luminous efficacy has exclusively been defined.

Concerning the implementation provisions for the candela, it is currently being discussed whether to include further photometric observers. Especially the mesopic observer for quantities in the range of the mesopic vision (twilight visual acuity), the 10° observer and also observers which take the age-dependent modification of the spectral sensitivity of the human eye into account, come into consideration.

A corresponding recommendation for the realisation of mesopic quantities has already been published by the CIE [10] and is currently being examined by the CCPR. Since the future mesopic weighting function – similar to the existing photopic and scotopic weighting functions – provides a clear imaging of different ranges of values of luminous intensity, a special identification of the photometric measured values for these ranges is necessary, but not one for all valid units.

But also for the other above-mentioned observers, the adequate application of new weighting functions is awaited by industry and planning offices. The goal to be achieved is to give the client a transparent description of what is technically feasible for certain, frequently requested edge

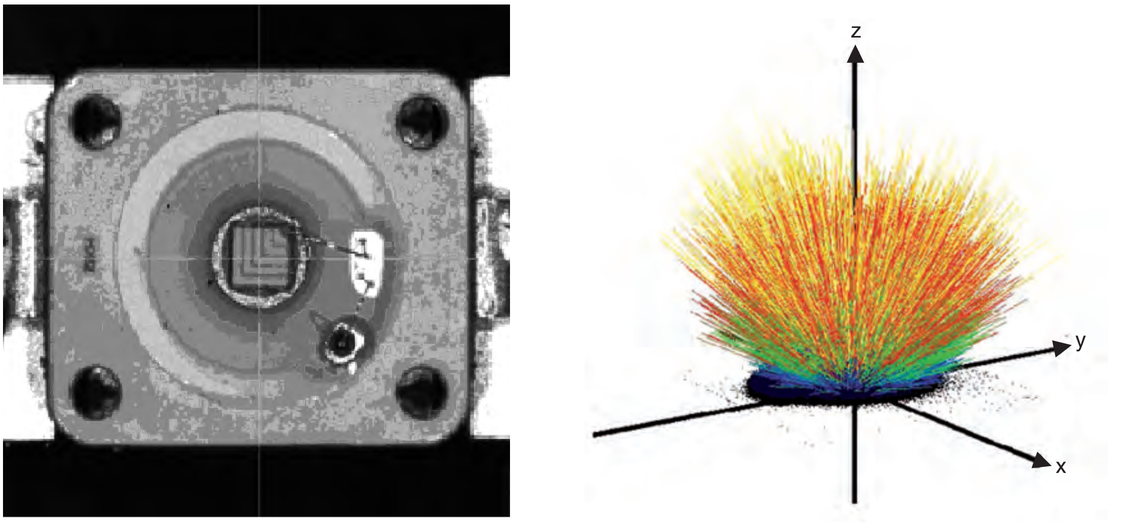

Figure 6:
LED chip of a high-power LED and corresponding ray files.

conditions. As suggested above, in all these cases, the definition and the name of the unit must remain unaltered. Since the observers in question, however, provide different quantitative assessments for identical lighting situations (lighting or signalling applications), it is indispensable to either always indicate the validity range of the photometric values measured or, instead, to determine dimensionless matching coefficients which are assigned to the previous standard observer as a possible correction value. How this will be realised ultimately is not settled yet.

It must be kept in mind that, similar to the other six SI base units, growing metrological possibilities on the one hand and the increasing requirements from industry due to technological progress on the other have made an adaptation of the candela and its implementation provisions to present needs desirable. Considering all possible requests for modification with regard to the SI base unit candela – and of the units derived from it – the coherence, stability and clearness of the system of units for all its users should remain in focus. ■

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Fundamental Constants and the “New SI”

Jörn Stenger[1] and Bernd R. L. Siebert[2]

Structure

Summary

The International Committee for Weights and Measures (CIPM) has recommended redefining the seven base units of the International System of Units (SI) by fixing the numerical values of fundamental constants. As long as consistence and completeness are guaranteed, the type and number of these fundamental constants can be freely selected. In the following, we will discuss their selection (which resulted from intensive international discussions), their mutual dependencies, and the uncertainties with which they can be measured in accordance with the existing SI definition.

1 Introduction

Measuring always means *comparing*. In each measuring process, the result is expressed as a part or multiple of a known reference which relates to the calibration of the measuring equipment. This reference must be traceable to units, so that the value of a measured quantity can be represented as a multiple of these units. This requires that defined units must also be physically realised. As a matter of principle, units can be defined and realised in different ways, i. e. as:

- **artefacts** (such as, for example, the prototype of the kilogram),
- **material parameters** (such as, for example, the triple point of water for the unit kelvin),
- **idealised measurement instructions** (such as, for example, in the case of the ampere), or
- **fundamental constants** (such as, for example, the speed of light in the case of the unit “metre”).

If a definition is made via an artefact, then this definition corresponds already to the realisation. Although this concept is simple and clear, it bears the disadvantage that comparisons with other primary realisations are, as a matter of principle, not possible and that a potential loss, damage or any kind of change whatsoever represent a risk. The other three types of unit definitions that are listed above are increasingly abstract or idealised. In the case of these three types, the realisations are separated conceptually from the definitions, so that the unit can, as a matter of principle, be realised at any place and at any time. In addition, by comparing primary realisations, it is possible to check their quality.

Although an increasing degree of abstraction renders the realisation increasingly complicated, it allows more stable and more exact measurements. Defining units based on fundamental constants is ideal, as they neither drift nor depend on material parameters. However, realising the respective unit for practical applications must be possible. The concept of the so-called “new SI” is to define all the base units – and, thus, indirectly also all the derived units – by fixing the values of these fundamental constants and by warranting their realisation and dissemination by means of so-called *mises en pratique*.

A historical review of metrology shows how this consequent approach developed. For several units, successive redefinitions – without artefacts or material parameters – were realised. This happened always when uncertainties due to drifts or insufficiently known material parameters had become unacceptable.

One example of this is the second. In former times, the second was defined as a fraction of the duration of a solar day. Later on – after it had become clear due to more exact measurements that the duration of the solar day is not always the same – it was defined as a fraction of the time which the Earth needed in the course of the year 1900 to orbit the Sun. The time which the Earth needs to orbit the Sun depends on the masses of the Sun, of the Earth, of the Moon and on other masses and parameters, which are not invariant. The “astronomic” second is, within the scope of the above categorisation, defined via material parameters. Its advantage: it could be measured

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anywhere on Earth in any suitably equipped laboratory. Its disadvantage, however, was an inherent drift. Finally, in 1968, the reference to a fundamental constant was chosen by defining the second as a multiple of the period of the radiation which corresponds to the transition between the two hyperfine levels of the ground state of caesium 133 atoms.

The different steps of development – from artefacts to a fundamental constant – become particularly clear when we look at the example of the unit "metre". Given a large number of independent artefacts such as cubits installed at market places, which could be compared selectively only, the attempt was made to achieve international harmonisation by defining the metre via a „primary" artefact, which was to correspond to one forty millionth of the circumference of the Earth at the equator. However, in 1960, the uncertainties achievable in this way had become insufficient and the metre was based on a fundamental constant and defined as the multiple of the wavelength of the radiation emitted in vacuum by ^{86}Kr atoms during the transition from the $5d_5$ state to the $2p_{10}$ state. Together with the caesium-based definition of the second, two base units had now been defined essentially in the same way, namely via the frequencies of atomic transitions, and they were interlinked via the fundamental relation $c = \lambda \nu$ Finally, in 1983, under the assumption that the speed of light c is constant in all realistically imaginable scale ranges for the metre and the second, the metre was linked to the second, which can be realised with a much smaller uncertainty, by fixing the value of the speed of light in vacuum.

The desire to realise units at any place without depending on an artefact or its copies led to definitions of several other units by specifying measurement procedures in sufficient detail such that any suitably equipped laboratory can realise them anywhere on Earth. Examples of this are the Weston standard element for the realisation of 1.01865 V (at 20 °C), or the triple point cell for water (gas-free and with defined isotopic composition) to realise the temperature of 273.16 K. The increase in stability and comparability gained in this way required increased efforts, because in order to implement these definitions, a great number of material parameters and measurement conditions have to be well known and controlled. Furthermore, some of the values of the material parameters are well measurable, but not understood in theory.

The proposed redefinitions of the base units intend fixing the elementary charge e, the Planck constant h, and the Boltzmann constant k_B. A primary realisation of the kelvin is then possible, for instance, via the thermodynamic temperature of a Planck radiator. It will then be possible to "officially" use the Josephson effect and the quantum Hall effect for primary realisations of the volt and the ohm, respectively, as has already been done for more than 20 years in the "SI_{90}". From this, another characteristic of the redefinitions becomes obvious: like the base unit "ampere", the volt and the ohm, too, can be related directly to the defined fundamental constants, which shows that the distinction between base units and derived units is basically needless.

Currently, the kilogram is the only unit that is still defined by an artefact. It is now suggested to redefine the kilogram by fixing the value of the Planck constant h. The implied conceptual change from the artefact to an abstract formulation is unprecedented in metrology. There is no realisation which could trace the kilogram exclusively back to the Planck constant, whose SI unit corresponds to a physical action $[h] = \text{kg m s}^{-1}$. This means that the kilogram is defined when the numerical value $\{h\}$ is determined in SI units and when the metre and the second are defined. Experimentally, it can be realised by means of the watt balance [1]. In addition to the determination of $\{h\}$, as well as of $\{\Delta\nu\,(^{133}\text{Cs})_{\text{hfs}}\}$ and $\{c\}$ for the second and the metre, this special equipment requires, however, also defined electric units which could be obtained, for example, by a determination of the elementary charge.

This obvious interrelation of the units raises the question as to what extent the determinations can be freely selected and whether and where this redundancy may cause inconsistencies.

In the following, we will discuss some general requirements which a system of units has to fulfil, and we will explicate – by means of a hypothetical, minimum system of units – in which way the units are interdependent. Finally, we will discuss the reliability of the latest values of those fundamental constants that are to be used in the new SI.

2 General Requirements for a System of Units

In 1960, the International System of Units – the SI – was introduced under this name by the General Conference on Weights and Measures (GCPM). Today, it has been officially established in almost all countries and is successfully used in practice. Since its introduction, the SI has experienced essential extensions and redefinitions and has been adapted several times to the latest state of metrology. The version which is presently valid was published in 2006 [2]. For a detailed survey of the SI and of international metrology, see [3] and [4].

Today, measurements are omnipresent in everyday life, as well as in industry and science. In all these fields, the requirements differ from each other, however [5]. To make clear that the

SI does not merely serve physics, but that it also serves innumerable applications in practice, and to understand why the system of units has been influenced to such an extent by the historical development and why each redefinition also bears a political component, we will briefly summarise these general requirements in the following.

Figure 1 shows the requirements the SI has to fulfil and which, as a matter of course, also the new SI will have to fulfil. The requirement *"À tous les temps, à tous les peuples" ("to all men and all times")*, formulated on the occasion of the foundation of the Metre Convention as an ideal, is also valid for the SI, irrespective of any modifications due to increasing and changing requirements today. People (i. e. *society*) expect units that are used for measurements in everyday life to be clear and easy to understand. From this it follows that it should be possible in practice to express the values of the frequently used quantities with as low a number of units as possible, and that composed units should be easy to understand. Furthermore, units and their definitions should change as little as possible because changes bring about costs and because experience has shown that the old definitions will continue to be used for a long time, parallel to the new ones. The requirements of industry (i. e. *the economy*) are, to a certain degree, the same as those of society, but the economy requires – in addition, and to a greater extent – that the system of units is valid and comparable worldwide and that the units are traceable. Worldwide validity prevents error-prone conversions and, in conjunction with traceability, enables the uniform standardisation of products and product parts and facilitates trade. Last but not least, *science* needs a coherent system of units in which the measurement values of all conceivable measurements can be easily expressed and converted.

Metrologists who are in charge of providing realisations that allow traceability of the measurement results to SI units face the following metrological requirements:
The units must be defined such that their realisations warrant the highest stability and the smallest measurement uncertainties. This needs to be checked by comparison measurements that use different measurement principles, if possible, and are carried out by different working groups. This requires a separation of the definition and the realisation of units.

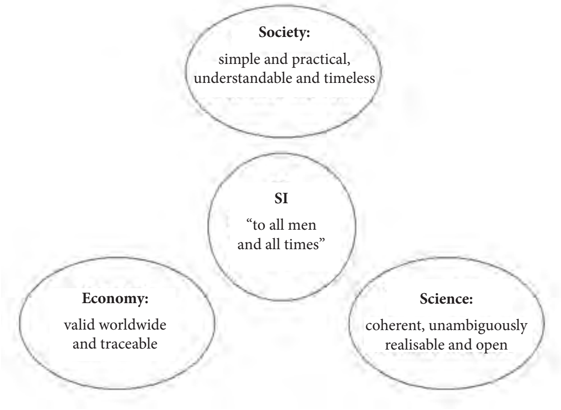

Figure 1: Requirements for the definition of base units.

3 A Hypothetical, Minimum System of Units

To illustrate the mutual dependencies of the units, and to show also how important the fundamental constants are in the definition of units, we will conceive, in the following, a hypothetical, minimum system of units. This system does, of course, not meet the requirements for a practical system of units as stated in the last section. Its intention is solely to show the mutual dependencies of the units and their dependence on fundamental constants.

In principle, for each phenomenon that can be described on a rational scale level, an own unit could be introduced. This, however, neither makes sense nor is it necessary as many phenomena can be described on the basis of physical relations by combining few base quantities.

If physical relations are applied to reduce the number of base quantities used – i. e. if a base quantity is, in a certain way, substituted by a physical law – the question of the validity of the law used arises. It is not necessary to assume that this law is universally valid. It is sufficient if the correctness is guaranteed within the scale range of the realised measurand and in the required and realistically feasible uncertainty range. Any deviations of the space-time from the Euclidian geometry in astronomic distances are, for example, not relevant, as a realisation of the metre over such distances cannot exist. Another example is the unit "second": It is defined via the frequency of a hyperfine structure transition in the caesium atom. If the second can now – realistically – not be realised and disseminated with a relative uncertainty of better than 10^{-18}, any possible drift of the fine structure constant α with time, which determines this frequency, is irrelevant, if $|\Delta\alpha/\alpha|$ is clearly smaller than 10^{-18} within a foreseeable period of time

Hence, the question as to whether and to what extent a system of units can be reduced is equivalent to the question as to whether it is possible as a matter of principle to build devices which interlink two measurands and whose functioning can be described with sufficient accuracy by the corresponding physical law within the scope of the scale range realised.

For further discussion, we assume without proof that all physical units can be realised with the aid of the base units, and we will, from now on, consider only the dependencies between the base units themselves:

time, t, with the unit *second*, s
length, l, with the unit *metre*, m
mass, m, with the unit *kilogram*, kg
electric current, I, with the unit *ampere*, A
temperature, T, with the unit *kelvin*, K
amount of substance, n, with the unit *mole*, mol
luminous intensity, I_v, with the unit *candela*, cd

We will now investigate the dependencies in the existing SI system.

The **second** is defined as *"the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium 133 atom."* The inverse period duration is described by $\Delta\nu\,(^{133}\mathrm{Cs})_{\mathrm{hfs}}$. The second is independent of all other units.

The **metre** is coupled to the second by the determination of the speed of light in vacuum, whose invariance is demanded by the special theory of relativity. The equation $c_0 = \nu_0\,\lambda_0$ holds for particles with zero rest mass in vacuum. The speed of light $c_0 = 299\,792\,458\ \mathrm{s}^{-1}\ \mathrm{m}$ is exactly defined; the relative uncertainty of the value listed by CODATA was $4 \cdot 10^{-9}$ just prior to the definition in 1983.

Thus, the metre and the second now jointly relate to $\Delta\nu\,(^{133}\mathrm{Cs})_{\mathrm{hfs}}$ and can be considered, due to the determination of the constant c_0, as two expressions of the same unit for the space-time.

The **kilogram**, the unit of mass, *"is equal to the mass of the international prototype of the kilogram"*, m(K) = 1 kg, and can obviously not be derived from other base units. Actually, a drift of the international prototype with time is possible and, as a matter of principle, not exactly definable.

The **mole** is defined as *"the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12"*. It is no more than a counting unit which corresponds to the Avogadro constant N_A. Obviously, the mole is not a fundamentally necessary base unit. As the quantity of atoms in 12 grams of carbon is countable, the atomic mass of ^{12}C is defined at the same time. The advantage of the unit mole lies in the fact that it allows simple weighing instead of an impracticable counting of approx. 10^{23} particles.

Basically, the **kelvin** is no more than a special energy unit and can, therefore, be defined as $[T] = k_B \cdot 1\ \mathrm{J} = 1\ \mathrm{K}$; where k_B is the Boltzmann constant which is a freely selectable scaling factor between the energy unit and the temperature unit. The kelvin, too, is not a fundamentally necessary base unit.

The unit of energy, $\mathrm{J = Nm = kg\ m^2\ s^{-2}}$, is a derived unit and can, for example, be related to the kinetic energy of the accelerated kilogram prototype[1] $E = \frac{1}{2} m\, v^2$.

It is relatively easy to build an apparatus which converts kinetic energy into thermal energy.

The **candela** is defined as "*the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540 \cdot 10^{12}$ hertz and that has a radiant intensity in that direction of 1/683 watt per steradian*". The candela corresponds to a power, as the steradian [sr] = [m^2/m^2] has the dimension one. The candela, too, is not a fundamentally necessary base unit.

The unit of power, $\mathrm{W = J\ s^{-1}}$, links up energy and time.

The **ampere** is defined as *"that constant current which, if maintained in two straight, parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, will produce between these conductors a force equal to $2 \cdot 10^{-7}$ newton per metre of length"*. The definition of the ampere is based on the electromagnetic laws of forces. The electrostatic force between charges follows Coulomb's law. The inverse interaction constant is called electric permeability $\varepsilon_{\mathrm{Index}}$, whereby the index designates the material into which the charges are embedded; 0 indicates the vacuum. Moving charges generate a magnetic field. A magnetic field acts on moving charges. Therefore, two conductors with the two parallel currents $I_{1,2}$, respectively, are attracted by a magnetic force. The interaction constant is called magnetic constant μ_{Index}. The two coupling constants are interlinked by the relation $\varepsilon_0^{-1} = \mu_0\, c_0^2$. In the SI system, the two relations read:

$$\boldsymbol{F} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^3}\boldsymbol{r} \qquad \text{and}$$

$$d^2\boldsymbol{F} = \frac{\mu_0}{4\pi}\frac{i_1\, d\boldsymbol{l}_1 \times \left(i_2\, d\boldsymbol{l}_2\right) \times \boldsymbol{r}}{r^3}, \tag{3.1}$$

where $d\boldsymbol{l}_1$ and $d\boldsymbol{l}_2$ are infinitesimal length vectors along the two thin wires and the symbol × indicates vector multiplication. By the definition of μ_0, the ampere relates to the unit of force "newton". If the left-hand equation in (3.1) were applied, using the charge instead of the current and determining ε_0 instead of μ_0, this would lead to an analogous result.

The ampere, thus, depends on the second to which the metre is connected, on the newton and on the definition of μ_0 or ε_0, respectively, which are interrelated via $\varepsilon_0^{-1} = \mu_0\, c_0^2$.

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[1] As the case may be, relativistic corrections must be taken into account.

In the currently valid SI definition, the elementary charge e_0 is a measurand. The electric current $I = \dot{e}_0$ corresponds to the number of elementary charges flowing through a conductor per time unit. A definition via the determination of the elementary charge would suggest itself. The electric current would be related exclusively to the unit second, and ε_0 and μ_0 would be measurands which would – of course – still be interrelated via $\varepsilon_0^{-1} = \mu_0 c_0^2$. When the measurand was defined in 1948, the advantage was the feasibility of the realisation, as it was at that time not possible to count single electrons in a sufficient quantity and with sufficient uncertainty. However, as described in (see *Ahlers, Siegner*, pp. 59–67), different approaches meanwhile exist for the counting of single electrons which allow sufficiently large currents and which, thus, come closer to the aim of realising the ampere via $I = \dot{e}_0$.

The unit of force N = m kg s^{-2} is a derived unit. It can be realised either via the heavy mass, by weighing the kilogram prototype, or via the inert mass, by accelerating the kilogram prototype. To the heavy mass, the law of gravitation

$$\boldsymbol{F} = -G \frac{M_1 M_2}{r^3} \boldsymbol{r} \text{ applies.}$$

Both basic interactions of nature which are relevant to metrology – i. e. the electromagnetic force and the gravitational force – are described theoretically in the same manner.

In this way, the kilogram and the coulomb (or the ampere) can be compared, making use of the gravitational and Coulomb’s law, respectively. The resulting consistency condition is reflected by two key experiments which will be dealt with further below: the *watt balanc*e and the *Avogadro experiment*.

Up to now, we have seen that the two base units “the second” and “the kilogram”, which are defined via $\Delta\nu\,(^{133}\mathrm{Cs})_{\mathrm{hfs}}$ and $m(\mathcal{K})$, are independent, and that they are also sufficient to define – with definitions for the numerical values for c_0, k_B, N_A and e_0 and with suitable measuring facilities – all other units.

To reduce this hypothetically to only one base unit, an additional physical relation, which connects a mass with a frequency, has to be applied. An approach is provided by the De-Broglie relation

$$E = m_0 c_0^2 \,/ \sqrt{1 - \left({}^{v}\!/\!{}_{c_0} \right)^2} = h\,f = h\,c_0\,\lambda^{-1} ,$$

with $c_0 = \lambda f$, so that for the unit of mass $[M]$ = const. · s^{-1} = 1 kg is valid. For a reduction to only one base unit via this relation, h would have to be determined. The determination of h would be arbitrary, and the numerical value would be selected in such a way that $m_0 = m(\mathcal{K})$ is valid. Although theoretically possible, constructing a realisation of a unit is difficult as macroscopic masses lead to extremely high frequencies.

It would be an alternative to relate the kilogram to the mole, i. e. by determining a fixed number of elementary particles such as carbon or silicon atoms for the Avogadro constant. In the case of carbon, this would correspond to the current definition of the mole, with the difference that in a reversed logic not the mass, but the Avogadro constant would be determined. The disadvantage of this definition would be, however, that for practical realisations, again material parameters such as impurities or crystal defects would inevitably have to be taken into account.

In this chapter we have shown that the existing SI can be transferred into a new system with the aid of values which would have to be consistently determined for $\Delta\nu\,(^{133}\mathrm{Cs})_{\mathrm{hfs}}$, c_0, k_B, N_A, e_0 and h. With the aid of simple, fundamental physical relations, this system corresponds to a hypothetical, minimum system of units, based on one base unit only. It is pointed out once again that this system is only one of many possible systems. It was chosen here because it is the system which has been selected for the redefinition.

4 Fundamental Constants

In the above discussion, it became clear which role fundamental constants and fundamental physical laws play for the definition of units, and it became evident that in order to make measurands quantifiable, one simply has to define constants which partly have the character of a scaling factor. The determinations of $\Delta\nu\,(^{133}\mathrm{Cs})_{\mathrm{hfs}}$, c_0, h, e_0, k_B and N_A proposed by CIPM offer the possibility of defining the SI as follows [6]:

- “The international system of units, the SI, is the system of units scaled so that
- the ground state hyperfine splitting frequency of the caesium 133 atom $\Delta\nu\,(^{133}\mathrm{Cs})_{\mathrm{hfs}}$ is exactly 9 192 631 770 hertz, Hz
- the speed of light in vacuum c is exactly 299 792 458 metre per second, m s^{-1}
- the Planck constant h is exactly 6.626 06X · 10^{-34} joule seconds, J s
- the elementary charge e_0 is exactly 1,602 17X · 10^{-19} coulomb, C
- the Boltzmann constant k_B is exactly 1,380 65X · 10^{-23} joule per kelvin, J K^{-1}
- the Avogadro constant N_A is exactly 6,022 14X · 10^{23} reciprocal mole, mol^{-1}
- the luminous efficacy K_CD of a monochromatic radiation of frequency 540 · 10^{12} hertz is exactly 683 lumen by watt, lm W^{-1}.“

The symbol X here designates the digit which still has to be determined until the redefinition.

In this chapter, we will examine how well these fundamental constants are known within the scope of the currently existing SI system in which some of them are still measurands.

The caesium hyperfine transition and the speed of light have already been exactly defined. In the logic of the discussion conducted so far, these two fundamental constants can be freely selected, as $\Delta\nu\,(^{133}\mathrm{Cs})_{\mathrm{hfs}}$ scales the entire system of units and as the general theory of relativity only specifies that c_0 is constant, but not the length of a metre.

The measurement values which are presently available for h and e_0 contain an inconsistency. This, we want to discuss on the basis of the two key experiments *watt balance* and d*etermination of the Avogadro constant*. For this discussion, we will consider an alternative possibility of defining the SI, which differs from the CCU proposal only by the fact that – instead of the Planck constant h – the mass $M(^{12}\mathrm{C})$ would be fixed. In the following, when speaking of this possibility, we will refer to it as the "alternative".

In the *watt balance experiment* [1], in a first step, a force is generated in a magnetic field on a coil flown through by a current which is compensated by acceleration due to the gravity g of a known mass m. The current measurement is realised by a resistance measurement ($R = r R_{\mathrm{K}}$; R_{K} being the von Klitzing constant and r an index) and a voltage measurement with Josephson contacts ($U = u f_{\mathrm{J}} / K$; f_{J} and K_{J} being the Josephson frequency and the Josephson constant) realised by means of the quantum Hall effect. In a second step, the coil is moved with a constant velocity v in the same magnetic field, and the voltage, which is thereby induced in the coil, is again measured with Josephson contacts. Assuming that the coil and the magnetic field are identical in the two steps, the respective parameters can be eliminated from the two conditional equations and the following is obtained:

$$m = \frac{1}{rR_{\mathrm{K}}}\frac{u_1 f_{\mathrm{J},1}}{K_{\mathrm{J}}}\frac{u_2 f_{\mathrm{J},2}}{K_{\mathrm{J}}}\frac{1}{gv} = \frac{u_1 f_{\mathrm{J},1} u_2 f_{\mathrm{J},2}}{rgv}\frac{1}{R_{\mathrm{K}} K_{\mathrm{J}}^2} \quad , (4.1)$$

with m being the mass and h the Planck constant. With $K_{\mathrm{J}} = 2e/h$ and $R_{\mathrm{K}} = h/e^{2,}$

$$h = m\frac{4rgv}{u_1 f_{\mathrm{J},1} u_2 f_{\mathrm{J},2}} \quad \text{is obtained.}$$

At present, the experiments yield the following for the Planck constant:

$h = 6.626\,068\,91(24) \cdot 10^{-34}$ Js, thus
$u_{\mathrm{rel}}(h) = 3.6 \cdot 10^{-8}$ (watt balance NIST [7])

$h = 6.626\,070\,95(44) \cdot 10^{-34}$ Js, thus
$u_{\mathrm{rel}}(h) = 6.6 \cdot 10^{-8}$ (watt balance NPL [8]), whereby a current evaluation indicates an uncertainty which has to be increased to $u_{\mathrm{rel}}(h) = 1.7 \cdot 10^{-7}$ for the NPL watt balance.

The Avogadro project [9] comprises several subtasks. Two spheres were prepared from a ^{28}Si-enriched silicon single crystal. From the lattice spacing measured by means of X-ray interferometry, the number density n of the silicon atoms is determined. The volumes V of the spheres are measured by means of a sphere interferometer. The number of the atoms is then given by $V\,n$. The relative isotopic distribution and, from that, the molar mass $M(\mathrm{Si}_{\mathrm{AVO}})$ are determined by means of modified isotopic dilution mass spectrometry, and finally the mass m_{AVO} of the spheres (weight: approx. 1 kg) is determined by weighing. From that, the Avogadro constant is obtained as follows:

$$N_{\mathrm{A}} = \frac{M(Si_{\mathrm{AVO}})}{m_{\mathrm{AVO}}} Vn \quad . \qquad (4.2)$$

At present, the current measurement result is $N_{\mathrm{A}} = 6.022\,140\,78\,(18) \cdot 10^{23}$ mol^{-1}, i. e. it reaches a relative measurement uncertainty of $u_{\mathrm{rel}}(N_{\mathrm{A}}) = 3.0 \cdot 10^{-8}$ [10].

The Planck constant and the Avogadro constant can be compared with each other via the following relation of the molar Planck constant:

$$h\,N_{\mathrm{A}} = h\frac{M_{\mathrm{e}}}{m_{\mathrm{e}}} = h\,M_{\mathrm{e}}\frac{c\alpha^2}{2R_\infty} = M_{\mathrm{u}}\frac{m_{\mathrm{e}}}{m_{\mathrm{u}}}\frac{c\alpha^2}{2R_\infty} \quad .$$

Here, M_{e} designates the molar electron mass, m_{e} the mass of a single electron, $M_{\mathrm{u}} = N_{\mathrm{A}} m_{\mathrm{u}} = 10^{-3}$ kg mol^{-1} the molar unit of mass, m_{u} the atomic unit of mass, $\alpha = e_0^2/2c\varepsilon_0 h$ the fine structure constant, and $R_\infty = m_{\mathrm{e}} e_0^4/8\varepsilon_0^2 h^3 c$ Rydberg's constant. The relative atomic mass of the electron $m_{\mathrm{e}}/m_{\mathrm{u}}$ can be measured via the cyclotron resonance in Penning trap experiments with an uncertainty of $2.1 \cdot 10^{-9}$, the fine structure constant can be determined with $6.8 \cdot 10^{-10}$, and Rydberg's constant with $6.6 \cdot 10^{-12}$ (see CODATA2006). For the overall uncertainty of the molar Planck constant, the following is obtained [11]:
$h\,N_{\mathrm{A}} = 3.990\,312\,682\,1\,(57) \cdot 10^{-10}$ J s mol^{-1},
i. e. $u_{\mathrm{rel}}(hN_{\mathrm{A}}) = 1.4 \cdot 10^{-9}$.

If this value is used and if the experimental value for N_{A} is converted into h, the following results:
$h = 6.626\,070\,07\,(20) \cdot 10^{-34}$ Js,
i. e. $u_{\mathrm{rel}}(h) = 3.0 \cdot 10^{-8}$.

This means that the results of the watt balance of NIST and of the Avogadro experiment differ significantly by $1.7 \cdot 10^{-7}$. The watt balances of NIST and NPL differ by $3 \cdot 10^{-7}$ – due to the larger measurement uncertainties in the case of the NPL watt balance, however, with less statistical significance. This situation can be basically resolved in two ways: either by detecting systematic errors by carrying out additional measurements, which would lead to a correction of the measurement results of one or both experiments, or by increasing, in a formal step, the stated measurement uncertainties up to statistical consistency. The latter procedure is scientifically unsatisfactory since the determination of the respective uncertainty contribution would be *ad hoc* instead of being based on a careful analysis of the measurements.

Table 1 shows the values which were indicated by CODATA [11] in 2006 for the fundamental constants which are relevant to the new SI and the relative uncertainties $u_{\mathrm{rel}} \cdot 10^8$ assigned to them. In addition, the relative uncertainties indicated by CODATA in 1986 and the relative difference between the values from 2006 and 1986: $\Delta_{\mathrm{rel}} = (x_{2006} - x_{1986})/x_{2006}$ are shown.

The last column shows the change which occurred between the value from 2006 and the value from 1986. It can be seen that – except for k_B – the changes are larger than the relative uncertainties indicated for 2006 as well as for 1986 ($u_{\mathrm{rel}} \cdot 10^8$ or $u_{\mathrm{rel,86}} \cdot 10^8$, resp.).

This raises the question of whether all uncertainties stated are comparable. To ensure consistency, all these uncertainties must be determined with one and the same procedure. The procedure that is generally mandatory is the one which has been proposed by the JCGM[2] [12] “Guide to the Expression of Uncertainty in Measurement” (abbreviated to: GUM). This procedure will be described in the Annex.

A general survey of the fundamental constants can be found in [15]. The numerical values of the fundamental constants determined by means of a fitting method can be found in CODATA [11]. (For a survey, see also the Annex).

5 Discussion and Conclusions

In the “new SI”, all units will be based – as recommended by the International Committee for Weights and Measures (CIPM) – on a set of exactly defined fundamental constants or “constants of nature”: $\Delta\nu(^{133}\mathrm{Cs})_{\mathrm{hfs}}$, c_0, h, e_0, k_B and N_A. In this way, the objective which has long been aimed at – namely to define “imperishable” units instead of basing them on “ephemeral” artefacts – will be reached.

The definitions of all seven base units are given a uniform form [6] which reads: *“The (name of the unit), (symbol of the unit), is the unit of (base unit). Its magnitude is set by fixing the numerical value of (name of the fundamental constant) to be exactly (numerical value), when it is expressed in (SI-unit(s)).”* In this way, the importance of the fundamental constants is emphasised.

The seven base units will be introduced in a new order, by which a certain hierarchy is indicated. This order is as follows: second, metre, kilogram, ampere, kelvin, mole, and candela. The method of their practical realisation is not explicitly defined. However, CGPM has pointed out that the existence of *mises en pratique* for all base units is a prerequisite for the redefinition.

According to the concept of the redefinition, it would not be necessary any longer to distinguish between base units and derived units. For historical reasons – and to ensure that the redefinition will find general acceptance – this distinction is, however, still adhered to. As long as consistency is ensured, the numerical values of the constants are arbitrary. A redefinition other than one leading to continuous numerical measurement values would not, however, be acceptable. This is guaranteed by using the measured values for the respective constants within the existing SI, which are affected by uncertainties, and by assigning the uncertainty zero to them. In effect, other quantities – such as the value of the kg prototype or the electric constant ε_0 – become measurable quantities with an associated uncertainty.

Tabelle 1:

Symbol	Value 2006	SI Unit	in base units	$u_{\mathrm{rel}} \cdot 10^8$	$u_{\mathrm{rel,86}} \cdot 10^8$	$\Delta_{\mathrm{rel}} \cdot 10^8$
h	6.626 068 96	10^{-34} J s	10^{-34} s^{-1} m^2 kg	5	60	99
N_A	6.022 141 79	10^{-23} mol^{-1}	10^{-23} mol^{-1}	5	60	85
e_0	1.602 176 487	10^{-19} C	10^{-19} s A	2.7	30	–53
K_J	4.835 978 91	10^{14} Hz V^{-1}	10^{14} s^2 m^{-2} kg^{-1} A	2.5	29	46
R_K	2.581 280 755 7	10^4 Ω	10^4 s^{-2} m^2 kg A^{-2}	0.070	4.6	7.6
k_B	1.380 650 4	10^{-23} J K^{-1}	10^{-23} s^{-2} m^2 kg K^{-1}	170	870	–550

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[2] Joint Committee for Guidance in Measurement

The third prerequisite which has been formulated by the CGPM [13] – in addition to a sufficiently good data quality for the constants and the formulations of the *mise en pratique* – is that the redefinition is made known to the public, that it is sufficiently discussed in public, and that it finds general acceptance. As the redefinition is abstract, a quantification of whether it finds general acceptance is difficult, so that this task – like the other two prerequisites – has to be regarded as having not yet been completely implemented.

Annex

The approach of GUM is that generally, not only one value can be assigned to a measured quantity but, based on given information, a probability distribution of reasonably possible values. If, for example, a voltage is measured very precisely by means of an ideal digital voltmeter whose last digit represents the multiple of $10^{-\mathrm{n}}$ volt, then all values from the interval given by the value ± $0.5 \cdot 10^{-\mathrm{n}}$ V are equally possible and a rectangular distribution is assigned to the measurand whose expected value is the read measurement value and whose variance is $^{1}/_{12} \cdot 10^{-2n}$ V^2. In practice, usually not the distribution, but the root of the variance is indicated which is referred to as uncertainty. Further uncertainties may be needed to be considered. The device itself can have a measurement deviation $\Delta V \pm u(\Delta V)$ which can be inferred from the calibration certificate. The resistances of the contacts are not exactly known, etc. GUM requires a model equation to be set up for the measurement which represents the output quantity Y – here the measured voltage – as a function of all relevant input and influence quantities $X_1,\dots,X_\mathrm{n}$. This model equation $Y = f(X_1,\dots,X_\mathrm{n})$ is linearised by a Taylor series of 1st order. This provides an equation for the possible values of Y – they are identified by η – as a function of the possible values of X_i, which are designated ξ_i:

$$\eta = f(x_1,\dots,x_n) + \sum_{i=1}^{n} \frac{\partial}{\partial X_i} f(X_1,\dots,X_n)\Bigg|_{X_i = x_i} \left(\xi_i - x_i\right). \tag{A.1}$$

The partial derivatives are referred to as sensitivity coefficients c_i. From equation (A.1), it follows that

$$\mathrm{E}Y = f(x_1,\dots,x_n) \quad \text{and} \quad \mathrm{Var}Y = \boldsymbol{c}^{\mathrm{T}} \boldsymbol{U}_x \boldsymbol{c}, \tag{A.2}$$

with $\boldsymbol{c}^{\mathrm{T}} = (c_1,\dots,c_n)$ and with $\boldsymbol{U}_\mathrm{x}$ being the uncertainty matrix for the input and influence quantities for whose elements, $u_{i,j} = u(x_i) r(x_i,x_j) u(x_j)$ applies, whereby the $r(x_i,x_j)$ are the correlation coefficients having the value 1 for $i = j$ so that $u_{i,i} = u^2(x_i)$ is valid. The expected value EY is referred to as best estimate y, and the root of the variance Var $\boldsymbol{Y}$ is referred to as the uncertainty $u(y)$ assigned to y. As many input quantities are given in most cases, it can be assumed that the probability distribution for Y is a normal distribution. In this case, the interval $[y - u(y), y + u(y)]$ covers the value of the measurand searched for with the probability $p = 0.68$. According to GUM, the complete measurement result must be indicated with a so-called expanded uncertainty which is to correspond to a coverage probability of $p = 0.95$. In the case of a normal distribution, $U = 1.96$ u is then valid or, rounded, $U = 2$ u. The equations (A.8) and (A.9) show an application example.

The fitting procedure used by CODATA is described in detail in the CODATA Report 1998 [14]. It is therefore sufficient to outline the procedure here only briefly. We keep closely to Appendix E in [14], but we adapt the notation to make things clearer. Instead of "covariance matrix", we use the concept "uncertainty matrix", and we write vectors with small letters and matrices with capital, bold-faced letters in italics. The procedure works on the assumption of n (mostly measured, but sometimes also calculated) values $\boldsymbol{q}^{\mathrm{T}} = (q_1,\dots,q_n)$, the uncertainty matrix $\boldsymbol{U_q}$ and a set of constants $z_{\mathrm{T}} = (z_1,\dots,z_m)$ to be adapted, $m<n$ selected, e. g. $z_1 = \alpha$ (fine structure constant), $z_2 = h$ (the Planck constant), etc. For each qi there is a so-called operational equation: $q_i = f(z_1,\dots,z_m)$. The selection of the z_i must comply with two requirements. First of all, they must be independent insofar that no z_i can be expressed as a function of the other $z_{j \neq i}$ and, secondly, each z_i must occur in at least one operational equation. Apart from that, the selection is free. The selection made has, however, a great influence on the values of the adapted constants; this is discussed, for example, by Milton et al. [16]. The operational equations are usually not linear and are, therefore, linearised by a Taylor series of 1st order, see equation (A.1). This yields:

$$q_i \doteq f_i(s_1,\dots,s_M) + \sum_{j=1}^{m} \frac{\partial}{\partial s_j} f_i(z_1,\dots,z_m)\Bigg|_{z_i = s_i} \left(z_j - s_i\right), \tag{A.3}$$

the initial values s_i being selected in such a way that they lie as closely as possible to the values expected for the z_i. This is why the s_i are often referred to as "fiducial value". The symbol $\doteq$ is to indicate that the relation is not exact.

To obtain a linear system of equations in the usual form, the vectors $\boldsymbol{s}^{\mathrm{T}} = (s_1,\dots,s_m)$, $\boldsymbol{f}^{\mathrm{T}} = (f_1(\boldsymbol{s}),\dots,f_n(\boldsymbol{s}))$, $\boldsymbol{y} = \boldsymbol{q} - \boldsymbol{f}$ and $\boldsymbol{x} = \boldsymbol{z} - \boldsymbol{s}$ and the design matrix $\boldsymbol{A}$ are now introduced; the elements $\alpha_{i,j}$ are the partial derivatives of the i-th operational equation according to the j-th "fiducial value" which are shown in equation

(A.3). In this way, we obtain the system of linear equations $\boldsymbol{y} \doteq \boldsymbol{A}\boldsymbol{x}$. The uncertainty matrix $\boldsymbol{U}_y$ is identical with the uncertainty matrix $\boldsymbol{U}_q$, as the components of vector f are constants to which no uncertainty is assigned. The solution according to the least squares method is:

$$\boldsymbol{x}^* = \boldsymbol{U}_{x^*}\boldsymbol{A}^T\boldsymbol{U}_y^{-1}\boldsymbol{y} \quad \text{with} \quad \boldsymbol{U}_{x^*} = \left(\boldsymbol{A}^T\boldsymbol{U}_y^{-1}\boldsymbol{A}\right)^{-1}, \tag{A.4}$$

with the components of $\boldsymbol{x}^*$ being the adapted values for the components $\boldsymbol{x}$, and $\boldsymbol{U}_{x^*}$ being the uncertainty matrix. With the aid of $\boldsymbol{x}^*$, it is now also possible to calculate fitted (adapted) values for the components of $\boldsymbol{y}$ and their uncertainty matrix: $\boldsymbol{y}^* = \boldsymbol{A}\boldsymbol{x}^*$and $\boldsymbol{U}_y{}^* = \boldsymbol{A}\boldsymbol{U}_{x^*}\boldsymbol{A}^{\mathrm{T}}$. The fitted values for $\boldsymbol{q}^*$ and $\boldsymbol{z}^*$ which are actually of interest are now obtained as:

$$\boldsymbol{z}^* = \boldsymbol{s} + \boldsymbol{x}^* \quad \text{and} \quad \boldsymbol{q}^* = \boldsymbol{f} + \boldsymbol{y}^*. \tag{A.5}$$

As the components of vector s as well as those of vector $\boldsymbol{f}$ are constants to which no uncertainty is assigned, $\boldsymbol{U}_{z^*} = \boldsymbol{U}_{x^*}$ and $\boldsymbol{U}_{q^*} = \boldsymbol{U}_{y^*}$ are valid. The procedure is now iterated k times by setting $\boldsymbol{s}^{(k+1)} = \boldsymbol{z}^{*(k)}$. The amount of k to be selected is determined by a termination criterion:

$$\sum_{j=1}^{m}\left(\frac{x_j^{*(k)}}{u(x_j^{*(k)})}\right)^2 < 10^{-20}. \tag{A.6}$$

If the procedure complies with this termination criterion, the consistency of the measured – or sometimes also calculated – input data is checked by means of the Birge Chi square test:

$$R_B = \sqrt{\chi^2 \big/ n-m} = \left(\boldsymbol{q} - \boldsymbol{q}^{*(k)}\right)^{\mathrm{T}} \boldsymbol{U}_q^{-1}\left(\boldsymbol{q} - \boldsymbol{q}^{*(k)}\right). \tag{A.7}$$

The difference $n - m$ is referred to as the effective degree of freedom ν. Consistency is assumed if R_B is not significantly larger than 1. It is to be noted that a bilateral χ^2 test would have to be preferred, as values which are too small also imply an inconsistency.

Here, a discussion of the convergence properties of the procedure will be dispensed with. Instead, reference is made to a fundamental work of D. W. Marquardt [17].

It is not possible to summarise all fundamental constants in one system of equations. The gravitational constant G is, for example, assessed separately. This represents the case m = 1. If one has $\boldsymbol{n}$ experimental results q_i and their uncertainty matrix $\boldsymbol{U}_q$, an analogous application of equation (A.4) yields the fitted value and the uncertainty assigned to it. Here, the “design matrix” is only a vector $\boldsymbol{a}^{\mathrm{T}} = (1,\ldots,1)$ with n components. The consistency test is carried out as described above. Iterations are not necessary here, as the system of equations is linear.

Although it is possible by means of the fitted values to achieve numerically consistent equations, it is not possible to obtain identical uncertainties on both sides of the equation [18]. As an example, we regard an equation which represents Rydberg’s constant as a function of the fine structure constant, the electron rest mass, the speed of light and the Planck constant: $R_\infty = \alpha^2 m_e c/2h$. The CODATA-2006 value for the left side is $R_\infty = 1.097\,373\,156\,8527(73) \cdot 10^7\ \mathrm{m}^{-1}$, i. e. the relative uncertainty is $6.67 \cdot 10^{-12}$. If now the right side is taken into account, one obtains the value $1.097\,373\,157\,457 \cdot 10^7\ \mathrm{m}^{-1}1$, which differs from the fitted value already from the 10th significant place onwards. Now, the sensitivity coefficient is calculated to determine the uncertainty:

$$\frac{\partial R_\infty}{\partial \alpha} = 2\frac{R_\infty}{\alpha}, \frac{\partial R_\infty}{\partial m_e} = \frac{R_\infty}{m_e} \text{ and } \frac{\partial R_\infty}{\partial h} = -\frac{R_\infty}{h}, \tag{A.8}$$

and according to equation (A.1), it follows that

$$\begin{aligned} \frac{u^2(R_\infty)}{R_\infty^2} = &\left(4\frac{u^2(\alpha)}{\alpha^2} + \frac{u^2(m_e)}{m_e^2} + \frac{u^2(h)}{h^2}\right) + \\ &2\left[2\frac{u(\alpha)}{\alpha}\begin{pmatrix} r(\alpha,m_e)\dfrac{u(m_e)}{m_e} - \\ r(\alpha,h)\dfrac{u(h)}{h}\end{pmatrix} - \frac{u(m_e)}{m_e}r(m_e,h)\frac{u(h)}{h}\right] \end{aligned} \tag{A.9}$$

If now, also CODATA-2006 are inserted, a relative uncertainty of $7.15 \cdot 10^{-8}$ is obtained from the first line in equation (A.9), i. e. without taking the correlations into account. If the correlations are taken into account, $1.24 \cdot 10^{-8}$ is obtained and, thus, $1.097\,373\,157(12) \cdot 10^7\ \mathrm{m}^{-1}$. This result is consistent, as the calculated value, $R_\infty = \alpha^2 m_e c/2h$, agrees – within the scope of the uncertainty stated for it – with the fitted value for R_∞. The result illustrates the great influence of correlations.

The reliability of the procedure depends decisively on the fact that the uncertainty matrix can be set up correctly for the input data. Although CODATA checks all input data used, it cannot guarantee in every case that all uncertainties stated have been determined strictly in accordance with GUM and that they have neither been determined too “generously” nor too “meticulously”. Another problem is the difficulty in determining the correlation between measurement results which may be correlated – although coming from different laboratories – due to the same measurement principle, or due to a reference to the same constants, e. g. in the case of electrical measurements. The deviations concerned are systematic measurement deviations which are sometimes hard to assess. This results in different corrections and assumed uncertainties for these corrections. ■

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