TASK GROUP ON THE SI (TG-SI) REPORT TO CCT

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Terms of reference: The Terms of Reference follow closely CIPM Recommendation 1 of 2005, (CI-2005), "Preparative steps towards new definitions of the kilogram, the ampere, the kelvin and the mole in terms of fundamental constants". The TG-SI is presently tasked with the following two terms:

- monitor closely the results of new experiments relevant to the possible new definition of the kelvin, and to identify necessary conditions to be met before proceeding with changing the definition;
- solicit input from the wider scientific and technical community on this important matter.

The TG-SI members met to review the present state of the Boltzmann constant determinations at the 9th International Temperature Symposium (ITS-9) in Los Angeles, CA, held from 19 to 23 March 2012.

Figure 1 shows a summary of determinations of the Boltzmann constant *k* since 2007. Motivated by the recommendation of the International Committee for Weights and Measures in 2005, numerous new experiments have subsequently been set up.

NIST deduced a value for the Boltzmann constant from measurements of the refractive index of helium (RIGT) at T_{TPW} with a relative standard uncertainty of 9.1×10^{-6} [1]. A significant limitation of this work was the assumption that the deformation of the assembled cavity under hydrostatic pressure could be accurately computed from the elastic constants of samples of the alloy used to manufacture the cavity. 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 was derived with a relative standard uncertainty of 3×10^{-5} [2]. DCGT determinations of *k* have a limitation similar to that of RIGT; specifically, the deformation under hydrostatic pressure of an assembled capacitor must be computed from measurements of the elastic constants of samples of the alloys and insulators used to manufacture the capacitor. For DCGT, the sensitivity coefficient and hence the influence on the uncertainty of *k* is a factor of two smaller. University Paris North, Laboratoire de Physique des Lasers (LPL) in cooperation with LNE-CNAM undertook a first proof of the Doppler broadening technique (DBT) with a relative uncertainty of 2×10^{-4} [3]. Within the iMERAPlus project [4] the Italian group at Second University of Naples and Polytechnic of Milan (UniNA) in cooperation with INRiM evaluated the Doppler broadening of a CO_2 line [5, 6].

The acoustic gas thermometry (AGT) measurements of LNE-CNAM [7, 8], NPL [9], and INRiM [10] all used resonators jointly developed within the European iMERAPlus project and achieved the smallest uncertainties to date (listed in table 1) of all methods. LNE-CNAM pioneered the design of several triaxial ellipsoid copper cavities of different volume. Some of these cavities were made available by LNE-CNAM to NPL and INRiM. The cooperation between NPL and Cranfield University further refined machining and finishing techniques for copper cavities. Stainless steel cavities of spherical shape have been designed, realized and used at INRiM and at the University of Valladolid (UVa) in cooperation with CEM [11]. For this simpler geometry, the degeneracy of microwave modes can be removed by slight misalignment of the two hemispheres comprising the cavity.

Significant effort was dedicated to the dimensional characterization of the acoustic cavities. Three alternative independent methods were investigated as suitable to provide the needed precision and accuracy, namely water pyknometry, coordinate measuring machines (CMM) and microwave resonances. While the microwave technique was jointly developed for all the experiments involved within the iMERAPlus project, the research group at NPL was the only to pursue a comparison of all three methods.

Progress was obtained in refining the acoustic models and the experimental practice of several perturbing effects. These improvements included: the extension of the model used to calculate the perturbation induced by geometry beyond the triaxial ellipsoid approximation. Thus, the more realistic expression of the geometrical internal shape of the resonant cavities, as inferred from the analysis of CMM data and expressed as a spherical harmonics series expansion, could be used to estimate and calculate appropriate corrections to the experimental data; measuring and modeling the acoustic impedance of the electroacoustic transducers; measuring and modeling the effects of coupling between the acoustic field and the vibrations of the cavity shell; measuring and modeling the perturbing effects of cylindrical holes (like the ducts used for flowing gas through the cavity interior); and estimating the perturbation induced by flow on the acoustic eigenfrequencies. Still, the uncertainty associated to the acoustic part of the experiment up to now limits the ultimate uncertainty achievable in the acoustic determination of k.

With the DBT LPL evaluated the same series of NH_3 spectra applying a Voigt absorption line profile [12], subsequently a Galatry profile [13], and corrected it for the hyperfine structure of the absorption lines [14]. Finally, they obtained a relative uncertainty for k of 50 ppm. PTB used DCGT with helium gas for the first time at the TPW [15] and with the new thermostat developed jointly with INRiM in the iMERAPlus project. Together with re-evaluated measurements at low temperatures [16] a relative standard uncertainty of k of 7.9 ppm was obtained. At NIST the Boltzmann constant k was measured by comparing the Johnson noise of a resistor at the TPW with a quantum-based voltage reference signal generated with a superconducting Josephson-junction waveform synthesizer [17]. It is NIST´s first measurement of k with this electronic technique, and the first noise-thermometry measurement to achieve a relative standard uncertainty of 12 parts in 10^6.

A single, fixed-path-length cylindrical-cavity resonator was used at NIM to measure the speed of sound in argon at the TPW. Three even and three odd longitudinal modes were used in this measurement. Based on the ratio M/γ_0 determined from an impurity and isotopic analysis of the argon used in the measurement and the measured speed of sound, a value was obtained for the Boltzmann constant k [18].This value of k has a relative standard uncertainty $u_r(k) = 7.9\times10^{-6}$. Several, comparatively large imperfections of NIM´s prototype cavity affected the even longitudinal modes more than the odd modes. The models for these imperfections are approximate, but they suggest that an improved cavity will significantly reduce the uncertainty of k.

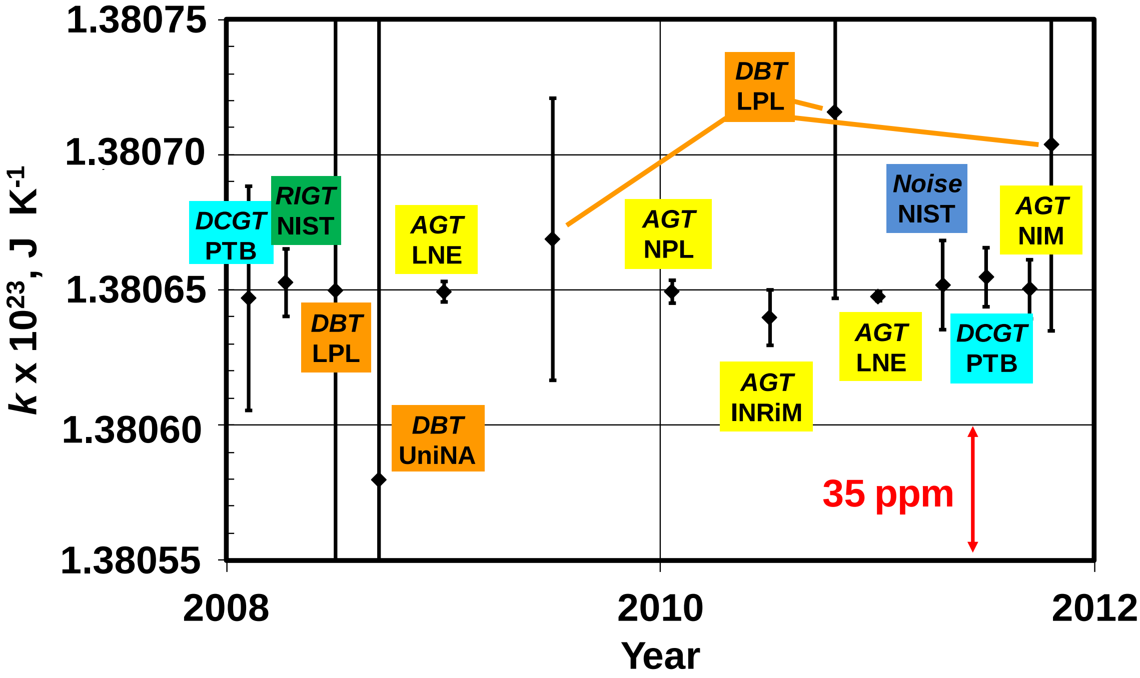

Figure 1a: Determinations of the Boltzmann constant since 2007. For the abbreviations see text. The error bars denote standard uncertainties.

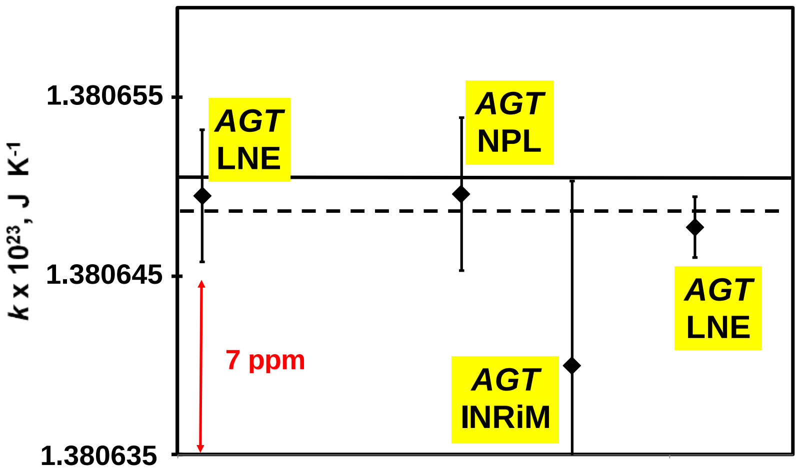

Figure 1b: Enlargement of Figure 1a depicting all new determinations contributing to the CODATA 2010 adjustment. The full line represents the CODATA value for the Boltzmann constant of 2006 [19] and the broken line the new value of 2010.

All results are highly consistent and agree with the CODATA value of 2006 which was based on the AGT work at NIST [20] and to much lesser extend to that of NPL [21]. The new results were recently exploited by CODATA in their 2010 adjustment of recommended values for fundamental constants. As a result, the CODATA group recommended a value for *k* with a relative standard uncertainty about a factor of two smaller than the previous $u_r(k)$ of 1.7×10^{-6}. The 2010 value of the CODATA group is shown in figure 1b.

year	1979	1988	2009	2010	2010	2011
k (10^{-23} J/K)	1.380656	1.3806503	1.3806495	1.3806496	1.380640	1.3806477
$k - k_{CODATA}$ (ppm)	5.21	1.09	0.51	0.58	-6.37	-0.80
$u_r(k)$ (ppm) (1σ)	8.5	1.7	2.68	3.11	7.49	1.24
Reference	[21]	[20]	[7]	[9]	[10]	[8]
weight	**0.011**	**0.275**	**0.111**	**0.082**	**0.014**	**0.517**

Table 1: All measurements contributing to the 2010 CODATA adjustment of the Boltzmann constant. All results are based on acoustic gas thermometry. The shaded values were used for the CODATA adjustment of 2006 but still affect the 2010 adjusted value by the weights stated in the bottom line.

All values contributing to the 2010 adjustment were based on acoustic gas thermometry (table 1). For the new definition of the kelvin this is insufficient as the recommendation T2(2010) [22] of the CCT states "that before proceeding with the redefinition of the kelvin a relative standard uncertainty of the value of *k* of order one part in 10^6 be obtained, based on measurements **applying different methods of primary thermometry**" and "that these measurements ideally include at least two fundamentally different methods such as acoustic gas thermometry and dielectric constant gas thermometry and be corroborated by other measurements such as Johnson noise thermometry, total radiation thermometry or Doppler broadening thermometry". Accordingly, in 2011 the CGPM [23] encouraged researchers "to continue their efforts and make known to the scientific community in general and to CODATA in particular, the outcome of their work relevant to the determination of *k*."

At the TG-SI meeting in 2012, the following current research efforts were discussed:

The AGT resonator of **CEM/University Valladolid** was polished and cleaned. A new turbomolecular pump has been installed in the equipment and all the ducts have been cleaned to decrease the effect of the impurities in the measurements. Oxygen and water impurities are removed from the argon used in the measurements by means of a gas clean filter. A new set of measurements has been carried out with these modifications and a reduction of the uncertainties has been achieved.

INRiM is working towards a new acoustic determination of the Boltzmann constant *k* based on the determination of the speed of sound in helium using a copper quasi-spherical cavity previously designed and assembled at LNE-CNAM. Recent work, conducted in cooperation with the Scottish Universities Environmental Research Center, focused on the estimate and control of the residual impurities and the isotopic composition of the helium samples used at INRiM. The current performance of the acoustic, microwave and temperature parts of the experiment indicates that a determination of *k* with relative standard uncertainty around 4 ppm may be achieved at INRiM within 2012. PTB is making its analytical facilities available for the analysis of the helium samples. INRiM will shortly get in contact with PTB to arrange the details of this.

LNE-CNAM concluded a series of isothermal measurements at the triple point of water in January 2012 using Helium gas with the 0.5 liter sphere. LNE-CNAM is now completing the analysis of the results. Special care was taken in investigating the LHe trap effect with different bottle impurity and different pressure. Ultra high purity is especially an issue with Helium gas as this light gas is much more sensitive to heavy molecule impurities than argon. A publication is on the way.

NIM reported in a paper presented at ITS-9 [24] an investigation on the redetermination of the Boltzmann constant using a fixed-path-length cylindrical resonator. They observed that perturbations arising from a non-well characterized shell motion yield a key disturbance to the speed-of-sound when comparing with the measurements of a reference spherical resonator. They investigated a number of cylindrical resonators of different length, suspension, gas fill duct and pure sample gas. The experimental observations show that the low modes of the 130 mm and 160 mm cylinders demonstrate significant diversity at low pressure. The cause is the low signal-to-noise ratio at low resonant frequencies of low modes. The high modes of the two resonators bear the perturbation of the natural vibration of the cylindrical shells and have their (400) mode close to the acoustic resonance. It is concluded that there exists an optimal length of 80 mm for single cylindrical fixed-path-length resonators. The investigation indicates that the performance of cylindrical resonators can be further improved to obtain an uncertainty of k below 4 ppm.

A quantum-voltage-calibrated Johnson-noise thermometer was developed at NIM [25]. It measures the Boltzmann constant k by comparing the thermal noise across a 100 Ω resistor at the TPW with the pseudo-random frequency-comb voltage waveform synthesized with a bipolar-pulse-driven quantum-voltage-noise source. A measurement with integration period of 10 hours and bandwidth of 640 kHz resulted in a relative offset of 0.5×10^{-6} from the current CODATA value of k, and a type A relative standard uncertainty of 23×10^{-6}.

NIST determined the ratios of the thermodynamic temperatures of three fixed points (T_{Hg}, T_{TPW}, and T_{Ga}) by measuring the refractive indices of helium and argon in the same quasi-spherical microwave cavities. The refractive index of helium is accurately known from theory; thus, the helium data enable to determine the temperature-dependent compressibility of the assembled microwave cavities. However, further measurement of the Boltzmann constant is not envisaged. In a paper presented at ITS-9 [26] NIST described the most recent improvements of their Johnson-noise thermometer that enabled the statistical uncertainty contribution to be reduced to seven parts in 10^6, as well as the further reduction of spurious systematic errors and electromagnetic interference effects.

NPL concluded a series of isothermal measurements at the triple point of water in July 2011 using Argon gas. They have now completed analysis of the results and are ready to publish a new low-uncertainty estimate for k, subject to the completion of final checks. These checks concern two areas. Firstly a number of suggestions were made by colleagues at ITS-9 on possible causes of the observed line narrowing. And secondly issues related to gas purity are investigated. Extensive purity and isotopic composition measurements were made on each bottle of argon and NPL found no variation among 4 bottles examined. However more recently they have found a bottle which gives a significantly different result and NPL is seeking to understand the origin of this as it may shed light on the dispersion amongst previously published measurements.

The additional research efforts in AGT have a twofold motivation. Firstly, they aim at a further reduction of previously achieved uncertainties by exploiting the improved acoustic features of newly designed larger cavities. Secondly, the same experiments, with minor modifications, may demonstrate their usefulness for primary and practical thermometry in the near future.

For the first determination of the Boltzmann constant by DCGT of **PTB** at the TPW, the two main uncertainty components are connected with the properties of the measuring cylindrical capacitor, namely with its instability and effective compressibility. Progress in decreasing significantly these components is expected by comparing the parameters of capacitors with quite different designs [27], and by using alternative electrode materials, e.g. tungsten carbide, the compressibility of which is smaller than that of stainless steel by a factor of two to three. Considering the experience gained during the first DCGT experiments at the TPW, it seems to be realistic to decrease the relative uncertainty of the Boltzmann constant to a level of only about 2 ppm within one year. Such result would be the required independent confirmation of AGT.

At **University Paris North** (LPL) in cooperation with LNE-CNAM a complete analysis of the lineshape of ammonia at 10.35 µm around the TPW has been performed to obtain accurate lineshape parameters considering a speed-dependent Voigt profile. LPL anticipates a large reduction of the main source of uncertainty in the measurement of *k* coming from collisional effects by the use of a multi-path gas cell (37 m absorption length) with low pressures between only 0.025 Pa and 0.25 Pa and derived type A uncertainties of 6.4 ppm. A determination of *k* with an uncertainty of about 10 ppm by measurement of the Doppler width in ammonia seems now reachable [14].

At **Second University of Naples** and **Polytechnic of Milan** (UniNA), in cooperation with INRiM, the analysis of spectra acquired in 2011 at different gas pressures between 10 Pa and 500 Pa, with the H_2O line at 1.38 µm was completed. A refined interpolation of the absorption spectra could be performed by using the symmetric version of the speed-dependent Voigt profile [28]. The application of the fitting procedure to a variety of numerically simulated spectra demonstrated that a further reduction of the uncertainty could be achieved. Due to the high gas density, they found a type A uncertainty of the determination of *k* of only 3.5 ppm. Simultaneously, a new approach to Doppler-width thermometry was invented, based on line-absorbance analysis. The application of this method to simulated spectra, as well as to real spectra, demonstrated its validity and great potential [29].

The DBT presents several differences as compared to other better-established methods of primary gas thermometry, besides the basic principles of operation. It can take advantage of recently developed technologies of optical-frequency metrology and, most importantly, a very well defined quantum state is probed. Although the involved molecule may have a natural abundance of other isotopes, only one species is interrogated and the results do not depend on the isotopic composition. The exact modeling of the absorption lineshape is presently the main drawback, but semiclassical models can be successfully employed, provided that the Doppler width is retrieved from an extrapolation to zero pressure with the required uncertainty. Therefore, this method may be complementary to AGT and DCGT.

Table 2 gives an updated summary overview of the potential of the currently relevant primary thermometers for the institutes where research work to determine *k* is continued. It was deduced from the meeting of TG-SI during the conference ITS-9 in March 2012 and compared to the findings of the 2nd Boltzmann workshop held at PTB in 2006 [30] and to the state at the CODATA adjustment of 2010. Within 2013, it exists the possibility of achieving a relative standard **uncertainty for the adjusted value of the Boltzmann constant *k* below one part in 10^6 (1 ppm) but based on measurements applying different methods.**

Table 2: Development of the relative standard uncertainties for determining the Boltzmann constant *k* applying different methods and involved active institutes.

Method	2nd WS 2006	2011	2013 possibility	institute
AGT	> 20 ppm	1.2 ppm	< 1 ppm	CEM+UVa, INRiM, LNE-CNAM, NPL, NIM
DCGT	15 ppm	8 ppm	2 ppm	PTB
Noise	-	12 ppm	5 ppm	NIST, NIM
DBT	200 ppm	50 ppm	10 ppm	LPL+LNE-CNAM, UniNA+INRiM

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