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

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Terms of reference: The Terms of Reference follow closely the Recommendation 1 of the 94th meeting of the CIPM in 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, and a few additional experts (Livio Gianfrani (Univ. Naples), Christophe Daussy (Univ. Paris North)) covering in particular the field of Doppler broadening thermometry, met to review the present state of the Boltzmann constant determinations at BIPM on 20 May 2014.

This report is an update of the minutes of the TG-SI meeting hold on 12 March 2013, document CCT/14-03. Compared to the state reported in document CCT/14-03 the following progress has been achieved with the different methods:

Acoustic gas thermometry

The **University of Valladolid**, in cooperation with CEM, derived from the measurements with argon gas described in document CCT/14-03 a value of k = 1.380 656 2 × 10^{-23} J/K. A complete uncertainty budget has been established with a final result for the relative standard uncertainty of 20 × 10^{-6}. The result has been submitted to Int. J. Thermophys.
(F. J. Pérez-Sanz et al., Progress Towards an Acoustic Determination of the Boltzmann Constant at CEM-UVa, Int. J. Thermophys. 2014, submitted)

INRiM is pursuing an accurate determination of the speed of sound in helium at 273.16 K with a 3-liter volume copper sphere assembled in 2013. Preliminary acoustic and microwave results indicate that the performance of the experiment has significantly improved with respect to previous INRiM achievements. Also, with three newly calibrated cSPRTs, temperature measurement and thermal gradients across the resonator are satisfactory. Thus, for three out of the four major uncertainty contributions significant progress has been obtained, the remaining fourth being an accurate and reliable assessment of the molar mass yet to be achieved. A cross-check of the current estimate of helium impurities is planned by using the mass spectrometry facilities made available by PTB, starting in April 2014. A reduction of the uncertainty associated to a determination of k at INRiM is expected within 2014.

LNE-CNAM is going to publish in summer 2014 the series of measurements of May 2012 and January 2013 using helium gas with the 0.5 liter copper quasi-sphere BCU3 (50 mm radius). The values are in good agreement with the earlier measurements in argon. The weighted mean of both measurements named LNE3 and LNE4 has a relative standard uncertainty of 0.9 × 10^{-6}, without taking into account

their correlation. For 2014 new results are expected with the 3.1 liter quasi-sphere BCU4 having 90 mm radius to be operated with helium and argon.
All energy for the moment is concentrated on the acoustic molar mass argon comparison. It is now a much more complex comparison because the argon gas samples of NPL, INRIM, NIM, LNE-CNAM are compared with the same acoustic apparatus at LNE-CNAM and then samples taken in the same way will be measured by mass spectroscopy at **KRISS**. The determinations of the isotopic composition of several argon gas samples used in recent acoustic gas thermometry experiments are under way. A separate document submitted by KRISS describes the detailed method and uncertainties of the mass spectrometer used for this purpose at KRISS.

NPL published the measurements of 2011 using argon gas and the 62 mm radius sphere with a value of $k = 1.380\,651\,56 \times 10^{-23}$ J/K and a relative uncertainty of 0.71×10^{-6}, the lowest uncertainty in the determination of the Boltzmann constant achieved so far. Of note was the level of agreement between acoustic modes ($u = 0.18 \times 10^{-6}$) and the exceptionally low level of excess half-width: the lowest ever reported. NPL had extensive gas purity and isotopic composition measurements made on each bottle of argon gas in cooperation with the Scottish Universities Environmental Research Centre revealing significant bottle-to-bottle variation in molar mass. Examination of the contributions to the measurement uncertainty in k shows that the largest single component (24.3%) is the uncertainty of the molar mass of atmospheric argon determined by Lee et al. If that estimate were to be revised then NPL´s estimate for k would need to be adjusted accordingly. The NPL estimate of k is 2.7×10^{-6} higher than the LNE-CNAM estimate and the possibility this difference is due to an error in the estimate of the molar mass by either NPL or LNE-CNAM is under joint investigation.
(M. de Podesta et al., A low-uncertainty measurement of the Boltzmann constant, Metrologia **50**, 354–376, 2013)

NIM reported improvements to the previous acoustic determination of the Boltzmann constant k using a single 80 mm long cylindrical cavity. Now, the shape of the gas-filled resonant cavity is closer to that of a perfect cylinder and the thermometry has been improved. NIM used two different grades of argon, each with measured relative isotopic abundances, and they used two different methods of supporting the resonator. The measurements with each gas and with each configuration were repeated several times for a total of 14 runs. NIM improved the analysis of the acoustic data by accounting for certain second-order perturbations to the frequencies from the thermo-viscous boundary layer. The weighted average of the data yielded $k = 1.380\,647\,6 \times 10^{-23}$ J/K with a relative standard uncertainty of 3.7×10^{-6}. The largest component of the uncertainty resulted from inconsistent values of k determined with the various acoustic modes and is 2.9×10^{-6}. In the previous work, this component was 7.6×10^{-6}.
NIM is presently studying the two-cylinder regime which has demonstrated good improvement. NIM is preparing a new publication for 2014 on the two-cylinder regime.
(H. Lin et al. Improved determination of the Boltzmann constant using a single, fixed-length cylindrical cavity, Metrologia **50**, 417-432, 2013)

Dielectric constant gas thermometry

At **PTB**, applying dielectric constant gas thermometry with helium gas, further reduction of uncertainties was achieved in 2013 by the use of tungsten-carbide cylindrical capacitors featuring at least a factor of 2 lower effective compressibility. Further, essential progress has been achieved concerning the design and the assembly of the measuring capacitors, the determination of its effective compressibility, the sensitivity of the capacitance bridge, the influence of stray capacitances, the purity of the measuring gas, the pressure measurement, and the scattering and the evaluation of the data. The resulting new value amounts to $k = 1.380\,650\,9 \times 10^{-23}$ J/K with a relative standard uncertainty of 4.3×10^{-6}.
Additional progress in decreasing the uncertainty is expected by using measuring capacitors of a quite different design, namely ring cross capacitors. The first stability tests of those cross capacitors gave encouraging results. This is important because it would be an independent check of the results

based on cylindrical capacitors. Cross capacitors have several advantages such as insensitivity to dielectric films on the electrodes and an effective compressibility very close to that resulting from the volume compressibility of the electrode material. Activities to decrease the uncertainty of the pressure measurement to a level of 1 x 10^{-6} are in progress. This concerns extensive cross-float comparisons between six independent primary piston–cylinder assemblies to improve consistency of their effective areas and pressure-distortion coefficients. Moreover, an uncertainty reduction is expected from taking into account the correlation between the zero-pressure effective areas and the pressure-distortion coefficients. Considering the experience gained during the DCGT experiments, it seems to be realistic to decrease the relative uncertainty of the Boltzmann constant to a level of only about 2 x 10^{-6} within 2014.
(C. Gaiser et al. Improved determination of the Boltzmann constant by dielectric-constant gas thermometry, Metrologia **50**, L7-L11, 2013)

Noise thermometry

The quantum-voltage calibrated Johnson-noise thermometer system has been pioneered, developed and improved by the **NIST** over a couple of years. The thermometer developed recently at the **NIM** in cooperation with the **NIST** and the **MSL** was further developed and first results were obtained. It measures *k* by comparing the thermal noise across a 100 Ω resistor with the pseudo-random frequency-comb voltage waveform synthesized with a bipolar-pulse-driven quantum-voltage-noise source. The flat ratio between the thermal noise and the calculated quantum voltage noise up to 800 kHz, and self-consistent fitting results with different bandwidths, indicate that the systematic uncertainties are greatly reduced. Measurements of *k* with an integration period of 19 h resulted in a relative offset of 1 × 10^{-6} from the CODATA 2010 value, and a type A relative standard uncertainty of 17 × 10^{-6}. Experiments are ongoing at NIST to understand the sources of spherical aberrations and at NIM to reduce the statistical uncertainty. It is anticipated to reach an electronic measurement of *k* with a combined relative uncertainty of 6 x 10^{-6} with both systems in the near future.
(J. Qu, Y. Fu, J. Zhang, H. Rogalla, A. Pollarolo, S. P. Benz, Flat Frequency Response in the Electronic Measurement of Boltzmann's Constant, IEEE Trans. Instrum. Measurem. **62**, 1518-1523, 2013;
J. Qu, J. T. Zhang, Y. Fu, H. Rogalla, A. Pollarolo, and S. P. Benz, Development of a Quantum-Voltage-Calibrated Noise Thermometer at NIM, Temperature: Its Measurement and Control in Science and Industry, Vol. 8, AIP Conf. Proc. **1552**, 29-33, 2013)

NIST is developing a more advanced system for a more efficient measurement: The 2 channel-system will be replaced by a 4 channel-system in a more compact setting with a 4-channel ADC-readout. The bandwidth of the system will be increased by switching to amplifiers with increased bandwidth, with lower or comparable noise and higher linearity. In the most recent measurements, NIST used a 200 Ω sense resistor that reduced the statistical uncertainty by 25 % in the same measurement period compared to that of a 100 Ω sense resistor. The measurements of the 200 Ω sense resistor show differences of -10 × 10^{-6} and +27 × 10^{-6} between the measured and 2006 CODATA values of *k* for waveforms of the 800 Hz and 100 Hz tones spacing, respectively. For both sets of data, the statistical uncertainty is 16 × 10^{-6}. The larger correlated current noise of this 200 Ω measurement appears not to affect the measurement of *k*, probably because all associated effects are removed by fitting, as are the other quadratic effects.
(A. Pollarolo, T. Jeong, S. P. Benz, P. D. Dresselhaus, H. Rogalla, and W. L. Tew, Johnson-Noise Thermometry Based on a Quantized-Voltage Noise Source at NIST, Temperature: Its Measurement and Control in Science and Industry, Volume 8, AIP Conf. Proc. **1552**, 23-28, 2013)

NMIJ/AIST has been developing a quantum-voltage calibrated Johnson-noise thermometer system to first measure thermodynamic temperatures or the Boltzmann constant *k*, and then aim to extend the temperature range to higher temperatures where T-T_{90} data is lacking. This system features that most of the key elements have been built from scratch independently from NIST and NIM; especially the Josephson junction array was built in house at AIST, and its driving method differs

from that of either NIST or NIM. The values for *k* should be ideally flat and be independent on the bandwidth. However, the adjustment level of the system is still premature and consequently there is some bandwidth dependency in the measurements. Also some EMI in the measurements have to be faced. Currently NMIJ/AIST is building another amplifier box to include the battery power supplies within the same casing. They expect further improvement in the Boltzmann constant measurements through the improvements in the hardware in 2014.
(K. Yamazawa et al., Boltzmann Constant Measurements using QVNS based Johnson Noise Thermometry at NMIJ, AIST; Int. J. Thermophys. 2014, preprint TEMPMEKO 2013)

Doppler Broadening Technique

At **University Paris North** a complete analysis of the lineshape of ammonia ($^{14}NH_3$) was published considering a speed-dependent Voigt profile (SDVP) corrected for hyperfine structure. The laser source, a frequency-stabilized CO_2 laser at 10.35 µm, exhibits a spectral width smaller than 10 Hz and a frequency stability of 0.1 Hz (3×10^{-15}) for a 100 s integration time. The absorption length of the gas cell is 37 cm in a single-pass configuration (SPC) or 3.5 m in a multipass configuration (MPC). The linear absorption of the chosen transition varies from 15% to 98% for pressures ranging from 1 Pa to 25 Pa in SPC and from 0.1 Pa to 2.5 Pa in MPC. University Paris North followed the line-absorbance-based analysis method recently proposed. Having extracted the line shape parameters related to the speed dependence of the collisional broadening and shift with good accuracy from data taken at high pressures, they were fixed when fitting the low-pressure data to be used to determine *k*. It was experimentally demonstrated that in the 1.7 Pa to 17 Pa pressure range, these parameters are independent of the molecular density and the SDVP is the most suitable line shape profile. Simulated SDVP spectra corresponding to the optimal experimental conditions in MPC (pressure below 2 Pa) were fitted and an uncertainty of 0.9×10^{-6} of the Doppler width measurement and a resulting total systematic uncertainty contribution to *k* of 2.3×10^{-6} are expected.
University Paris North ís currently developing a compact spectrometer based on a widely tunable laser source—a quantum cascade laser. The tunability of the spectrometer will be increased by more than three orders of magnitude. Together with the higher available intensity and the potentially lower amplitude noise of the quantum cascade laser, a large reduction in the time needed to record absorption spectra, limited by the currently used complexity of the CO_2 laser frequency tuning technique, is expected. Such improvements will contribute to a reduction in the type A uncertainty of the Doppler width and, in turn, to a reduction in the time needed to reach the 10^{-6} level on *k*.
(C. Lemarchand et al., A revised uncertainty budget for measuring the Boltzmann constant using the Doppler broadening technique on ammonia, Metrologia **50**, 623-630, 2013)

At **Second University of Naples** and Polytechnic of Milan the analysis of spectra acquired in 2011 at different gas pressures between 200 Pa and 500 Pa, with the $H_2{}^{18}O$ line at 1.39 µm was published. The new implementation of Doppler broadening thermometry is based on precision absorption spectroscopy by means of a pair of offset-frequency locked extended-cavity diode lasers at 1 39 µm. A sophisticated and extremely refined spectral analysis procedure is adopted for the retrieval of the Doppler width as a function of the gas pressure, taking into account the Dicke narrowing effect, the speed dependence of relaxation rates, and the physical correlation between velocity-changing and dephasing collisions. This is the so-called partially correlated speed-dependent hard-collision model. A determination of the Boltzmann constant with a value of $1.380\,631 \times 10^{-23}$ J/K with a combined (type A and type B) uncertainty of 24×10^{-6} is reported. This is the best result obtained so far by means of an optical method.
Further reduction of uncertainties is expected by the use of a low-pressure long path absorption cell, by increasing the number of spectra, by improving the signal-to-noise ratio and by removing the dither on the reference laser. As for this latter upgrade, they are presently implementing a technique known as noise-immune cavity-enhanced optical heterodyne molecular spectroscopy for the highly sensitive detection of the sub-Doppler line.
(L. Moretti et al., Determination of the Boltzmann Constant by Means of Precision Measurements of $H_2{}^{18}O$ Line Shapes at 1.39 µm, PRL, **111**, 060803, 2013)

Table 1 gives a **summary overview** of the achievements of the presently relevant primary thermometers. It has been deduced from the meeting of TG-SI in May 2014 and compared to the findings described in the report of 2013, document CCT/14-03 and in the report of 2012, document CCT/12-13. The uncertainties of the four recent determinations taken into account in the **CODATA adjustment of 2010** are marked in **bold** in the third column. The denominations of the six determinations taken into account in the **CODATA interim adjustment of 2013** are marked in **bold** in the last column. Not listed here is the AGT reference work of Moldover of 1988 with a relative standard uncertainty of 1.7×10^{-6} which contributed to both adjustments. The preliminary uncertainty of the 2014 determination of the LNE-CNAM with Helium gas is derived from a weighted mean of measurements LNE 3 and LNE 4 (see above) without consideration of correlations. The uncertainties with a question mark are present estimations of TG-SI. Within 2014, the possibility exists of achieving a relative standard uncertainty for the adjusted value of the Boltzmann constant *k* at around 0.5 parts in 10^6 based on measurements applying different methods.

For the detailed results of the CODATA interim adjustment of 2013 see figure 1.

Table 1: Recent development of the relative standard uncertainties $u(k)/k$ for determining the Boltzmann constant *k* applying different methods and involved institutes.

method	gas	up to 2011 $u(k)/k$ / 10^{-6}	2013 $u(k)/k$ / 10^{-6}	2014 $u(k)/k$ / 10^{-6}	institute or denomination in figure 1
AGT	Ar	-	-	20	CEM+UVa
AGT	He	**7.5**	-	?	INRiM
AGT	He	**2.7**	-	0.9	**LNE-09**
AGT	Ar	**1.2**	-	?	**LNE-11**
AGT	Ar	7.9	3.7	?	**NIM-13**
AGT	Ar	**3.1**	0.7	-	**NPL-10, NPL-13**
DCGT	He	7.9	4.3	2 ?	**PTB-13**
JNT	-	-	-	6 ?	NIM
JNT	-	12	-	6 ?	NIST
JNT	-	-	-	< 20 ?	NMIJ
DBT	NH_3	50	-	< 10 ?	LPL+LNE-CNAM
DBT	H_2O	160	24	< 10 ?	UniNA+INRiM

Figure 1 CODATA 2013 interim adjustment of the Boltzmann constant *k* including the CODATA 2006 and CODATA 2010 values. All 7 experimental determinations taken into account are shown. For the abbreviations see table 1, NIST-88 denotes the determination by Moldover et al., J. Res. Natl. Bur. Stand. **93**, 85-144, 1988.
The graph is taken from the "Report by the CODATA Task Group on Fundamental Constants (TGFC) on the analysis of currently available data" given by David Newell at the CCU meeting, BIPM, 11 June 2013.