Int J Thermophys (2010) 31:1360–1370
DOI 10.1007/s10765-010-0728-6

Design and Capabilities of the Temperature Control System for the Italian Experiment Based on Precision Laser Spectroscopy for a New Determination of the Boltzmann Constant

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Received: 17 December 2009 / Accepted: 11 March 2010 / Published online: 10 April 2010

Abstract This article reports on the construction details of an isothermal cell, referenced to the triple point of water (TPW), together with characterization of its temperature uniformity and stability. The traceability of the temperature measurements is also defined and reported. The cell has an inner chamber of 15 mm diameter, and it is 150 mm long. Its temperature is actively controlled and maintained stable within 0.1 mK, for an unlimited time. The temperature gradient is limited to less than one millikelvin over the length of the cell which is kept in a horizontal position. This accurate temperature control is achieved by means of a series of three vacuum chambers, one inside the other. A special heater, reflectors, standard platinum resistance thermometers, several feedthroughs, an auxiliary thermostat, specific electronics, and dedicated software are used for the active control. The device represents a mixture of cryogenic and contact thermometry techniques, and it has been designed, assembled, and characterized at the Istituto Nazionale di Ricerca Metrologica. This temperature-stabilized cell is a part of a more complex experimental setup, based on near-infrared precision laser spectroscopy, devoted to the experimental determination of the Boltzmann constant.

Keywords Boltzmann constant · Definition of the kelvin · Doppler broadening thermometry · Laser spectroscopy · Temperature metrology

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1 Introduction

Modern optics and laser spectroscopy provide several tools for fast and non-intrusive temperature measurements in the gas phase. For instance, we have seen in the last decade several successful implementations of the so-called "two-line ratio method," based on laser absorption spectroscopy either with near-infrared diode lasers [1–3] or using coherent sources of mid-infrared radiation [4]. A radically different method exploits coherent Rayleigh scattering (CRS), and it has been applied to temperature measurements in plasmas, analyzing the profile of a CRS diffusion spectrum [5]. So far, regardless of the employed optical method, precision and accuracy levels in temperature determinations only rarely have been better than 1 %.

Nevertheless, much better results can be obtained by exploiting the well-known Doppler broadening effect in laser absorption spectroscopy. In fact, Doppler broadening thermometry (DBT) has recently proved to be a very promising method of primary gas thermometry [6]. Taking advantage of the capabilities of precision laser spectroscopy, when applied to molecular vibration–rotation spectra, highly accurate observations of the absorption line shape of a given line are possible for a gaseous sample at thermodynamic equilibrium. This feature, in conjunction with the use of the most refined methods of line fitting and spectral analysis [7,8], has recently allowed performance of a spectroscopic determination of the Boltzmann constant k_B, with a relative uncertainty of 1.6×10^{-4} [9,10].

In order to improve the accuracy of the spectroscopic determination of k_B, one of the key requirements is that the interaction between the laser beam and the molecular sample takes place in an isothermal cell, back-traced to the triple point of water (TPW), with temperature stability and uniformity a few millikelvin at the TPW.

The cell used for the Italian DBT experiment of the second generation has been studied and designed to meet this requirement. For this purpose, a cylindrical shape has been adopted, both for the inner chamber, where the gas sample is contained, and for the cell itself thus limiting the radial temperature differences. The length has been defined to allow a sufficient laser path and, at the same time, to reduce the axial temperature gradient. The radius of the cell, also, has been determined to obtain a good compromise between control capabilities and thermal inertia: the stainless steel mass of the cell, therefore, helps to keep the temperature stable and make the stability control loops easy to implement. The cylindrical symmetry has also been used for all the other components of the overall system: both vacuum chambers, the inner reflector, the heater displacement, the support frames, and structures all have been studied and assembled to reduce any thermal asymmetry at a minimum.

The measurement accuracy must also be carefully defined to reduce the overall uncertainty to the same order. For this reason, temperature measurements are performed using the best instrumentation available for thermal metrology at the Italian Istituto di Ricerca Metrologica (INRiM). Capsule type standard platinum resistance thermometers (C-SPRTs) have been chosen for this experiment. An Automatic System Laboratory (ASL) F18 resistance bridge is used for both temperature measurements and control. A standard TPW cell is used to evaluate the resistance of C-SPRTs at the TPW temperature. For this experiment, the TPW cell is the same that was used in the recent K7 key comparison and that will be also compared to the other TPW

cell involved in all the other experiments and methods for the determination of k_B in Europe [11].

2 Apparatus

Due to the dimensions of the apparatuses and the temperature controls required, most of the Boltzmann experiments use a common technique to keep the temperature of the apparatuses constant and uniform. Usually, for experiments based on acoustic gas thermometry (AGT), the vessels containing the resonators are immersed in a liquid bath [12]. The same approach is also adopted for the dielectric constant gas thermometry (DCGT) experiments, using, for example, a large dimension thermostat [13]. For the French DBT experiment, an ice bath is used [6] and will also be replaced by a liquid bath. For our experiment we adopted a different solution: the cell is not immersed in a liquid bath. The overall system, schematically reproduced in Fig. 1, is based on three chambers placed one inside the other. The inner one is 15 mm diameter and 150 mm long inner chamber which is placed inside the 70 mm diameter and 150 mm long stainless steel cell.

A constantan heater wire, wound in 13 loops directly around the cell body, is used to provide a maximum of about 3 W heating power directly to the cell. This power value has been determined according to several parameters such as the thermal inertia

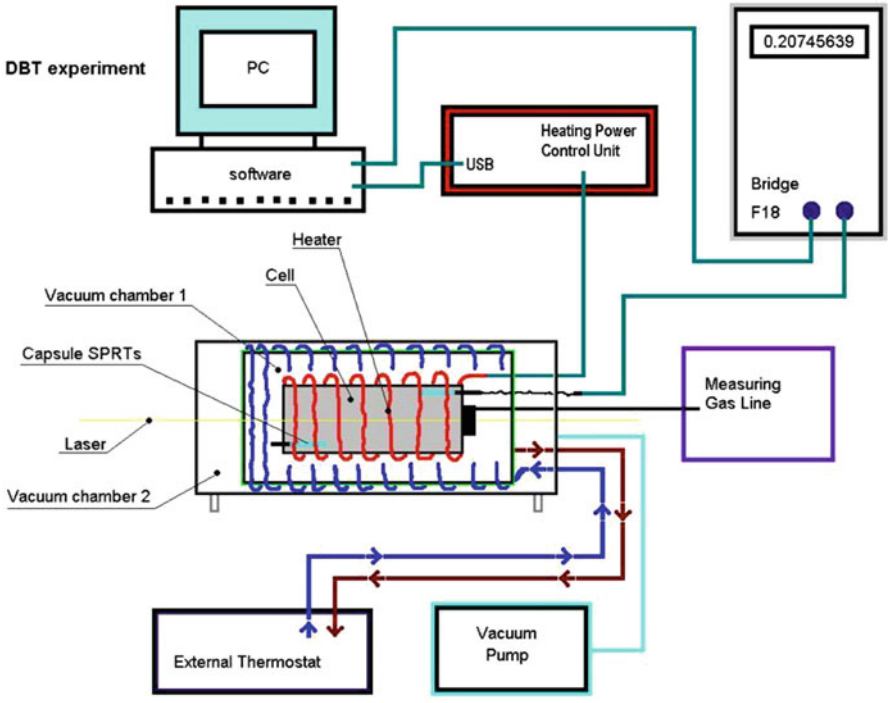

Fig. 1 Schematic view of the system

of the cell, the capabilities of the external thermostat, the loop cycle duration, heat losses, heater maximum current, etc.

The cell is suspended inside an intermediate chamber by means of purposely designed structures made from Bakelite. This structure is used to keep the cell in the horizontal position inside this second chamber and, at the same time, to reduce the heat transfer to and from the chamber and cell walls. The second chamber is a 318 mm long and 102 mm diameter stainless steel cylinder, closed at both ends by DN 100 ISO-K flanges. On the inner wall of this second chamber, a copper reflector is placed. It has two uses, since it helps to maintain good temperature axial and radial uniformity and partially reflects the irradiating heat from the heater. Twelve loops of 8 mm diameter copper tube are wound uniformly around the outer wall of this central secondary chamber; good thermal contact is guaranteed by a layer of tin used to mechanically weld the copper tube to the stainless steel outer wall of the chamber. An external commercial thermostat, Polyscience Model 9712 (range −40 °C to 200 °C), is used to keep the temperature of the intermediate chamber close to the selected value. Inside this pipeline the external thermostat fluid circulates.

The second chamber is contained in the third structure. This last structure is a 213 mm diameter and 530 mm long cylinder made from stainless steel. The second chamber is suspended in this third one by means of another specially designed structure made of Plexiglas rods and hangers, as shown in Fig. 2. Again the requirements are the mechanical stability and reduced thermal exchange to the outer wall of the third chamber. The external chamber has a couple of positioning frames use to keep the whole apparatus on the optical table.

The inner chamber hosting the gas sample has an independent gas line that passes through a series of thin wall tubes and pressure line connectors until exiting from the external chamber where the vacuum is controlled and the gas sample injected. A

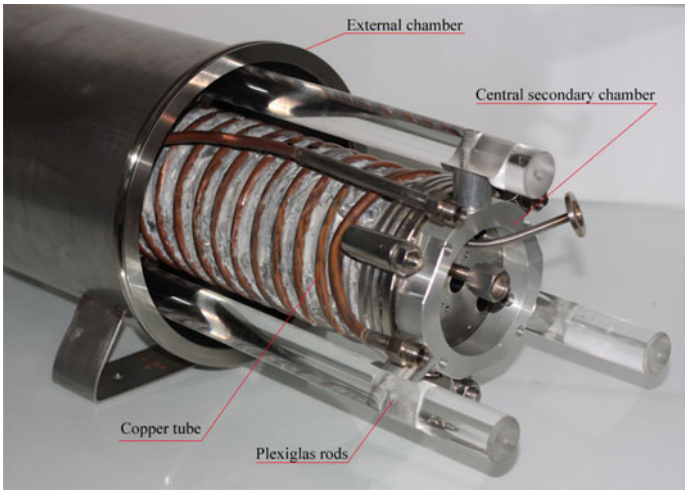

Fig. 2 Photograph of the second chamber while half-inserted in the external third chamber; the hanging rods and the copper pipeline for the external thermostat are shown. The cell is contained inside

separate vacuum line is used to avoid moisture inside the chambers that causes freezing on the structures and on the optical windows.

Two thermometer wells have been drilled 120 mm deep directly in the cell body, on the front and the rear sides of the cell with a displacement of 180 ° between them. They host the two capsule-type SPRTs, Hart Scientific Model 5686, designated HS118 and HS175 used to perform both the temperature control and measurements. They are 25 Ω thermometers with a 18 mm long sensor in a glass sheath of 5.5 mm diameter and 55 mm length. These dimensions allow the entire SPRT to be encased in the cell front and rear ends. The HS118 has been positioned on the front of the cell, and the HS175 on the rear. The resulting displacement of the SPRT sensing elements allows evaluation of the maximum temperature gradient, since they are positioned in both radial and axially opposite positions, at both ends of the cell.

Dedicated electronics has been studied and assembled at INRiM for this application. Very briefly, it consists of a power supply driven by a BJT transistor that receives a TTL signal from a USB card connected to a computer. The voltage supplied to the heater by this system is shown on a liquid crystal screen and can be manually adjusted for fine control or quick temperature changes.

A Visual Basic code has been developed for both temperature measurements and control. In particular, the software allows manual heating, bridge reading and data saving, and automatic temperature control, acquisition or temperature changes.

3 Temperature Control

The temperature control is achieved by means of a combination of cryogenic and contact thermometry techniques. The stability is obtained by using two independent control stages: an auxiliary thermostat and fine heating control. Coarse temperature control is provided by the circulation in the heat exchanger helical tube placed in contact with the second chamber external wall of a fluid supplied by the external commercial liquid bath.

The thermostat is programmed to maintain the temperature of the fluid at a set point approximately 0.1 K below the target cell temperature. This temperature difference is due to the capabilities of the thermostat that can keep the cell temperature stable on the order of a tenth of a kelvin, as reported in Fig. 3.

The difference between the targeted temperature set point and the external thermostat set point has to be larger than the temperature fluctuations of the thermostat. At the same time, this difference must not be too high which would require an excessive current for fine control, causing sawtooth-type instability. Moreover, an excessive temperature difference could also originate strong parasitic heat fluxes, from the heater to the copper pipes, thus degrading the temperature uniformity of the cell.

The fine control is achieved by carefully heating the cell containing the inner chamber with the gas sample. The DC voltage of the power supplied to the heater can be varied between 9 V and 23 V corresponding to a power ranging from 0.43 W to 2.97 W. The limiting values have been selected to obtain a minimum effect for the lower limit and a non-excessive current for the higher. The lower the voltage supplied, the finer the control achieved, but for temperature change tests, a higher voltage can be used.

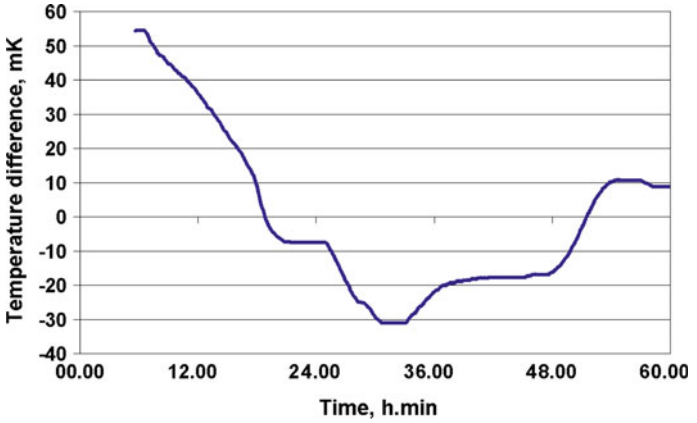

Fig. 3 Cell temperature fluctuations using only the external auxiliary thermostat

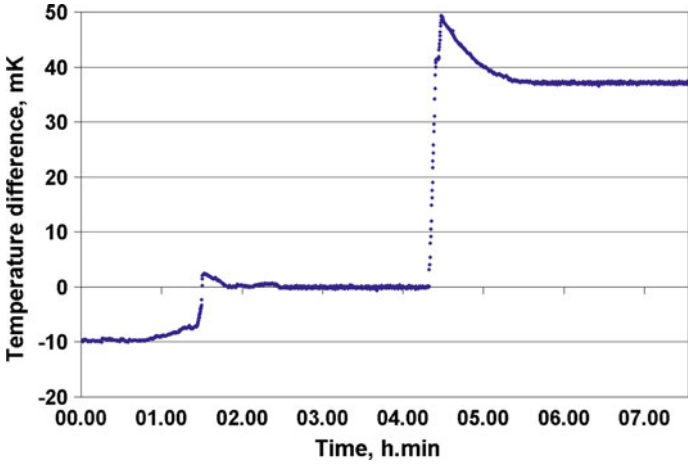

Fig. 4 Automatic temperature changes

Indeed, in Fig. 4, we report an example of two successive stabilization tests where the power supplied to the heater was at minimum and maximum allowed values. In particular, in the first test, we decided to set the power supply to its minimum voltage to stabilize the temperature after a small temperature step (less than 10 mK). In the second test, the power supply voltage was set to 23 V to obtain a temperature jump of about 40 mK.

The control loop is based on a 55 s reading-controlling cycle. This interval has been decided after several tests and considering the thermal response of the cell due to its mass. The feedback loop is based on the reading of one of the two C-SPRTs connected to the F18 bridge. The thermometer time constant is very small, and so its effects are assumed to be negligible. The software reads the resistance ratio values from the F18 and determines the time the power has to be supplied to the heater by means of a pro-

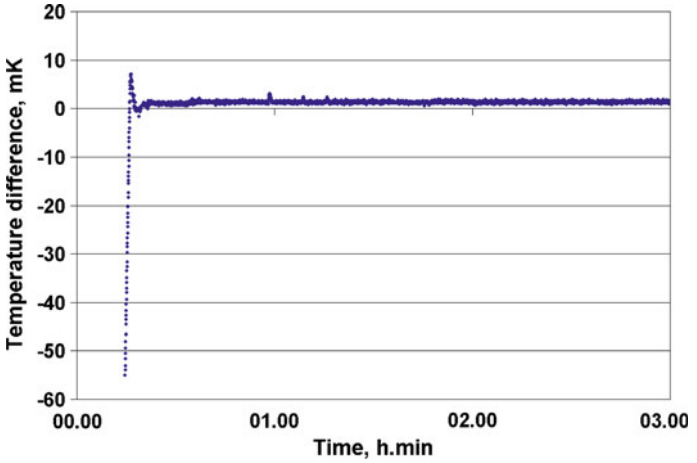

Fig. 5 Automatic set-point achievement and control

portional algorithm. The proportional system was found to be a satisfactory method to obtain a temperature stability well within the value required for the experiment. When the operator decides the set point, the system automatically starts to evaluate the heating periods to increase the temperature from the floating conditions due to the auxiliary thermostat control, to the fine control. It takes a few minutes to reach the best control capabilities as shown in Fig. 5.

4 Temperature Measurements

A first characterization campaign has been performed at INRiM using an F18 resistance bridge and the standard resistor. The thermometers involved in the k_B experiments do not have to be "calibrated" in the usual sense of this concept. They have to be considered a transfer standard from the thermodynamic temperature of the TPW to the temperature of the device used to determine k_B. In this case, the temperature of the gas sample inside the cell has then to be kept as close as possible to that of the TPW. The C-SPRT's resistances are thus measured at the TPW using the same cell that took part in the recent K7 key comparison and that will be also compared to the other TPW cell involved in all the other experiments and methods for the determination of k_B in Europe. No other fixed-point cells are required for the calibration of the C-SPRTs, since the temperature values are obtained in terms of differences from that of the TPW. Since the measurand, namely, the temperature of the gas sample, is kept and controlled at a value close to that of the TPW temperature, the ITS-90 formula does not have to be applied, reducing the temperature calculation to the resistance-to-temperature ratios of the platinum used for the C-SPRT's sensing element.

The resistance of the thermometers is measured using the automatic resistance bridge, ASL F18, with a switch box unit ASL 148/158. The bridge reading is the resistance ratio of the thermometer and a reference resistance of 100 Ω calibrated at

the electromagnetic division of INRiM. The reference resistances are two standard resistors, Tinsley 5685A, placed in their temperature-controlled enclosures, Tinsley 5648. The F18 ASL bridge has an uncertainty of 0.1 ppm of the maximum ratio, a resolution of 0.1 ppm of the reference resistor, and an overall linearity of 0.08 ppm for any ratio. Personal computers control the bridges for automatic measurement, digital data recording, and for the temperature control.

The self-heating effect of the thermometers has been evaluated both during the measurements in the TPW cell and when inserted in the cell. When inserted in the TPW cell, the HS118 showed self-heating of 1.9 mK and the HS 175 of 1.6 mK, while when the C-SPRTs are positioned in the cell, they showed self-heating of 2.0 mK and 2.9 mK, respectively. Finding a similar self-heating enforces the validity of the calibration method adopted: with similar self-heating values, the uncertainty due to the correction applied for the zero current extrapolation is strongly reduced, thus increasing the accuracy of the temperature measurements.

With both C-SPRTs inserted in opposite ends of the cell, the eventual reciprocal self-heating effect has also been evaluated by changing the current in one C-SPRT and measuring the eventual resistance change in the other. No effect has been observed in both thermometers, meaning that the cell does not receive a significant temperature increase due to the measuring current passing through the C-SPRT sensing elements.

4.1 Calibration Techniques

In order to be inserted inside the fixed-point cells for calibration, each capsule thermometer is mounted inside a long stem adapting probe, made at INRiM for the specific use. A fitted copper sleeve surrounds the sensing element of the thermometer in the probe.

Due to the quartz-to-glass welding process used to manufacture the C-SPRTs, the two glass capsules are not exactly of the same shape. Therefore, two different long-stem probe adapters, one for each C-SPRT, were manufactured. Every time a C-SPRT has to be calibrated, it must be removed from the cell and mounted in its dedicated long-stem adapting probe. The first calibration has been performed while keeping the C-SPRTs connected to the same wires and feedthroughs used when they are inserted in the cell. This care was taken to evaluate eventual systematic components due to the several connections required to allow the current to pass through the three chambers. A second measurement has then been performed directly connecting the C-SPRT cables to the resistance bridge, without any connecting cable and connection. The readings showed no differences between the two configurations, with respect to the F18 resolution.

The TPW cell used to calibrate both C-SPRTs is the same that was used in the K7 comparison and that is one of the four defined as Italian national standards. This cell, coded IMGC-31, will also be used in the TPW special comparison organized inside the iMERA T1.J1.4 joint research project. The traceability to the national standard and to the other experiments involved in the determination of k_B is therefore guaranteed at the best level.

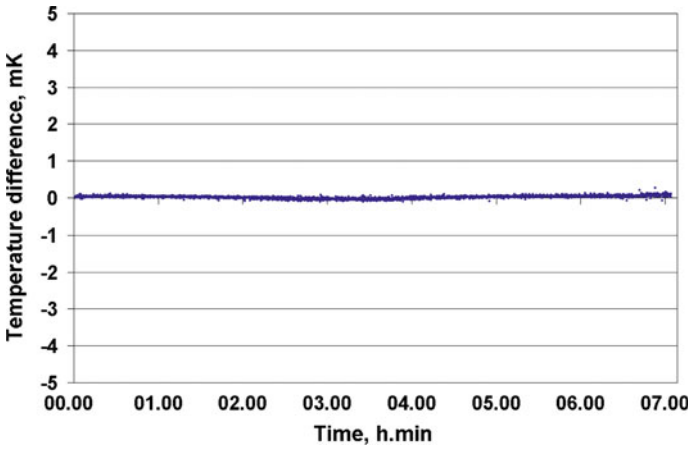

Fig. 6 Temperature stability inside the cell

4.2 Temperature Stability Evaluation

For the temperature stability evaluation, both short- and long-term evaluations have been performed. After having adjusted the control parameters and power values, the temperature has been controlled and kept stable well within 0.15 mK as reported in Fig. 6.

This behavior, free of any systematic oscillation, demonstrates that the control-loop capability is of the same order as the instrumentation resolution. The use of the C-SPRT as a controlling sensor and the F18 as a resistance reading instrument allows one to obtain such control and measurement accuracy result.

4.3 Temperature Uniformity Evaluation

The temperature gradient along the cell has been evaluated by repeating temperature readings on both C-SPRTs when satisfactory stability has been achieved. All resistance values are expressed as pure numbers as they are evaluated as ratios between the C-SPRT resistance $R(T)$ at temperature T and the resistance of the standard resistor R_s connected to the F18 bridge. Note that the resistor used for the temperature measurements in this experiment is the same as used for the C-SPRT calibrations, thus eliminating the need of accuracy in the R_s value and the value itself from the temperature calculations since its stability with time is sufficient to consider any drift negligible.

The temperature gradient ΔT is then obtained as two temperature differences from the front and rear temperatures of the cell, T_f and T_r, and the temperature of the TPW, T_{TPW}, as in the following equation:

$$\Delta T = T_f - T_r \frac{\left[\frac{R_{f0}(T)}{R_{f0}(T_{TPW})} - 1\right]}{\frac{\delta W}{\delta T}} - \frac{\left[\frac{R_{r0}(T)}{R_{r0}(T_{TPW})} - 1\right]}{\frac{\delta W}{\delta T}} \tag{1}$$

Table 1 Evaluation of the temperature uniformity of the cell

Test no	$R_{f0}(T)$	R_{f0}(TPW)	$R_{r0}(T)$	R_{r0}(TPW)	T_f (mK)	T_r (mK)	ΔT (mK)
1	0.25558913	0.25559062	0.25326126	0.25326269	−1.47	−1.42	0.05
2	0.25558924	0.25559062	0.25326136	0.25326269	−1.36	−1.32	0.04
3	0.25558942	0.25559062	0.25326154	0.25326269	−1.18	−1.14	0.04

where $R_{f0}(T)$ and $R_{r0}(T)$ are the zero current extrapolated resistances ratios, respectively, of the front (HS118) and rear (HS175) placed C-SPRTs at the cell temperature T, controlled close to that of the TPW, and $R_{f0}(T_{TPW})$ and $R_{r0}(T_{TPW})$, respectively, are the zero current extrapolated resistances ratios of the same C-SPRTs when inserted in the TPW cell. $\frac{\delta W}{\delta T}$ is the value of the resistance ratio change over a temperature change, where W denotes the ratio of the resistance value of a SPRT $R(T)$ at temperature T over the same SPRT resistance value at the TPW temperature. Since the temperature of the cell is always close to that of the TPW temperature, the temperature calculation can be performed using only the resistance change over temperature change $\frac{\delta W}{\delta T}$ for an ITS-90 SPRT.

In Table 1, we have reported the results of the three repeated tests we have performed to evaluate the temperature uniformity of the cell. Expressed as differences in millikelvin from the TPW, these results show that any temperature gradient along the cell can be completely neglected, being well below the temperature stability.

5 Conclusions

A special apparatus has been studied, designed, and assembled at INRiM to obtain satisfactory temperature control of a 150 mm long stainless steel gas absorption cell. The device is based on three chambers placed coaxially one inside the other. During the design of this apparatus, the goal was to reach a temperature stability and uniformity within 1 mK. This goal has been well satisfied, and the Italian experiment can now have a cell controlled within a few tenths of a millikelvin for an indefinite time, showing a temperature uniformity well within 0.1 mK. The accuracy of the measurements is obtained using two C-SPRTs inserted in the front and rear sides of the cell and calibrated with the national TPW cell, to reduce any uncertainty due to the traceability chain. The system has been integrated in a complex laser-based apparatus to determine the Boltzmann constant by means of precision molecular spectroscopy in water vapor. A detailed description of this experiment would be beyond the aims of the present article, so here, we will be limiting ourselves to highlighting the most important features that should allow us to approach the ppm target accuracy in the k_B determination. Very briefly, the water spectrometer is based on a reference extended-cavity diode laser (master laser), frequency stabilized against the saturated absorption of a vibration–rotation line of $H_2^{17}O$ at 1384.5919 nm. A second extended-cavity diode laser (slave laser) is offset-frequency locked to the master one and probes a vibration–rotation line of $H_2^{18}O$ at 1384.6008 nm in a ^{18}O-enriched water sample. This latter is contained in the developed isothermal cell and temperature stabilized to the TPW.

In the near future, a final characterization of the temperature control capabilities will be performed with all of the experiments in operation. The complete uncertainty budget on temperature measurement will then be evaluated.

The results achieved and presented here fully satisfy the requirement of the experiment and what is expected for the iMERA T1.J1.4 4.4 and 4.3 deliverables.

References

1. M.P. Arroyo, R.K. Hanson, Appl. Opt. **32**, 6104 (1993)
2. M.P. Arroyo, T.P. Birbeck, D.S. Baer, R.K. Hanson, Opt. Lett. **19**, 1091 (1994)
3. D.S. Baer, R.K. Hanson, M.E. Newfield, N.K.J.M. Gopaul, Opt. Lett. **19**, 1900 (1994)
4. R. Wehr, E. McKernan, A. Vitcu, R. Ciurylo, J.R. Drummond, Appl. Opt. **42**, 6595 (2003)
5. X. Pan, P.F. Barker, A. Meschanov, J.H. Grinstead, M.N. Shneider, R.B. Miles, Opt. Lett. **27**, 161 (2002)
6. C. Daussy, M. Guinet, A. Amy-Klein, K. Djerroud, Y. Hermier, S. Briaudeau, Ch.J. Bordé, C. Chardonnet, Phys Rev. Lett **98**, 250801 (2008)
7. R. Ciurylo, Phys. Rev. A **58**, 1029 (1998)
8. G. Casa, R. Wehr, A. Castrillo, E. Fasci, L. Gianfrani, J. Chem. Phys. **130**, 184306 (2009)
9. G. Casa, A. Castrillo, G. Galzerano, R. Wehr, A. Merlone, D. Di Serafino, P. Laporta, L. Gianfrani, Phys. Rev. Lett. **100**, 200801 (2008)
10. A. Castrillo, G. Casa, A. Merlone, G. Galzerano, P. Laporta, L. Gianfrani, C. R. Phys. **10**, 894 (2009)
11. A. Peruzzi, R. Bosma, O. Kerkhof, R. Peter, M.D. Campo Maldonado, M. Smid, D. Zvizdic, M.B. Nielsen, M. Anagnostou, E. Grudnewicz, M. Nedea, P.P.M. Steur, E. Filipe, I. Lobo, I. Antonsen, E. Renaot, T. Weckstrom, J. Bojkovski, E. Turzó-András, M. White, E. Tegeler, M. Dobre, J. Ranostaj, A. Kartal Dogan, V. Augevicius, A. Pokhodun, S. Simic, Metrologia **46**(1A), 03001 (2009)
12. G. Benedetto, R.M. Gavioso, R. Spagnolo, P. Marcarino, A. Merlone, Metrologia **41**, 74 (2004)
13. A. Merlone, F. Moro, T. Zandt, C. Gaiser, B. Fellmuth, Int. J. Thermophys. doi:10.1007/s10765-010-0708-x