Director's Report on the Activity and Management of the International Bureau of Weights and Measures

Supplement: scientific Departments

(1 January 2014 – 31 December 2014)

March 2015

Bureau International des Poids et Mesures

BIPM Mass Department

Interim Director: M. Stock[1]

(1 January 2014 to 31 December 2014)

1. Measurement services

1.1 Calibrations

1.1.1 Extraordinary calibrations with respect to the IPK in anticipation of the redefinition of the kilogram (P. Barat, M. Milton, E. de Mirandés, M. Stock)

In December 2013 the Mass Department started a campaign of calibrations with respect to the International Prototype of the Kilogram (IPK) in anticipation of the planned redefinition of the kilogram (*Extraordinary Calibrations*). This campaign will meet one of the prerequisites for the redefinition of the kilogram requested by the Consultative Committee for Mass and Related Quantities (CCM). It will enable the mass standards used in the watt balance and X-ray crystal density (XRCD) experiments, which will contribute to fixing the numerical value of the Planck constant, to be compared as directly as possible with the IPK. This is essential to ensure continuity from the present definition of the kilogram (based on the IPK) to the future definition (based on the numerical value of the Planck constant). Another objective of this campaign is to recalibrate the BIPM reference and working standards with respect to the IPK. At the beginning of this campaign, the traceability of the BIPM working standards to the IPK depended on measurements made in the context of the 3rd Periodic Verification (3rd PV) of National Prototypes, carried out from 1988 to 1992.

In the first phase of the Extraordinary Calibrations, the six official copies of the IPK and the BIPM working standards have been compared with the IPK for the first time since the 3rd PV. The definition of the kilogram was realized according to the procedure outlined in the 8th Edition of the SI Brochure. Thus, the IPK and its six official copies have been cleaned and washed following the BIPM procedure. The cleaning of the IPK resulted in a mass loss of 17 µg, after 22 years since the last cleaning and washing. The average mass loss of the six official copies was 15 µg, with the individual mass losses ranging from 13 µg to 17 µg.

The differences in mass between the IPK and the official copies, after cleaning and washing, have changed on average by only 1 µg since the 3rd PV. These results do not confirm the trend for the masses of the six official copies to diverge from the mass of the IPK that was observed during the 2nd and 3rd PVs. In the present calibration campaign, the IPK and its six official copies have behaved as a consistent set of mass standards. During the same period prototype n° 34 of the French Academy of Sciences, which had not been used since the 3rd PV, was calibrated. Its mass was found to be 1 µg lower than its mass observed during the 3rd PV.

All BIPM working standards have been calibrated with respect to the IPK and they were all found to have lower masses than when they were calibrated during the 3rd PV. As a consequence, the BIPM 'as-maintained' mass unit has been found to be offset by 35 µg with respect to the IPK. Mass calibrations based on the 'as-maintained' BIPM mass unit resulted in values which were 35 µg higher than those based on the IPK.

To understand how the offset of 35 µg in 2014 has evolved over time, extensive mathematical modelling has been carried out. The results of all mass comparisons between the BIPM working standards that were carried out between the 3rd PV and now have been used as input data. Different deterministic models were tested against these data and we have identified the model that describes the data most satisfactorily. The phenomena included in this model are: the mass increase of a standard after cleaning and washing, and mass changes proportional to the number of weighings in the two comparators used most often during this time. As a consequence of this, it is

[1] A. Picard (Director of the Mass Department) was absent in 2014 due to ill health

planned that the BIPM's mass comparators will be investigated for eventual anomalous wear. As boundary conditions, the model assumes that the mass of the IPK was exactly 1 kg after cleaning and washing in 1992 and in 2014. This model allows retrospective calculation of revised mass values for previous calibrations. The correction is below 5 µg for calibrations carried out before 2003. The correction increases up to about 35 µg in 2010 and remains constant during the following years. The uncertainty of the revised mass values has been estimated as 3 µg. The NMIs involved in accurate determinations of the Planck or the Avogadro constant have been informed of the revised mass values for previous mass calibrations. This has allowed them to recalculate their results, where the effect of the correction was significant, and to submit revised values for the 2015 CODATA fundamental constants adjustment.

During the second phase of the *Extraordinary Calibrations,* transfer standards from NMIs involved in determinations of the Planck or the Avogadro constant, will be calibrated (see section 1.1.2).

The results of this calibration campaign have been discussed with a Support Group of mass experts, which was set up by the CCM. The results will be presented and discussed in detail at the CCM meeting in February 2015. Following this meeting, all mass calibration customers will be informed of the results.

1.1.2 *Calibration of 1 kg Pt-Ir prototypes and stainless steel standards* (P. Barat)

The mission of the BIPM is to ensure and promote the global comparability of measurements. In the field of mass measurements, the Mass Department is in charge of providing mass calibrations to Member States that are traceable to the IPK.

Since the 3rd Periodic Verification of the National Prototypes of the Kilogram (1988-1992), the mass unit of the BIPM was maintained by means of the BIPM working standards in platinum-iridium, which were directly calibrated with respect to the IPK in 1992.

The establishment of improved traceability to the International System of Units (SI) by making use of the IPK is considered to be an essential step toward the planned redefinition of the kilogram by the CCM. The BIPM therefore started with the first phase of the "Extraordinary calibrations with respect to the IPK for the redefinition of the kilogram" in December 2013 (see section 1.1.1).

Under the framework of the extraordinary calibrations only a selection of 1 kg mass standards, used by NMIs that contribute to the redefinition of the kilogram, could be calibrated as close as possible with respect to the IPK. These NMIs are: LNE (France), METAS (Switzerland), MSL (New Zealand), NIM (China), NIST (USA), NMIJ/AIST (Japan), NRC (Canada) and PTB (Germany). The extraordinary calibrations of the 1 kg mass standards belonging to these NMIs, for a total of eleven standards, started in December 2014 and will be completed in January 2015, except for one standard which is expected to arrive at the BIPM at the end of January.

To ensure the global comparability of mass measurements, the BIPM provides 1 kg mass prototypes to Member States. During 2014 five new 1 kg mass prototypes, which were manufactured at the BIPM in 2013, have been calibrated: Nos. 102, 104 and 105 for the NIST, No. 106 for the NRC and No. 103 for the BIPM. Prototype No. 12 of the Russian Federation has been recalibrated. The calibration of the prototype No. 93, reallocated to Saudi Arabia (SASO), is also ongoing and will be completed in early 2015.

The Mass Department has issued certificates for the calibration of stainless steel standards from the LATU (Uruguay), the IPQ (Portugal) and the VSL (The Netherlands).

1.1.3 *Air-to-vacuum transfer characterizations* (P. Barat)

The realization of the new kilogram definition by watt balance or x-ray crystal density experiments must be made under vacuum. As a consequence, the laboratories involved in these experiments are required to evaluate the amount of water desorbed from the test artefacts when they are transferred from air to vacuum. The amount of desorbed water can be deduced using sorption artefacts composed of one 1 kg mass prototype (a cylinder) and one 1 kg stack of discs made of the same material.

The BIPM has provided the NIST and the NRC with such artefacts made of platinum-iridium:

- for the NRC: a new stack of discs (F18) with one of the new prototypes (No. 106) fabricated in 2013.
- for the NIST: an already existing stack of discs (C18) and two of the three new prototypes belonging to the NIST and fabricated in 2013 (Nos. 104 and 105).

The BIPM has characterized the mass changes following air-to-vacuum transfers of these five artefacts.

1.1.3 *Mass determinations of the AVO28 spheres* (P. Barat, M. Stock)

In order to reduce the uncertainty of the Avogadro constant (and of the Planck constant which can be derived from it), the Avogadro consortium is carrying out a new determination with the re-polished spheres AVO28-S5 and AVO28-S8, made of isotopically pure ^{28}Si, and an improved apparatus for the determination of the other parameters. The BIPM is responsible for coordinating the determination of the sphere masses, which is being carried out at the BIPM, the NMIJ and the PTB.

All measurements at the BIPM were carried out using the Sartorius CCL 1007 mass comparator. Before weighing, the two spheres were cleaned three times, using the cleaning procedure that was recommended by the National Metrology Institute of Australia (NMIA). A set of air buoyancy artefacts made of stainless steel, consisting of a tube (Cp) and a hollow cylinder (Cc), was used to determine the air density, for the buoyancy correction. A set of sorption artefacts made of Pt-Ir, consisting of a cylinder (A0) and a stack of 8 disks (A18), was used to establish the link between masses in air and vacuum. The masses in air were determined during three periods from 18 February to 18 March 2014, with weighings made in-between in vacuum. The relative humidity during the measurements in air was 45 % on average. The vacuum pressure was 2 mPa. After each change of condition, a period of at least 3 days was allowed for stabilization before the start of the measurements.

The two spheres were weighed directly after the first phase of the Extraordinary Calibrations. The spheres were compared in air with BIPM working standard No. 77, which itself had been weighed against working standards Nos. 91 and 650. The latter two working standards had been compared directly with the IPK, in air. The values for the masses under vacuum determined by the three institutes agree well within the uncertainties. The weighted mean has an uncertainty of 3.5 µg, corresponding to a relative uncertainty of 3.5 parts in 10^9. A publication on the new determination of the Avogadro constant has been submitted by the consortium.

The NMIs contributing to the mass determinations of the ^{28}Si spheres used for the previous determination of the Avogadro constant in 2011 have been informed of the estimated offsets of the 'as-maintained' BIPM mass unit at the time of their previous BIPM mass calibrations. This has allowed them to calculate revised sphere masses, which are required for a revised value of the Avogadro constant. The revised result of the previous determination has been included in the new publication.

A study was undertaken at the BIPM to determine the mass of the chemisorbed water layer present on the surface of a natural silicon sphere. Two methods were applied: baking the sphere under vacuum and immersing the sphere in bi-distilled water. For both methods, the chemical adsorption coefficient was obtained by determining the mass difference under vacuum conditions (to reduce the uncertainty) prior to and after placing the sphere in air, in order to reintroduce the chemisorbed water on the surface of the sphere. The mean chemical adsorption coefficient thus obtained was 0.026 µg cm^{-2} with a standard uncertainty (k = 1) of 0.012 µg cm^{-2}. The BIPM results confirm those obtained by the NMIJ/AIST (Japan) which had measured the adsorption isotherms on SiO_2/Si(100) plane surfaces.

1.1.3 Mass determinations for the BIPM Ensemble of Reference Mass Standards (P. Barat)

The four prototypes which are part of the BIPM Ensemble of Reference Mass Standards have been calibrated in the framework of the extraordinary calibrations (section 1.1.1). Their masses are now linked as closely as possible to the IPK.

The calibration of the 1 kg mass standards in stainless steel will be carried out in early 2015 as soon as the calibration of the selected NMI standards is completed (1.1.2).

1.1.4 Volume calibrations of mass standards (D. Bautista[2], H. Fang, C. Goyon-Taillade[3])

A newly hired technician, Mr Bautista, was trained by Dr Fang in the density and volume determination of mass standards ranging from 200 g to 1 kg, including mass prototypes. This training was validated by the density determination of a 1.02 kg platinum-iridium cylinder (JM57), which was used as travelling density standard for a bilateral comparison with the PTB in 2009. The difference between the new determination and the one carried out during the previous comparison is consistent, at the 95 % level of confidence with the uncertainties, and proves the validity of our new measurements. Density determinations of three new 1 kg prototypes have been carried out.

Mr Bautista has taken over the ongoing work to improve the hydrostatic weighing facility. The aim is to replace distilled water as the density reference with two 500 g cylinders of single-crystal silicon in a transfer liquid (Fluorinert Electronic Liquid FC40). The use of this liquid instead of water should lead to a significant simplification in the determination of the density of "stacks", made up of several disks separated by spacers. These stacks play an important role in the air-to-vacuum transfer process, which is needed for the future realizations of the kilogram (section 1.1.3). To this end, and with a view to reducing operator interventions, modifications have been made to the control and data acquisition software.

1.1.5 Pressure calibrations (F. Idrees)

Calibrations of BIPM manometers, with respect to the pressure balance maintained by the Mass Department, were carried out during two campaigns in 2014. Sixteen internal certificates were issued.

1.2 Comparisons (P. Barat, A. Picard[4], M. Stock, S. Davidson[5])

The BIPM has piloted the key comparison of stainless steel 1 kg mass standards, CCM.M-K4. The final report was published in the BIPM key comparison database (KCDB) in 2014. This comparison had 16 participants, each of which had to measure two 1 kg mass standards. The measurements were made between August 2011 and May 2012. The stability of the mass standards was monitored by the BIPM. The key comparison reference value was calculated by a General Linear Least Squares method. The result obtained by one participant was considered to be an outlier, all other results agree within their uncertainties.

The BIPM will act as the pilot laboratory for the planned pilot study of primary realizations of the kilogram. The purpose of this comparison is to check the realization and the dissemination of the new kilogram, as described in the *mise en pratique* for the definition of the kilogram. A draft technical protocol was developed during the secondment of Dr Davidson (NPL).

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[2] Since 1 July 2014
[3] Until 28 February 2014
[4] A. Picard was absent in 2014 due to ill health
[5] On secondment from NPL (16 June – 25 July, 22 September – 31 October 2014)

1.3 Maintenance of the mass comparators (P. Barat)

In cooperation with the BIPM workshop, some improvements have been made to the Vacuum Transfer System (VTS) which equips the Sartorius CCL1007 mass comparator. The hanging system that allows the bell of the containers to be attached has been completely modified. The transfer of standards from BIPM containers, manufactured for the Ensemble of Reference Mass Standards (ERMS), and those made by Sartorius for the VTS can now be carried out securely for both types of container.

2. **Manufacturing 1 kg artefacts in Pt-Ir for NMIs** (F. Boyer - BIPM Workshop, P. Barat)

Three new 1 kg mass prototypes are being manufactured at the BIPM: one for Pakistan and two that have yet to be allocated.

3. **Ensemble of Reference Mass Standards** (P. Barat, F. Idrees and E. de Mirandés)

In 2014, work on the BIPM Ensemble of Reference Mass Standards focused on daily maintenance and data analysis. No major development work has been carried out due to the high work load that the Extraordinary Calibrations involving the IPK has imposed on the staff responsible for the ensemble. It is expected that the activities related to the ensemble will resume in 2015.

4. **Watt balance** (F. Bielsa[6], R. Chayramy, A. Dupire, H. Fang, A. Kiss, T. Lavergne, Y. Lu[7], E. de Mirandés, L. Robertsson, S. Solve and M. Stock)

A watt balance is being developed at the BIPM to enable the realization of the expected new definition of the kilogram in terms of the Planck constant. Preparations are under way for a new version of the apparatus with the objective of reducing measurement uncertainties, in particular the type B uncertainty due to misalignment. The new apparatus will comprise several new and improved measurement facilities.

Some elements of the new apparatus have already been assembled for testing *in situ*, most importantly a dynamic alignment mechanism that is based on four pairs of push-pull piezo-elements. The mechanism allows dynamic correction of the coil trajectory during its travel whilst in working mode. It also helps to align the coil with respect to the magnetic field. The performance of the system has been successfully validated under real working conditions. All five undesirable degrees of freedom of the coil (horizontal translations in two directions and rotations around all three axes) were servo-controlled via a closed loop. The rotation around the vertical axis was controlled by means of electrostatic actuators. The horizontal translation of the freely moving coil of up to 120 µm was reduced to almost zero, with some residual deviations up to 10 µm due to the low bandwidth of the servo-control loop below one hertz. Concerning the rotation, a small deviation of 15 µrad was corrected and the residual noise was of a few µrad. A second method is based on a correction of the coil trajectory which is deduced from the highly reproducible coil motion. This method avoids problems due to oscillations, a characteristic of closed-loop operation, and is easier to operate. The noise from the feedback was thus minimized and the remaining noise was limited by electric and vibrational noise intrinsic to the system. Additional modifications to further facilitate the operation and improve the reliability of the system are anticipated.

Alignment techniques for the coil and the magnetic field continue to be refined. A new optical bench has been designed and prepared to improve the alignment accuracy of 150 µrad achieved so far on a test coil. This consists of two spatially separated alignment systems which allow the alignment the two orthogonal axes of the coil at the same location, inside the uniaxial magnetic field produced by a horizontally aligned precision solenoid. The coil, once horizontally aligned, will allow the alignment of the magnetic field of the watt balance

[6] Since 15 July 2014
[7] On secondment from NIM, China, since 1 September 2014

magnet. In parallel, a new method based on a rotating Hall probe has been developed to independently align the magnetic field. The technique consists of the alignment of the magnetic field orthogonally to a Hall probe, vertically aligned, at several locations inside the air gap of the magnetic circuit. The vertical reference is the axis of a rotation stage, which is aligned vertically by means of a tiltmeter. The directional Hall probe is mounted on the axis of the rotating stage so that it rotates around itself at each chosen location in the air gap of the magnetic circuit. The probe output as a function of the rotation angle is mainly composed of a sum of harmonics. The DC component represents the tilt of the magnetic field. The first harmonic contains information about the misalignment of the probe. Higher order harmonics are due to parasitic effects such as the planar Hall effect and default of centring of the probe. In practice, careful alignment of the probe is required in order to reduce any bias due to these unwanted effects. Measurements carried out on the simple magnetic circuit used for the first version of the watt balance showed an alignment resolution better than 50 µrad. The technique will soon be applied on the definitive magnetic circuit. To adapt the alignment set-up on this magnet, various mechanical support components and adjustable mounts have been designed. It is expected that the results obtained by both alignment methods will be compared.

The BIPM watt balance experiment requires the simultaneous operation of two Josephson voltage standards (JVSs), one for the measurement of the induced voltage and one for the measurement of the current. A new 1 V SNS programmable array for the voltage measurement was delivered by NIST in June 2014 to replace a previous chip for which the array carrier (NIST *flexboard*) was damaged as a consequence of it undergoing too many temperature cycles between liquid He temperature and laboratory temperature. This array is based on a newly designed board and will be tested in the future. The development work has focused on the assembly and testing of the JVS dedicated to the measurement of the current. Once assembled, the JVS was compared to the BIPM JVS primary reference maintained in the Electricity Department and a relative voltage difference of a few parts in 10^{11} was achieved. As a second step, the capabilities of the JVS in operation were investigated: it was connected in series opposition to a resistor coupled to commercial current source, simulating its use in the watt balance. The system produced very satisfactory results and was transferred to the watt balance laboratory for the final validation step (more details are available in the Electricity Department report). The JVS was successfully tested on the watt balance apparatus. The short-term noise of the current source could be evaluated as 50 nV (using a digital voltmeter with an integration time of 4 s). This noise includes a significant contribution from the digital voltmeter. Further tests will allow the assignment of a numeric value to each contribution.

Development of a new interferometer has advanced well. It has been carefully designed to allow for a small non-linear error, high signal-to-noise ratio and high phase resolution. The new interferometer is based on space-separated heterodyning techniques. It uses non-polarizing elements and has a minimal number of optical surfaces. The interferometer signals are differential outputs with a “common mode” reference signal. The laser source is based on a commercial Nd:YAG laser with a useful power of at least 35 mW at a wavelength of 532 nm. The frequency of this laser has been stabilized on a hyperfine-line of iodine by the saturated absorption technique. The whole set-up is installed on a portable optical table for easy implementation. Three outputs via optical fibres are used, two to feed light into the interferometers and one for the calibration of the laser frequency. The mounting and alignment of the optical set-up of three interferometers is being tested. Set-ups for signal conditioning and phase detection are in progress.

A new support structure for the watt balance has been designed in order to facilitate the alignment of the apparatus. The new structure has an open design that allows easy access to all key components of the watt balance. In addition to being rigid and stable for a total load of around 50 kg, the new structure has been designed to avoid low frequency resonance peaks, especially at frequencies present in the environment. It is composed of three stages of a symmetric pentapod structure. Finite elements analysis showed that only three eigenfrequencies below 200 Hz exist for the new support structure, compared to five frequencies in the present one. A new compact mass loading and exchange system has been designed in order to make space for the installation and alignment of the interferometers. The mechanism is based largely on a translation arm which can move horizontally and vertically. The loading of the test mass on the weighing pan is ensured by the vertical motion of the translation arm, while the transfer between the weighing pan and the mass storage carrousel is done by combing both horizontal and vertical motions. Both the new support structure and the new mass exchanger are being fabricated. The two lower stages of the new structure will allow the installation of the mechanical set-up for the alignment of the magnetic circuit.

7. Activities related to the work of Consultative Committees (R. Davis and A. Picard[8])

A. Picard is Executive Secretary of the CCM (until the end of 2014) and the Consultative Committee for Thermometry (CCT) and is a member of several working groups (WGs) and task groups (TGs) of these Consultative Committees (CCs).

R. Davis is the Interim Acting Executive Secretary of the CCM (until the end of 2014) and has provided support to the new CCM President, P. Richard (METAS) since his appointment in late 2012. Of particular note, R. Davis is the co-editor with H. Bettin (PTB) of the *mise en pratique* of the (new) definition of the kilogram being drafted within the CCM. H. Fang has been nominated as Executive Secretary of the CCM from January 2015.

8. Activities related to external organizations (E. de Mirandés, M. Stock)

M. Stock acted as the BIPM liaison with the International Avogadro Coordination project, the EURAMET Technical Committee of Mass and Related Quantities (TC-M) and for the European Metrology Research Programme (EMRP) joint research projects SIB-05 (NewKILO) and SIB-03 (kNOW). On 8 October 2014 a NewKILO progress meeting was held at the BIPM.

E. de Mirandés is member of the CODATA Task Group on Fundamental Constants.

9. Publications

1. Fang H., Kiss A., Picard A., Stock M., A watt balance based on a simultaneous measurement scheme, *Metrologia*, **51**, S80-S87.
2. Fang H. *et al*., Recent progress on the BIPM watt balance, *EPJ Web of Conferences*, 2014, **77**, 00023.
3. Becerra L.O., *et al*., Final report on CCM.M-K4: Key comparison of 1 kg stainless steel mass standards, *Metrologia*, 2014, **51**, *Tech. Suppl*., 07009.
4. Davis R.S., Milton M.J.T., The assumption of the conservation of mass and its implications for present and future definitions of the kilogram and the mole, *Metrologia*, 2014, **51**(3), 169-173.
5. Fang H., Kiss A., Lavergne T., Robertsson L., de Mirandés E., Solve S., Picard A., Stock M., Update from the BIPM Watt Balance, *Proc. 2014 Conference on Precision Electromagnetic Measurements (CPEM)*, 2014, 710-711.
6. Azuma Y., Barat P., et al., An improved result on the measurement of the Avogadro constant from a 28Si crystal *Metrologia* **52** (2015) 360 –375.
7. Stock M., Barat P., Davis R., Picard A., Milton M., Calibration campaign against the International Prototype of the kilogram: Part I: comparison of the International Prototype with its official copies, *Metrologia* **52** (2015) 2010-316.
8. Barat P., Mémoire d'ingénieur Cnam, "Projet international Avogadro: Détermination de la masse de la couche d'eau chimisorbée à la surface d'une sphère en silicium naturel", 2015

[8] A. Picard was absent in 2014 due to ill health

10. Travel (conferences, lectures and presentations, visits)

M. Stock to:

- LNE, Trappes (France), 2-3 April 2014, to attend the EURAMET TC-PR meeting and to present information from the CCPR and the JCRB;
- Brno (Czech Republic), 9-11 April 2014, to attend the EMRP NewKILO project meeting and the EURAMET TC-M meeting and to present BIPM activities related to the planned kilogram redefinition;
- Rio de Janeiro (Brazil), 22-28 August 2014, to attend the CPEM conference and CCEM and CCM satellite meetings, and to present the results of the *Extraordinary Calibrations*;
- PTB, Berlin (Germany), 1 December 2014, to give a lecture on determinations of the Planck constant at a PTB seminar.

P. Barat to:

- NMIJ/AIST, Tsukuba (Japan), 26-28 March 2014, to deliver the ^{28}Si Avogadro spheres and to give a presentation about BIPM activities in mass.

R. Davis to:

- LNE, Paris (France), 31 March 2014, to participate in the mid-term review of EMRP projects funded from the 2011 SI Broader Scope call;
- NMC A*STAR (Singapore), 27-28 October 2014 for a peer review of mass calibration services and 29-30 October for consultations on wider mass issues.

H. Fang to:

- Rio de Janeiro (Brazil), 23-28 August 2014, to attend the CPEM conference and the CCEM WGkg (monitoring the kilogram) meeting, and to give two oral and one poster presentation on the BIPM watt balance.

11. Visitors

- L.F. Vitushkin, VNIIM (Russian Federation), to collect prototype No. 12 following calibration, 6 February 2014;
- H. Bettin, PTB (Germany), to deliver the ^{28}Si Avogadro spheres for mass measurements and to work on the *mise en pratique* of the (new) definition of the kilogram, 9-10 February 2014;
- D. Arneson, Professional Instruments Company (USA), and E. Marsh, Penn State University (USA), to visit the watt balance, 24 March 2014;
- M. Götz, PTB (Germany), to visit the watt balance, 3 April 2014;
- O. Zakaria, NML-SIRIM (Malaysia), to collect two 1 kg mass standards in stainless steel following calibration, 9 April 2014;
- C. Bock and M. Hirayama, METAS (Switzerland), to visit the watt balance, 15 May 2014;
- G. Tsorbatzoglou and H. Al Kaabi, ADQCC - Emirates Metrology Institute, EMI (Abu Dhabi) accompanied by J. Lüscher, Mettler-Toledo AG (Switzerland), to visit the mass laboratories and to make a presentation on their NMI, 16 May 2014;
- F. Kelly, Christ's College, Cambridge, (UK) and T. Quinn, to visit the watt balance, 21 May 2014;
- P. Taquet, President Académie des Sciences (France), to visit the watt balance, 13 June 2014;
- P. Richard, METAS (Switzerland), to discuss results of Phase 1 of the Extraordinary Calibrations and to discuss CCM matters, 25 June 2014;

- J. Bienfang, NIST (USA), to collect new mass standards, 4 July 2014;
- C. Müller-Schöll, Mettler-Toledo (Switzerland), for general discussions, 15 July 2014;
- J. Pratt, NIST (USA), to visit the watt balance, 4 September 2014;
- D. Rovera, SYRTE (France), to visit the watt balance, 25 September 2014;
- M. Borys, PTB (Germany), to deliver prototype No. 55 for phase 2 of the Extraordinary Calibrations, 7 October 2014;
- I. Rahneberg, Ilmenau University (Germany), to visit the watt balance, 8 October 2014;
- S. Mizushima, NMIJ/AIST (Japan), to deliver prototype No. 94 and 1 kg mass standard in platinum-iridium E59 for Phase 2 of the Extraordinary Calibrations, 10 October 2014;
- F. Nez, LKB (France) and F. Piquemal, LNE (France), to visit the watt balance, 3 November 2014;
- B. Wood, NRC (Canada), to visit the watt balance, 5 November 2014;
- P. Richard, METAS (Switzerland) to complete plans for next CCM meeting, 14 November 2014;
- J. Champagne, Canadian Embassy in France (Canada), to deliver prototype No. 74 for Phase 2 of the Extraordinary Calibrations, 24 November 2014;
- S. Akretche, B. Harchaoui, A. Cheblal, K. Bey Benagliz (all NAFTAL, Algeria), M. Bekhadda (Embassy, Algeria) and J-F. Lipskier (LNE) to visit the BIPM laboratories, 27 November 2014.
- K. Chesnutwood, NIST (USA), to deliver prototypes Nos. 20 and 79 for Phase 2 of the Extraordinary Calibrations, 2 December 2014;
- X. Ni and J. Wang, NIM (China), to deliver prototype No. 60 for Phase 2 of the Extraordinary Calibrations and to visit the watt balance, 3 December 2014;
- Journalists, Le Journal du Dimanche (France), to visit the watt balance, 3 December 2014;
- M. Mecke, PTB (Germany), to collect prototype No. 55 following calibration, 4 December 2014;
- P. Otal and P. Pinot, LNE (France), to deliver prototype No. 17 and 1 kg mass standard in platinum-iridium JM15 for Phase 2 of the Extraordinary Calibrations, 5 December 2014;
- X. Ni and J. Wang, NIM (China), to collect prototype No. 60 following calibration, 10 December 2014;
- J. Champagne, Canadian Embassy in France (Canada), to collect prototype No. 74 following calibration and new 1 kg mass prototype No. 106 and new 1 kg stack of discs F18, 17 December 2014;
- K. Chesnutwood, NIST (USA), to collect prototypes Nos. 20 and 79 following calibration, 19 December 2014.

BIPM Time Department

Director: E.F. Arias

(1 January 2014 to 31 December 2014)

1. International Atomic Time (TAI), Coordinated Universal Time (UTC) and Rapid UTC (UTCr)

(E.F. Arias, A. Harmegnies, Z. Jiang, H. Konaté, W. Lewandowski[1], G. Panfilo, G. Petit and L. Tisserand)

The reference time scales, International Atomic Time (TAI) and Coordinated Universal Time (UTC), are computed from data reported regularly to the BIPM by the various timing centres that maintain a local UTC; monthly results are published in *Circular T*. The UTC rapid solution (UTCr) is published every Wednesday at 18 h UTC at the latest. All information related to the publication of UTC and UTCr can be accessed at www.bipm.org/en/scientific/tai/ftp_server/introduction.html.

The *BIPM Annual Report on Time Activities for 2013*, volume 8, provides the definitive results for 2013 and is available on the BIPM website at www.bipm.org/en/bipm/tai/annual-report.html.

2. Algorithms for time scales (G. Panfilo, G. Petit, A. Harmegnies, L. Tisserand and F. Parisi[2])

The algorithm used to calculate the time scales by the Time Department is an iterative process that starts by producing a free atomic scale (*Échelle atomique libre,* EAL) from which TAI and UTC are derived. Research into time-scale algorithms is ongoing in the department, with the aim of improving the long-term stability of EAL and the accuracy of TAI.

The revision of the algorithm was completed at the start of 2014 with the official introduction of the new clock weighting algorithm in UTC. The new procedure is based on the concept of clock frequency predictability. The weight assigned to a clock reflects its predictability rather than its stability, as was the case in the previous procedure. The result is a more balanced distribution of weights between caesium clocks and hydrogen masers and enhances the influence of the hydrogen masers in the ensemble. An improvement in the short- and long-term stability of EAL is foreseen by applying the new weighting algorithm.

Work started on updating the method to evaluate the uncertainties of [$UTC\text{-}UTC(k)$] reported in Section 1 of *Circular T*. The current algorithm provides underestimated values for the pivot laboratory (currently PTB) which does not correspond to real physical values. This is due to the fact that some correlations are not taken into account.

2.1 EAL stability

Some 88 % of the clocks used in the calculation of time scales are either commercial atomic clocks with high performance caesium tubes or active hydrogen masers. A weighting procedure was developed to guarantee the long-term stability of EAL. To prevent domination of the scale by a small number of very stable clocks, a maximum relative weight is used each month which depends on the number of participating clocks. On average, about 10 % of the participating clocks were at the maximum weight during 2014; almost all of these were hydrogen masers. The total weight of hydrogen masers and caesium clocks is about 50 % while the number of these clocks in the ensemble is significantly different, about 300 caesium clocks and 100 hydrogen masers. This means that the time scale implicitly relies on the hydrogen masers in the short term and on caesium clocks in the

[1] Retired on 1 May 2014

[2] Department of Mathematics, University of Torino, Italy, on a six-month secondment from 1 November 2014

long term, which was an aim of the new weighting procedure. Both the short- and long-term stability of EAL are expected to improve by 20 %. The stability of EAL at the end of 2014, expressed in terms of an Allan deviation, is about three parts in 10^{16} for averaging times of one month. A long-interval estimation of the frequency stability of EAL after the introduction of the new weighting procedure indicates that it will decrease by up to 1.8 parts in 10^{16} over the next few years.

2.2 TAI accuracy

To characterize the accuracy of TAI, estimates are made of the relative departure, and its uncertainty, of the duration of the TAI scale interval from the SI second, as produced on the rotating geoid, by primary and secondary frequency standards. Since January 2014, individual measurements of the TAI frequency have been provided by eleven primary frequency standards, including nine caesium fountains (LNE-SYRTE FO1, LNE-SYRTE FO2, NIST F1, NIST F2, IT CSF2, SU CSFO, NPL CSF2, PTB CSF1 and PTB CSF2), and by a rubidium secondary frequency standard (LNE-SYRTE FO2Rb). Reports on the operation of the primary and secondary frequency standards are regularly published on the BIPM website and collated in the *BIPM Annual Report on Time Activities*.

Since January 2014, the global treatment of individual measurements has led to a relative departure of the duration of the TAI scale unit from the SI second on the geoid ranging from $+0.46 \times 10^{-15}$ to -0.99×10^{-15}, with a maximum standard uncertainty of 0.28×10^{-15}. No steering corrections have been applied since October 2012, demonstrating the positive impact of the new algorithms on the accuracy of TAI.

2.3 Independent atomic time scales: TT(BIPM)

TAI is computed in 'real-time' and is subject to operational constraints; as a result it does not provide an optimal realization of TT, the time coordinate of the geocentric reference system. The BIPM therefore computes an additional realization, TT(BIPM), in post-processing, which is based on a weighted average of the evaluation of the TAI frequency by the primary frequency standards. The Time Department provided an updated computation of TT(BIPM), known as TT(BIPM13), valid until December 2013, which had an estimated accuracy of about 2-3 parts in 10^{16} over recent years. Moreover, the Time Department provides a formula to extend TT(BIPM13) based on the most recent TAI computation. Such an extension is useful for pulsar analysis pending on the yearly updates of TT(BIPM). Studies to improve the computation of TT(BIPM) are ongoing, in order to keep it in line with improvements in the primary and secondary frequency standards.

2.4 Local representations of UTC in national laboratories as broadcast by the GNSS

The Time Department continues to calculate and publish the differences between the predictions of UTC(USNO) and UTC(SU) (as broadcast by GPS and GLONASS) and UTC in BIPM *Circular T*. As a consequence of the alert made by the BIPM on the offset of GLONASS time and the broadcast prediction of UTC(SU) with respect to UTC, work is under way with the VNIIFTRI, Russian Federation, and the GLONASS authorities on the absolute calibration of a BIPM receiver and the receiver at the AOS, Poland, that provides data for the offset evaluation.

3. **Primary frequency standards and secondary representations of the second** (E.F. Arias, G Panfilo, G. Petit and L. Robertsson)

Members of the BIPM Time Department actively participate in the work of the CCL-CCTF Frequency Standards Working Group (WGFS), and the Consultative Committee for Time and Frequency (CCTF) Working Group on

Primary and Secondary Frequency Standards (WGPSFS). These Working Groups seek to encourage comparisons, knowledge-sharing between laboratories, the creation of better documentation, the use of high-accuracy primary frequency standards (Cs fountains) and secondary frequency standards for TAI. In 2014, the WGPSFS reviewed four new Cs fountains that had been submitted by four different laboratories.

The WGFS maintains a list of recommended values of standard frequencies for applications including secondary representations of the second. The latest changes to the list, as recommended by the CCTF in September 2012 as secondary representations of the second have been endorsed by the CIPM in Recommendation 1(CI-2013). Work is under way to prepare the elements necessary for the revision of the list of recommended frequencies at the WGFS meeting in September 2015.

Secondary representations of the second reported in BIPM Circular T

Since January 2012 the LNE-SYRTE has reported frequency measurements of the Rb microwave transition obtained with a double Cs-Rb fountain (FO2Rb). Eight measurement reports of FO2Rb were submitted in 2014 and have been officially used for the accuracy of TAI. For the first time, FO2Rb measurements were used for the computation of TT(BIPM13) in January 2014.

4. **Time links used for UTC** (E.F. Arias, A. Harmegnies, Z. Jiang, H. Konaté, W. Lewandowski, G. Panfilo, G. Petit, L. Tisserand, A. Kanj[3] and W. Wenjun[4])

At the end of 2014, 73 time laboratories supplied data for the calculation of UTC at the BIPM. The laboratories are equipped with GNSS receivers and some of them also operate two-way satellite time and frequency transfer (TWSTFT) stations.

Data from three independent techniques are included in the process of comparison of laboratories' clocks based on tracking GPS and GLONASS satellites, and TWSTFT.

The GPS all-in-view method is widely used and takes advantage of the increasing quality of the International GNSS Service (IGS) products (clocks and IGS time). Clock comparisons are possible using C/A code measurements from GPS single-frequency receivers, or dual-frequency, multi-channel GPS geodetic-type receivers (P3). The older GPS single-channel single-frequency receivers are almost obsolete, having been replaced by either multi-channel single- or dual-frequency receivers.

The Time Department also regularly computes combined GPS/GLONASS links resulting in improved link uncertainty. About five GPS/GLONASS links are regularly computed for *Circular T*.

Fifteen TWSTFT links are officially submitted for use in the computation of UTC, representing 19 % of the time links. The combination of TWSTFT and PPP (so called TWPPP) is used whenever possible. This generally concerns about a dozen links for which the two techniques are available. This combination takes advantage of the small noise of the GPSPPP and of the accuracy of the TWSTFT links.

The GPS phase and code data provided by time laboratories which operate geodetic-type receivers is processed each month using the Precise Point Positioning (PPP) technique. The NRCan's PPP software is used for the time link calculation. The current version of the software is capable of processing both GPS and GLONASS data but only GPS results are used operationally. Comparisons with other PPP software have been carried out. Studies are continuing to improve long-term stability, using new processing techniques, in collaboration with software developers at NRCan, the *Observatoire Royal de Belgique* (ORB), the *Centre National d'Études Spatiales* (CNES) and also with other institutes. A novel PPP technique using integer phase ambiguities (IPPP) has been successfully developed within the framework of a post-doctoral project. It significantly improves the stability in the medium term (several hours) and long term (days).

[3] Post-doctoral research under a two-year BIPM-CNES contract starting on 1 January 2013
[4] Chinese Academy of Sciences, NTSC (Xi'an, China), on a one-year secondment starting 3 June 2014

GPS PPP alone or in combination with TWSTFT are in use for UTC clock comparisons in 55 % of the links, where the statistical uncertainty of time transfer is well below the nanosecond, the best value is 0.3 ns for 46 % of the time links.

Comparisons of the different possible links on a baseline linking two contributing laboratories are computed and published monthly on the Time Department's ftp server.

4.1 Global Positioning System (GPS) and Global Navigation Satellite System (GLONASS) code measurements

All GNSS time and frequency transfer data are corrected for satellite positions using IGS and European Space Agency (ESA) precise satellite ephemerides. The measurement data obtained by using single-frequency receivers are corrected for ionospheric delays using IGS maps of the total electron content of the ionosphere.

4.2 Phase and code measurements from geodetic-type receivers

Techniques that use dual-frequency, GNSS carrier-phase measurements in addition to the codes, are widely used by the geodetic community, and have been adapted to the needs of time and frequency transfer. This topic is studied within the framework of the IGS Working Group on Clock Products, which has a physicist from the Time Department as a member.

Data from world-wide geodetic-type receivers are collected for UTC computation, using procedures and software developed in collaboration with the ORB. These P3 time links are routinely computed and compared to other available techniques, notably two-way time transfer. The software producing iono-free has been implemented in some receivers, and these now automatically produce both formatted GPS and GLONASS P3 code results. These newly available data will be used in multi-GNSS system time links, but further studies on GLONASS inter-frequency biases have to be carried out first.

4.3. Two-way time transfer

Two meetings of the TWSTFT participating stations were held during 2014. The 22nd annual meeting of the CCTF WG on TWSTFT was held at the VNIIFTRI, Mendeleevo, Russian Federation, on 16-17 September 2014. The outcomes of these meetings that will have an impact on the Time Department's activities are: the organization of calibration trips between TW stations, where the BIPM is charged with the validation of the reports and introduction of the calibration parameters in the calculation of UTC, and the recommendation to elaborate a document with the guidelines for TWSTFT links. The BIPM has been invited to lead the group that is preparing the guidelines.

The TWSTFT technique is currently operational in twelve European, two North American and nine Asia-Pacific time laboratories. Fifteen TWSTFT links are routinely used in the computation of UTC; they are combined with GPS PPP solutions. The TWSTFT technique applied to clock comparisons in UTC is at its maximum potential with sessions scheduled every two hours.

Some of the TWSTFT links involved in the computation of UTC are used for particular experiments such as the Time Transfer by Laser Link (T2L2). The BIPM is interested in developing studies on this technique which could be used to validate less accurate time links and their calibrations.

The BIPM is also involved in the calibration of two-way time-transfer links by comparison with the corresponding GPS links. This is necessary to maintain the stability of the TWSTFT links in case of a loss of their direct calibration.

Campaigns with a travelling calibration station that were organized and funded by the participating laboratories in 2014, resulted in the calibration of seven TW UTC links. The parameters obtained have been implemented for UTC computation following validation of the results by the Time Department.

Results of the time links and link comparison using GNSS single-frequency, dual-frequency and TW observations are published monthly on the Time Department's ftp server (ftp://tai.bipm.org/TimeLink/LkC).

4.4 Calibration of delays of time-transfer equipment and time links

Calibration of time transfer equipment in the contributing laboratories is necessary to improve the uncertainty of [*UTC*-*UTC*(*k*)] and for the accuracy of UTC dissemination. As part of the process of maintaining UTC, the BIPM organizes and runs campaigns to measure the relative delays of GPS time equipment in participating time laboratories.

The method previously developed by the Time Department to perform absolute calibration of the Ashtech Z12-T hardware delays allows the use of this receiver in differential calibrations of the same type of receivers world-wide; calibration campaigns have continued since January 2001 and have been expanded to include other types of receivers (Septentrio PolaRx2-3-4, Dicom GTR50 and GTR51, Javad JPS E-GGD, PikTime TTS3 and TTS4). New types of receivers are being investigated in collaboration with the laboratories that use the equipment. In all cases, at least two receivers remain at the BIPM to serve as a local reference to which the travelling receivers are compared between calibration trips. Results of the differential calibration exercises are made available on a dedicated web page (www.bipm.org/jsp/en/TimeCalibrations.jsp), where past calibration results are also provided.

Based on a successful pilot experiment run by the Time Department in 2012-2013, a time transfer system consisting of two or three GNSS receivers, antennas and auxiliary equipment has been developed, together with a calibration procedure, with the aim of performing GPS time link calibrations that can be transferred to any other technique on the same baseline. The system and procedures have been validated, and the process, named METODE (MEasurement of TOtal DElay), has been used regularly in 2014 for direct calibration of GPS links, and for transferring the calibration to links between Asia and Europe.

Following a recommendation by the CCTF, the Time Department has issued the '*BIPM Guidelines for GNSS equipment calibration in UTC contributing laboratories*'. This document is intended for Regional Metrology Organizations (RMOs) and aims to establish a permanent cooperation for sharing the organization of campaigns to determine the relative delays of time transfer equipment in UTC contributing laboratories. The *Guidelines* are being continuously improved and this led to a revised edition of the *Guidelines* being produced in 2014 and the elaboration of standard processing and reporting procedures. Global processing of all measurements using METODE was carried out in 2013 and 2014, completing the measurement campaign being conducted by selected laboratories in APMP and EURAMET. Measurements are continuing in COOMET and SIM, and after the end of the BIPM campaign, regional calibration trips will be implemented in accordance with the *BIPM Guidelines*. By applying this new procedure time transfer accuracy is expected to improve by a factor of 2.

The BIPM Time Department is not directly involved in specific TWSTFT calibration trips, but is responsible for validating the calibration reports and implementing the results in the calculation of UTC. It also provides support whenever necessary to maintain a TW calibration by alignment with a calibrated GPS link (see section 4.3).

The CCTF WG on TWSTFT decided, in September 2014, to establish guidelines for TWSTFT link calibration, and appointed a task group to prepare a draft document, under the leadership of the Department. The first draft of the guidelines has been completed and is being revised before final approval by the WG.

4.5 Advanced time and frequency transfer

One of the Time Department's innovative activities in this field is related to the establishment of optical fibre links between certain laboratories which maintain local representations of UTC. A successful experiment was conducted using the BIPM GPS equipment in parallel with the optical fibre link regularly operated between two institutes that represent UTC in Poland. This experiment demonstrated excellent agreement (at the level of the GPS PPP uncertainty) between the GPS PPP link calculated with the BIPM equipment and the optical fibre link. The optical fibre link can be used to assess the calibration of a UTC link calculated with the current time transfer techniques as a result of the small (hundred picoseconds) and stable calibration uncertainty. This experiment enabled the validation of the new BIPM calibration system with u_B within 1 ns. It also allowed validation of the results of the newly developed IPPP processing technique. Several other fibre links between contributing laboratories are calculated on a regular basis and are anticipated to achieve a potential measurement uncertainty of about 100 ps in the future. In order to benefit from the quality of these links, the Time Department has initiated discussions with the laboratories that already implement time transfer via optical fibres with the aim of establishing standards for data transmission and to validate the compatibility of the different techniques.

In parallel, the Time Department continued its activities in the framework of the CCTF WG on Coordination of the Development of Advanced Time and Frequency Transfer Techniques (WGATFT), and followed the progress in the NMIs and other institutes in this field of activity.

5. **Key comparisons** (E.F. Arias, H. Konaté, Z. Jiang, W. Lewandowski, G. Panfilo, G. Petit, L. Tisserand, A. Harmegnies and L. Robertsson)

Key comparison in Time CCTF-K001.UTC

Results of the key comparison in time, CCTF-K001.UTC, involving the time laboratories participating in the CIPM MRA, are published monthly as BIPM *Circular T*.

Key comparison of stabilized lasers CCL-K11

Following a decision at the 98th meeting of the CIPM in 2009 the BIPM continues to support the CCL-K11 key comparison by participating in measurement campaigns and by providing general advice whenever solicited. This comparison is the internationally recognized traceability chain to the SI metre and is supervised by the CCL. In 2014, dialogue with the participants helped towards the development of the measurement campaigns and reporting.

6. **Rapid UTC** (A. Harmegnies, G. Panfilo, G. Petit and L. Tisserand)

Since January 2013 the Time Department has published a UTC rapid solution 'UTCr', that is, daily values of [*UTCr* – *UTC*(*k*)] evaluated on a weekly solution on one-month batches of data. About 44 laboratories traceable to UTC contribute to UTCr, together representing 60 % to 70 % of the clocks participating in UTC.

UTCr attained the expected quality, providing a weekly solution which is consistently better than ±3 ns peak to peak with the values published monthly in BIPM *Circular T*. The results (ftp://tai.bipm.org/UTCr) have been published every Wednesday, without interruption since the end of February 2012.

UTCr does not change the procedures for the monthly calculation of UTC, which remains the only key comparison on time. However, UTCr favourably impacts on the quality of the local representations UTC(k) in national laboratories, and on the steering of GNSS times to UTC via some UTC(k).

7. New proposed definition of UTC (F. Arias)

The BIPM has actively participated in discussions about a possible redefinition of UTC without leap seconds since 2000. This proposal favours systems that require precise time synchronization and does not allow a discontinuity in the time scale that they use as a reference.

BIPM delegates have had a critical role during this process at the International Telecommunication Union (ITU), and also in disseminating information and promoting decision making at the level of national representatives. In 2014 the work has focused on the preparation of the relevant documents for the World Radiocommunication Conference to be held in Geneva, Switzerland, from 2-27 November 2015 (WRC15), where a decision is to be taken on the redefinition of UTC without leap second adjustments.

8. Pulsars (G. Petit)

Collaboration continues with radioastronomy groups that observe pulsars and which analyse pulsar data to study the possibility of using millisecond pulsars as a means of sensing the very long-term stability of atomic time. The Time Department provides these groups with its post-processed realization of Terrestrial Time, TT(BIPM). Additionally it participates in a Working Group on pulsars and time scales established by the International Astronomical Union (IAU).

9. Space-time references (E.F. Arias and G. Petit)

Activities related to the realization of reference frames for astronomy and geodesy are ongoing in cooperation with the International Earth Rotation and Reference Systems Service (IERS). In these domains, improvements in accuracy will increase the need for a full relativistic treatment and it is essential to continue to participate in international working groups in this field.

Cooperation continues on the maintenance of the international celestial reference system within the framework of the activities of a working group created by the IAU in August 2012; the target is to report on the features of the next realization of the International Celestial Reference Frame (ICRF3) to the IAU General Assembly in 2015 and to provide the set of coordinates in ICRF3 in 2018.

As part of its participation in the Conventions Centre of the IERS, the BIPM maintains the web and ftp sites for the *IERS Conventions* (http://tai.bipm.org/iers/). The Conventions describe the latest realizations of the celestial and terrestrial reference frames, and the model for the transformation between them. They also describe conventional models for the gravitational field, the displacement of markers on the Earth's crust and for the propagation of electromagnetic signals. In addition, the *Conventions* now provide a complete set of associated conventional software. Since the completion of the latest reference edition, *IERS Conventions* (2010) in December 2010, work is continuing with the help of an Editorial Board to provide updates to the *Conventions* (2010) which are posted on the website (http://tai.bipm.org/iers/convupdt).

10. Comb activities (L. Robertsson)

The BIPM comb activities are limited to the maintenance of the BIPM frequency comb for internal use related to laser applications only and in other departments when needed.

11. Publications

External publications

1. Jiang Z., Total Delay and Total Uncertainty in UTC Time Link Calibration, *Proc. 45th PTTI Meeting*, 2014, 112-125.
2. Jiang Z., Lewandowski W., Evolution of the Uncertainty of [*UTC-UTC(k)*], *Proc. 45th PTTI Meeting*, 2014, 208-216.
3. Jiang Z., Accurate time link calibration for UTC time transfer - Status of the BIPM pilot study on the UTC time link calibration, *Proc. 28th European Frequency and Time Forum*, 2014.
4. Jiang Z., Tisserand L., Stability of the BIPM GNSS travelling calibrator, *Proc. 28th European Frequency and Time Forum*, 2014.
5. Jiang Z., Czubla A., Nawrocki J., Nogaś P., (2014) Calibration comparison between optical fiber and GPS time links, *Proc. ION/PTTI2014*.
6. Jiang Z., Lewandowski W., An Approach to the Uncertainty Estimation of [UTC-UTC(*k*)], *Proc. ION/PTTI2014*.
7. Konaté H., Arias E.F., The BIPM Time Department Database, *Proc. 45th PTTI Meeting*, 2014, 1-13.
8. Panfilo G., Harmegnies A., A new weighting procedure for UTC, *Metrologia*, 2014, **51**, 285-292.
9. Petit G., Arias E.F., Harmegnies A., Panfilo G., Tisserand L., UTCr: a rapid realization of UTC, *Metrologia*, 2014, **51**, 33-39.
10. Petit G., A timescale based on the world's fountain clocks, *Proc. PTTI meeting*, Bellevue, WA, December 2013.
11. Petit G., Kanj A., Harmegnies A., *et al*., GPS frequency transfer with IPPP, *Proc. 28th European Frequency and Time Forum*, 2014, 451-454,.
12. Petit G., Wolf P., Delva P., Atomic time, clocks and clock comparisons in relativistic space-time: a review, in *Frontiers of Relativistic Celestial Mechanics*, Volume 2, *Applications and Experiments*, Sergei M. Kopeikin Ed., De Gruyter, 2014, 266pp.

BIPM publications

13. *BIPM Annual Report on Time Activities for 2013*, 8, 121 pp., available only at http://www.bipm.org/en/publications/time_activities.html.
14. *Circular T* (monthly), 8 pp.
15. *Rapid UTC* (*UTCr*) (weekly), 1 pp.

12. Activities related to the work of Consultative Committees

E.F. Arias is Executive Secretary of the Consultative Committee for Time and Frequency (CCTF). She is the Secretary of the CCTF Working Group on TAI (WGTAI) and the CCTF Working Group on Strategic Planning (WGSP).

Z. Jiang is Secretary of the CCTF Working Group on TWSTFT (WGTWSTFT).

G. Panfilo is Secretary of the CCTF Working Group on the CIPM MRA (WGMRA) and the CCTF Working Group on Time Scale Algorithms (WG-ALGO).

G. Petit is Secretary of the CCTF Working Group on Primary and Secondary Frequency Standards (WGPSFS) and the Working Group on Global Navigation Satellite Systems (WGGNSS).

L. Robertsson is Executive Secretary of the Consultative Committee for Length (CCL), a member of the CCL Working Group on Strategic Planning (WG-S) and of the Discussion Group DG-11 (Lasers). He is the BIPM representative on the CCM Working Group on Gravimetry (WGG). He is also Secretary for the CCTF WG on

Coordination of the Development of Advanced Time and Frequency Transfer Techniques (WGATFT) and shares the secretariat of the CCL-CCTF Frequency Standards WG (WGFS) with E.F. Arias.

13. Activities related to external organizations

E.F. Arias is a member of the IAU and participates in its working group on the International Celestial Reference Frame (ICRF), she is vice-president of Commission 31 (Time) and co-chaired the working group on the redefinition of UTC. She is an associate member of the IERS, a member of its International Celestial Reference System Centre, and of the Conventions Centre. E.F. Arias is a member of the International VLBI Service (IVS). She is the BIPM representative to the Governing Board of the International GNSS Service (IGS). She is the BIPM representative to the UN sponsored International Committee on GNSS (ICG) and the chairperson of its Task Force on Time References. E.F. Arias is a member of the IAG Global Geodetic Observing System (GGOS) Steering Committee representing the BIPM. She is a member of the Argentine Council of Research (CONICET) and an associate astronomer at the LNE-SYRTE, Paris Observatory. She is a corresponding member of the *Bureau des longitudes* and the BIPM representative to the Working Party 7A of Study Group 7 of the International Telecommunication Union – Radiocommunication Sector (ITU-R).

G. Petit is co-director of the Conventions Centre of the IERS. He is an associate member of the IGS and member of the IGS Working Groups on Clock Products and on Bias Calibration. He is a member of the IAU Working Groups on Numerical Standards in Fundamental Astronomy and on Pulsar Time Scale.

G. Panfilo collaborates with the Joint Committee for Guides in Metrology (JCGM) Working Group 1 (WG1) on the Expression of Uncertainty in Measurement (GUM) to provide a section on uncertainty of time measurements for the new version of the GUM.

14. Travel (conferences, lectures and presentations, visits)

E.F. Arias to:

- Delft (The Netherlands), 17-18 March 2014, for a meeting of the EURAMET Time and Frequency Technical Committee;
- Paris (France), 9 April 2014, for a discussion on the IERS Conventions;
- Geneva (Switzerland), 6-14 May 2014, for the meeting of the ITU-R WP7A;
- Neuchâtel (Switzerland), 23-26 June 2014, to the 28th European Frequency and Time Forum and for the meetings of CCTF Working Groups;
- Neuchâtel (Switzerland), 27 June 2014, to the Workshop "frequency standards with trapped ions";
- Beijing (China), 18-23 August 2014, for the URSI General Assembly, and as convener of a session on UTC;
- Hendaye (France), 17 September 2014, to give a training course on Time Scales at the Chateau d'Abbadia (expenses paid by the Chateau d'Abbadia Foundation);
- Geneva (Switzerland), 30 September to 7 October 2014, for the meeting of the Working Party 7A at the ITU;
- Luxembourg, 14 October 2014, to the meeting of the IAU Working Group on the ICRF3;
- Boston (USA), 1-5 December 2014, for the 46th PTTI Meeting, as convener of a session and for the meeting of TW participating stations.

Z. Jiang to:

- Nanjing and Beijing (China), 21-28 May 2014, for the China Satellite Navigation Conference, organizing a session, for the Interoperability Workshop, for a meeting with BeiDou time experts;
- Neuchâtel (Switzerland) to the 28th European Frequency and Time Forum (giving presentations) and for the meetings of CCTF Working Groups,;
- Mendeleevo (Russian Federation), 15-16 September 2014, for the 22nd Meeting of the CCTF Working Group on TWSTFT;
- Boston (USA), 1-5 December 2014, for the 46th PTTI Meeting (giving presentations) and for the meeting of TW participating stations.

A Kanj to:

- Neuchâtel (Switzerland), 23-26 June 2014, to the 28th European Frequency and Time Forum and for the meetings of CCTF Working Groups (expenses paid by the CNES);
- Boston (USA), 1-5 December 2014 for the 46th PTTI Meeting and for the meeting of TW participating stations.

W. Lewandowski to:

- Krakow (Poland), 6-7 February 2014, for the "Industrial policy of the European Union. The Economic Weimar Triangle";
- Geneva (Switzerland), 6-14 May 2014, for the meeting of the ITU-R WP7A;
- Namur (Belgium), 19-20 May 2014, for the meeting of the ESA Programme Board on Satellite Navigation (PB-NAV);
- Nanjing and Beijing (China), 21-28 May 2014, for the China Satellite Navigation Conference, for the Interoperability Workshop, and for a meeting with BeiDou time experts.

G. Petit to:

- Toulouse (France), 16 January 2014, to visit the CNES time laboratory and for a Workshop "Precise positioning Using Carrier Phase Measurements" ;
- Paris (France), 9 April 2014, for a discussion on the IERS Conventions;
- Vienna (Austria), 27 April 2014, to participate in the IERS Directing Board;
- Paris (France), 13 June 2014, to participate in a PhD jury;
- Neuchâtel (Switzerland) 23-27 June 2014, to attend the EFTF 2014 meeting, to give an oral presentation, a CCTF WG meeting and a CCL-CCTF WG meeting;
- Besançon (France), 1-2 July 2014, to give two lectures at the European Frequency and Time Seminar;
- Luxembourg, 13-14 October 2014, to attend the REFAG 2014 workshop;
- Paris (France), 23 October 2014, to attend a CNES workshop on GRASP;
- Prague (Czech Republic), 12-14 November 2014, for the ninth meeting the International Committee on GNSS (ICG), with presentations.

G. Panfilo to:

- Rome (Italy), 8 October 2014, invited to give a presentation on the BIPM Time Department activities at the Sapienza – Università di Roma, Rome.

L. Robertsson to:

- Toulouse (France), 12 February 2014, for the "Journée peignes de fréquence optique";
- Neuchâtel (Switzerland), 23-26 June 2014, to the 28th European Frequency and Time Forum and for the meeting of four CCTF Working Groups;

- Neuchâtel (Switzerland), 27 June 2014, to the Workshop “frequency standards with trapped ions”.

W. Wenjun to:

- Neuchâtel (Switzerland), 23-26 June 2014, to the 28th European Frequency and Time Forum (to give presentations) and for the meeting of four CCTF Working Groups (expenses paid by the Chinese Academy of Sciences);
- Mendeleevo (Russian Federation), 15-16 September 2014, for the 22nd Meeting of the CCTF Working Group on TWSTFT (expenses paid by the Chinese Academy of Sciences).

15. Visitors, secondees

- A. Kanj as a post-doctoral researcher under a BIPM-CNES contract for the optimization of GNSS time transfer, 1-15 February and 1 August - 31 December 2014;
- J. Faller (JILA, USA) for a BIPM seminar and discussions on gravity measurements associated with BIPM activities, 20 March 2014;
- P. Fisk (NMIA, Australia) for discussions on the activities of the CCTF WG on TAI, 28 March 2014;
- S. Junqueira (ONRJ, Brazil) and a team from the Observatory for discussions on time transfer at ONRJ, 23 April 2014;
- W. Wu (NTSC, Chinese Academy of Sciences) on a one-year secondment starting on 3 June 2014, for activities on time transfer and calibration;
- A. Bauch (PTB, Germany) for discussions on time transfer and calibrations, 12 June 2014;
- C. Lin (TL, Chinese Taipei) for a discussion on GNSS calibrations, 1 July 2014;
- G. Garcia (INMETRO, Brazil) for discussions on the Brazilian contribution to UTC, 26 September 2014;
- F. Parisi from the University of Torino (Italy) to study an independent time scale based on the Kalman Filter, 1 November 2014 – 6 February 2015.

BIPM Electricity Department

Director: M. Stock

(1 January 2014 to 31 December 2014)

1. Electrical potential difference (voltage) (R. Chayramy, S. Solve)

1.1 Compact NIST 10 V programmable Josephson voltage standard for ac voltage measurements

Investigations into the leakage resistance to ground of the BIPM 10 V programmable Josephson voltage standard (PJVS), which was donated by the NIST, continued and the following results were presented during an oral session at the CPEM conference held in Rio de Janeiro, Brazil, in August 2014.

The PJVS leakage resistance to ground (LRG) is defined as the electrical resistance of the measurement leads from one side of the array to ground. Under certain measurement conditions, this resistance can produce a significant systematic error of the PJVS output voltage. In particular, if the low potential side of the array is grounded, for instance in a direct comparison measurement with another JVS, the LRG from the high potential side will reduce the PJVS output voltage. At 10 V, an error of 0.5 nV can result from a LRG of 50 GΩ if the measurement leads have a total resistance of 2.5 Ω. The LRG and the path of the leakage current to ground are difficult to determine. Furthermore, since the bias source needs to remain connected during operation, the corresponding voltage error also remains present. It is therefore important to apply different measurement techniques to compare the corresponding LRG values.

- The leakage resistance of the precision leads to ground at the voltage output of the PJVS can vary by one order of magnitude (from 10 GΩ to 100 GΩ) depending on the isolation quality of some main components of the Josephson voltage standard;
- The PJVS bias source is equipped with six commercial digital to analogue converters (DAC), the isolation resistance of each of these devices will contribute to the total isolation resistance of the JVS precision voltage leads by adding a parallel current path. Therefore a card with low isolation resistance or a defective card can significantly decrease the total resistance to ground of the PJVS.
- The leakage resistance to ground of the DC power supply which biases the PJVS electronics is a major contributor to the total leakage resistance to ground, even if the DAC cards are already equipped with optical isolators which considerably increase the isolation of the PJVS current source.
- A PXI chassis which can be fully powered from batteries was put into service. By using this chassis, the PJVS biasing source is floating from the ground. The remaining equipment required to operate the PJVS (DVM, RF source, computer and screen) is powered from a 2.7 kW UPS. This setup allowed the isolation resistance of the PJVS to be increased by making it floating from ground. To investigate the remaining effect, the voltage difference when the PJVS was directly compared to the BIPM primary SIS-based JVS unit was measured. This primary voltage standard offers the possibility of being fully floating from ground. Several measurement configurations could be analyzed with respect to this experimental reference. Compared to the PXI chassis powered from the mains, a significant decrease by a factor of 2 could be observed in the dispersion of the measurements. However, the total leakage resistance to ground of the PJVS was not affected at a level comparable to the noise floor of the measurement setup (0.25 nV).

1.2 Upgrade of the automatic Zener measurement system for measurements at 10 V

The automatic Zener calibration system has been upgraded by using a new programmable 10 V SNS Josephson voltage array, donated by the PTB to replace a 1 V SINIS programmable array. The BIPM can therefore increase its capabilities to 10 V. This array consists of 69 632 Josephson junctions, divided into 17 individual segments, for which the number of junctions varies from 1 to 34 816.

This measurement system had originally been designed to calibrate the 1.018 V output of our Zener-based secondary voltage standards. To increase the voltage output to 10 V, we had to select a proper configuration of the array, to test its behaviour and to implement it in the measurement setup.

The biasing source had been designed to drive six individual segments and we therefore had to find the best arrangement of the segments in series compatible with the requirements of achieving two nominal voltages (1.018 V and 10 V) in a close frequency domain, as the biasing current should also be the same for the two voltages.

Two suitable configurations were obtained:

1- U = 10.00190414 V at f =72.88 GHz with 66 368 JJ biased from the combination of three different segments;

2- U = 1.017878365 V at f =73.12 GHz with 6 732 JJ biased from the combination of five different segments.

Furthermore, the current capabilities of the biasing source had to be extended to reach a larger value of the biasing current (typically I = 3.6 mA to reach the middle of the Shapiro voltage step). This goal was achieved by changing the type of the operational amplifiers which equip our bias source and by increasing the power supply voltage from 12 V to 18 V.

The PJVS was then directly compared to the BIPM primary voltage reference and a relative voltage difference of 2×10^{-12} was achieved as the mean value of 24 measurement points with a relative Type A uncertainty of 2.8×10^{-11}. For this exercise, the biasing current of the programmable array was varied and the result shows a perfect agreement between the two quantum voltage standards.

As the final step, the new 10 V PJVS was integrated into the automated measurement setup. The preliminary measurement tests performed on the Zener at the level of 10 V show a small systematic discrepancy of a few parts in 10^8 with respect to the results obtained with the conventional measurement setup based on a commercial array of SIS junctions. Further investigations are required to cross-check the equivalence of the two systems before the new setup can be qualified as the designed primary DC voltage standard for the calibration of the Zeners and the BIPM bilateral Zener comparison programme.

1.3 Quantum Voltage reference for the watt balance

A Josephson Voltage Standard (JVS) dedicated to the measurement of the current sent to the coil of the watt balance (WB) experiment has been assembled, tested and delivered. The heart of this primary voltage standard is a SNS array of Josephson junctions from the NIST. The selected array cells have been organized to produce 1 V from 26 388 junctions in series when irradiated with a radio frequency signal at f = 18.5 GHz. A single current biasing source is required to operate the array. In order to cancel out the thermal electromotive forces (EMFs) developed along the Josephson voltage probe, a very low residual thermal EMFs computer-controlled reversal switch has been designed and assembled. This capability allows a measurement of the voltage drop across the resistance (1 kΩ) through which the current to the coil flows (1 mA) using a nanovoltmeter. The voltage across the resistor is opposed to the one generated by the primary voltage standard. A first evaluation of the measurement setup was performed in the BIPM voltage laboratories where a secondary voltage standard was used to simulate the ensemble of resistor and current source of the WB experiment. A relative type A uncertainty of 10^{-8} was achieved on repeated measurements performed overnight. This uncertainty corresponds to the noise floor (1/*f* noise) of a good Zener-based secondary voltage standard. The software designed to control the switch and to carry out the measurements was adjusted in order to protect the array from receiving a current intensity that was too large. The secondary voltage standard was then replaced by a resistance and a dedicated current source as a second step in simulating the corresponding WB apparatus. The immunization of the junctions against magnetic flux trapping was investigated. When the measurement setup was judged to be working satisfactorily, *i.e.* when the limiting factor of the measurement setup was clearly the accuracy of the current source and the resistance, the JVS and related equipment were transferred to the watt balance laboratory to be incorporated into the experiment. Several measurement series were performed overnight that demonstrated very satisfactory metrological behaviour of the PJVS. The limiting factor is so far on the side of the ensemble resistor and current source of the watt balance.

2. Electrical impedance (resistance and capacitance)

2.1 DC resistance and quantum Hall effect (N. Fletcher, R. Goebel[1], P. Gournay[2] and B. Rolland)

The quantum Hall resistance (QHR) standard maintained by the BIPM is the basis for all services (calibrations and comparisons) in resistance and capacitance, and is also essential for the watt balance and calculable capacitor projects. The QHR cryostat was operated three times during 2014 to update the drift lines on our secondary working standards. In resistance, these served as the basis for the calibration of 31 standards from nine NMIs during the year (a mixture of 1 Ω, 100 Ω and 10 kΩ standards). Mr Goebel retired from the BIPM in May 2014, and responsibility for resistance services has now passed to Mr Fletcher, with ongoing support from Mr Rolland. Dr Gournay, who started working at the BIPM in April 2014, has also participated in the operation of the QHR standard, in order to ensure that there is redundancy in technical competences.

A major project in 2014 was the refurbishment of the 'Warshawsky bridge', which is used for the calibration of 10 kΩ standards. The basic principle of the bridge remained unchanged, but the system was completely rebuilt with modernized instrumentation; in particular a replacement motorized selector switch that allows for automated calibrations was developed in house. Commercially available solutions were considered, but none offered the required combination of low-thermal-emf switch contacts and high isolation resistance needed in this application. New software to operate the bridge and calculate measurement results was developed using LabVIEW. By the end of 2014, the updated system had been brought into routine use for calibrations, under the control of the BIPM Quality Management System. The previous bridge had given around 20 years of service before running into reliability problems, and we hope that the updated system will have a similarly long and useful life.

The BIPM series of onsite quantum Hall comparisons (BIPM.EM-K12) restarted with a successful visit to the PTB, Germany, in November 2013. This comparison highlighted a limiting factor for 1 Ω measurements, which has been the subject of further study in 2014 in collaboration with the PTB. The effect of Peltier heating in a range of different 1 Ω standards has now been comprehensively characterized, with the results presented at the CPEM conference and submitted for publication. With this improved knowledge it should be possible to minimize these effects in future comparisons, and ensure comparability of 1 Ω measurements to the level of around 10 nΩ/Ω. The effect is less significant for higher value resistors, and comparisons of 100 Ω and 10 kΩ standards against the quantum Hall reference are possible at uncertainties approaching 1 nΩ/Ω, as seen in the PTB comparison. The comparison series will continue with two onsite visits planned for 2015. In preparation for this, we have constructed an additional thermo-regulated resistance enclosure which now houses a 100 Ω standard and completes our set of robust transportable standards. Experience with the enclosure design for 1 Ω measurements during the Peltier tests at the PTB was very positive, showing no problems related to

[1] Until 31 May 2014
[2] Since 1 April 2014

electrical interference when connected to a sensitive superconducting quantum interference device (SQUID) system.

The very-low frequency (1 Hz or below) room temperature current comparator bridge technology that the BIPM uses for onsite resistance comparisons is being investigated as part of a EURAMET research project on next generation quantum Hall reference systems based on graphene. The BIPM has been collaborating with the PTB and MIKES, Finland, to test new resistance bridges that can give primary standards level accuracy without the need for liquid helium. Initial tests have shown successful ratio measurements using MIKES-built current comparators and the existing BIPM electronics. This technology, combined with graphene devices, is now in development and promises simpler, more robust primary standards for resistance.

2.2 Maintenance of a reference of capacitance (R. Chayramy, N. Fletcher, R. Goebel[1], P. Gournay[2])

With the retirement of Mr Goebel in 2014, the responsibility for capacitance services has been passed from Mr Fletcher to Dr Gournay (with support provided by Mr Chayramy as before), after a period of overlap for training on the specifics of the BIPM coaxial bridge systems. The quadrature transfer chain from the dc resistance standard provided by the QHR reference to the capacitance standards maintained at 1592 Hz has been operated several times in 2014 as usual. Based on this reference, 14 standards have been calibrated for five NMIs during the year (this is less than the average over the past few years, but within the normal range of variations for calibration requests).

The discrepancies found in the 2011 EURAMET.EM-S31 comparison of 10 pF and 100 pF standards remain unresolved. An exchange of reference ac-dc resistors (which are a critical part of the quadrature traceability chain) between the PTB, the LNE (France), the METAS (Switzerland) and the BIPM was completed in early 2014, and the results showed excellent agreement of the measured frequency dependence. Following this reassuring result, it was decided after a discussion meeting at the CPEM conference in August 2014 to organise a new circulation of capacitance standards. This time, the NMIA (Australia) will be included, giving one point traceable to a Thompson-Lampard calculable capacitor (in contrast to the QHR traceability of all the original participants). The BIPM is due to receive the standards at the start of 2015, and will perform measurements before and after transport to Australia. The BIPM calculable capacitor should be ready to give a first useable result at the same time, and this comparison will be an excellent test of the measurement systems required for the measurement of R_K.

3. **Calculable capacitor** (N. Fletcher, R. Goebel[1], P. Gournay[2], L. Robertsson, M. Stock)

A first uncertainty budget has been established for the calculable capacitor, which includes the results of a theoretical model of the frequency dependence. The present alignment accuracy of the capacitor's electrode bars limits the relative uncertainty of determinations of the von Klitzing constant to about 1 part in 10^7. A number of measurements involving the calculable capacitor and the dedicated coaxial ac-bridge have been carried out to investigate possible systematic errors and noise sources. The bridge was studied in detail, including calibrations of the transformer, verification of the current equalization in all loops and testing the injection ratios. These investigations allowed improvements of the measurement chain to give an overall repeatability of 1 part in 10^8 or better.

Two causes of systematic errors have been detected in the calculable capacitor. One of them was related to problems in locking the interferometer laser to the iodine frequency reference cell. An optical fibre link has been installed between the BIPM laser laboratory and the calculable capacitor, which allowed comparison of the suspect laser with a more stable reference, and this problem has now been resolved. The second concerns the mechanical stability of the bottom mounts of the main electrode bars in the capacitor. Displacements of the order of a few nm of the electrodes have been observed when applying force to the external electrical connectors.

These effects have been eliminated in the measurement sequence by avoiding direct contact with the cables, but a possible voltage effect due to the electrostatic forces experienced by the bars has not yet been fully investigated. These difficulties have delayed the first determination of the von Klitzing constant (at the 10^{-7} level), which is now planned for early 2015. This will be followed by a careful re-alignment of the electrode bars using a new alignment probe which has been fabricated in the BIPM workshop, and is now undergoing electrical calibration. The ultimate goal remains a determination of the von Klitzing constant at the 10^{-8} level.

4. BIPM ongoing key comparisons in electricity (R. Chayramy, N. Fletcher, R. Goebel[1], P. Gournay[2], S. Solve, M. Stock)

Two on-site comparisons of Josephson voltage standards with the INM (Romania) and the PTB have been successfully completed at 10 V. The reports are in a Draft B and Draft A stages, respectively.

Five bilateral voltage comparisons using Zener voltage standards as transfer standards were carried out with the NSAI (Ireland) in March 2014; the DMDM (Serbia) in February 2014; the NIS (Egypt) in September 2014; the SMD (Belgium) in October 2014; and the NIMT (Thailand) in November 2014. The comparison with NSAI was made at 10 V; the other comparisons were made at 1.018 V and 10 V. The reports have been published for NSAI and DMDM and the Draft A reports are in preparation for the other participants.

Bilateral comparisons of resistance measurements for 1 Ω and 10 kΩ (BIPM.EM-K13.a and BIPM.EM-K13.b) were carried out with NSAI NML (Ireland, measurements started September 2014). Comparisons with the BIM (Bulgaria) and the NPLI (India) had been completed in September 2013 and reports are currently being published.

5. Calibrations (R. Chayramy, N. Fletcher, R. Goebel[1], P. Gournay[2], B. Rolland, S. Solve, M. Stock)

During the period from January 2014 to December 2014 the Electricity Department calibrated the following standards:

Two Zener diode-based voltage standards at 1 V and 10 V for the SMD (Belgium) and the NCM (Bulgaria);

One Zener diode-based voltage standard at 1 V and 10 V for the BIPM Ionizing Radiation Department.

A study note on a Zener diode-based voltage standard at 1 V and 10 V was also issued for the SMD (Belgium).

1 Ω, 100 Ω or 10 kΩ resistors were calibrated for: MKEH (Hungary), DFM (Denmark), NMC (Singapore), DMDM (Serbia), CMI (Czech Republic), INM (Romania), IPQ (Portugal), SMU (Slovakia) and GUM (Poland) - in total 31 certificates for nine NMIs.

1 pF, 10 pF or 100 pF capacitors were calibrated for: INMETRO (Brazil), GUM (Poland), IPQ (Portugal), NIS (Egypt) and SMU (Slovakia) - in total 14 certificates for five NMIs.

6. Publications

1. Burroughs C. J., Rüfenacht A., Waltrip B.C., Solve S., Dresselhaus P.D., Benz S.P., AC Waveform Source Referred to a Programmable Josephson Voltage Standard, *Proc. 2014 Conference on Precision Electromagnetic Measurements (CPEM)*, 2014, 736-737.

2. Solve S., Chayramy R., Rüfenacht A., Burroughs C. J., Benz S.P., "The leakage resistance to ground of a NIST Programmable Josephson Voltage Standard", *Digest CPEM 2014*, *2014 Conference on Precision Electromagnetic Measurements*, pp. 462-463.

3. Fang H., Kiss A., Lavergne T., Robertsson L., de Mirandés E., Solve S., Picard A., Stock M., Update from the BIPM Watt Balance, *Proc. 2014 Conference on Precision Electromagnetic Measurements (CPEM)*, 2014, 710-711.

4. Fletcher N., Goebel, R., "A measurement chain for the determination of R_K using a calculable capacitor", *Digest CPEM 2014, 2014 Conference on Precision Electromagnetic Measurements*, pp.474-475.

5. Fletcher N, Götz M., Goebel R., Rolland B., "On the definition of DC in resistance measurements", *Digest CPEM 2014, 2014 Conference on Precision Electromagnetic Measurements*, pp.688-689.

6. Fletcher N., Rietveld G., Olthoff J., Budovsky I., "Predicted impact of latest *h* and *e* values on resistance and voltage traceability in the new SI (système international)", *Digest CPEM 2014, 2014 Conference on Precision Electromagnetic Measurements*, pp.432-433.

7. Satrapinski A., Pontynen H., Götz M., Pesel E., Fletcher N., Goebel R., Rolland B., "A low-frequency current comparator for precision resistance measurements", *Digest CPEM 2014, 2014 Conference on Precision Electromagnetic Measurements*, pp.760-761.

8. N. Fletcher, G. Rietveld, J. Olthoff, I. Budovsky and M. Milton , "Electrical Units in the New SI: Saying Goodbye to the 1990 Values", *NCSLI Measure J. Meas. Sci*, Vol. 9, No. 3, pp 30-35, 2014.

9. M.J.T. Milton, R. Davis, and N. Fletcher, "Towards a new SI: a review of progress made since 2011," *Metrologia*, 2014, **51**(3), R21.

10. Power O., Chayramy R., Solve S., Stock M., "Bilateral comparison of 10 V standards between the NSAI–NML (Ireland) and the BIPM, January to February 2013 (part of the ongoing BIPM key comparison BIPM.EM-K11.b)", *Metrologia*, 2014, **51**, *Tech. Suppl.*, 01006.

11. Solve S., Chayramy R., Power O., Stock M., Bilateral comparison of 10 V standards between the NSAI-NML (Ireland) and the BIPM, March 2014 (part of the ongoing BIPM key comparison BIPM.EM-K11.b), *Metrologia*, 2014, **51**, *Tech. Suppl.*, 01008.

12. Solve S., Chayramy R., Stock M., Simionescu M., Cirneanu L., "Bilateral comparison of 1 V and 10 V standards between the INM (Romania) and the BIPM, August to October 2013 (part of the ongoing BIPM key comparison BIPM.EM-K11.a and b)", *Metrologia*, 2014, **51**, *Tech. Suppl.*, 01005.

13. Solve S., Chayramy R., Stock M., Yuan G., Honghui L., Zengmin W., "Comparison of the Josephson Voltage Standards of the NIM and the BIPM (part of the ongoing BIPM key comparison BIPM.EM-K10.b)", *Metrologia*,2014, **51**, *Tech. Suppl.*, 01009.

14. R Goebel, N Fletcher, B Rolland, M Götz and E Pesel, "Final report on the on-going comparison BIPM.EM-K12: Comparison of quantum Hall effect resistance standards of the PTB and the BIPM", *Metrologia*, 2014, **51** 01011, 2014.

7. Activities related to the work of Consultative Committees (M. Stock)

M. Stock is the Executive Secretary of the Consultative Committee for Electricity and Magnetism (CCEM) and the Consultative Committee for Photometry and Radiometry (CCPR) and a member of several of their working groups. At the 28th CCEM meeting on 14-15 March 2013 a task group was set up to consider the effects of the redefinitions on the electrical units. The conclusions were presented by BIPM staff at the CPEM conference and the NCSLI conference in 2014 and in the related conference papers.

The CCPR and its working groups met in September 2014 at the BIPM. The work on the *mise en pratique* for the definition of the candela is nearly complete and it is being reviewed by members of the CCPR and the CIE (International Commission on Illumination).

8. Activities related to external organizations (M. Stock)

M. Stock is a member of the Executive Committee of the Conference on Precision Electromagnetic Measurements (CPEM). S. Solve and M. Stock are members of the Technical Committee for the CPEM 2014.

M. Stock is the contact person for the BIPM liaison with the CIE.

P. Gournay represents the BIPM in the Organizing Committee and the Scientific Committee of the International Congress of Metrology, CIM.

The BIPM is an external collaborator on the EMRP projects "Quantum Resistance based on Graphene (GraphOhm)" and "Automated Impedance Metrology extending the Quantum Toolbox for Electricity (AIMQuTE)".

9. Travel (conferences, lectures and presentations, visits)

M. Stock to:

- LNE, Trappes (France), 2-3 April 2014, to attend the EURAMET TC-PR meeting and to present information from the CCPR and the JCRB.
- Brno (Czech Republic), 9-11 April 2014, to attend the EMRP NewKILO project meeting and the EURAMET TC-M meeting and to present the BIPM activities related to the planned kilogram redefinition.
- Rio de Janeiro (Brazil), 22-28 August 2014, to attend the CPEM conference and CCEM and CCM satellite meetings; he presented the results of the *Extraordinary Calibrations*.
- PTB, Berlin (Germany), 1 December 2014, to give a lecture on determinations of the Planck constant at a PTB seminar.

S. Solve and R. Chayramy to:

- INM, Bucharest (Romania), 17-25 June 2014, to carry out a direct on-site BIPM Josephson voltage standard comparison.
- PTB, Braunschweig (Germany), 6-10 October 2014 to carry out a direct on-site BIPM Josephson voltage standard comparison.
- La Défense, Paris (France) to attend LabVIEW© software courses, December 2014.

S. Solve to:

- SMD (Belgium), 15-16 May 2014 to provide support for the start-up of the Belgium primary quantum voltage standard after a long period of maintenance.
- Rio de Janeiro (Brazil), 23-29 August 2014 to attend the CPEM conference and to give a talk entitled "The leakage resistance to ground of a NIST Programmable Josephson Voltage Standard".
- Ecole Superieure de Metrologie, Douai (France), 25 April 2014, to give a talk on "traceability to primary standards in voltage metrology".

N. Fletcher to:

- LNE, Paris (France) 27-28 January 2014, to attend a EURAMET TC-EM meeting on EMPIR projects.
- PTB, Braunschweig (Germany), 2-3 July 2014, to deliver a resistance standard and for discussions on the EURAMET GraphOhm collaboration and the EURAMET.EM.S31 capacitance comparison.
- Rio de Janeiro (Brazil), 23-31 August 2014, to attend the CPEM conference and CCEM and CODATA TG satellite meetings, to present three oral papers at the conference, and to INMETRO to discuss a future onsite quantum Hall comparison.

P. Gournay to:

- PTB, Braunschweig (Germany), 2-3 July 2014, to deliver a resistance standard and for discussions on the EURAMET GraphOhm collaboration and the EURAMET.EM.S31 capacitance comparison.
- Rio de Janeiro (Brazil), 23-29 August 2014, to attend the CPEM conference and CCEM satellite meetings.
- PTB, Braunschweig (Germany), 27 October – 1 November 2014, for collaborative measurements on low-frequency current comparators (part of the GraphOhm project).

B. Rolland to:

- PTB, Braunschweig (Germany), 2-3 July 2014, to deliver a resistance standard and for discussions on the EURAMET GraphOhm collaboration and the EURAMET.EM.S31 capacitance comparison.
- PTB, Braunschweig (Germany), 27 October – 1 November 2014, for collaborative measurements on low-frequency current comparators (part of the GraphOhm project).

10. Visitors

- D. Vlad, SMD (Belgium), to visit the BIPM voltage laboratory and discussions on future collaboration work, 28 March 2014;
- M. Götz, PTB (Germany), for discussions on resistance measurements and the GraphOhm collaboration, 2-4 April 2014;
- A. Pollarolo, NIST (USA), to visit the voltage laboratory, 26 May 2014;
- O. Thevenot, G. Thuillier, LNE (Trappes, France), to use a BIPM spot welding machine for the fabrication of ac-dc reference resistors, 18-19 May and 16 September 2014;
- E. Cabrera Herebia, INTN (Paraguay), to visit the electricity laboratories, 25 July 2014;
- Y. Tatsuji, NMIJ (Japan), to visit the electricity laboratories, 4 September 2014;
- H. Abdelmegeed, NIS (Egypt), to transport the secondary voltage transfer standards involved in a bilateral comparison between the BIPM and the NIS, 2 and 15 September 2014;
- J.-M. Reiff, P. Kadok, ILNAS (Luxembourg), to visit the electricity laboratories, 1 October 2014;
- B. Wood, NRC (Canada), to discuss issues with voltage measurements on the watt balance experiment, 5 November 2014;
- Delegates from the CGPM to visit the Electricity Department laboratories on 18 November 2014;
- S. Akretche, B. Harchaoui, A. Cheblal, K. Bey Benagliz (all NAFTAL, Algeria), M. Bekhadda (Embassy, Algeria) and J-F. Lipskier (LNE, France) to visit the BIPM laboratories, 27 November 2014.

BIPM Ionizing Radiation Department

Director: J.M. Los Arcos

(1 January 2014 to 31 December 2014)

1. X- and γ-rays (D.T. Burns, C. Kessler, S. Picard and P. Roger)

1.1 Dosimetry standards and equipment

The project to develop an absorbed-dose standard for medium-energy x-rays, based on the existing standard for air kerma, has made significant progress. A system for raising and lowering a small water phantom has been developed to allow ionization chambers in water to be set up accurately and rapidly. The transfer standards constructed at the BIPM have been measured in air and in this new water-phantom arrangement over the range of x-ray energies. Corresponding Monte Carlo calculations of the relative response of the chambers under these conditions continue; the first indications are that the target standard uncertainty of 1 % in the determination of absorbed dose is likely to be achieved down to the 100 kV radiation quality.

Work on the development and characterization of cavity ionization chambers continues. Two new graphite-walled cavity standards were built and characterized in the ^{60}Co and ^{137}Cs beams. The standard with graphite walls, which was built in 2013 for use as a transfer standard in the determination of absorbed dose in medium-energy x-rays, was tested and characterized in ^{60}Co radiation.

The Department coordinated the seventh and eighth comparison in the series BIPM.RI(I)-K6 for absorbed dose to water in high-energy photon beams, with the NPL (UK) and the VSL (the Netherlands). The measurements were made in the 6 MV, 10 MV and 25 MV beams of the NPL Elekta accelerator from 23 September to 20 October and the corresponding Monte Carlo calculations (for a depth of 10 g cm^{-2}) were made at the BIPM using photon spectra supplied by the NPL. The BIPM equipment was shipped to the NPL in advance, with the exception of the calorimeter core and ionization chambers which were carried by hand. This comparison enabled the NPL to verify robustly the present UK primary standard to realize absorbed dose to water in accelerator beams. The VSL brought and used its newly-constructed water calorimeter, which is of a unique design, and made a successful determination of absorbed dose to water in the same beams. A problem with one of the BIPM transfer instruments was identified at the beginning of the comparison, but was easily resolved by using a spare chamber. This highlights the value of travelling with a back-up system for key devices, and most key elements now have a spare. This back-up system now includes a second calorimeter core, which is being tested. Substantial modifications to the electronic support have also been made to reduce the number of manual operations it requires.

For these two comparisons which were made in parallel, the BIPM used a remote-controlled motorized monitoring and shutter system for the first time, to reliably track and correct for intrinsic intensity variations in the beams. The new design is compact and showed high reproducibility in the positioning of the shutter. The remotely controlled system avoids staff having to enter the radiation area between irradiations, which improves radiation protection of the operator and saves time. The report of the previous comparison with the ARPANSA, Australia, was published, and a comparison to be carried out with the NMIJ/AIST, Japan, in April 2015 was prepared.

The accumulated data from the BIPM.RI(I)-K6 comparison series and from the work on ionization chamber volume measurements were used for a re-determination of the value for W_{air}, the mean energy required to create an ion pair in air. This important parameter is being reviewed by a report committee of the International Commission on Radiation Units and Measurements (ICRU), which will produce a report on Key Data for

Dosimetry during 2015. The result of the BIPM determination of W_{air} was published in *Physics in Medicine and Biology*, 2014 **59**, 1353-1365.

The comparison series BIPM.RI(I)-K8 for the reference air kerma rate for HDR Ir-192 brachytherapy sources was re-launched. A new protocol was agreed and adopted and the results of previous comparisons were re-analysed following the new protocol. The corresponding comparison reports were produced and published and the KCDB has been updated accordingly. Two new comparisons with the NRC, Canada, and the LNE-LNHB, France, were carried out; the comparison reports are in progress.

Primary measurements and reference chamber calibrations have continued in all of the reference x- and γ-ray beams. Comparisons and calibrations are underpinned by a significant effort in equipment calibration and maintenance, as required by the BIPM Quality System. This system was subject to a successful internal audit in December 2014.

1.2 Dosimetry comparisons

Sixteen comparisons were carried out in the x- and gamma-radiation beams in terms of air kerma with the PTB (4), ENEA (2), BEV (3), NIM (1), NRC (1) and NMIJ (1). Two high-energy absorbed-dose comparisons were carried out in the NPL's accelerator beams with the NPL and the VSL. Two comparisons were carried out in terms of reference air kerma rate for HDR ^{192}Ir brachytherapy sources at the NRC and at the LNE-LNHB.

Fifteen comparison reports were published in the *Metrologia Technical Supplement* for the PTB (5), ENEA (1), BEV (2), VSL (3), NPL (1), ARPANSA (1), NIST (1) and for the METAS (1).

1.3 Characterization of national standards for dosimetry

Fourteen characterizations of national standards were carried out: five for the STUK in low-energy x-rays (1), mammography beams (1) medium-energy x-rays (1) and ^{60}Co (2); eight for the IAEA in the ^{60}Co and ^{137}Cs radiation protection beams and one for the ENEA in the ^{137}Cs radiation protection beam.

The IAEA/WHO dosimetry assurance programme continues to be supported by reference irradiations, which involved only one series of irradiations in 2014 for the radiotherapy level in the ^{60}Co beam.

2. **Radionuclides** (J.M. Los Arcos, S. Courte, C. Michotte, M. Nonis and G. Ratel)

Within the framework of maintenance of the primary activity measurement systems based on the coincidence method, a new digital system for the measurement of dead times by the two-oscillator method has been developed and validated. The system is based on a NI 9402 counter and on a double oscillator that was built at the BIPM and which is compatible with the NI acquisition system. It follows the description and recommendations on the two-oscillator method[3-3]. The frequencies selected are 9729.2 Hz and 6097.5 Hz enabling measurements of dead times up to 51 μs. This new digital system has been validated to better than 1.5 parts in 10^4 for non-extended dead-time values of 5 μs, 10 μs and 50 μs by comparison with the module developed in 1981[4].

[3] Müller J.W., Une méthode simple pour mesures précises de temps mort, *Rapport BIPM*-1969/03.
[2] Gostely J.-J. and Carval E., NIM, 1978, **150**, 459 – 464.
[3] Gostely J.-J. and Carval E., NIM, 1979, **158**, 537 – 544.
[4] Bréonce P., Description d'un dispositif automatique de mesure précise de temps mort, *Rapport BIPM*-1981/01.

2.1 International Reference System (SIR) for γ-ray emitting radionuclides

2.1.1 SIR submissions in 2014

During 2014, the BIPM received twelve ampoules filled with ten different radionuclides from seven laboratories (i.e. one ampoule each containing ^{22}Na (LNE-LNHB), ^{59}Fe (NMIJ), ^{60}Co (NIM), ^{68}Ge (NMIJ and NIST), ^{89}Sr (PTB), ^{90}Y (PTB),), ^{134}Cs (NRC), ^{137}Cs (NRC), ^{177}Lu (PTB) and ^{223}Ra (NPL and PTB). A further ampoule filled with ^{222}Rn gas with a short half-life ($T_{1/2}$ = 3.8235 d) that was prepared by the LNE-LNHB, was measured first at the BIPM, sent back to the LNE-LNHB and then forwarded to the ENEA. All these submissions had been made to generate equivalence values for the associated ongoing BIPM key comparisons BIPM.RI(II)-K1.

In parallel, measurements of a set of three ampoules of different shapes and sealed at various heights, filled with ^{222}Rn gas and provided by the LNE-LNHB, were carried out to study the influence of the form of the ampoules on the ionization chamber currents. These results were added to a more general study carried out at the LNE-LNHB and presented at a conference in Japan.

2.1.2 SIR reports and quality assurance

Updated reports of four comparisons were published in the *Metrologia Technical Supplement* covering ^{131}I, ^{133}Ba, ^{152}Eu and ^{177}Lu including the linked APMP.RI(II)-K2.I-131, CCRI(II)-K2.Lu-177 and COOMET.RI(II)-K2.Eu-152 comparisons. Two other reports are in circulation. With the exception of four results: reporting forms for ^{51}Cr and ^{125}Sb which are still with the NMIs concerned and ^{111}Ag and ^{222}Rn which are being evaluated by the BIPM, all the Draft A reports have been circulated.

There are 43 SIR results awaiting publication in the KCDB and every effort will be made to ensure that reports are published as quickly as possible, particularly when NMIs make submissions that are to replace outdated results that have already been removed from the KCDB.

All SIR measurements are covered by the BIPM Quality Management System and an internal audit, including the extension to short-lived radionuclides, was carried out on 15 September 2014 by the BIPM Quality, Health and Safety Manager, Mr Maggi (assisted by Mr Fletcher, BIPM).

Following a recommendation made by Prof. Dr Bochud from the IRA-METAS (Switzerland) during a previous external audit, a hand-foot contamination monitor was acquired in 2013 and installed in 2014. To complete the installation and to control the entrance to the hot laboratory, where open radioactive sources are manipulated, a sliding door controlled by the monitor has also been installed.

2.2 Gamma spectrometry

Since the failure of the Ge(Li) spectrometer in July 2013, measurements of potential impurities in SIR ampoules have been suspended. Efficiency measurements of the replacement HPGe spectrometers were carried out several years ago but the data analysis was pending because operation of the SIRTI (see below) was given a higher priority. In 2014, Dr Antohe on secondment from IFIN-HH, Romania, made some additional measurements, analyzed all the measured spectra and evaluated the pile-up corrections. He produced efficiency curves at two distances from the detector, for which only the small true coincident summing correction still needs to be applied. The uncertainty budget needs to be finalized. New procedures will be drafted and the entire process validated before re-offering the gamma-ray spectrometry service to the SIR participants.

2.3 Extension of the SIR to short-lived radionuclides

The BIPM.RI(II)-K4.Tc-99m ($T_{1/2}$ = 6.0 h) key comparison using the SIR Transfer Instrument (SIRTI) continued in 2014 with the VNIIM, Russian Federation, and the ENEA-INMRI, Italy, participating. The NMISA, South Africa, is the next planned participant. The result of the comparison in Romania in 2013 has been published. To date all the degrees of equivalence based on the SIRTI, except the secondary result from Argentina, agree with the KCRV for ^{99m}Tc.

The link SIRTI-SIR for ^{99m}Tc was re-measured after six years of use giving a slightly lower result (12 132(26)). Consequently, the weighted mean linking factor changed from 12 173(20) to 12 165(23), and the latter value will be used for all BIPM.RI(II)-K4.Tc-99m comparisons to be published in future, starting with the VNIIM.

The original SIRTI equipment which had been in Argentina since a comparison in November 2012 was returned to the BIPM in spring 2014. The stability of the SIRTI using the niobium reference source No. 1 was re-measured and no significant change was observed. It is remarkable that, in spite of being transported around the world, the SIRTI has shown a very high reproducibility since 2007, with a relative standard deviation of 2×10^{-4} for the count rate of the ^{94}Nb reference source measured world-wide.

Significant efforts were made to extend the SIRTI to ^{18}F ($T_{1/2}$ = 1.8 h), which is one of the most frequently used radionuclides in positron emission tomography (PET), e.g. to study of the influence of the pulse shape, reproducibility of measurements, production of a copy of the PVC liner and tests of a new centrifuge for the SIR ampoules. A new specific protocol was established and the link SIRTI-SIR was measured for ^{18}F using both a commercial solution and a solution from the LNE-LNHB. The validation was made at the NPL by comparing the SIRTI result with the NPL's SIR result from 2003. Monte Carlo simulations of the SIRTI response as a function of the ampoule shape and filling height need to be finalized for the evaluation of the corresponding uncertainty components of the SIRTI measurements.

A significant milestone in 2014 was the effective use of the SIRTI for ^{18}F through a new BIPM.RI(II)-K4.F-18 ongoing comparison, on-site at each participating NMI's premises, starting with comparisons at the VNIIM, the NPL and the ENEA-INMRI. Other NMIs that have expressed an interest in the ^{18}F comparison are the ANSTO (Australia), BARC (India), BEV (Austria), CNEA (Argentina), IFIN-HH (Romania), KRISS (Republic of Korea), LNMRI/IRD (Brazil), NIM (China), NIST (USA), NMIJ (Japan), NMISA (South Africa), NRC (Canada) and SMU (Slovakia).

Finally, trial measurements of ^{11}C, a PET radionuclide with a 20 min half-life, have been carried out at the NPL with encouraging results.

2.4 Extension of the SIR to pure beta emitters

A significant step towards the extension of the SIR to β-emitters was made in November 2014. A trial exercise was launched to measure samples of ^{3}H, ^{14}C, ^{55}Fe and ^{63}Ni using three commercial liquid-scintillation spectrometers (Beckman TS 6000 TA, Perkin Elmer Tri-Carb 2910 TR and Perkin-Elmer Quantulus 1220) and a TDCR counter that was fabricated at the BIPM. The samples were sent by 14 NMI/DIs (ANSTO, CIEMAT, ENEA, IFIN-HH, IRMM, LNE-LNHB, MKEH, NIM, NIST, NMIJ, NPL, NRC, PTB, POLATOM-RC). These samples were prepared using four different commercial scintillators (Ultima Gold, HiSafe III, Hionic Fluor and Bio Fluor +) in two different scintillator volumes, 10 mL and 15 mL. These measurements will extend over five to seven months and will serve to demonstrate the appropriateness of using the universal efficiency curves (UEC), based on the commercial spectrometers or the apparent efficiencies relying on TDCR measurements, to extend the SIR to β-emitters.

3. Thermometry (S. Picard, M. Nonis)

The Ionizing Radiation Department provides internal calibration services for thermometry at the BIPM under the terms of the BIPM Quality Management System. A problem occurred with the BIPM high-precision resistance bridge during 2014 that prevented calibration certificates from being issued for SPRTs. Work has been carried out during the second half of the year to resolve the problem. Six calibration certificates for commercial laboratory thermometers belonging to the Chemistry and Mass Departments were issued.

4. Publications

1. Alvarez J.T., de Pooter J.A., Andersen C., Aalbers A.H.L., Allisy-Roberts P.J. Kessler C., Comparison BIPM.RI(I)-K8 of high dose-rate Ir-192 brachytherapy standards for reference air kerma rate of the VSL and the BIPM, *Metrologia*, 2014, **51,** *Tech. Suppl.*, 06022.
2. Alvarez J.T., Sander T., de Pooter J.A., Allisy-Roberts P.J., Kessler C., Comparison BIPM.RI(I)-K8 of high dose rate ^{192}Ir brachytherapy standards for reference air kerma rate of the NPL and the BIPM, *Metrologia*, 2014, **51,** *Tech. Suppl.*, 06024.
3. Anton M., Allisy-Roberts P.-J., Kessler C., Burns D.T., A blind test of the alanine dosimetry secondary standard of the PTB conducted by the BIPM, *Metrologia*, 2014, **51**, *Tech. Suppl*., 06001
4. Arias F., Los Arcos J M., Stock M., Wielgosz R., Milton M., News from the BIPM laboratories-2013, *Metrologia*, 2014, **51**, (2014) 121-125.
5. Bailat C.J., Keightley J., Nedjadi Y., Mo L., Ratel G., Michotte C., *et al.*, International comparison CCRI(II)-S7 on the analysis of uncertainty budgets for 4πβγ coincidence counting, *Metrologia*, 2014, **51,** *Tech. Suppl.*, 06018.
6. Burns D.T., Picard S., Kessler C., Roger P., Use of the BIPM calorimetric and ionometric standards in megavoltage photon beams to determine W_{air} and I_c, *Phys. Med. Biol*., 2014, **59,** 1353−1365.
7. Burns D.T., Kessler C., de Prez L., Joulaeizadeh L., Key comparison BIPM.RI(I)-K2 of the air-kerma standards of the VSL, Netherlands and the BIPM in low-energy x-rays, *Metrologia*, 2014, **51,** *Tech. Suppl*., 06010.
8. Burns D.T., Kessler C., Büermann L., Key comparison BIPM.RI(I)-K2 of the air-kerma standards of the PTB, Germany and the BIPM in low-energy x-rays *Metrologia*, 2014, **51,** *Tech. Suppl*., 06011.
9. Burns D.T., Kessler C., Pinto M., Cappadozzi G., Silvestri C., Toni M.P., Key comparison BIPM.RI(I)-K3 of the air-kerma standards of the ENEA, Italy and the BIPM in medium-energy x-rays, *Metrologia*, 2014, **51,** *Tech. Suppl*., 06020.
10. Burns D.T., Kessler C., Büermann L., Key comparison BIPM.RI(I)-K3 of the air-kerma standards of the PTB, Germany and the BIPM in medium-energy x-rays, *Metrologia*, 2014, **51,** *Tech. Suppl.*, 06016.
11. Kessler C., Burns D.T., Büermann L., Key comparison BIPM.RI(I)-K1 of the air-kerma standards of the PTB, Germany and the BIPM in ^{60}Co gamma radiation, *Metrologia*, 2014, **51,** *Tech. Suppl*., 06012.
12. Kessler C., Allisy-Roberts P.J., Miniti R., Comparisons of the radiation protection standards for air kerma of the NIST and the BIPM for ^{60}Co and ^{137}Cs gamma radiation, *Metrologia*, 2014, **51,** *Tech. Suppl.*, 06013.
13. Kessler C., Burns D.T., Büermann L., Key comparison BIPM.RI(I)-K5 of the air-kerma standards of the PTB, Germany and the BIPM in ^{137}Cs gamma radiation, *Metrologia*, 2014, **51,** *Tech. Suppl.*, 06015.
14. Kessler C., Burns D.T., de Prez L., Joulaeizadeh L., Key comparison BIPM.RI(I)-K7 of the air-kerma standards of the VSL, Netherlands and the BIPM in mammography x-rays, *Metrologia*, 2014, **51,** *Tech. Suppl.*, 06025.

15. Michotte C., Ratel G., Courte S., Caffari Y., Fréchou C., Thiam C., Brettner-Messler R., Maringer F.J., Update of the BIPM comparison BIPM.RI(II)-K1.Ba-133 of activity measurements of the radionuclide ^{133}Ba to include the 2009 result of the IRA (Switzerland) and the 2012 results of the LNE-LNHB (France) and BEV (Austria), *Metrologia*, 2014, **51**, *Tech. Suppl.*, 06017.

16. Michotte C., et al., BIPM comparison BIPM.RI(II)-K1.Lu-177 of activity measurements of the radionuclide ^{177}Lu for the NPL (UK) and the IRMM (EU), with linked results for the comparison CCRI(II)-K2.Lu-177, *Metrologia*, 2014, **51**, *Tech. Suppl.*, 06002.

17. Michotte C., et al., BIPM comparison BIPM.RI(II)-K1.Eu-152 of activity measurements of the radionuclide ^{152}Eu for the VNIIM (Russia), the LNE–LNHB (France) and the CNEA (Argentina), with linked results for the COOMET.RI(II)-K2.Eu-152 comparison, *Metrologia*, 2014, **51**, *Tech. Suppl.*, 06004.

18. Michotte C., *et al*., BIPM comparison BIPM.RI(II)-K1.I-131 of activity measurements of the radionuclide ^{131}I for the NMIJ (Japan), the NIST (USA) and the LNE-LNHB (France), with linked results for the APMP.RI(II)-K2.I-131 comparison, *Metrologia*, 2014, **51**, *Tech. Suppl.*, 06003.

19. Michotte C., Sahagia M., Ioan M.R., Antohe A., Luca A., Activity measurements of the radionuclide ^{99m}Tc for the IFIN-HH, Romania in the ongoing comparison BIPM.RI(II)-K4.Tc-99m, *Metrologia*, 2014, **51**, *Tech. Suppl.*, 06014.

20. Picard S., *et al*., Key comparison BIPM.RI(I)-K6 of the standards for absorbed dose to water of the ARPANSA, Australia, and the BIPM in accelerator photon beams, *Metrologia*, 2014, **51**, *Tech. Suppl.*, 06006.

5. Activities related to the work of Consultative Committees

J.M. Los Arcos is the Executive Secretary of the CCRI, an *ex-officio* member of all CCRI working groups and Coordinator of the CCRI(II) Working Group on the Extension of the SIR to beta-emitters using liquid scintillation (ESWG(II)). During 2014 the Key Comparisons Working Group (KCWG(II)) met in April and September.

D.T. Burns is a member of the CCRI(I) Key Comparisons Working Group (KCWG(I)) and the Brachytherapy Standards Working Group (BSWG(I)). He is also a member of an *ad hoc* group evaluating the effect of excess charge on the value for W_{air}. Since 2009 he has been *rapporteur* at annual meetings of the CCRI.

C. Kessler is the Coordinator of the CCRI(I) Brachytherapy Standards Working Group (BSWG(I)).

C. Michotte is a member of the Key Comparisons Working Group (KCWG(II)) which met in April and September 2014.

S. Picard is Executive Secretary of the Consultative Committee for Acoustics, Ultrasound and Vibration (CCAUV). She is the Interim Acting Executive Secretary of the Consultative Committee for Thermometry (CCT) which held its 27th meeting on 21-23 May 2014.

G. Ratel is a member of the CCRI(II) Working Group on the Extension of the SIR to beta-emitters using liquid scintillation (ESWG(II)) and of the KCWG(II), which met in April and September 2014.

6. Activities related to external organizations

J.M. Los Arcos evaluates scientific projects for the Spanish National Evaluation and Foresight Agency (ANEP) and is a technical auditor for the Spanish accreditation body.

D.T. Burns is a Fellow of the Institute of Physics (FInstP) in the UK and elected Commissioner of the ICRU. In 2014 he was appointed Chairman of the ICRU Committee on Fundamental Quantities and Units. He is a member of the ICRU Report Committee on Key Data for Dosimetry and is Commission Sponsor for three ICRU reports (Key Data for Dosimetry, Operational Quantities for Radiation Protection, and Small and Non-Standard Fields). He is a member of the Scientific Committee of the IAEA/WHO Network of Secondary Standards Dosimetry Laboratories.

C. Michotte is the Scientific Secretary and *rapporteur* for the JCGM-WG1 meetings, which were held in June and October 2014.

G. Ratel is the BIPM representative on the International Committee for Radionuclide Metrology (ICRM) and is the President of the ICRM Nominating Committee. He is a member of the Scientific Committee for the 20th International Conference on Radionuclide Metrology and its Applications (ICRM 2015), which will be held in Vienna (Austria) on 8-11 June 2015.

7. **Travel** (conferences, lectures and presentations, visits)

D.T. Burns to:

- Vienna (Austria), 10-14 March 2014, to participate in a meeting of the Scientific Committee of the IAEA/WHO Networks of SSDLs.
- Bethesda (Maryland, USA), 10-16 May 2014, to attend the annual meeting of the ICRU.
- Teddington (UK), 26-29 September 2014, to participate in the BIPM.RI(I)-K6 comparison of absorbed dose to water in accelerator beams with the NPL.
- Brussels (Belgium), 29-30 September 2014, to participate in a meeting of the Commission Sponsors for the ICRU Report on Small-field Dosimetry.
- Teddington (UK), 12-24 October 2014, to participate in the BIPM.RI(I)-K6 comparison of absorbed dose to water with the VSL in the accelerator beams of the NPL.
- Paris (France), 3 November 2014, to participate in a meeting of the ICRU Report Committee on Operational Quantities for Radiation Protection, held at the LNE.

C. Kessler to:

- Ottawa (Canada), 21-29 August 2014, to carry out the BIPM.RI(I)-K8 comparison for reference air kerma rate for HDR Ir-192 brachytherapy sources with the NRC.
- Saclay (France), 16-19 September 2014, to carry out the BIPM.RI(I)-K8 comparison for reference air kerma rate for HDR Ir-192 brachytherapy sources with the LNE-LNHB.
- Oslo (Norway), 29-31 October 2014, to participate in the EURAMET Technical Committee for Ionising Radiation.

J. M. Los Arcos to:

- Madrid (Spain), 12-14 February 2014, to give two lectures at the Master in Metrology-Ionizing Radiation, organized by the Universidad Complutense de Madrid and the Centro Español de Metrología.

S. Picard to:

- Cavtat (Croatia), 2 April 2014, to attend the EURAMET TC-T workshop on "Comparisons: Regional, Key, Linkage and Associated CMC Review".
- Cavtat (Croatia), 3-4 April 2014, to participate at the EURAMET TC-T meeting and to present recent

news from the BIPM and the CCT.

- Brdo (Slovenia), 15-16 September 2014, to participate at the Workshop Metrology for Meteorology and Climate, where she gave the talk "BIPM: Climate and Environment". She also gave a talk on behalf of Dr R.I. Wielgosz (Chemistry Department, BIPM) entitled "Linking Essential Climate Variables to SI Traceable Measurements: BIPM Gas Standard Comparison Activities".
- Teddington (UK), 23 September to 9 October 2014, to carry out two parallel BIPM.RI(I)-K6 comparisons of absorbed dose to water in accelerator beams with the NPL and the VSL at the medical accelerator facility of the NPL.
- Teddington (UK), 1 October 2014, to visit the thermometry laboratories at the NPL.

C. Michotte to:

- NPL, Teddington (UK), 22-26 September 2014, to validate the SIRTI-SIR link for ^{18}F, to carry out an activity comparison of ^{18}F (BIPM.RI(II)-K4.F-18) and to make trial measurements of ^{11}C using the SIR Transfer Instrument.
- Casaccia (Italy), 23 October to 1 November 2014 to carry out activity comparisons of ^{99m}Tc (BIPM.RI(II)-K4.Tc-99m) and ^{18}F (BIPM.RI(II)-K4.F-18) at the VNIIM using the SIR Transfer Instrument.

C. Michotte and M. Nonis to:

- St Petersburg (Russia), 19-28 June 2014 to carry out activity comparisons of ^{99m}Tc (BIPM.RI(II)-K4.Tc-99m) and ^{18}F (BIPM.RI(II)-K4.F-18) at the VNIIM using the SIR Transfer Instrument.

G. Ratel to:

- Vienna, (Austria) 23-24 April 2014, to attend the International Conference on Radionuclide Metrology and its Applications (ICRM) Executive Board.
- Vienna, (Austria) 25-26 November 2014, to attend the ICRM Scientific Committee of the 20th ICRM Conference.
- Vienna, (Austria) 27 November 2014, to attend the ICRM Executive Board.

G. Ratel and C. Michotte to:

- Issy-les-Moulineaux (France), 13-14 November 2014, to attend the "Neuvième rencontre des personnes compétentes en radioprotection".

P. Roger to:

- Teddington (UK), 23 September to 9 October and 20-21 October 2014, to carry out two parallel BIPM.RI(I)-K6 comparisons of absorbed dose to water in accelerator beams with the NPL and the VSL at the medical accelerator facility of the NPL.

8. Visitors

A number of delegations from different countries or organizations visited the Ionizing Radiation Department in 2014:

- M. Hirayama, President of the Institute Council of the Federal Institute of Metrology (METAS) and C. Bock, Director of METAS, 15 May 2014
- E. Cabrera Herebia - General Director of the National Metrology Institute of Paraguay, 25 July 2014
- J.-M. Reiff, Director of the Bureau luxembourgeois de métrologie (ILNAS), Director of ILNAS and P.

Kadok (ILNAS), 1 October 2014

- Delegates attending the 25th CGPM, 17 November 2014

9. Guest workers

- L. Büermann (PTB, Germany), 24 March to 4 April 2014
- M. Pinto (ENEA, Italy), 7-18 April 2014
- A. Antohe (IFIN-HH, Romania), 5 May to 31 July 2014
- L. Czap (IAEA), 23-27 June 2014
- P. Wang and D. Li (NIM, China), 1-5 September 2014
- L. Rodríguez (ex-CIEMAT, Spain), 8 September to 31 December 2014
- E. Mainegra-Hing (NRC, Canada), 15-19 September 2014
- M. Shimizu and T. Tanaka (NMIJ, Japan), 27-31 October 2014

BIPM Chemistry Department

Director: R.I. Wielgosz

(1 January 2014 to 31 December 2014)

1. Gas metrology programme (J. Viallon, E. Flores, P. Moussay, F. Idrees and R.I. Wielgosz)

1.1 Greenhouse gases standards

1.1.1 Key comparison on methane standards (CCQM-K82)

Alternative proposals for key comparison reference values (KCRV's) were calculated for the CCQM-K82 comparison and distributed to participants in March 2014, following on from the initial discussion of results at the November 2013 CCQM Working Group on Gas Analysis (GAWG) meeting in South Africa. Agreement on the KCRV to be used was reached during the GAWG meeting held at the BIPM in April 2014. A new version of the report that was distributed in July 2014 and presented at the GAWG meeting held at the BIPM in October 2014 was approved in November 2014 and published, demonstrating that the level of agreement amongst standards improved by a factor of ten compared to a similar comparison exercise performed in 2003 (CCQM-P41).

Measurements performed during the validation phase and during the comparison itself were presented at the European Geophysical Union General Assembly. A paper demonstrating equivalence between standards made in whole and synthetic air measured by cavity ring-down spectroscopy (CRDS) and gas chromatography – flame ionization detection (GC-FID) for atmospheric monitoring applications was submitted to *Analytical Chemistry* in November 2014.

1.1.2 Preparation for the key comparison on carbon dioxide (CCQM-K120)

A new vacuum Fourier transform infrared spectroscope (FTIR) was acquired in preparation for the comparison CCQM-K120 on carbon dioxide in air standards. The standards that were selected to span both the target amount fraction and isotope ratio ranges have been obtained through collaborative work with partner NMIs (NIST, USA, and NPL, UK). A subset of these standards, all of which have different isotope ratios, were sent to the Max Planck Institute for Biogeochemistry in Jena, Germany, for assignment of $\delta^{13}C$ and $\delta^{18}O$ values. This laboratory has been designated as the Central Calibration Laboratory for CO_2 isotope ratios by the World Meteorological Organization (WMO). This information was used together with the carbon dioxide mole fractions assigned by the NIST and the NPL using gravimetry to validate the FTIR measurements of $\delta^{13}C$ in the CO_2/air mixtures. The FTIR work was supported by the secondment of Dr Marta Doval Miñarro to the BIPM from the NPL.

In parallel, a new system to measure carbon dioxide in air amount fractions with traceability to the BIPM pressure standards is being installed in a new laboratory. The system makes use of cryogenic separation of carbon dioxide from its air matrix and accurate measurements of pressure and temperature, first in air then in pure carbon dioxide. The system includes an all-glass ensemble of five spheres of different volumes. They will be used to accurately characterize the ratio of the largest to the smallest of these volumes, designed respectively to contain the air sample and the carbon dioxide extracted from it. Corrections for the presence of N_2O will be made based on gas chromatography–electron capture detection (GC-ECD) measurements, with the funds for the purchase of a system donated from the KRISS, Republic of Korea.

1.2 Air quality gas standards

1.2.1 Ongoing ozone photometer comparison and calibration programme (BIPM.QM-K1)

In 2014, three laboratories brought or sent their ozone national standards to the BIPM for comparison with the BIPM-SRP27 reference standard as part of the key comparison BIPM.QM-K1: the NIM, China, in April, the VNIIM, Russian Federation, in June, and the ISCIII, Spain, in December. The Directorate of Measures and Precious Metals (DMDM), Serbia, participated in the comparison for the first time in November 2014, using the NIST as a link. All reports of comparisons performed in 2013 were published and reports of comparisons performed in 2014 are either under review or in preparation. In addition, the calibration of the ozone national standard belonging to the NMISA, South Africa, was performed in July 2014.

1.2.2 Ozone absorption cross-section value

Work on new ozone absorption cross-section measurements was completed in early 2014, leading to the proposal of a new value of 11.27×10^{-18} cm^2 $molecule^{-1}$ with an expanded relative uncertainty of 0.86 %. This is lower than the conventional value currently in use that was measured by Hearn in 1961 with a relative difference of 1.8 %. This research has highlighted that the historically reported ozone concentrations should be increased correspondingly by 1.8 %. A paper describing the measurements and this significant finding was published on-line in *Atmospheric Measurement Techniques Discussions* and is currently under revision following the receipt of reviewers' comments.

Work restarted on a gas phase titration (GPT) system in 2014. A new reaction chamber was designed and new standard mixtures of nitrogen monoxide and nitrogen dioxide were purchased to compare ozone measurements traceable to those gravimetric standards with UV absorption measurements, anchored to the ozone absorption cross-section. Final measurements are planned for 2015 and a GPT-based value of the ozone cross-section will be deduced.

1.2.3 Key comparison on Formaldehyde standards (CCQM-K90)

The set of 14 cylinders of formaldehyde in nitrogen was selected and purchased to act as transfer standards for the comparison CCQM-K90. The cylinders were delivered later than anticipated, in mid-2014 instead of February, after an issue with the regulations on their transportation was solved by the BIPM with assistance from the NIST. Validation measurements of the BIPM's two dynamic generation systems, one based on paraformaldehyde permeation and the other on trioxane diffusion followed by conversion to formaldehyde, were undertaken. The comparison was launched with the registration of the eight expected participants and measurements began at the BIPM in December 2014.

1.2.4 Preparation for a repeat key comparison on nitrogen dioxide (CCQM-K74.2018)

The development of a dynamic generation system for nitric acid in nitrogen standards was carried out during the secondment of Céline Pascale from METAS. The generation of dynamic gas mixtures containing nitric acid mole fractions in the range of 200 nmol mol^{-1} to 500 nmol mol^{-1} with a standard relative uncertainty of 3 % was demonstrated. An important component of this uncertainty comes from the quantification of water vapour emitted with nitric acid from the permeation tube, which was performed using a CRDS analyser calibrated by the NPL. The nitric acid in nitrogen standard mixtures were analysed using a Fourier Transformed Infrared spectrometer equipped with a gas cell with the inner surfaces coated with a Silcosteel® layer. This coating allowed a reduction of the response time of the FTIR by a factor of four compared to a traditional electropolished stainless steel gas cell of the same volume. The standard mixtures were used to calibrate the FTIR spectrometer, reducing the relative uncertainty of measurements of nitric acid by a factor of three. As a result the uncertainty in the reference value for nitrogen dioxide standards in future key comparisons (CCQM-K74.2018) will be reduced.

1.2.5 Gas metrology programme quality system

The Quality System that underpins the Gas Metrology work programme was reviewed during an internal audit and also during a two day External Audit, undertaken in November 2014. No major non-conformities in the documentation and implementation were reported by the auditors. A series of actions to address minor non-conformities and observations raised in the audit report will be undertaken in 2015.

2. **Organic analysis programme** (S. Westwood, R. Josephs, N. Stoppacher, S. Maniguet, A. Daireaux, T. Choteau, and R.I. Wielgosz)

2.1 Purity methodology and small molecule purity analysis

A revised "White Paper" that describes an objective approach to the use of data from organic purity assignment comparisons coordinated by the BIPM was prepared and circulated. These comparisons demonstrate a general capability for purity assignment of organic primary calibrators and for linking the results of key comparisons to the reporting and assessment of CMC claims. The revision included an extensive compilation of the results by all NMIs that have participated in BIPM coordinated purity comparisons. The approach described in the White Paper has been accepted for implementation by the CCQM Working Group on Organic Analysis (OAWG) and the CCQM Working Group on Key Comparisons and CMC Quality (KCWG).

The BIPM has led an International Union of Pure and Applied Chemistry (IUPAC) working group, with members from 12 NMIs and two international organizations. Two meetings were held in 2014 to draft technical guidelines on 'Methods for the SI Value Assignment of the Purity of Organic Compounds for use as Primary Reference Materials and Calibrators'. The BIPM organized and hosted the first meeting of the working group in April 2014. A draft report from this working group is expected in 2015.

The BIPM's laboratory facilities for supporting purity key comparisons were augmented through collaboration with the NMIJ/AIST, Japan, the first deliverable of which has resulted in the donation to the BIPM of a high-field nuclear magnetic resonance (NMR) spectrometer from an instrument manufacturer. This was followed by training of BIPM staff at the NMIJ and the NRC, Canada, and the installation and commissioning of the NMR instrument at the BIPM. In a lead up to this collaboration, the BIPM participated successfully in the CCQM-P150 pilot study, coordinated by the NMIJ, on the use of qNMR for the purity assignment of a sample of dimethyl sulfone using bis-3,5-triflurormethylbenzoic acid as the internal standard.

2.2 Organic programme quality system

The Quality System that underpins the Organic work programme was reviewed during a two-day External Audit undertaken in November 2014. No major non-conformities in documentation and implementation were reported by the auditors. A series of actions to address minor non-conformities and observations raised in the audit report will be undertaken in 2015.

2.3 Purity comparison CCQM-K55.c [(L)-Valine]

The CCQM-K55.c Final Report was approved and published in the KCDB. The CCQM-P117.c Final Report was finalized and has been approved by the participants for publication in *Metrologia*.

2.4 Purity comparison CCQM-K55.d [Folic acid]

The characterization of the CCQM-K55.d candidate material has continued, including sorption balance studies relating the water content of the material to the relative humidity of the laboratory. A draft protocol for the comparison, taking into account the sorption balance studies was prepared and discussed at the CCQM OAWG meeting in October 2014.

2.5 Organic large molecule purity – Angiotensin I and Insulin model studies

The development and validation of a range of analytical methods for the purity determination of the intact decapeptide Angiotensin I (ANG I) and Insulin (INS) was completed by the BIPM. The ANG I activities have received additional support through a collaborative agreement with the NIST. ANG I, a hypertension marker, is frequently monitored and is important in clinical chemistry. INS plays an important role in the treatment and monitoring of diabetes. Pure peptide primary calibrator materials are a fundamental requirement for pharmaceuticals, laboratory medicine and clinical chemistry, and both molecules provide model systems for developing future large organic molecule purity comparisons for the CCQM.

Analytical methods developed, validated and implemented for the identification and quantification of structurally related peptide impurities for use in the characterization of the model peptides ANG I and INS include: LC-hrMS/MS (Orbitrap), LC-MS/MS (Qtrap), and LC-UV-CAD.

A peptide impurity corrected amino acid (PICAA) analysis approach, requiring quantification of constituent amino acids (AAs) following hydrolysis of the material and correction for AAs originating from impurities, has been developed and validated. It is an alternative to the full mass balance approach that could require unviably large quantities of peptide materials.

The purity mass fraction values of the pure ANG I material and the corresponding measurement uncertainties obtained by both the mass balance and the PICAA approach are in agreement with results obtained by quantitative nuclear magnetic resonance spectroscopy (qNMR) and elemental analyses (CHN/O) corrected for impurities. Both qNMR and CHN/O analyses were undertaken by external providers to provide confirmatory data and would not deliver an accurate purity mass fraction value without impurity correction.

The purity mass fraction values of the pure INS material and the corresponding measurement uncertainties obtained by both the mass balance and the PICAA approach were found to be in agreement. NMR spectroscopy has been used to provide data to confirm the characterization of the INS.

The BIPM has successfully finalized the cross-validation of different approaches for the purity mass fraction value assignment for both model peptides ANG I, in collaboration with the NIST, and INS. The methods developed will be used in the planned CCQM key comparison on peptide purity. External publications of the study results are being prepared.

2.6 Organic large molecule purity – Human C-peptide

The first CCQM key comparison on peptide purity (CCQM-K115) coordinated by the BIPM in collaboration with the NIM, China, was launched. Dr M. Li and Dr D. Song from the NIM joined the BIPM as visiting scientists to work on method development and to study material characterization, in preparation for the key comparison.

The assignment of the mass fraction content of high-purity C-peptide (hCP) has been accepted as the most appropriate choice of study material for a first CCQM key comparison (CCQM-K115/P55.2) that will investigate competencies to perform peptide purity mass fraction assignment. The hCP was chosen to be an applicable model system from which performance on other molecules could be inferred, whilst simultaneously focusing on a material directly relevant to existing CMC claims.

hCP is an important clinical and forensic analyte in its own right for which accurate reference measurement systems are required. It is a chemically-synthesized linear peptide of known sequence, without cross-links, that contains 31 amino acids. It will directly support NMI services and certified reference materials (CRMs) which are currently provided by NMIs. A paper (*SI value assignment of purity – a model for the classification of peptides for primary structure purity determinations*) describing how this comparison supports a wider range of NMI capabilities was presented and approved by the CCQM Working Group.

The NIM, China, was responsible for the synthesis and supply of the hCP material to the BIPM. The comparison samples were filled under nitrogen using a glove box to avoid contamination. Homogeneity and stability studies have been completed at the BIPM.

Different methods have been developed and implemented for the identification and quantification of structurally-related impurities for the characterization of materials. These are: LC-hrMS/MS (Orbitrap), LC-MS/MS (Qtrap), and LC-UV-CAD. The additional methods for use in the characterization of the hCP material that have been developed or investigated are GC-MS, KFT, TGA, DVS as well as supporting data from ion chromatography, CHN/O and NMR measurements.

A PICAA analysis approach, requiring quantification of constituent amino acids following hydrolysis of the material and correction for amino acids originating from impurities, has been developed and is in use.

The impurity profile of the batch and the outcome of the homogeneity and stability studies have been found to be appropriate for the purposes of the comparison. The key comparison and a parallel pilot study began in early December 2014. The study samples were shipped to the participants by 48h express service using insulated shipping containers and cooling pads. The boxes were equipped with temperature loggers to control and exclude exposure to high temperatures that could alter the impurity profile.

3. **Activities related to the JCTLM** (S. Maniguet and R.I. Wielgosz)

Dr Wielgosz is the Executive Secretary of the Joint Committee for Traceability in Laboratory Medicine (JCTLM), and leader of its review team on Quality Systems and Implementation. Dr Maniguet coordinates the development of the JCTLM Database, and is a member of the review team on Quality Systems and Implementation.

In February 2014, the WG1 Cycle 10 reference materials, and measurement methods, and WG2 Cycle 8 reference measurement laboratory services approved by the Executive Committee during its 12th annual meeting in December 2013 were published in the database.

As of December 2014 the JCTLM Database contained:

- 319 available certified reference materials that cover 11 categories of analytes. Of these reference materials, 33 are in List II, which includes reference materials that are value-assigned using internationally agreed protocols, and three are in List III, which covers reference materials with nominal properties;
- 167 reference measurement methods or procedures that represent about 80 different analytes in nine categories of analytes;
- 106 reference measurement services, delivered by ten reference laboratories and two NMIs in eight countries and which cover seven categories of analytes.

The WG1 Cycle 10 call for nominations of higher order reference materials and reference measurement methods or procedures, and the WG2 Cycle 8 call for nominations of reference measurement laboratory services were announced on the JCTLM website in February 2014, and email notifications were sent to about 350 potential contributors to the JCTLM. As of July 2014, 12 nominations for materials, 9 nominations for methods, and 31 nominations for services had been received and sent to Review Teams for evaluation.

The first issue of the JCTLM Database Newsletter was released in April 2014 and distributed to JCTLM contacts by email. Positive feedback was received on this first issue as well as requests to include external contributions in future issues to promote measurement result traceability in laboratory medicine.

The annual joint meeting of the JCTLM Working Group 1 and 2 was held at the BIPM on 3 December 2014, and was followed by the 13th meeting of the JCTLM Executive Committee on 4-5 December. During its meeting the Executive decided to establish a Working Group on Education and Promotion on Traceability which would come into force in 2015 as well as an *ad hoc* Working Group on JCTLM Governance. The latter will be tasked with revising JCTLM procedures and proposing the most appropriate structure and assignment of duties to the JCTLM Executive, WG Chairs and Secretariat.

ISO TC 212 WG2 is currently revising two normative standards of particular importance to the JCTLM processes, notably ISO 17511 and ISO 15195. The BIPM participates actively as a liaison organization to ISO TC 212.

4. Publications

1. Viallon J., Moussay P., Idrees F., Wielgosz R., Sweeney B., Quincey P., Final report of the ongoing key comparison BIPM. QM-K1: Ozone at ambient level, comparison with NPL (May 2013), *Metrologia*, 2014, **51**, 08004.
2. Viallon J., Moussay P., Idrees F., Wielgosz R., Norris J.E., Guenther F., Final report of the ongoing key comparison BIPM. QM-K1: Ozone at ambient level, comparison with NIST (February 2013), *Metrologia*, 2014, **51**, 08005.
3. Viallon J., Moussay P., Idrees F., Wielgosz R., Lagler F., Final report of the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with JRC (October 2013), *Metrologia*, 2014, **51**, 08006.
4. Viallon J., Moussay P., Wielgosz R., Li H., Hui W.L., Norris J.E., Guenther F., Final report of the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with NMC, A*STAR, May 2013, *Metrologia*, 2014, **51**, 08007.
5. Viallon J., Lee S., Moussay P., Tworek K., Petersen M., Wielgosz R.I., Accurate laser measurements of ozone absorption cross-sections in the Hartley band, *Atmos. Meas. Tech. Discuss*., 2014, **7**, 8067-8100.
6. Flores, E., *et al*., International comparison CCQM-K82: methane in air at ambient level (1800 to 2200) nmol/mol (2014) *Metrologia*, 2014, **52**, 08001.
7. Flores, E., Rhoderick, G., Viallon, J., Choteau, T., Moussay, P., Guenther, F.R., Gameson, L., Wielgosz, R.I. *Anal. Chem*. (Submitted) 2014.
8. Westwood S., Josephs R., Choteau T., Daireaux A., Wielgosz R *et al*., Final Report on key comparison CCQM-K55.c (L-Valine): Characterization of organic substances for chemical purity, *Metrologia*, 2014, **51**, 08010.
9. Josephs R.D., Daireaux A., Choteau T., Westwood S., Wielgosz R.I., Normal phase-liquid chromatography-tandem mass spectrometry with atmospheric pressure photoionization for the purity assessment of 17β-estradiol, *Anal. Bioanal. Chem.*, 23 September 2014 (Epub ahead of print), in print.

5. Activities related to the work of Consultative Committees

The CCQM held its 20th meeting on 10-11 April 2014 at the BIPM. It was preceded by meetings of the CCQM Working Groups.

R.I. Wielgosz is the Executive Secretary of the CCQM and a member of the CCQM Strategic Planning Working Group (SPWG).

S. Westwood is a member of the CCQM Working Group on Organic Analysis (OAWG).

R. Josephs is a member of the CCQM Working Group on Bioanalysis (BAWG), the CCQM Working Group on Organic Analysis (OAWG) and the *ad hoc* Steering Group on Microbial Measurements (MBSG).

J. Viallon is a member of the CCQM Working Group on Gas Analysis (GAWG).

E. Flores is a member of the CCQM Working Group on Gas Analysis (GAWG).

S. Maniguet is a member of the CCQM Working Group on Organic Analysis (OAWG) and the CCQM Working Group on Key Comparisons and CMC Quality (KCWG).

6. Activities related to external organizations

R.I. Wielgosz is a BIPM representative to the International Union of Pure and Applied Chemistry, Interdivisional Committee on Terminology, Nomenclature and Symbols (IUPAC ICTNS), ISO TC 212, Clinical laboratory testing and *in vitro* diagnostic test systems, Working Group 2 on Reference Systems, and ISO TC 146 on Air Quality, and is a member of the editorial board of Accreditation and Quality Assurance. He is a member of the World Meteorological Organization (WMO)-BIPM Joint Liaison Group.

S. Westwood is the chair of the IUPAC Project 2013-025-2-500: Methods for the SI Value Assignment of Purity of Organic Compounds, and the BIPM liaison to the ISO/REMCO and the REMCO/CASCO Joint Working Group 43, and a member of the World Anti-Doping Agency (WADA) Laboratory Expert Group.

R. Josephs is the BIPM representative to the Inter-Agency Meeting and the Codex Committee on Methods of Analysis and Sampling (CCMAS) of the Codex Alimentarius Commission.

J. Viallon is the BIPM representative at ISO TC 146/SC 3 on Air Quality – Ambient Atmospheres.

7. Travel

R.I. Wielgosz to:

- Teddington (UK), 5 - 7 February 2014, to attend the EURAMET Metchem Plenary Session and Gas sub group;
- Marnes la Coquette (France), 28-30 April 2014, to participate in revision of standards for ISO TC 212 WG2 (Reference Systems – Laboratory Medicine);
- Warsaw (Poland), 19 - 20 May 2014, to give an invited lecture at the workshop organized for the 95th anniversary of GUM, Poland;
- Gaithersburg (USA), 16 - 19 June 2014, to participate in the National Academies Review of the NIST MML laboratory;
- OSTP, Washington (USA), 20 June 2014, to give a presentation on activities and comparisons in greenhouse gas standards in support of climate change monitoring; and USP, Rockville (USA), to present BIPM activities on peptide purity comparisons;

- Teddington (UK), 3 July 2014 to participate in the NMS Chem/Bio-metrology advisory working group;
- PTB, Braunschweig (Germany), 24-25 July 2014, to discuss collaborative projects in metrology in chemistry;
- Vienna (Austria), 3 - 5 September 2014, to attend the Technical Meeting on Stable Isotope Reference Materials at the IAEA headquarters;
- Tsukuba (Japan), 14 - 17 October 2014, to attend meetings of the CCQM Working Group on Gas Analysis.

S. Westwood to:

- Tsukuba (Japan), 6 - 10 June 2014, for discussions on the BIPM-NMIJ qNMR project;
- Tsukuba (Japan), 14 - 17 October 2014, for meetings of the IUPAC Organic Purity Technical Report and the CCQM Organic Analysis Working Groups;
- Geneva (Switzerland), 10 - 11 December 2014, for the first meeting of the REMCO/CASCO Joint Working Group 43.

J. Viallon to:

- Vienna (Austria), 29 April - 2 May 2014, to attend the European Geosciences Union general assembly and to the IAEA for a visit of the Terrestrial Environment Laboratory;
- Vienna (Austria), 3-5 September 2014, to attend the Technical Meeting on Stable Isotope Reference Materials at IAEA headquarters;
- Tsukuba (Japan), 14 - 17 October 2014, to attend meetings of the CCQM working group Gas Analysis and to visit the National Institute for Environmental Studies;
- Daejeon (Republic of Korea), 20 - 22 October 2014, to attend the 5th WMO-GAW Expert workshop on Volatile Organic Compounds.

R. Josephs to:

- IAM, Budapest (Hungary), 28 February - 2 March 2014, to represent the BIPM at the Inter-Agency Meeting of the Codex Alimentarius Commission and to attend the 6th Joint IAM/MoniQA Workshop on Sampling;
- USP, Rockville (USA), 30 September - 3 October 2014, to participate in the USP Peptide Workshop and to give a presentation at the USP Peptide Expert Panel;
- NIMJ, Tsukuba (Japan), 13 - 17 October 2014, to attend the IUPAC purity meeting, CCQM BAWG/OAWG meetings, Workshop and to visit the NMIJ.

E. Flores to:

- Vienna (Austria), 29 April - 2 May 2014, to attend the European Geosciences Union general assembly. To present the poster: Accurate measurements of Primary Standard Gas Mixtures (PSMs) of CH_4 in synthetic and scrubbed real air analyzed by two independent measuring techniques: CRDS and GC-FID;
- PTB, Braunschweig (Germany), 9 - 10 October 2014, to attend the EUMETRISPEC Workshop on Traceable spectral reference line data for atmospheric monitoring. To present the poster: HITRAN Vs Gas Standards Calibration for measurements of NO_2 in the v3 band and HNO_3 in the v2 band.

S. Maniguet to:

- JEOL Ltd, Welwyn Garden City (UK), from 29 July to 1 August 2014, to attend a training session on NMR spectrometer maintenance and operation, as well as NMR experiments, data analysis;
- NRC, Ottawa (Canada), from 8 - 12 September 2014, for training on qNMR measurements.

N. Stoppacher to:

- Tsukuba (Japan), 6 June to 8 August 2014, for training in the implementation of qNMR for organic purity assignments;

T. Choteau to:

- JEOL Ltd, Welwyn Garden City (UK), from 29 July to 1 August 2014, to attend a training session on NMR spectrometer maintenance and operation, as well as NMR experiments, data analysis;
- Ottawa (Canada), 1 September to 3 October 2014, for training in the operation and maintenance of a NMR spectrometer.

8. Visitors

- Z. Bi (NIM), 7 - 11 April 2014
- F. Guenther (NIST), 3 - 4 November 2014
- J. Warren (LGC), 3 - 4 November 2014
- T. Saito and T. Yamazaki (NMIJ), 11 April 2014, for discussions on the BIPM-NMIJ qNMR project.

9. Guest workers

- C. Pascale (METAS, Switzerland), 3 March to 31 July 2014
- M. Doval Miñarro (NPL, UK), 1 September to 30 November 2014
- D. Song (NIM, China), 2 June to 29 November 2014
- M. Li (NIM, China), until 30 May and since 3 November 2014.