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

Supplement: scientific Departments

(1 January 2013 – 31 December 2013)

March 2014

Bureau International des Poids et Mesures

BIPM Mass Department
Interim Director: M. Stock[1]
(1 January 2013 to 31 December 2013)

1.1 Measurement services

1.1.1 Calibrations

1.1.1.1 Calibrations of 1 kg prototypes and stainless steel standards (P. Barat)

From 1 January to 31 December 2013, certificates were issued for the following 1 kg prototypes in platinum-iridium: No. 2 (Romania), No. 3 (Spain), No. 4 (USA) and No. 70 (Germany). Calibration of the 1 kg prototype No. 12 for the Russian Federation was started in 2013 and will be completed in early 2014. One certificate was issued for a 1 kg mass standard in platinum-iridium designated "A" (NPL, UK).

Certificates for 1 kg mass standards in stainless steel were issued: four for the NML-SIRIM (Malaysia) and one for the INM (Romania). Calibrations were carried out in 2013 for one 1 kg mass standard in stainless steel from the LATU (Uruguay), three from the IPQ (Portugal) and two from the VSL (the Netherlands). The certificates for these calibrations will be issued in early 2014.

In preparation for the expected redefinition of the kilogram, the Mass Department is carrying out a series of "extraordinary calibrations" with respect to the International Prototype of the Kilogram (see §1.1.1.2). As a consequence of the high priority attached to this work and the heavy workload associated with this calibration campaign, the Mass Department temporarily suspended the mass calibration service from October 2013. The BIPM will inform the NMIs when the mass calibration service is to be restarted.

Since 1993, the BIPM Mass Department has offered National Metrology Institutes (NMIs) a service to determine the magnetic properties of new 1 kg mass standards in stainless steel in order to check their conformity with the technical requirements for primary mass standards. Due to the high priority being given to the upcoming redefinition of the kilogram and consequently to the BIPM watt balance, it was decided to suspend this service.

1.1.1.2 Extraordinary calibrations with respect to the IPK for the redefinition of the kilogram (P. Barat)

As requested by the Consultative Committee for Mass and Related Quantities (CCM) and following an announcement of intent to the CIPM in October 2011, the BIPM intends to carry out calibrations in air of 1 kg platinum-iridium (Pt-Ir) prototypes for NMIs involved in experimental determinations of the Planck constant, h, and the Avogadro constant, N_A, as well as determinations in vacuum of two silicon spheres used in the Avogadro Project. 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. It will be the first time that the IPK has been used since the Third Periodic Verification of National Prototypes of the Kilogram (1988-1992).

This work will be carried out in two phases. Phase 1 will consist of determining how much the mass of the IPK has increased since its last cleaning and washing carried out at the end of the Third Verification, approximately 20 years ago. The official copies will be included in these measurements as well as the BIPM's collection of eight 1 kg working standards in Pt-Ir and the two prototypes that are reserved for exceptional use. The effect of cleaning and washing on the IPK and its six official copies will be studied, and then the mass of the remaining artefacts will be determined with respect to the IPK. Following these studies, the masses of the BIPM working standards with respect to the IPK will be known with minimal uncertainty.

Phase 2 will consist of calibrating a selection of Pt-Ir prototypes used by NMIs that contribute to the redefinition

[1] A Picard (Director of the Mass Department) was absent in 2013 due to ill health

of the kilogram with respect to the BIPM working standards linked to the IPK during Phase 1. In parallel we will determine the mass of the ^{28}Si spheres AVO28-S5 and AVO28-S8 in the context of the programme already agreed by the CCM Working Group on the Avogadro Constant (WGAC). Although the mass of the spheres will be determined using a vacuum comparator, none of the Pt-Ir standards mentioned above, including the IPK and its six official copies, will be used in vacuum. The transfer of the mass unit from air to vacuum is made using surface artefacts developed by the BIPM and which have already been used successfully in the Avogadro project.

Phase 1 was launched in December 2013 and involves only BIPM working standards in Pt-Ir in order to select two working standards on the basis of their stability as reference standards for the measurements that involve the IPK and its six official copies. Comparisons among the IPK, its six official copies, two BIPM prototypes reserved for exceptional use and the two selected working standards have been undertaken to establish baseline values prior to any cleaning-washing operations. The process of cleaning-washing started at the end of December 2013. Phase 1 is expected to be completed by the end of February 2014.

A detailed report of the results will be presented at the next CCM meeting in February 2015.

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

The BIPM Ensemble of Reference Mass Standards (ERMS) comprises four 1 kg Pt-Ir cylinders, four 1 kg stainless steel cylinders and four 1 kg natural silicon spheres. In addition to these 12 mass standards, two surface artefacts (stacks), one in Pt-Ir and the other in stainless steel, each consisting of a stack of eight discs, are part of the ensemble. A second stack in stainless steel and one in silicon, consisting of seven discs, will be added in 2014.

Each storage condition (air, nitrogen, argon and vacuum) will receive one 1 kg Pt-Ir cylinder, one 1 kg stainless steel cylinder, one 1 kg natural silicon sphere and one surface artefact (in Pt-Ir for air, in stainless steel for argon and nitrogen environments, and in natural silicon for vacuum).

Before the mass standards are placed definitively in their respective storage containers, the mass stability has been investigated in air. This preliminary study shows that the behaviour of the 1 kg Pt-Ir cylinders is similar. A mass increase of about 2 µg was observed over a period of one year. The mass stability for the four 1 kg stainless steel cylinders has been between 2 µg and 4 µg over the last six months. Both surface artefacts showed a mass stability of about 1 µg to 2 µg over a period of one year.

Knowing that the combined standard uncertainty for the mass determination of 1 kg Pt-Ir mass standards is 7 µg and for 1 kg mass standards in stainless steel is 15 µg, these results reveal a good mass stability of these standards in air and reinforce our decision that 2014 will be the starting point for the definitive placement of these standards in their respective environments.

Volume determinations of three of the four natural silicon spheres were carried out in 2013 by the NMIJ/AIST (Japan). The fourth was carried out by the PTB (Germany). The PTB is also performing surface characterization of all the spheres; this work will be completed in 2014. The BIPM Mass Department appreciates the PTB's contribution and thanks them for their strong support. As soon as the Mass Department receives the four natural silicon spheres, a mass stability study will be undertaken in air before placing them in their respective storage conditions.

1.1.1.4 Volume calibrations of mass standards (C. Goyon-Taillade and F. Idrees)

Density determinations of four new 1 kg prototypes have been carried out. In addition, the volume was determined for one stack of eight Pt-Ir disks that belong to the NIST (USA).

To improve the hydrostatic weighing facility, work is in progress to replace doubly distilled water, used as the density reference, by two 500 g cylinders of single-crystal silicon in a transfer liquid other than water.

The densities of the two cylinders were determined by the NMIJ/AIST. New software has been written for data acquisition and analysis. We plan to improve the measurement algorithm so that the balance sensitivity would be determined during each weighing series. At present, the sensitivity is determined separately, just prior to weighing the mass standards.

Following completion of the cleaning process, volume calibration was carried out on the stainless steel samples which are dedicated for surface analysis and which are linked to the Ensemble of Reference Mass Standards (ERMS) experiment (see §1.5).

1.1.1.5 Pressure (C. Goyon-Taillade and F. Idrees)

Calibration of BIPM manometers, with respect to the pressure balance maintained by the Mass Department were carried out during three campaigns in 2013. Nineteen internal certificates were issued.

1.1.1.6 Quality Management System (P. Barat, C. Goyon-Taillade and F. Idrees)

In conformity with the BIPM Quality Management System (QMS), the mass service and the internal pressure calibration service underwent successful external audits. These peer-reviews were carried out by Dr P. Fuchs (METAS) for mass and volume measurement capabilities and by Mr P. Otal (LNE) for pressure measurement.

1.1.2 Comparisons (P. Barat, C. Goyon-Taillade and A. Picard)

The BIPM is the pilot laboratory for the key comparison CCM.M-K4 with 16 participants, organized in four petals. Each participating NMI has determined the masses of two 1 kg mass standards in stainless steel. Measurements were carried out between September 2011 and April 2012. The Draft A report was sent to the participants last November and the deadline for comments is 21 January 2014.

1.1.3 Support for NMIs (P. Barat)

The realization of the new kilogram definition by watt balances or the x-ray crystal density method (usually referred to as the Avogadro method) 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 BIPM is able to provide this service using its surface artefacts for laboratories that are not able to characterize their own test standard with respect to the air/vacuum transfer. At the request of the NRC, the BIPM conducted a study of the water sorption effect on the 1 kg prototype No. 50 following air/vacuum transfers.

1.1.4 Mass comparators to support the measurement services (P. Barat)

The Mass Department has three 1 kg mass comparators: the Metrotec from Mettler-Toledo which only works in air and the M_one 6V-LL from Mettler-Toledo and the CCL1007 from Sartorius, both of which work in air/gas and vacuum environments.

Until now, mass calibrations provided for NMIs of Member States have been performed with the Metrotec mass comparator only. As mentioned in §1.3, the realization of the new kilogram definition must be made under vacuum. In order to anticipate the expected redefinition of the kilogram, the M_one 6V-LL and CCL1007 mass comparators have been integrated into the BIPM QMS for mass calibrations carried out not only in air but also under vacuum from October 2013.

1.2 **Manufacturing 1 kg artefacts in platinum-iridium for NMIs** (F. Boyer - BIPM Workshop)

Four new 1 kg mass prototypes were manufactured at the BIPM in 2013: three for the NIST (USA) and one for the NRC (Canada). One platinum-iridium surface artefact consisting of a stack of eight discs, each separated by three rods, was manufactured for the NRC (Canada).

1.3 **Cooperation between the METAS and the BIPM** (P. Fuchs (METAS) and P. Barat)

In preparation for the *mise en pratique* of the new definition of the kilogram, cleaning efficiency is currently being investigated under the umbrella of the European Metrology Research Programme (EMRP) as a Joint Research Programme (JRP) designated as SIB-05 (NewKILO): "Developing a practical means of disseminating the redefined kilogram".

Within this framework, the BIPM and the METAS are undertaking a study which is focused on cleaning effects on 1 kg Pt-Ir mass standards. Three cleaning methods are under investigation: the nettoyage-lavage technique (BIPM method), hydrogen low-pressure plasma cleaning (METAS method) and UV/Ozone cleaning (NPL method).

Two aspects are evaluated in the comparison: the amount of contaminants removed after cleaning and the mass stability of the 1 kg mass standard after cleaning.

To accomplish this study, two of the cleaning methods (hydrogen low-pressure plasma cleaning and UV/Ozone cleaning) are performed by the METAS using its own equipment. Chemical analysis of the surface of the standard is carried out before and after each cleaning operation, using the METAS XPS system as well as mass measurements to determine the effect of each cleaning operation using METAS mass comparators. Mass measurements to determine the stability of the 1 kg mass standard in Pt-Ir will be carried out at the BIPM.

This study started in April 2011 with a one-year investigation into the mass stability of a 1 kg Pt-Ir mass standard after having proceeded to the BIPM cleaning method. No chemical analysis of the surface of the standard was performed so as not to change the behaviour of the standard due to XPS measurements which are carried out under ultra-high vacuum. The 1 kg mass standard was then exposed to laboratory air at the BIPM from April to June 2012 in order to achieve natural contamination of its surface. Further to this contamination, the 1 kg mass standard was cleaned three times using the hydrogen low-pressure plasma method at the METAS. This time, chemical analyses of the surface were performed before and after each cleaning operation. The mass stability was studied over 10 months at the BIPM. From April to June 2013, the 1 kg mass standard was contaminated in the same way as before. In August 2013, the 1 kg mass standard was cleaned two times using the BIPM method but this time a chemical analysis of its surface was carried out before and after each cleaning. Determination of the mass stability has been ongoing since August 2013.

A complete and detailed report will be issued at the end of the study, after evaluation of the UV/Ozone cleaning method.

P. Barat would like to thank the METAS, particularly Peter Fuchs, Kilian Marti and Stefan Russi for their strong support and warm welcome.

1.4 **A new analysis of BIPM historical mass comparison data** (C. Goyon-Taillade and E. de Mirandés)

A new analysis of all available experimental data from historical mass comparisons at the BIPM during the period 1889 to 2009 has been undertaken. The purpose of this analysis has been to carry out an independent data treatment taking advantage of modern computational tools and to compare the results with the mass values historically assigned by the BIPM to the international prototype of the kilogram (IPK, when it had not been cleaned), its six official copies and 11 BIPM working standards during the period.

Two different approaches have been developed successfully. One of them has aimed at re-treating the data while respecting most of the hypotheses historically used by the BIPM on the temporal evolution of those mass standards that act as references. This has been done by using least squares analysis and Lagrange multipliers. By contrast, in the second approach we chose to make hypotheses based on explicit mathematical criteria without regard to their agreement with the ones historically assumed; the outcome of each possible hypothesis was examined and we retained the group of hypotheses leading to the most similar results as being valid.

Both approaches have been thoroughly investigated and both have been able to reproduce the historical mass values assigned by the BIPM from 1889 to 2009 with differences which stay typically within 5 micrograms.

This work will be the subject of a peer reviewed article which is expected to be published during 2014.

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

During 2013, work on the BIPM Ensemble of Reference Mass Standards concentrated on three major areas: the conception and construction of a new vacuum storage network; the development of a new surface analysis project based on an international collaboration; and the optimization of a large number of different experimental aspects.

The vacuum storage network constructed in 2012 was found to have three significant limitations. These limitations have been corrected in a second version of the network that has been successfully completed during 2013. Manual valves have been replaced by computer controlled electric valves. These valves can be used to dynamically select the network container(s) to be analyzed by the residual gas analyzer (RGA); a mass spectrometer able to detect minute traces of impurities present in a low-pressure environment. The new network has had most of its connections soldered to help minimize the risk of future vacuum leaks. The mass containers used to store the standards in the vacuum network have been changed. The new containers have been designed to be compatible with the vacuum transfer system (VTS) of the CCL 1007 mass comparator. This will allow the mass standards which are stored under vacuum and which are to be transferred to the mass comparator to be weighed under vacuum without interrupting the low pressure environment.

A new surface analysis project in connection with the ensemble started in 2013. Six surface samples of the same material will be stored inside each container that hosts a standard of the ensemble. These samples are discs of 1.5 mm thickness, manufactured with a surface finish as similar as possible to the surface finish on the standard they share a container with. The samples will experience the same environmental conditions as the main standards and therefore we expect them to react to external contamination in a similar way. The samples should be subjected to periodic surface analysis (possibly twice a year over several years) to monitor the evolution of the surface contaminants. These measurements are planned to be carried out through partnerships with selected NMIs. The envisaged surface analysis methods include X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS) and secondary ion mass spectroscopy (SIMS). As a first step prior to contamination monitoring, a collaboration with the Laboratoire Commun de Métrologie LCM-LNE-CNAM (St Denis, France) started in 2013 to compare the surface roughness of the samples to that of the standards manufactured from the same material. An optical contact-less technique is used, where monochromatic polarized light is shone onto the samples with a fixed incidence angle and the diffused light is collected over a certain solid angle. Angle-resolved scattering theory is then used to link the angular distribution of the diffused light with the surface roughness. This collaboration will be pursued in 2014 with the objective of measuring the surface roughness of one third of the Pt-Ir, stainless steel and silicon samples.

In addition to these two major activities, several experimental improvements have been implemented. They concern aspects such as data treatment, operation protocols, security of the networks against a sudden leak, optimization of the measurement sequence and similar issues. All these improvements have been directed towards the achievement of our main goal for 2014 which is the definitive placement of some of the standards of the ensemble inside their storage containers and the official start of operations of the BIPM Ensemble of Reference Mass Standards.

1.6 Watt balance (R. Chayramy, A. Dupire, H. Fang, A. Kiss, T. Lavergne[2], E. de Mirandés, A. Picard, L. Robertsson, S. Solve and M. Stock)

The BIPM is developing a watt balance in order to be able to realize the expected new definition of the kilogram in terms of the Planck constant. A relative type A uncertainty of 10^{-6} and a type B uncertainty of 10^{-5} was achieved using the first version of the experiment which was conducted in a non-ideal environment inside a temporary laboratory. The type A uncertainty was limited mainly by the laboratory environment whereas the type B uncertainty was limited mainly by alignment capabilities.

Development of an improved apparatus operating in a more suitable environment progressed during 2013. In particular, a vacuum chamber has been installed in a dedicated new laboratory with improved temperature stability and vibration isolation. The existing apparatus was transferred and assembled inside the vacuum chamber in early 2013 to repeat previous measurements and to evaluate improvements that resulted from the better environment. As the vacuum chamber is designed for the future improved apparatus, modifications were necessary to temporarily accommodate the existing apparatus. Some components of the future version are already in use, in particular, a new vacuum-compatible weighing cell.

Measurements carried out in the new laboratory showed several large low-frequency velocity noise peaks, in particular a peak at 18 Hz whose amplitude reached as much as 10 % of the velocity of the moving coil (0.2 mm s^{-1}). In addition, large-band noise was observed on the velocity data with relative amplitude of about 5 parts in 10^4. The latter can be explained by the periodic non-linearity error of the interferometer measurements. The velocity of the coil is measured by a three-axis interferometer which consists of three home-built single-beam Michelson heterodyne interferometers. As the original apparatus needed to be adapted to meet the space limitations of its temporary accommodation inside the vacuum chamber, the optical alignments were less well optimized compared with those in the old laboratory, which leads to larger non-linearity errors. This error is caused by crosstalk between the two interferometer arms. In order to reduce this error, a test interferometer was studied on an independent bench, which is composed of the same optical elements mounted in a similar optical arrangement as in the watt balance. The aim was to find an alignment configuration which reduces the non-linearity error and which is easily reproducible in the watt balance. This investigation allowed a reduction of the non-linearity effect to 2 parts in 10^4 which corresponds to a peak-to-peak position error of about 3 nm. This error was then further reduced mathematically. Several methods have been evaluated, two of which were easily implemented in practice. Both gave similar results under the present measurement conditions. This led to an improvement in the standard deviation of the residuals of the voltage-to-velocity ratio U/v (from the fitted magnetic profile) by a factor of more than two. The relative standard deviation was about 8×10^{-5} for the results deduced from a single measurement with the coil moving upwards or downwards. The signal-to-noise (S/N) of the U/v ratio was mainly limited by a 28 Hz noise peak, which needs to be better understood and minimized in the future. The residual non-linearity error might become a potential limiting error source in the future, especially in the case of the BIPM watt balance where the velocity is very small compared to other watt balances and the vibration noise is large. Imperfect cancelling of the vibration noise in the U/v ratio and the resolution of the present phase detection system are other sources of error. Therefore, we have started to develop a new interferometer which has very small non-linearity errors. The new interferometer is based on two spatially separated beams and uses non-polarizing optical components. The first bench top tests have shown very promising results.

In the BIPM watt balance, the force-to-current F/I and U/v ratios are continuously and simultaneously measured while the coil is moving. The force signal is sensitive to undesirable accelerations due to the moving masses and in particular the vibrations. For the U/v ratio, the vibration noise, common to both signals, is significantly reduced when calculating the ratio of the two. However, for the F/I ratio, the vibration noise influences the force determination, but not the current, so that it does not cancel out by calculating the ratio and therefore needs to be carefully reduced or corrected. Vibration isolation is thus of particular importance for the BIPM watt balance

[2] Since 1 May 2013

operating in the simultaneous measurement scheme. Investigations were carried out to better understand and evaluate these unwanted effects. The time synchronization scheme for data acquisition was significantly improved by enabling the acceleration data to be acquired in perfect synchronization with the force data. This allowed a correlation analysis of the force and the acceleration signals to be undertaken. An improvement by a factor of two was achieved on the S/N ratio of the F/I ratio after applying a correction for the acceleration to the raw force data. The relative standard deviation was about 3×10^{-5} for the results deduced from a single coil movement upwards or downwards. However, the corrected data still shows significant residual variation due to the imperfect correlation. More work is required to further reduce the effect of vibration–related acceleration.

Following the improvement of the interferometry and the force determination, a short measurement campaign was carried out to assess the improvement on measurements of the Planck constant. In total, five series of measurements were performed. Each series took about one night. Both the day-to-day relative repeatability of the F/I and U/v ratios were reduced to 4×10^{-7}, corresponding to a factor of reduction of about five. In addition to the refinement on the velocity and the force determinations, the better thermal stability also contributed to the improvements. The standard deviation of measurements of the Planck constant in air was consequently reduced from 1.4 parts in 10^6 to about 5 parts in 10^7.

Significant efforts have been made to identify the environmental vibration sources and to understand the way vibrations propagate inside the apparatus. Vibrations were intensively recorded on the concrete block and the surrounding floor using a high precision seismometer. Measurements showed that the concrete block damps the vibration noise above 50 Hz but has a negligible effect at lower frequencies. The results were confirmed by the measurements performed by a colleague from the LNE using the LNE's accelerometers. An investigation showed that three air-conditioning units were particularly noisy. All have been subsequently replaced or removed. To identify the source of the observed large low-frequency noise peaks and to assess the vibration propagation, small accelerometers were placed at a large number of locations on the experimental set-up. The 14 Hz peak seems to be due to the internal structure supporting the weighing cell and the entire suspension, while the 18 Hz peak was amplified by some elements of the suspension. The internal structure has since been reinforced. Measurements will be repeated in the near future to confirm the expected noise reduction due to the 'quieter' air conditioners and the more rigid internal structure.

Progress was also made on the fabrication of the definitive magnetic circuit. It is based on an original design, employing two disks of Sm_2Co_{17} magnets in a closed yoke structure with a horizontal symmetry plane, creating a radial and horizontal magnetic flux density in the air gap. The geometry of the yoke structure leads to a highly constant flux density over the travel range of the coil, which is advantageous for watt balance operation. The coil in the air gap is completely surrounded by the high permeability yoke, made of a FeNi-alloy, which acts as a shield against external electromagnetic perturbations. The air gap has a width of 13 mm and a diameter of 250 mm. This geometry has recently been applied in the construction of magnets for several other watt balances.

To achieve the theoretically expected high uniformity of the flux density in practice requires a highly constant width of the air gap, which leads to very tight tolerances, at the level of 1 µm, on the elements of the yoke. All parts, except the outer housing, have been pre-machined by the BIPM workshop. Fabrication of the housing and the ultra-high precision machining of all parts has been carried out by Professional Instruments, USA. Accuracy of the machined parts was controlled by the Fraunhofer IPT (Institute for Production Technology), Aachen, Germany. Assembly was carried out at the BIPM, using a specially developed device, which allowed positioning of the components with micrometre accuracy in the presence of very strong magnetic forces, up to about 10 kN. Parallelism of the pole faces of 2 µm over 30 mm and centering of the outer and inner pole to within 10 µm could be achieved. The magnetic flux density in the gap was about 0.45 T with uniformity along a length of 40 mm at the level of 10^{-4}.

Work has advanced to apply a separately developed alignment technique to the watt balance coil. As a first step, the electric plane of the watt balance coil as well as an adjustable mirror fixed onto the coil were aligned to be horizontal to within about 150 µrad. A home-made auto-collimation system was used for the alignment of the mirror because of its small size. As this reference mirror is still too large to be placed inside the air gap of the magnet, the next step will be to transfer its alignment to a smaller mirror directly fixed to the watt balance coil. The coil will finally be integrated in the watt balance and will be used to align the magnetic field horizontally.

The Josephson voltage array developed for the determination of the induced voltage had been damaged. New arrays have been tested at the NIST for its replacement. At the same time, the current bias source for the Josephson voltage standard (JVS) has been improved to avoid trapping magnetic flux. Work on the second JVS dedicated to the measurement of the coil current has started: several 2 V arrays have been tested at the NIST by Dr Solve from the BIPM, and the design of the probe is complete. Both systems are expected to be tested in the watt balance in 2014.

The previous watt balance equipment has been transferred back to the old laboratory and will be used as a test apparatus. We have started to assemble an improved watt balance with several new components, most importantly a device based on piezo-elements for accurate control of the coil position and angle, which will lead to a significant reduction of the Type B uncertainty. The new magnet has been installed in the vacuum chamber of the watt balance. A new coil based on a stiffer ceramic Macor former was wound and it is expected that the deformation observed on the plastic PVC coil which is currently in use, will be reduced.

1.7 **Activities related to the work of Consultative Committees** (R. Davis and A. Picard)

A. Picard[3] is Executive Secretary of the Consultative Committee for Mass and Related Quantities (CCM) 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 Interim Acting Executive Secretary of the CCM[4] and has supported the new CCM President, P. Richard (METAS) since his appointment in late 2012; the position of President having previously been vacant for several months. A CCM meeting was held in February 2013. Among other activities, the Interim Executive Secretary has assisted in drafting the *mise en pratique* of the new definition of the kilogram and has supported the President in his development of the CCM Roadmap to reach the redefinition of the kilogram by autumn 2018.

1.8 **Activities related to external organizations** (E. de Mirandés and A. Picard)

A Picard acts as the BIPM liaison with the International Avogadro Coordination project (IAC), IMEKO Technical Committee 3 (TC3) and EURAMET Technical Committee of Mass and Related Quantities (TC-M) and Technical Committee of Thermometry (TC-T).

A. Picard is coordinator for mass measurements in the former International Avogadro Coordination project/CCM Working Group on the Avogadro Constant (WGAC).

A. Picard is the contact person for the European Metrology Research Programme (EMRP) joint research project SIB-05 (NewKilo) and SIB-03 (kNOW).

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

1.9 Publications

1. Fang H. *et al*., Status of the BIPM watt balance, *IEEE Trans. Instrum. Meas.*, 2013, **62**, 1491-1498.

[3] A Picard was absent in 2013 due to ill health

[4] In the absence of A. Picard

2. Solve S. *et al.*, A bias source for the voltage reference of the BIPM watt balance, *IEEE Trans. Instrum. Meas.*, 2013, **62**, 1594-1599.
3. Stock M., Watt balance experiments for the determination of the Planck constant and the redefinition of the kilogram, *Metrologia*, 2013, **50**, R1-R16.
4. Stock M., Watt balance experiments for the determination of the Planck constant and the redefinition of the kilogram, in *Metrology and Physical Constants*, IOS press, Amsterdam, ISBN 978-88-7438-083-1, 415-446.
5. Quinn T., Parks H., Speake C., Davis R., Improved determination of *G* using two methods, *Phys. Rev. Lett.*, 2013, **111**, 101102.
6. Barat P. *et al*., Report detailing requirements of NMIs for storage and transfer equipment compatible with existing apparatus, *NPL REPORT ENG 43*, ISSN 1754-2987, January 2013.
7. Berry J.J. *et al*., Report on the CCM WG TG1 pilot comparison to measure water vapour sorption on stainless steel mass standards, *NPL REPORT ENG 46*, ISSN 1754-2987, November 2013.

1.10 Travel (conferences, lectures and presentations, visits)

M. Stock to:

- Poznan (Poland), 16-17 May 2013, for an invited talk at the Quantum Metrology Conference.
- Fraunhofer Institute for Production Technology (IPT) in Aachen (Germany), 23 May 2013, for trial assembly of the watt balance magnetic circuit.
- Turin (Italy), 18-19 September 2013, to give two presentations at the kNOW workshop and to attend the EMRP kNOW project meeting.

P. Barat to:

- METAS, Bern-Wabern (Switzerland), 14 July-5 August 2013, to work on the second part of a study into the cleaning effect on 1 kg mass standards in platinum-iridium.
- INRIM, Turin (Italy), 18-20 September 2013, to attend the kNOW Workshop and the EMRP NewKILO project meeting.
- LCM LNE-Cnam (France), 11 and 30 October 2013, for surface analysis of some standards from the Ensemble of Reference Mass Standards (ERMS).

R. Davis to:

- Dubrovnk (Croatia), 21-22 March 2013, EURAMET TC-M meeting, to attend the plenary session and to give an invited presentation on work within the CCM related to the redefinition of the kilogram.
- Turin (Italy), 17-18 September 2013, kNOW Workshop organized by project SIB-03 of the European Metrology Research Programme (EMRP) to give invited presentations on the evolution of the definitions of the kilogram from 1799 through the proposed redefinition, and the *mise en pratique* of the new definition of the kilogram.

H. Fang to:

- Ottawa (Canada), 18-19 June 2013, Watt Balance Technical Meeting to give a presentation on the BIPM watt balance.
- NRC (Canada), 20 June 2013 to visit the NRC watt balance.
- LNE, Trappes (France), 6 August 2013, to discuss interferometry for watt balances with the LNE and the METAS.
- LNE (France), 26 September 2013, to visit the LNE watt balance.
- 16th International Congress of Metrology, Paris (France), 8 October 2013 to give a presentation on recent progress on the BIPM watt balance.
- NIM (China), 14-18 October 2013, to visit and discuss the NIM Joule balance and to give an invited presentation on the redefinition of the kilogram and the BIPM watt balance.

- LNE, Trappes (France), 18 December 2013, to attend the meeting on vibration problems in watt balances and to give a presentation on the BIPM watt balance and vibration measurements.

E. de Mirandés to:

- 16th International Congress of Metrology, Paris (France), 8 October 2013 to give a presentation on the Ensemble of Reference Mass Standards.

C. Goyon-Taillade to:

- LCM LNE-Cnam (France), 16-17 December 2013, to perform surface analysis of some standards from the Ensemble of Reference Mass Standards (ERMS).

A Kiss to:

- Ottawa (Canada), 18-19 June 2013, Watt Balance Technical Meeting.
- NRC (Canada), 20 June 2013, to visit the NRC watt balance.

T. Lavergne to:

- LNE (France), 26 September 2013, to visit the LNE watt balance.
- LNE, Trappes (France), 18 December 2013, to attend the meeting on vibration problems in watt balances.

L. Robertsson to:

- LNE, Trappes (France), 6 August 2013, to discuss interferometry for watt balances with the LNE and the METAS.

1.11 Visitors

- R.J. Hocken (The William States Lee College of Engineering), 23 January 2013;
- M. Schreiber (Sartorius) and U. Bartsch (SIOS), to perform maintenance on the CCL1007 mass comparator, 29 January-1 February 2013;
- P.J. Abbott (NIST), to deliver prototype No. 4, 18 February 2013;
- D. Mutter and R. Farley (MBW), to commission two new dew point meters, 19 February 2013;
- M. Shih Mean Lee (NMC, A*Star), to visit the watt balance, 22 February 2013;
- Channel Korea film crew, 26 February 2013;
- J. Pratt (NIST) and C. Sanchez (NRC), to visit the watt balance, 12 March 2013;
- H. Laiz (INTI), to collect two 1 kg mass standards in stainless steel, 15 March 2013;
- T. Nelson (NIST), to collect prototype No. 4, 15 March 2013;
- *Comité* "*Science et Métrologie*" of the French Academy of Sciences, to visit the watt balance, 8 April 2013;
- F.J. Gamarra and M. Bautista (CEM), to deliver prototype No. 3, 9 April 2013;
- O. Zakaria (NML-SIRIM), to deliver two 1 kg mass standards in stainless steel and to collect two 1 kg mass standards in stainless steel, 15 and 19 April 2013;
- L.F. Vitushkin (VNIIM), to deliver prototype No. 12, 24 April 2013;
- E. Lo, General Manager of NATA Australia, 30 April 2013;
- Delegation from Colombia, to visit the watt balance, 15 May 2013;
- M. Van Camp (Royal Observatory of Belgium), to visit the watt balance, 23 May 2013;

- M. Meunier (Canadian Embassy in France), to deliver prototype No. 50, 24 May 2013;
- J. Berry and M. Perkin (NPL), to deliver the 1 kg mass standard in platinum-iridium “A”, 5 June 2013;
- H. Bettin (PTB), to deliver prototype No. 70, 9 June 2013;
- D. Newell (NIST), to visit the watt balance, 11 June 2013;
- F.J. Gamarra and M. Bautista (CEM), to collect prototype No. 3, 11 June 2013;
- Abdel Monem Sallam (NIS), to visit the watt balance, 22 July 2013;
- J. Berry and S. Reilly (NPL), to collect the 1 kg mass standard in platinum-iridium “A”, 7 August 2013;
- M. Meunier (Canadian Embassy in France), to collect prototype No. 50, 21 August 2013;
- M. Schreiber (Sartorius), to carry out some adjustments on the CCL1007 mass comparator, 26-29 August 2013;
- P. Girault (Mettler Toledo), to perform maintenance on an AT1004 mass comparator, 3 September 2013;
- A. Razet (LNE-CNAM), to visit the Mass laboratories and the watt balance, 4 September 2013;
- O. Hupe and F. Schirdewahn (PTB), to collect prototype No. 70, 5 September 2013;
- P. Otal (LNE) to peer-review the pressure measurement capabilities, 30 September 2013;
- G.F. Popa (INM), to collect prototype No. 2 and one 1 kg mass standard in stainless steel, 2 October 2013;
- M. Kliebenschaedel (Mettler Toledo), to perform maintenance on the M_one mass comparator, 2-4 October 2013;
- P. Fuchs (METAS), to peer-review mass and volume measurement capabilities and to discuss surface analysis on the standards of the Ensemble of Reference Mass Standards (ERMS), 3-4 October 2013;
- M. Schreiber and T. Fehling (Sartorius), to carry out improvements to the CCL1007 mass comparator, 9 October 2013;
- D. Mutter (MBW) and R. Kurte (WIKA), for a technical discussion on humidity measurements, 15 November 2013;
- A. van der Veen (VSL), to collect two mass standards in stainless steel, 12 December 2013.

BIPM Time Department

Director: E.F. Arias

(1 January 2013 to 31 December 2013)

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

(E.F. Arias, A. Harmegnies, Z. Jiang, H. Konaté, W. Lewandowski, 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*. Starting on 1 July 2013 the official UTC rapid solution *UTCr* has been 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 2012*, volume 7, provides the definitive results for 2012 and is available electronically on the BIPM website at www.bipm.org/en/publications/time_activities.html.

2.2 Algorithms for time scales (W. Lewandowski, G. Panfilo, G. Petit, A. Harmegnies and L. Tisserand)

The algorithm ALGOS used for the calculation of the time scales 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 continues in the department with the aim of improving the long-term stability of EAL and the accuracy of TAI.

As a consequence of the introduction of the quadratic clock frequency prediction since September 2011, no drift of EAL has been observed during 2013. A new clock weighting procedure has been developed based on the concept of clock frequency predictability. It results in a more balanced distribution of clock weights and enhances the influence of the H-masers in the ensemble. An improvement on the short- and long-term stability of EAL is observed by applying the new weighting algorithm.

2.2.1 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. In the current weighting procedure the weight attributed to a clock reflects its long-term stability in order 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 and depends on the number of participating clocks. On average during 2013, about 14 % of the participating clocks were at the maximum weight. Since 2001, when the present weighting procedure was adopted, the number of hydrogen masers doubled, whilst the number of caesium clocks increased by 50 %. In order to optimize the impact of the hydrogen masers on the time scale, and for better distribution of the weight among the caesium clocks and hydrogen masers, a new weighting procedure based on the concept that a good clock is not a stable clock but instead is a predictable clock has been developed and validated. This new prediction model will be implemented in UTC calculation starting on 1 January 2014. Tests over the past eight years demonstrated that a better distribution among the clock weights is achieved, with a 40 % increase in hydrogen masers at the maximum weight. Both short- and long-term stability of EAL will improve by 20 %. The stability of EAL, as at the end of 2013, expressed in terms of an Allan deviation, is about 3 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 up to 1.8 parts in 10^{16} in the next few years.

2.2.2 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 2013, individual measurements of the TAI frequency have been provided by eight primary frequency standards, including six caesium fountains (LNE-SYRTE FO1, LNE-SYRTE FO2, NIST F1, NPL CSF2, PTB CSF1 and PTB CSF2). Reports on the operation of the primary frequency standards are regularly published on the BIPM website and collated in the *BIPM Annual Report on Time Activities*.

During 2013, measurements of the TAI frequency by a rubidium secondary frequency standard (LNE-SYRTE FO2Rb) have been reported in *Circular T*. They have been used for TAI steering since July 2013, after the publication of the CIPM 2012 recommendations.

Since January 2013, 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 $+0.7 \times 10^{-15}$ to -0.6×10^{-15}, with a standard uncertainty of maximum 0.3×10^{-15}. No steering corrections have been applied in 2013, showing the positive impact of the new algorithm on the accuracy of TAI.

2.2.3 Independent atomic time scales: TT(BIPM)

Because TAI is computed in 'real-time' and has operational constraints, 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(BIPM12), valid until December 2012, which had an estimated accuracy of about 2-3 parts in 10^{16} over recent years. Moreover, the Time Department provides a monthly extension of TT(BIPM12) based on the most recent TAI computation. Such an extension is useful for pulsar analysis pending 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.

2.2.4 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*.

2.3 **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 CCTF Working Group on Primary and Secondary Frequency Standards (WGPSFS), seeking 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.

The WGFS maintains a list of recommended values of standard frequencies for applications including secondary representations of the second. At its meeting in September 2012 it proposed additions and updates to microwave and optical atomic transitions in the list. 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).

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). Fifteen measurement reports of FO2Rb were submitted in 2013. With the agreement of the CCTF Working Group on Primary and Secondary Frequency Standards (WGPSFS), the Time Department updated its procedures and programs in order to include secondary frequency standards in the estimation of TAI accuracy (see §2.2.2) and in the computation of TT (see §2.2.3). These measurements have been officially used for the accuracy of TAI since July 2013 and will be used in January 2014 for the computation of TT(BIPM13).

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 some laboratories which maintain local representations of UTC. A successful experiment was conducted using BIPM GPS equipment in parallel to the fibre link regularly operated between two representations of 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 allowed the validation of the new BIPM calibration system with u_B within 1 ns. Several other fibre links between contributing laboratories are calculated on a regular basis, with a potential measurement uncertainty of about 100 ps in the future. In order to benefit from the quality of these links, the Time Department initiated a discussion with the laboratories already implementing time transfer via optical fibres with the aim of establishing standards for data transmission and validating the compatibility of the different techniques.

In parallel, the Time Department continued with activities in the frame 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.

2.4 **Time links used for TAI** (E.F. Arias, A. Harmegnies, Z. Jiang, H. Konaté, W. Lewandowski, G. Panfilo, G. Petit and L. Tisserand)

At the end of 2013, 73 time laboratories supplied data for the calculation of TAI 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 have almost disappeared from use, 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 TAI, 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.

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 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.

GPS PPP alone or in combination with TWSTFT are in use for TAI clock comparison 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.

Testing continues on other time and frequency comparison methods and techniques.

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.

2.4.1 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 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.

2.4.2 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 in 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 TAI computation, using procedures and software developed in collaboration with the ORB. These P3 time links are now routinely computed and compared to other available techniques, notably two-way time transfer. After one year of operation, the software that produces GPS P3 (iono-free) data has been upgraded and is now able to produce GLONASS P3. It will be implemented in some receivers to automatically produce both formatted GPS and GLONASS P3 code results. In the future, these newly available data are likely to be used in multi-GNSS system time links, but further studies on inter-frequency biases have to be carried out.

2.4.3 Two-way time transfer

Two meetings of the TWSTFT participating stations were held during 2013. The 21st annual meeting of the CCTF WG on TWSTFT was held at the TL premises in Chinese Taipei in September 2013.

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 TAI; fourteen are combined with GPS PPP solutions. Some of the TWSTFT links are used for particular studies such as the Time Transfer by Laser Link (T2L2) experiment. The TWSTFT technique applied to clock comparisons in TAI is at present reaching its maximum potential with sessions scheduled every two hours.

The BIPM is also involved in the calibration of two-way time-transfer links by comparison with GPS.

Results of 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).

2.4.4 Calibration of delays of time-transfer equipment

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. The BIPM continues to organize and run campaigns to measure the relative delays of GPS time equipment in time laboratories that contribute to TAI.

The method developed to perform absolute calibration of the Ashtech Z12-T hardware delays has allowed the BIPM to use this receiver for differential calibrations of similar receivers world-wide; calibration campaigns began in January 2001 and have been continued and expanded to include other types of receivers (Septentrio PolaRx2-3-4, Dicom GTR50 and Javad JPS E-GGD). New types of receivers are being investigated in collaboration with the laboratories that are equipped with them. In all cases, at least two receivers remain at the BIPM to serve as a local reference to which the travelling receiver is 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.

Starting in 2012, the BIPM initiated work to adopt a new organization for calibrations:

- In the frame of the Pilot Project of the UTC time link calibration, a time transfer system, consisting of two GNSS receivers, antennas, additional equipment and a calibration scheme has been developed with the aim of performing time link calibrations that could be transferred to any other technique on a same baseline. In 2013 this equipment had visited five laboratories in Europe and Asia under the pilot experiment to validate METODE (MEasurement of TOtal DElay).
- Following a recommendation by the CCTF, the Time Department has issued BIPM Guidelines for GNSS equipment calibration in UTC contributing laboratories, which are in the process of being revised by the CCTF Working Groups on GNSS and on the CIPM MRA. This process will be concluded in early 2014. This document is addressed to Regional Metrology Organizations with the aim of establishing a permanent cooperation for sharing the organization of campaigns to determine the relative delays of time transfer equipment in UTC contributing laboratories.

Work continues on absolute calibration of GNSS receivers in collaboration with the CNES.

The BIPM is not directly involved in TWSTFT calibration trips, but provides support whenever requested using a GPS receiver from its time laboratory.

2.5 **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 regularly in the form of the monthly BIPM *Circular T*.

Key comparison of stabilized lasers CCL-K11

The BIPM continues to support the CCL-K11 key comparison in terms of participation in measurement campaigns as well as by providing general advice. This follows a decision at the 98th meeting of the CIPM in 2009. This comparison is the internationally recognized and CCL supervised traceability chain to the SI metre. Even though this adds to the work load of the pilot and the four node laboratories that run the comparison, it effectively provides traceability to the metre for some eight NMIs per year. During 2013, staff from the Time Department were only involved in the reporting of measurement results and no BIPM presence for measurement campaigns took place.

Activities in gravimetry

The contribution of the Time Department to gravimetry covers two aspects:

a) The follow-up of the International Comparison of Absolute Gravimeters (ICAG), which has been under the responsibility of the NMIs since 2010. The key comparison CCM.G-K1 has been defined as part of the ICAG. The ICAG 2013 took place in Luxembourg piloted by the METAS. The BIPM provided support to the organization of this comparison and a member of the Time Department was present during the measurement campaign. The Time Department has also contributed to the CCM Working Group on Gravimetry (WGG).

b) A series of relevant publications related to gravity measurements at the BIPM, including a contribution to the watt balance experiment have been published.

2.6 **Rapid UTC** (F. Arias, A. Harmegnies, G. Panfilo, G. Petit and L. Tisserand)

From January 2012 until the end of June 2013 the Time Department conducted a pilot experiment to produce a "rapid UTC" (UTCr), that is, daily values of [*UTCr* – *UTC*(*k*)] evaluated on a weekly solution. About 40 laboratories that contribute approximately 60 % to 70 % of the clocks in UTC contributed to the pilot experiment.

UTCr became an official publication of the BIPM on 1 July 2013. This followed CCTF approval of a report which demonstrated that UTCr has reached the expected quality, providing a weekly solution which is consistently better than ± 2 ns peak to peak with the values published in the monthly BIPM *Circular T*. The results (ftp://tai.bipm.org/UTCr) have been published every Wednesday, without interruption since the end of February 2012.

The new product 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).

2.7 **New proposed definition of UTC** (F. Arias and W. Lewandowski)

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

The actions of BIPM delegates during this process have been critical at the International Telecommunication Union (ITU), and also in disseminating information and promoting decision making at the level of national representatives. Particularly important in 2013 was the organization of a joint workshop by the BIPM and the ITU on the future of the international time scale. This event was held in Geneva, Switzerland, on 19-20 September 2013. The workshop was in preparation for the next World Radiocommunication Conference in 2015 (WRC15), where a decision is to be taken on the redefinition of UTC without leap second adjustments. This meeting provided a unique opportunity to solicit input from most of the relevant communities, among then the two fully operational GNSS providers: GPS and GLONASS, the forthcoming GNSS Galileo and BeiDou, the telecommunications sector, time stamping authorities, and scientific organizations that represent astronomers, geodesists and geophysicists.

2.8 **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) and participates in a Working Group on pulsars and time scales established by the International Astronomical Union (IAU).

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

Activities related to the realization of reference frames for astronomy and geodesy are being developed 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 on these matters.

Cooperation continues for 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 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 of 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. These tasks are carried out with the help of the Advisory Board for the *IERS Conventions* updates, including representatives from all groups involved in the IERS. Since the completion of the latest reference edition, *IERS Conventions* (2010) in December 2010, work is continuing to provide updates to the *Conventions* (2010) which are regularly posted on the website (http://tai.bipm.org/iers/convupdt).

2.10 Comb activities (L. Robertsson)

As a result of the reorganization of activities in the Time Department, 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.

2.11 Publications

External publications

1. Defraigne P., Aerts W., Harmegnies A., Petit G. *et al.*, Advances in multi-GNSS time transfer, *Proc. IFCS-EFTF 2013*, 2013, 508-512.
2. Fang H., Kiss A., de Mirandés E., Lan J., Robertsson L., Solve S., Picard A., Stock M., Status of the BIPM watt balance, *IEEE Trans. Instrum. Meas.*, 2013, **62**, 1491-1498.
3. Harmegnies A., Defraigne P., Petit G., Combining GPS and GLONASS in all-in-view for time transfer, *Metrologia*, 2013, **50** (3), 277-287.
4. Jiang Z., *et al.*, On the gravimetric contribution to watt balance experiments, *Metrologia*, 2013, **50**, 452–471.
5. Jiang Z., Arias E.F., Use of the Global Navigation Satellite Systems for the construction of the international time reference UTC, *Proc. China Satellite Navigation Conference*, 457-468.
6. Jiang Z., Improving the time link calibration for the generation of UTC, *Proc. Asia-Pacific Time and Frequency Workshop*, on the internet only, Session A3 – Time and Frequency Transfer, http://www.apmpweb.org/fms/workshop3.php?tc_id=TF.

7. Jiang Z., Petit G., Tisserand L., Uhrich P., Rovera G.D. and Lin S.Y., Progress in the link calibration for UTC time transfer, *Proc. IFCS-EFTF 2013*, 2013, 861-864.
8. Jiang Z., Konaté H. and Lewandowski W., Review and Preview of Two-way Time Transfer for UTC generation – from TWSTFT to TWOTFT, *Proc. IFCS-EFTF 2013*, 2013, 501-504.
9. Panfilo G. and Harmegnies A., A new weighting procedure for UTC, *Proc. IFCS-EFTF 2013*, 2013, 652-653.
10. Panfilo G., Harmegnies A., Tisserand L., Arias E.F., The algorithm for the generation of UTC: latest improvements, *Proc. 45th PTTI Meeting*, 2013.
11. Petit G., Arias E.F., Harmegnies A., Panfilo G., Tisserand L., UTCr: a rapid realization of UTC, *Metrologia*, **51,** 2014, 33-39.
12. Solve S., Chayramy R., Picard A., Kiss A., Fang H., Robertsson L, de Mirandés E., Stock M., A bias source for the voltage reference of the BIPM watt balance. *IEEE Trans. Instrum. Meas*., 2013, 1594-1599.
13. Zucco M., Robertsson L. and Wallerand J.-P., Laser-induced fluorescence as a tool to verify the reproducibility of iodine-based laser standards: a study of 96 iodine cells. *Metrologia* **50**, 2013, 402–408.

BIPM publications

14. *BIPM Annual Report on Time Activities for 2012*, 7, 121 pp., available only at http://www.bipm.org/en/publications/time_activities.html.
15. *Circular T* (monthly), 8 pp.
16. *Rapid UTC* (*UTCr*) (weekly), 1 pp.
17. Panfilo G., Harmegnies A., Tisserand L., A new weighting procedure for UTC. Report to the CCTF Working Group on TAI and to the CCTF working group on Time Scale Algorithms, December 2013.

2.12 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).

W. Lewandowski 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) since June 2013.

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.

2.13 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 the Commission 31 (Time) and co-chairs 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 associated 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 the Study Group 7 of the International Telecommunication Union – Radiocommunication Sector (ITU-R).

W. Lewandowski is the BIPM representative to the Civil GPS Service Interface Committee and chairman of its Timing Sub-Committee. He is a member of the Scientific Council of the Space Research Centre of the Polish Academy of Sciences. He is also a member of a consultative Group on the Reform of Metrology at the Polish Ministry of Economy, an adviser to a Parliamentary Group on Space, and a member of the Committee on Research on Space Techniques of the Polish Academy of Sciences. He is member of European Commission Advisory Group on Galileo Time Infrastructure. Together with E.F. Arias, he is the BIPM representative to Working Party 7A of the Study Group 7 of the ITU-R, and to the ICG.

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 Working Group 1 (WG1) on the Expression of uncertainty in Measurement (GUM) of the Joint Committee for Guides in Metrology (JCGM) to provide an example for the new version of the GUM.

2.14 Travel (conferences, lectures and presentations, visits)

E.F. Arias to:

- Tokyo (Japan), 5-8 February 2013, for the NICT workshop on optical frequency standards (invited as a lecturer) and for a visit to the NMIJ;
- Geneva (Switzerland), 10-18 September 2013, for meetings of Study Group 7 and Working Party 7A of the International Telecommunication Union (ITU-R);
- Geneva (Switzerland), 19-20 September 2013, for the ITU/BIPM Workshop on the future of the international time scale at the International Telecommunication Union; charged with its organization and for giving presentations;
- Dubai (United Arab Emirates), 10-15 October 2013, for the 8th meeting of the International Committee on GNSS (ICG), with presentations and chairmanship of task group meetings;
- Bellevue (Washington, USA), 2-6 December 2013, for the PTTI2013 meeting with oral presentations, a panel discussion and two CCTF WG meetings;
- San Francisco (California, USA), 8 December 2013, for the IGS Governing Board meeting.

A. Harmegnies to:

- Prague (Czech Republic), 22-25 July 2013, to attend the IFCS-EFTF 2013 meeting and to give an oral presentation;
- Besançon (France), 26-30 August 2013, for training at the European Frequency and Time Seminar.

Z. Jiang to:

- Wuhan (China), 4-7 May 2013, for the China Satellite Navigation Conference 2013;
- Prague (Czech Republic), 22-25 July 2013, to attend the IFCS-EFTF 2013 meeting;
- Zdiby (Czech Republic), 26 July 2013, for a visit to the Research Institute of Geodesy, Topography and Cartography (VÚGTK/RIGTC);
- Taipei (Chinese Taipei), 4-9 September 2013, for the 21st meeting of the CCTF Working Group on TWSTFT, the AP-RASC'13 and the ATF Workshop;

- Bellevue (Washington, USA), 2-6 December 2013, for the PTTI 2013 meeting with oral presentations, a panel discussion and two CCTF WG meetings.

W. Lewandowski to:

- Vienna (Austria), 17-18 February 2013, for the preparatory meeting of the 8th ICG;
- Warsaw (Poland), 5-12 February and 18-23 April 2013, to the Space Research Centre and Space Commission;
- Brussels (Belgium), 4-5 June 2013, for GNSS Program Board;
- Warsaw-Poznan (Poland), 11-16 July 2013, for a GNSS calibration trip and experiment with fibre links;
- Taipei (Chinese Taipei), 4-9 September 2013, for the 21st meeting of the CCTF Working Group on TWSTFT, the AP-RASC'13 and the ATF Workshop;
- Geneva (Switzerland), 18-21 September 2013, for the ITU/BIPM Workshop on the future of the international time scale at the International Telecommunication Union;
- Dubai (United Arab Emirates), 10-15 October 2013, for the 8th meeting of the International Committee on GNSS (ICG), with presentations and task group meetings;
- Warsaw (Poland), 25-28 November 2013, for the Metrology Working Group and the Conference "Metrology - the engine of innovation";
- Bellevue (Washington, USA), 2-6 December 2013, for the PTTI2013 meeting with oral presentations.

G. Petit to:

- New Delhi (India), 20-23 February 2013, to attend the 8th International Conference of Advances in Metrology, with an invited talk and to visit the NPLI time laboratory;
- Toulouse (France), 26 March 2013, to visit the CNES time laboratory for collaboration in GNSS analysis and calibration;
- Paris (France), 10-11 April 2013, to attend the GRAMAP workshop and to give an oral presentation;
- Paris (France), 23-24 May 2013, to participate in the IERS Retreat;
- Toulouse (France), 3-7 June 2013, for training on GNSS processing and to visit the CNES time laboratory with a travelling GNSS receiver;
- Ottawa (Canada), 12-14 June 2013, to attend the GNSS Precise Point Positioning Workshop, to give an oral presentation and to visit the NRC time laboratory;
- Brussels (Belgium), 26 June 2013, to visit the ORB time laboratory for collaboration in GNSS analysis;
- Prague (Czech Republic), 22-25 July 2013, to attend the IFCS-EFTF 2013 meeting, to give oral presentations, a CCTF WG meeting and a CCL-CCTF WG meeting;
- Besançon (France), 27-29 August 2013, to give two lectures at the European Frequency and Time Seminar;
- Paris (France), 16-17 September 2013, to attend the Journées 2013 SRST and to give an oral presentation;
- Bellevue (Washington, USA), 2-6 December 2013, for the PTTI2013 Meeting with oral presentations and two CCTF WG meetings.

L. Robertsson to:

- Walferdange (Luxembourg), 10-14 November 2013 for the ICAG 2013, being a member of the steering committee.

2.15 Visitors

- P. Nogaś from the Polish Space Research Centre (SRC) for a cooperation on the improvement of GNSS time transfer, 23 April – 1 May 2013;
- T. Bartholomew (NIST, ITU) for a cooperation on ITU-R activities, 15-19 July 2013;
- Ł. Śliwczyński and P. Krehlik from the AGH University of Science and Technology, Krakow, Poland for discussions on the use of optical fibres for time transfer, 20 November 2013;
- M. Khalid Al-Dawood, Supervisor of Time and Frequency Laboratory (SASO) and R. Hamid, Head of the Time, Frequency and Wavelength Laboratory (TÜBİTAK - UME), and Chair of the EURAMET Technical Committee for Time and Frequency, for discussions on the participation of SASO in the key comparison CCTF-K001.UTC, 3 October 2013.

BIPM Electricity Department

Director: M. Stock

(1 January 2013 to 31 December 2013)

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

3.1.1 Development of a compact NIST 10 V Programmable Josephson Voltage Standard (PJVS) for the BIPM

Dr S. Solve completed his secondment with the Quantum Voltage Project group of NIST in Boulder, USA in July 2013. The secondment started in July 2012. During this time, the programmable Josephson Voltage Standard (PJVS) with compact electronics, which is designed to be transportable, was developed for the BIPM under a cooperative research and development agreement. This new system will be used in the future to develop a comparison scheme for AC Josephson voltage standards. The new system has been compared against a second PJVS and the smallest uncertainty achieved to date when comparing PJVS standards has been obtained. The relative difference was found to be 2.6 parts in 10^{11}, with a total combined uncertainty of 3.4 parts in 10^{11}, at the level of 10 V. To achieve this low uncertainty, several error sources have been carefully investigated:

- The input of the nanovoltmeter which measures the voltage difference between the two quantum standards was reversed in order to monitor any possible rectification of an AC voltage perturbation arising from inductive coupling between the measurement loop and its surroundings.
- The precision voltage leads of the PJVS were carefully twisted along the waveguide to filter a significant AC noise arising from a coupling effect between the RF coaxial line and the biasing wires.
- Different grounding schemes of the measurement setup were investigated. Similar results were obtained when the setup was completely floating, or if the low potential side of one or the other array was grounded or if the low potential side of the detector was grounded.
- The excellent temperature regulation in the laboratory made it possible to study the influence of the non-linear part of the thermal electromotive forces in the measurement setup on the voltage difference.
- The leakage resistance to ground of the systems was carefully measured and a model was derived explaining the contribution of the biasing source.
- The frequency accuracy of the RF sources was precisely measured using a Phase Noise Test unit provided by the NIST Time and Frequency department.
- The quantization margins of the 10 V Shapiro steps of the arrays were regularly checked under the conditions of the comparison configuration.
- A trigger signal was set up in order to accurately synchronize the timing of the voltage changes of the two PJVS from +10 V to −10 V in such a way that the comparison could be performed automatically without overloading the analogue detector.

An Allan variance was computed from 500 consecutive measurements, from which the noise floor, corresponding to the ultimate internal detector noise, was found to be 0.2 nV.

A detailed uncertainty budget was derived for the final comparison result. The major uncertainty contribution of 2.9×10^{-11} arises from the leakage resistance to ground. Leakage resistance to ground allows small currents to flow from components of the measurement circuit directly to ground, which can lead to a systematic voltage error. This effect is of particular importance for programmable Josephson voltage standards, since the bias current continues to flow during the voltage measurements. In conventional Josephson voltage standards the bias current is switched off during the voltage measurement. The effect was studied by using a technique which had previously been developed and demonstrated by the BIPM. This effect can lead to systematic errors at the level of 1 nV at 10 V, which is 1 part in 10^{10}. The work also demonstrated that trapped magnetic flux can lead to small systematic and reproducible voltage errors, which are difficult to detect. Details are described in a recent joint BIPM-NIST publication in *Metrologia*.

The transportable BIPM PJVS is equipped with a compact RF source associated to an amplifier in order to provide 21 dBm (125 mW) power at the input of the waveguide at the top of the cryoprobe. The functioning of this new microwave assembly was investigated by comparison to the traditional RF sources operated on a NIST 10 V PJVS. A frequency scan was repeated several times in the range from 18 GHz to 24 GHz with a 1 MHz frequency increment. We observed oscillations of the transmitted power with frequency (up to 2 dB peak-to-peak) which can be explained by the reflection amplitude of the signal along the whole propagation line consisting of the source assembly, the coaxial line and the array. These RF power variations have a direct impact on the operating margins exhibited by the subarrays and are at the origin of their frequency dependence. A careful mapping of the array response with frequency is therefore required on a regular basis.

The average gain value varies from 22 dB for the compact amplifier to 27 dB and 35 dB for the other two devices tested. A 20 dB gain is required to operate a 10 V NIST programmable array and therefore, all the devices tested fit this requirement.

3.1.2 Differential sampling measurements

As part of Dr Solve's training on the use and the applications of AC Josephson voltage standards at the NIST, the metrological characteristics of several AC calibrators were investigated. The calibrators generate at their output AC sinewaves of 1 V rms at a frequency of 62.5 Hz. The measurements were based on the differential sampling method, which might also be used in the future to compare AC voltage standards at the BIPM. This technique allows the comparison of a stepwise approximated sinewave from a Josephson Voltage Standard to the pure sinewave of the same amplitude and frequency, produced by the generator to be calibrated. The voltage values of each plateau of the stepwise sinewave are exactly known, because they are quantized. The comparison is performed using a sampling voltmeter.

The most important requirement for this measurement is that the two signals are well synchronized. In addition the sampling windows of the voltmeter need to be triggered in such a way that no measurements of the voltage difference are made during the transition of the PJVS between two quantized voltage levels.

Furthermore, verification is needed that the measurement results do not depend on the following parameters:

1- Number of samples of the PJVS approximated sinewave;

2- Sampling delay required to adjust the integration window of the voltmeter;

3- Value of the biasing current of the PJVS while remaining on the voltage step.

The independence on those parameters was investigated and a Type A uncertainty of a few ppm was achieved. This uncertainty is limited by the noise of the calibrator.

3.1.3 Quantum Voltage reference for the watt balance

The measurement of the induced voltage in the BIPM watt balance will be carried out by using a programmable Josephson voltage standard (as in any other watt balance). If the watt balance is operated in the special one-phase mode, where the force and velocity modes are carried out simultaneously, a second Josephson system will be needed for the determination of the coil current, measured as the voltage drop over a calibrated resistor.

Two NIST arrays capable of producing 1 V and 2 V were selected from the tests carried out on three different wafers. Each array was carefully characterized for its current margins as a function of RF power amplitude and frequency sweep response. The selected arrays will be bonded on a chip carrier at the NIST, Boulder, before being shipped to BIPM where they will again be carefully characterized.

3.2 Electrical impedance (resistance and capacitance)

3.2.1 DC resistance and quantum Hall effect (N. Fletcher, R. Goebel and B. Rolland)

The quantum Hall resistance (QHR) standard maintained by the BIPM is used not only as the reference for resistance comparison and calibration services offered to NMIs, but also as the starting point for the capacitance activity, and as one essential input to the watt balance project. For its regular work, the QHR cryostat is operated twice per year to characterize secondary working resistors which are used for daily traceability. This normal activity was supplemented by the first in a new series of on-site QHR comparisons (a continuation of the existing ongoing key comparison BIPM.EM-K12), carried out at the PTB, Germany, in November 2013.

The equipment used for the first series of on-site QHR comparisons (carried out in 1993-1999) has been largely replaced and modernized over the last couple of years. Previous tests with new types of resistance elements for use in the thermo-regulated enclosures that form an essential part of the transportable setup proved to be disappointing. The final versions of the 1 Ω and 10 kΩ resistors now house older commercial types of standards and these have been well characterized in 2013 prior to the first on-site visit. A 100 Ω standard of similar design will be mounted in 2014. The journey to the PTB was by road and the new resistors were deliberately left in the van over a weekend on the return journey to simulate the temperature excursion that could be seen during air transport. We observed that the standards needed several weeks after such a temperature shock to reach the stability required for precision comparisons (relative drifts at the level of 1×10^{-9}). This stabilization time will be planned into the transport schedules for future comparisons where supervised road transport is not possible.

Along with the new resistors, a completely rebuilt 'version 2' of the 1 Hz room temperature current comparator bridge (the unique part of the on-site apparatus) is now in service. This bridge, including new data acquisition and analysis software written in LabVIEW, was thoroughly tested against the old bridge, giving reliable results consistent at the 1×10^{-9} level. These preparations allowed us to proceed with confidence to the first on-site visit in November 2013.

During a two week stay at the PTB, all the measurements for the calibration of a 100 Ω standard against the QHR, and subsequent 100:1 scaling ratios down to 1 Ω and up to 10 kΩ were successfully performed. For the 100 Ω and 10 kΩ measurements, excellent agreement with the PTB system was found (relative agreement to around 1×10^{-9}, close to the limits imposed by the noise and stability of the resistors under test). The 1 Ω measurements proved more problematic, due to a known effect of Peltier heating in the resistor terminals, which makes the measured four-terminal resistance value dependent on the timing of DC current reversals. We were able to carry out some extra and very valuable investigations into this effect in collaboration with the PTB, and it now appears that this problem of the definition of the measurand can limit the relative uncertainty for 1 Ω comparisons to around 1×10^{-8}. Studies of this problem are continuing in collaboration with the PTB, and form the subject of a contribution to the Conference on Precision Electromagnetic Measurements (CPEM) to be held in Rio de Janeiro, Brazil, in August 2014. The full comparison report is being prepared for publication in early 2014.

During autumn 2013, the resistance laboratories were out of service for three months due to the major works required to replace the air-conditioning systems. This down-time, followed by the necessary time to recalibrate and monitor our working standards has delayed a number of calibrations for NMIs, and the backlog remains to be cleared at the start of 2014. During 2013 we also replaced the temperature controlled air bath used to house 10 kΩ standards undergoing calibration on our Warshawsky Bridge with a new commercial unit. Our facilities for in-house electronics development have been upgraded with a reorganization of the workshop areas for electronics and mechanical production, and the installation of a new software suite for electronics designs.

3.2.2 Maintenance of a reference of capacitance (R. Chayramy, N. Fletcher, R. Goebel)

The capacitance unit at the BIPM is maintained by a group of four 10 pF standards, which are calibrated every six months with respect to the QHR dc resistance standard. The transfer using a quadrature bridge and associated measurement chain is performed directly following the use of the QHR to calibrate the working resistance standards. From the historical drift data of the reference capacitors (now maintained for over 10 years) we can be confident in the continuity of our measurements to the relative level of 1 or 2 parts in 10^8. These routine measurements were successfully carried out twice in 2013, allowing the ongoing support of our calibration services to NMIs (at the level of 1 pF, 10 pF and 100 pF).

A 2011 comparison of 10 pF and 100 pF standards traceable to the QHR (EURAMET.EM-S31) had revealed some worrying inconsistencies, particularly in the frequency dependence of standards. During 2013, the BIPM participated in follow-up measurements with an exchange of ac-dc resistance standards with the LNE, PTB and METAS. This provided an opportunity to work on the coaxial ac-dc reference resistors and associated bridge that form an essential part of our traceability chain. The final results of this comparison will not be known until early 2014, but the resolution of any outstanding discrepancies will be a key priority for 2014.

3.3 **Calculable capacitor** (N. Fletcher, R. Goebel, L. Robertsson, M. Stock)

The main scientific effort of the Electricity Department in the field of impedance metrology has been taken up with the on-site QHR comparison in 2013, and this combined with a significant staff absence due to ill-health has not allowed much progress to be made on the calculable capacitor project. Investigations of the capacitance traceability chain and ac-dc resistors mentioned in activity 2.2 are however vital for the measurement of R_K using the calculable capacitor. The final mechanical alignment of the capacitor remains to be done, and some studies on the detail of the interferometer are still required. However, the measurement systems are in good shape, and significant progress is expected in 2014.

3.4 **BIPM ongoing key comparisons in electricity** (R. Chayramy, N. Fletcher, R. Goebel, S. Solve, M. Stock)

One on-site comparison of Josephson voltage standards (BIPM.EM-K10) with NIM (China) has been successfully completed at 10 V. The report is in the Draft A stage.

Two bilateral voltage comparisons (BIPM.EM-K11) using Zener voltage standards as transfer standards were carried out at the level of 10 V with the NSAI (Ireland) in March 2013 and with the INM (Romania) at both 1 V and 10 V. The Draft B reports have been submitted to the Chairman of the CCEM Working Group on Low-Frequency Quantities (WGLF) for final approval.

In December 2013 a questionnaire was sent to 27 NMIs to explore their interest in future on-site Josephson voltage comparisons, to allow us to plan the future activities. The replies are expected by January 2014.

As described in section 3.2, the first of a new series of on-site comparisons of quantum Hall resistance standards (BIPM.EM-K12) has been carried out with the PTB. The full comparison report is being prepared for publication in early 2014.

Resistance comparisons using BIPM transfer standards (BIPM.EM-K13) have been carried out with the NPL of India and the BIM (Bulgaria), at 1 Ω and 10 k Ω. The measurements have finished but we are still waiting for the participants' results.

3.5 **Calibrations** (R. Chayramy, N. Fletcher, R. Goebel, B. Rolland, S. Solve, M. Stock)

The Electricity Department calibrated the following standards during January to December 2013:

Zener diode-based voltage standards at 1 V and 10 V for: DMDM (Serbia).

Resistance at 1 Ω, 100 Ω or 10 k Ω was calibrated for: NIMT (Thailand), NIS (Egypt), BEV (Austria), SMD (Belgium), NMC (Singapore), MSL (New Zealand) - in total 24 certificates for 6 NMIs.

1, 10 or 100 pF capacitors were calibrated for: CMI (Czech Republic), SMD (Belgium), SIRIM (Malaysia), KRISS (Republic of Korea), BEV (Austria), CENAM (Mexico), NMC (Singapore), BIM (Bulgaria), INMETRO (Brazil), EIM (Greece) - in total 33 certificates for 10 NMIs.

3.6 Publications

1. Avilés D., Navarrete E., Hernández D., Solve S., Chayramy R., Direct comparison of Josephson voltage standards at 10 V between BIPM and CENAM, *IEEE Trans. Instrum. Meas.*, 2013, 1640-1645.
2. Chayramy R., Solve S., A very low thermal EMF computer-controlled scanner, *Meas. Sci. Technol.*, 2013, **24**, 035008.
3. Fang H., Kiss A., de Mirandés E., Lan J., Robertsson L., Solve S., Picard A., Stock M., Status of the BIPM watt balance, *IEEE Trans. Instrum Meas.*, 2013, **62**, 1491-1498.
4. Solve S., Chayramy R., Picard A., Kiss A., Fang H., Robertsson L, de Mirandés E., Stock M., A bias source for the voltage reference of the BIPM watt balance, *IEEE Trans. Instrum. Meas.*, 2013, 1594-1599.
5. Solve S., Rüfenacht A., Burroughs C.J., Benz S.P., Direct comparison of two NIST PJVS systems at 10 V, *Metrologia*, 2013, **50**(5), 441-451.
6. Stock M., Watt balance experiments for the determination of the Planck constant and the redefinition of the kilogram, *Metrologia*, 2013, **50**(1), R1-R16.
7. Stock M., Watt balance experiments for the determination of the Planck constant and the redefinition of the kilogram, in *Metrology and Physical constants*, IOS press, Amsterdam, ISBN 978-88-7438-083-1, 415-446.

3.7 Activities related to the work of Consultative Committees

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. The 28th CCEM meeting was held on 14-15 March 2013. The main topics were the planned redefinition of the SI, the CCEM strategy and the organization of comparisons. A task group was set up to consider the effects of the redefinitions on the electrical units.

The CCPR working groups met in April 2013 at the BIPM and a workshop on "SI units for Photometry and Radiometry" was organized, to which representatives of the International Commission on Illumination (CIE) were invited. The main topics were the future *mise en pratique* for the definition of the candela and the question of whether the lumen should be proposed as the photometric base unit of the SI, replacing the candela. This proposal was rejected.

R. Goebel organizes the review of comparisons reports and protocols within the CCPR Working Group on Key Comparisons (WG-KC).

3.8 Activities related to external organizations

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 was a member of the Scientific Committee for the 4th International Conference on Quantum Metrology (QM2013), held in Poznan, Poland, on 15-17 May 2013, and gave the opening speech.

M. Stock is the contact person for the BIPM liaison with the CIE. Representatives of the CIE were invited to the CCPR workshop on "SI units for Photometry and Radiometry" to discuss questions of common interest (see section 3.7). M. Stock was invited to give a speech at the CIE Centenary General Assembly meeting in Paris, on 14 April 2013.

N. Fletcher represents the BIPM on the 'Stakeholder Committee' for the EMRP Project GraphOhm.

3.9 Travel (conferences, lectures and presentations, visits)

M. Stock to:

- Paris (France), 14 April 2013, to give an invited speech at the CIE Centenary General Assembly meeting;
- Poznan (Poland), 16-17 May 2013, to give the opening speech at the 4th International Quantum Metrology Conference;
- IPT (Fraunhofer Institute for Production Technology), Aachen (Germany), 23 May 2013, for a trial assembly of the BIPM watt balance magnet;
- INRIM, Turin (Italy), to give two presentations at the EMRP kNOW workshop and to attend the kNOW project meeting on 18-19 September 2013;
- GUM, Warsaw (Poland), 17-18 October 2013, to attend the EURAMET TC-EM meeting.

M. Stock gave a presentation about the status of determinations of the Planck constant to the working group "Science et Métrologie" of the French Academy of Science, at the BIPM, on 8 April 2013.

S. Solve to:

- NIST (USA), 1 July 2012 - 31 July 2013, as a guest researcher;
- PTB, Braunschweig (Germany), 9-13 December 2013 to perform tests on the PTB Josephson arrays using a BIPM probe equipped with an oversized circular waveguide.

S. Solve and R. Chayramy to:

- NIM, Beijing, (China), 6-15 November 2013, to carry out a direct on-site BIPM Josephson voltage standard comparison.

R. Goebel and B. Rolland to:

- PTB, Braunschweig (Germany), 9-11 September 2013, for a pre-comparison test for BIPM.EM-K12, running the PTB's setup.

R. Goebel, N. Fletcher and B. Rolland to:

- PTB, Braunschweig (Germany), 11-22 November 2013, for the first of the new series of on-site comparisons of quantum Hall resistance standards.

B. Rolland to:

- LabVIEW France (Nanterre), 8-10 July 2013, to attend LabVIEW Core 1 training.

3.10 Visitors

- H.D.A. Sepulveda, Director of the NMI of Columbia to visit the laboratories of the Electricity Department, on 15 May 2013;
- M. Götz and E. Pesel from PTB (Germany), to discuss the planned on-site comparison of quantum Hall standards, 16 May 2013;
- Abdel Monem Sallam, NIS (Egypt), to collect calibrated resistance standards, to visit the laboratory and for technical discussions, 21-26 July 2013;
- M. Pavicevic and Z. Sofranac, DMDM (Serbia), to discuss the BIPM Zener bilateral comparison protocol, 18 September 2013;
- S. Benz, NIST (USA), to install a NIST 10 V PJVS for the future BIPM activity dedicated to AC voltage differential sampling, 19-25 September 2013;
- Po Gyu Park, Yound Gyun Kim and Jeong Tae from the KRISS (Republic of Korea) to visit the Electricity Department on 27 September 2013;
- Khalid Al-Dawood (SASO, Saudi Arabia) and Prof. Ramiz Hamid (UME, Turkey) to visit the Electricity Department, 3 October 2013;
- Delegation from Bangladesh: Mr Muhammed Musharraf Hossain Bhuiyan (Cabinet Secretary), Mr Mohammed Moinuddin Abdullah (Secretary, Ministry of Industries), Mr Abu Abdullah (Director General, Bangladesh Accreditation Board (BAB), Mr Iqramul Haque (Director General, Bangladesh Standards & Testing Institution (BSTI)), Mr Md Lutfor Rahman Tarafder (Joint Chief, Ministry of Industries & Project Director, BQI-BEST), Dr Franz Hengstberger (Technical Advisor, BQI-BEST), to visit the Electricity Department, on 11 October 2013.

BIPM Ionizing Radiation Department

Director: J.M. Los Arcos

(January 2013 to 31 December 2013)

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

4.1.1 Dosimetry standards and equipment

Following the installation of the new ^{60}Co source in the Theratron head in October 2012 and work during 2013 to ensure radiation protection, important modifications were made to the calibration bench for measurements in water and in air, including the design of a new chamber set-up for measurements in air. Beam characterization has continued, aided by the installation of a new laser system, with horizontal and vertical beam profiles measured in air and horizontal profiles in water; these data are used to evaluate correction factors for the non-uniformity of the beam. Reference air-kerma measurements have started using the new primary standard constructed for this beam. The water phantom has been installed and preliminary measurements made using the new and existing (CISbio) reference standards.

A significant development in 2013 was a change in the data acquisition software for all facilities, which until now was based on TestPoint software. New computers were installed and LabVIEW software developed for the seven measurement services – low- and medium-energy x-rays, mammography, radiotherapy-level ^{60}Co (air kerma and absorbed dose), and radioprotection-level ^{60}Co and ^{137}Cs. Validation of the changes and incorporation in the QMS documentation was completed in time for the internal audit in November 2013.

Work on the development and characterization of cavity ionization chambers continues. The standard built in 2012 for absorbed dose to water measurements in the new Theratron ^{60}Co source was tested. A study of the response of transfer chambers in the Theratron beam has started; calibration coefficients for chambers calibrated in the new beam are compared with those determined in the existing reference (CISbio) beam. Two chambers were constructed to a new design, for use as transfer standards in the determination of absorbed dose in medium-energy x-rays. The defining characteristic of these chambers is that they are waterproof and therefore do not require the use of a waterproof envelope. The first of these, with plastic walls, was characterized in ^{60}Co radiation and correction factors determined for orientation, polarity and ion recombination. The second chamber, with graphite walls, remains to be tested.

A sixth comparison was made in the series BIPM.RI(I)-K6. The BIPM equipment was shipped to the NPL (UK) in advance, with the exception of the calorimeter core and ionization chambers which were carried by hand. The comparison measurements were planned for the period 16 September to 4 October 2013 in the 6 MV, 10 MV and 25 MV beams of the Elekta accelerator at the NPL. However, a number of technical problems with the accelerator resulted in an incomplete comparison and the BIPM had to return to complete the measurements from 18 to 22 November. The codes of practice for dosimetry applied in the countries already having participated in the K6 comparison series employ a mass thickness of 10 g cm^{-2}. However, the UK currently follows a code of practice where mass-thicknesses of 5 g cm^{-2} or 7 g cm^{-2} are recommended, depending on the beam energy. For this reason, these depths have been adopted by the NPL and the BIPM has adapted its equipment to these requirements. The BIPM was already equipped for measurements at 5 g cm^{-2} as this configuration is applied for measurements in the BIPM Co-60 reference beam. In order to achieve 7 g cm^{-2}, a graphite plate of well-known density was fabricated to realize the additional mass-thickness of 2 g cm^{-2}. Furthermore, to allow rapid and regular switching between the beam qualities, this plate was placed in a frame fixed on a sliding carriage. The mass-thickness was easily altered between 5 g cm^{-2} and 7 g cm^{-2} by sliding the frame in and out of the beam. This solution is applicable due to the cancellation of first order effects using ratios, both in the measurement routine as well as in the Monte Carlo calculations.

The preliminary results have been evaluated. Two reports of previous comparisons in the series, with the NIST (USA) and the LNE-LNHB (France) were published in 2013. The report of the comparison carried out at the ARPANSA (Australia) in 2012 is close to completion, having been delayed by the ARPANSA which discovered a problem with its primary standard after the comparison measurements. The method for establishing degrees of equivalence for the BIPM.RI(I)-K6 series, as agreed at the meeting of the CCRI in May was published in 2013. The comparison results have been analysed accordingly, are now available on the KCDB and are updated after each comparison. The calorimeter continues to be used at regular intervals in the BIPM reference ^{60}Co beam, not only for the absolute determination of absorbed dose in this beam but also for quality assurance in BIPM.RI(I)-K6.

Monte Carlo calculations for the absorbed-dose conversion from graphite to water have continued, with calculations being made for the comparisons with the ARPANSA and the NPL using photon spectra supplied by these NMIs; calculations for 6 MV were also made for METAS (Switzerland) before the comparison scheduled for March 2014 was postponed. The calculations for the NPL were for a different reference depth and required new Monte Carlo geometry codes to be constructed. A study of the effect of detector radius on the calculation of $TPR_{20,10}$ was made in collaboration with the ARPANSA. The results showed that the value used to date (r = 22.5 mm) was too large; henceforth calculations will be made for r = 10 mm and r = 3 mm (simultaneously). New calculations with these smaller radii were made for all previous comparisons (NRC, PTB, NIST and LNE-LNHB) in the context of the work on W_a described below.

The project to develop an absorbed-dose standard for medium-energy x-rays, carried forward from the previous programme, has continued. The plan is to base the standard on the existing free-air chamber standard using a set of waterproof transfer standards of different wall materials and shape. As noted above, the first of these chambers, with walls of air-equivalent plastic (C552) and a waterproof outer layer of PMMA, was constructed. Following tests in x-rays, this chamber was found to have a significant leakage current. After detailed investigation, it was deduced that this leakage was due to an unexpected interaction between the C552, which has a polarizing potential of 80 V, and the outer PMMA – the same effect is not present in a graphite chamber subject to the same waterproofing. The solution was to coat the outer PMMA surfaces using a conductive graphite spray. The second chamber, with graphite walls, is ready for testing and preliminary measurements indicate that current leakage should not be a problem.

Also in the context of absorbed-dose for medium energy x-rays, the experiment to test the photon interaction cross-section data (μ-values) used by the simulation code PENELOPE continued with improved calculations. Interestingly, while the calculated values for air (μ_a), graphite (μ_c) and water (μ_w) are each lower than the corresponding measured value by 2 to 4 parts in 10^2, each of the calculated ratios $\mu_{a,c}$ and $\mu_{a,w}$ agrees with its measured value at the level of around 5 parts in 10^3 (the statistical uncertainty), except at 100 kV where a difference of 1 to 2 parts in 10^2 is observed. This latter effect is considered to be due to μ_a because the calculated ratio $\mu_{w,c}$ agrees with the measured value within the statistical uncertainty of 4 parts in 10^3 for all energies. An improved measurement of μ_a at 100 kV is planned.

Following publication of a global analysis of the W_a-value for ^{60}Co radiation in *Metrologia* in 2012, a paper has been submitted to *Physics in Medicine and Biology* on the W_a value for accelerator photon beams. This work pulls together various elements of the BIPM work programme, including the results of the BIPM.RI(I)-K6 comparisons in the NMI accelerator beams, Monte Carlo calculations and cavity volume measurements for ionization chambers constructed at the BIPM. The conclusion that there is no evidence for an energy variation for W_a is an important finding that will reduce the uncertainty of clinical reference dosimetry for these beams. A by-product of this work has been a new determination of the I_c-value for graphite, which is in close agreement with the value published by the BIPM in *Metrologia* in 2012. These results will be incorporated into report on Key Data which is being prepared by the International Commission on Radiation Units and Measurements (ICRU).

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 Quality System. This system, which includes new procedures and technical instructions which arose from the update of the data acquisition and storage systems, was subject to a successful internal audit in November 2013.

4.1.2 Dosimetry comparisons

Three comparisons were carried out in the ^{60}Co gamma radiation beam: one comparison in terms of air kerma with the LNE-LNHB and two comparisons in terms of absorbed dose to water with the LNE-LNHB and METAS. One high-energy absorbed-dose comparison was carried out in the NPL's accelerator beams, as described earlier.

Eleven comparison reports were published in the *Metrologia Technical Supplement*, three reports for the LNE-LNHB, two reports for the NMIJ (Japan), two for the NIST and one each for the GUM (Poland), the ININ (Mexico), the VNIIM (Russian Federation) and the IAEA.

The Summary comparison report for the K5 Cs-137 air-kerma key comparison and the report on degrees of equivalence for the K6 high-energy x-ray beam key comparison were also published in the *Metrologia Technical Supplement*.

4.1.3 Characterizations of national standards for dosimetry

Forty-two characterizations of national standards were carried out; five in low-energy x-rays for the NMISA (South Africa), NRPA (Norway) and the IAEA, one in mammography x-rays for the NRPA, nine in medium-energy x-rays for the NMISA, the CRRD (Argentina), the NRPA, the IAEA and the LNMRI (Brazil), twenty four in ^{60}Co for the NMISA, the CRRD, the GUM, the NRPA, the IAEA and the LNMRI and three in ^{137}Cs for the NMISA and the NRPA.

The IAEA/WHO dosimetry assurance programme continues to be supported by biannual reference irradiations, which in 2013 involved one series of irradiations for the radiotherapy level in the ^{60}Co beam and one for the radiation-protection level in the ^{137}Cs beam.

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

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

4.2.1.1 SIR submissions in 2013

During 2013, the BIPM received seven ampoules filled with seven different radionuclides from four laboratories (i.e. one ampoule each containing ^{57}Co (RC), ^{59}Fe (LNE-LNHB), ^{109}Cd (LNE-LNHB), ^{137}Cs (RC), ^{166m}Ho (PTB), ^{177}Lu (IFIN) and ^{222}Rn (LNE-LNHB). All the submissions had been made to generate equivalence values in the associated ongoing BIPM key comparisons BIPM.RI(II)-K1.

Measurements of ^{222}Rn, which is a radioactive gas with a short half-life ($T_{1/2}$ = 3.8235 d, u = 0.0003 d), were repeated to try and remove a systematic bias detected in the activity determination of this gas. Analysis is presently ongoing.

For the first time the ININ tried to submit three ampoules filled with radioactive solutions of ^{60}Co, ^{137}Cs and ^{241}Am but unfortunately the parcel did not reach the BIPM due to transportation or customs formalities which are being investigated.

Three further ampoules containing ^{14}C, ^{134}Cs and ^{137}Cs from the NRC are expected to be sent before the end of 2013.

4.2.1.2 SIR Reports and quality assurance

Updated reports of three comparisons were published in the *Metrologia Technical Supplements* covering ^{64}Cu, ^{134}Cs, ^{137}Cs including the linked COOMET.RI(II)-K2.Cs-137 comparison. One other report is in circulation. All results prior to 2009 have now been published in the *Metrologia Technical Supplement* except for one which is still to be received from the NMI concerned. To date, all the Draft A reports have been circulated except for 4 results (^{51}Cr, ^{111}Ag, ^{125}Sb, ^{222}Rn) that are still to be received from the NMIs concerned.

There are 40 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 already removed from the KCDB.

All the 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 28 November 2013 by the BIPM Quality, Health and Safety Manager, Mr C. Maggi.

A hand and foot contamination detector has been ordered in response to a recommendation made by the external auditor, Prof. Dr F.O. Bochud from the IRA-METAS (Switzerland), during the last external audit carried out on 21 September 2012. In compliance with the BIPM QMS Manual, an internal audit was carried out in 2013.

4.2.2 Gamma spectrometry

Routine measurements of potential impurities in SIR ampoules are made using the Ge(Li) and HPGe spectrometers. The Ge(Li) preamplifier failed in July 2013 and attempts to repair it have been unsuccessful to date. The service for measuring activity of impurities in SIR ampoules, when required and following the protocol CCRI(II)/01-01, has thus been temporarily suspended. The service could be restarted when the Ge(Li) is repaired or the HPGe calibrated. However, no time was available to analyse the calibration measurements of the HPGe and the BIPM Ionizing Radiation Department is offering an NMI secondment to collaborate on this project.

The impurity ^{177m}Lu was identified as expected in the ^{177}Lu submitted to the SIR by the IFIN-HH (Romania). The analysis of these measurements made with the HPGe detector is ongoing. Measurements of several swabs for a leakage test of an SIR ampoule of ^{68}Ge were carried out.

4.2.3 Extension of the SIR to short-lived radionuclides

The BIPM report which describes the SIRTI in detail and the tests made during its development has been finalized and submitted for publication.

The BIPM.RI(II)-K4.Tc-99m ($T_{1/2}$ = 6.0 h) key comparison using the SIR Transfer Instrument (SIRTI) is running at a rate of two comparisons per year: the LNMRI-IRD (Brazil) and the IFIN-HH participated in 2013. The results of the comparisons in China, Argentina and Brazil have been published. The VNIIM is the next planned participant. The SIRTI has remained very stable since 2007 even though it is regularly transported around the world, showing a relative standard deviation of 6×10^{-5} for the counting rate of the ^{94}Nb reference source.

The extension of the SIRTI to measure ^{18}F ($T_{1/2}$ = 1.8 h) is in development. Stability and reproducibility tests were carried out successfully. Further tests of the electronics are planned before calibration against the SIR. Monte Carlo simulations of the SIRTI response to ^{18}F agree with preliminary measurements within 4×10^{-3} in relative terms. A trial comparison at a European NMI which has already participated in the SIR will be organized. NMIs that expressed an interest in the ^{18}F comparison are the ENEA-INMRI (Italy), NIST, NIM (China), ANSTO (Australia), CNEA (Argentina), IFIN-HH, LNMRI-IRD and the VNIIM.

4.2.4 Extension of the SIR to pure beta emitters

The analysis of the comparison initiated by the Working Group for the extension of the SIR to the measurement of pure beta emitters has continued. Results obtained for the submissions by the eight participating laboratories (ENEA (Italy), IRMM (EU), LNE-LNHB, NIST, NMISA, NPL, PTB (Germany) and POLATOM RC (Poland)) with the BIPM TDCR system have been evaluated and compared with those obtained with the same technique at the LNE-LNHB.

The results of these measurements were presented together with those obtained using the universal efficiency curves (UEC) during the CCRI(II) meeting held at the BIPM in May 2013 and at the ICRM 2013 Conference held in Antwerp, Belgium, on 17-21 June 2013.

A larger scale exercise involving 19 interested NMIs and the radionuclides ^{3}H, ^{14}C, ^{55}Fe and ^{63}Ni, was approved by the CCRI(II) in May 2013.

4.3 **Thermometry** (S. Picard, M. Nonis)

The Ionizing Radiation Department provides internal calibration services for thermometry at the BIPM, under the BIPM Quality Management System. In June 2012, the BIPM was invited by the Consultative Committee for Thermometry (CCT) to take part in the CCT-K9 comparison which was already under way and piloted by the NIST. For this purpose, the second part of the comparison measurements were carried out at the BIPM in April 2013 after being returned from the NIST.

In 2013, eighteen SPRTs and eight commercial laboratory thermometers belonging to the Electricity, Mass, Time and Ionizing Radiation Departments were calibrated.

4.4 Publications

External publications

1. Allisy-Roberts P.J., Kessler C., Burns D.T., Summary of the BIPM.RI(I)-K5 comparison for air kerma in ^{137}Cs gamma radiation, Metrologia, 2013, 50, Tech. Suppl., 06001.
2. Andreo P., Wulff J., Burns D.T., Palmans H., Consistency in reference radiotherapy dosimetry: resolution of an apparent conundrum when ^{60}Co is the reference quality for charged-particle and photon beams, *Phys. Med. Biol.*, 2013, **58**, 6593-6621.
3. Burns D.T., Kessler C., Knyziak A.B., Key comparison BIPM.RI(I)-K3 of the air-kerma standards of the GUM, Poland and the BIPM in medium-energy x-rays, Metrologia, 2013, 50, Tech. Suppl., 06003.
4. Kessler C., *Développement et mise en place au BIPM d'un système international de comparaison et d'étalonnage pour la dosimétrie en mammographie*, Ph.D. thesis (LNE-INM/Cnam, La Plaine-Saint-Denis), 2013, 151 pp.
5. Kessler C., Allisy-Roberts P.J., Minniti R., Comparison of the standards for air kerma of the NIST and the BIPM for ^{60}Co gamma radiation, Metrologia, 2013, 50, Tech. Suppl., 06002.
6. Kessler C., Alvarez Romero J.T., Tovar-Muñoz V.M., Key comparison BIPM.RI(I)-K1 of the air-kerma standards of the ININ, Mexico and the BIPM in ^{60}Co gamma radiation, Metrologia, 2013, 50, Tech. Suppl., 06017.
7. Kessler C., Burns D.T., Czap L., Csete I., Gomola I., Comparison of the air kerma standards of the IAEA and the BIPM in mammography x-rays, Metrologia, 2013, 50, Tech. Suppl., 06005.
8. Kessler C., Burns D.T., Delaunay F., Donois M., Key comparison BIPM.RI(I)-K1 of the air-kerma standards of the LNE-LNHB, France and the BIPM in ^{60}Co gamma radiation, Metrologia, 2013, 50, Tech. Suppl., 06018.

9. Kessler C., Burns D.T., Delaunay F., Donois M., Key comparison BIPM.RI(I)-K4 of the absorbed dose to water standards of the LNE–LNHB, France and the BIPM in ^{60}Co gamma radiation, Metrologia, 2013, 50, Tech. Suppl., 06019.
10. Kessler C., Burns D.T., Oborin A.V., Villevalde A.Y., Key comparison BIPM.RI(I)-K7 of the air-kerma standards of the VNIIM, Russian Federation and the BIPM in mammography x-rays, Metrologia, 2013, 50, Tech. Suppl., 06013.
11. Kessler C., Saito N., Kurosawa T., Key comparison BIPM.RI(I)-K1 of the air kerma standards of the NMIJ, Japan and the BIPM in ^{60}Co gamma radiation, *Metrologia*, 2013, **50**, *Tech. Suppl.*, 06006.
12. Kessler C., Saito N., Kurosawa T., Key comparison BIPM.RI(I)-K5 of the air kerma standards of the NMIJ, Japan and the BIPM in ^{137}Cs gamma radiation, Metrologia, 2013, 50, Tech. Suppl., 06007.
13. Michotte C., Nonis M., Liang J.C., Chen J., Liu H.R., Zhang M., Zhao Q., Yang Y.D., Activity measurements of the radionuclide ^{99m}Tc for the NIM, China in the ongoing comparison BIPM.RI(II)-K4.Tc-99m, Metrologia, 2013, 50, Tech. Suppl., 06010.
14. Michotte C., Ratel G., Courte S., Kharitonov I. A., Zanevsky A. V., Sahagia M., van Wyngaardt W. M., van Staden M. J., Lubbe J., Simpson B. R. S., Maringer F. J. and Brettner-Messler R., Update of the BIPM comparison BIPM.RI(II)-K1.Cs-137 of activity measurements of the radionuclide ^{137}Cs to include the 2007 results of the VNIIM (Russia), the 2009 result of the IFIN-HH (Romania), the 2010 result of the NMISA (South Africa) and the 2011 result of the BEV (Austria), Metrologia, 2013, 50, Tech. Suppl., 06014.
15. Michotte C., Ratel G., Courte S., Maringer F.J., Caffari Y., van Wyngaardt W.M., Update of the BIPM comparison BIPM.RI(II)-K1.Cs-134 of activity measurements of the radionuclide ^{134}Cs to include the 2008 results of the BEV (Austria), the 2009 result of the IRA (Switzerland) and the 2010 results of the NMISA (South Africa), Metrologia, 2013, 50, Tech. Suppl., 06009.
16. Michotte C., Ratel G., Courte S., Sochorovà J., Auerbach P., Keightley J., Johansson L., Bakhshandeiar E., Cassette P., Moune M., Capogni M. and De Felice P., Update of the BIPM comparison BIPM.RI(II)-K1.Cu-64 of activity measurements of the radionuclide ^{64}Cu to include the 2009 results of the CMI-IIR (Czech Rep.) and the NPL (UK), the 2010 result of the LNE-LNHB (France) and the 2011 result of the ENEA-INMRI (Italy), *Metrologia*, 2013, **50**, *Tech. Suppl.*, 06021.
17. Picard S., Burns D.T., Roger P., Bateman F.B., Tosh R.E., Chen-Mayer H., Key comparison BIPM.RI(I)-K6 of the standards for absorbed dose to water of the NIST, USA and the BIPM in accelerator photon beams, Metrologia, 2013, 50, Tech. Suppl., 06004.
18. Picard S., Burns D.T., Roger P., Delaunay F., Gouriou J., Le Roy M., Ostrowsky A., Sommier L., Vermesse D., Key comparison BIPM.RI(I)-K6 of the standards for absorbed dose to water of the LNE-LNHB, France and the BIPM in accelerator photon beams, Metrologia, 2013, 50, Tech. Suppl., 06015.
19. Picard S., Burns D.T., Los Arcos J.M., Establishment of degrees of equivalence of national primary standards for absorbed dose to water in accelerator photon beams, Metrologia, 2013, 50, Tech. Suppl., 06016.
20. Michotte., Nonis M., Arenillas P., Cerutti G., da Silva C. J., Lima da Cruz P. A., Moreira D. S., Iwahara A., Delgado J. U., Poledna R., da Silva R. L., de Oliveira A. E. and dos Santos Gomes R., Activity measurements of the radionuclide ^{99m}Tc for the CNEA, Argentina and the LNMRI/IRD, Brazil in the ongoing comparison BIPM.RI(II)-K4.Tc-99m, Metrologia, 2013, 50, Tech. Suppl., 06023.

BIPM publications

1. C. Michotte, M. Monis, C. Bobin, T. Altzizoglou, G. Sibbens, The SIRTI : a new tool developed at the BIPM for comparing activity measurements of short-lived radionuclides world-wide, *Rapport BIPM-2013/02*, 24pp.

4.5 Activities related to the work of Consultative Committees

J.M. Los Arcos is the Executive Secretary of the CCRI, *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 2013 there were meetings of the CCRI, its three sections, CCRI(I), CCRI(II) and CCRI(III), as well as the ADWG(I), KCWG(II), BqWG(II), TIWG(II), ESWG(II) and KCWG(III).

D.T. Burns is a member of the CCRI(I) Key Comparisons Working Group (KCWG(I)), Accelerator Dosimetry Working Group (ADWG(I)) and 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 the coordinator of the CCRI(II) Transfer Instrument Working Group (TIWG(II)), which met in October 2013, and a member of the Key Comparisons Working Group (KCWG(II)) which met in May and October 2013.

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)), which met on May 2013 and for which he was the *rapporteur*, the KCWG(II) and the Working Group on the Realization of the becquerel (BqWG(II)), which met in May and October 2013, and the Transfer Instrument Working Group (TIWG(II)) which met in October 2013.

S. Picard is Executive Secretary of the Consultative Committee for Acoustics, Ultrasound and Vibration (CCAUV), which held its 9th meeting on 29 to 31 October 2013. She is a member of the CCAUV Working Group for RMO Coordination (CCAUV-RMOWG), the CCAUV Working Group on Strategic Planning (CCAUV-SPWG) and the CCAUV Working Group for Key Comparisons (CCAUV-KCWG), which met on 28-29 October 2013. She is the Interim Acting Executive Secretary of the Consultative Committee for Thermometry (CCT).

4.6 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. He is a member of the ICRU Committee on Fundamental Quantities and Units and of the ICRU Report Committee on Key Data for Dosimetry. He is Commission Sponsor for three reports (Key Data for Dosimetry, Operational Quantities for Radiation Protection, and Small and Non-Standard Fields). He is the BIPM representative on the IAEA Secondary Standards Dosimetry Laboratory (SSDL) Scientific Committee.

C. Michotte is the contact person at the BIPM and *rapporteur* for the JCGM-WG1 meetings in May and December 2013.

G. Ratel is the BIPM representative on the International Committee for Radionuclide Metrology (ICRM) and is the President of the ICRM Nominating Committee. He was a member of the Scientific Committee for the 19th International Conference on Radionuclide Metrology and its Applications (ICRM 2013), which was held in Antwerp (Belgium) on 17-21 June 2013. He refereed seven papers presented at the ICRM 2013, and papers for the journals *ARI*, *Cal Lab Magazine*, *NSCLI* and *Metrologia*.

4.7 Travel (conferences, lectures and presentations, visits)

D.T. Burns to:

- Teddington (UK), 16-20 September 2013, to participate in the BIPM.RI(I)-K6 comparison of absorbed dose to water in accelerator beams with the NPL.
- Paris (France), 8 October 2013, to participate in the 16th International Congress of Metrology and to present a poster entitled "The BIPM Calorimetric Standard for Accelerator Dosimetry".
- Paris (France), 2-4 December 2013, to participate in a meeting of the ICRU Report Committee on Operational Quantities for Radiation Protection, held at the LNE.

S. Picard to:

- St Denis (France), 19 February 2013, to visit the thermometry department of the LNE/INM-Cnam.
- Berlin (Germany), 12 March 2013, to attend the CCT/TG-SI progress meeting at the PTB on the determination of the Boltzmann constant.
- Berlin (Germany), 13 March 2013, to visit the laboratory on dielectric constant gas thermometry at the PTB.
- Prague (Czech Republic), 10 April 2013, to attend the EURAMET TC-T workshop on thermophysical properties.
- Prague (Czech Republic), 10-12 April 2013, to attend the EURAMET TC-T meeting and to present news from the BIPM and the CCT.
- Teddington (UK), 17 September to 2 October and 18 to 22 November 2013, to carry out the BIPM.RI(I)-K6 comparison of absorbed dose to water in accelerator beams with the NPL.
- Teddington (UK), 30 September 2013, to visit the ultrasound, acoustics and underwater acoustics laboratories at the NPL.
- Teddington (UK), 1 October 2013, to visit the thermometry laboratories at the NPL.
- Paris (France), 8 October 2013, to participate in the International Congress of Metrology in Paris and to give a poster presentation entitled "The BIPM Calorimetric Standard for Accelerator Dosimetry".
- Paris (France), 15 November 2013, to attend an award ceremony at the LNE.
- Teddington (UK), 19 November 2013, to visit the humidity laboratories at the NPL.

G. Ratel to:

- Barcelona, (Spain) 18-22 March 2013, to attend the LSC 2013 conference and to co-chair the session "Radionuclide Metrology using LSC".
- Antwerp, (Belgium) 17-21 June 2013, to attend the 19th International Conference on Radionuclide Metrology and its Applications, ICRM 2013, and to chair the sessions "Aspects of International Metrology" and "Intercomparisons".
- Paris, (France) 8 October 2013, to attend the 16th International Congress of Metrology to give a talk entitled "Some thoughts about the extension of the International Reference System (SIR) to β emitters".
- LNE-LNHB, Saclay (France) 21 November 2013, to attend as an examiner the defence of the "*Habilitation à diriger les recherches*" of Marie-Noëlle Amiot.
- LNE-LNHB, Saclay (France) 5 December 2013, to attend the "*Journées Utilisateurs LNHB*" to make a presentation entitled "*Système International de Référence*".

G. Ratel and C. Michotte to:

- Antwerp (Belgium), 17-21 June 2013, to attend the 19th International Conference on Radionuclide Metrology and its Applications, where G. Ratel made an oral presentation entitled "Pilot study organized in view of using liquid scintillation to extend the SIR to pure beta emitters" and chaired the sessions "Aspects of International Metrology" and "Intercomparisons".

C. Michotte to:

- NPL, Teddington (UK), 7-8 November 2013, to attend a meeting to celebrate the 20th Anniversary of the GUM.
- Bucharest (Romania), 18-22 November 2013, to carry out an activity comparison of ^{99m}Tc (BIPM.RI(II)-K4.Tc-99m) at the IFIN-HH using the SIR Transfer Instrument.

C. Michotte and M. Nonis to:

- Rio de Janeiro (Brazil), 1-8 July 2013, to carry out an activity comparison of ^{99m}Tc (BIPM.RI(II)-K4.Tc-99m) at the LNMRI-IRD using the SIR Transfer Instrument.

4.8 Visitors

A number of delegations from different countries or organizations visited the Ionizing Radiation Department in 2013:

- M. Gröning, Laboratory Head, Terrestrial Environment Laboratory, Department of Nuclear Sciences and Applications, IAEA, 1 March 2013;
- J. Stenger, PTB Board and EURAMET EMRP Chair, 12 June 2013;
- Delegation from the 102nd meeting of the CIPM: B. Bowsher, H.S. Brandi, K. Carneiro, K.H. Chung, Y. Duan, L. Érard, B. Inglis, R. Kaarls, W. Louw, J.W. McLaren, W.E. May, H. Nava Jaimes, H. Uğur, J. Ullrich, T. Usuda, J. Valdés, T.J. Quinn (Emeritus Director), P. Richard (President of the CCM) A.J. Wallard (Emeritus Director), 20 June 2013;
- L. Pereira Neves and A.P. Perini (IPEN, Brazil), 2 July 2013;
- Saudi Arabia: Mr Khalid Al-Dawood, Supervisor of Time and Frequency Laboratory, Metrology and Quality Organization (SASO), Mr Ahmed Hamed Aljawana, Time and Frequency Laboratory, Metrology and Quality Organization (SASO), Prof. Ramiz Hamid, Head of Time, Frequency and Wavelength Laboratory (TÜBİTAK - UME, Turkey) and Chair of EURAMET Technical Committee for Time and Frequency, 3 October 2013;
- Bangladesh Delegation: Mr Muhammad Musharraf Hossain Bhuiyan, Cabinet Secretary, Mr Mohammad Moinuddin Abdullah, Ministry of Industries, Mr Md Abu Abdullah, Director General, Bangladesh Accreditation Board (BAB), Mr Iqramul Haque, Director General, Bangladesh Standards and Testing Institution, Mr Md Lutfor Rahman Tarafder, Joint Chief, Ministry of Industries and Project director, BQI-BEST, Dr Franz Hengstberger, Technical Advisor, BQI-BEST, 11 October 2013.

4.9 Guest workers

- H. Bjerke (NRPA, Norway), 16 September 2013,
- L. Czap (IAEA), 14-18 October 2013,
- P. Rosado (LNMRI, Brazil), 21-31 October 2013.

BIPM Chemistry Department
Director: R.I. Wielgosz
(1 January 2013 to 31 December 2013)

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

5.1.1 Ozone photometer comparison and calibration programme

In 2013, five laboratories brought their ozone national standards to the BIPM for a comparison with the BIPM-SRP27 reference standard as part of the key comparison BIPM.QM-K1: the NIST (USA) in February; the NPL (UK) in May, the METAS (Switzerland) in July; the CHMI (Czech Republic) in September; and the EC-JRC (Ispra, Italy) in October. Two of the comparison reports have been reviewed and published in the *Metrologia Technical Supplement,* two are under review by the CCQM Working Group on Gas Analysis (GAWG) and one is in progress.

5.1.2 Maintenance of the NO_2 facility and CCQM-K74, CCQM-P110 coordination

The paper "*Accurate measurements of nitrogen dioxide (NO_2) and nitric acid (HNO_3) mole fraction by FT-IR spectroscopy calibrated by gas standards and synthetic spectra*" was published in the peer reviewed journal *Applied Spectroscopy*. The paper "*Final report on Pilot Study CCQM-P110: Study on the accuracy and uncertainty of FT-IR methods calibrated with synthetic spectra for NO_2 concentration measurements*" has been reviewed and published in the *Metrologia Technical Supplement*.

5.1.3 Key comparison on methane standards

The measurements of the CCQM-K82 international comparison were carried out and completed during 2013. The Draft A report was distributed to participants and presented during the 30th Meeting of the CCQM-GAWG (November 2013), together with proposals for the Key Comparison Reference Value. Draft B of the comparison report is in preparation.

5.1.4 Formaldehyde

Validation studies required for the key comparison CCQM-K90 have continued. In particular, the one year stability study of transfer standards that started in June 2012 was successfully completed. The gas mixtures under test were proven to be suitable as transfer standards and a new set of the same mixtures is expected to be delivered to the BIPM in February 2014 to allow the start of measurements for the comparison. The BIPM dynamic generation system based on paraformaldehyde permeation was also further characterized with reduced uncertainties for the measurement of the water emitted together with the formaldehyde.

In parallel, an alternative dynamic source of formaldehyde in nitrogen based on trioxane diffusion followed by conversion to formaldehyde was developed. A conversion efficiency of more than 99.7 % was evaluated by FTIR spectroscopy, which can detect low levels of both trioxane and formaldehyde. The BIPM, the pilot laboratory for the key comparison CCQM-K90, will value assign the mole fraction of formaldehyde in the transfer standards by reference to both sources.

5.1.5 Development of a laser-based SRP and ozone absorption cross-section measurements

The setup and the associated process to perform the measurements of the ozone cross-section were improved during 2013 with the development of an optimized configuration for measurements. Particular attention was paid to ensure that only highly inert materials were in contact with ozone, with the result that the rate of loss of ozone within the system was reduced. More importantly, the production process for liquid ozone was improved with the study of the best conditions of the starting oxygen pressure and the cooling temperature of the cryostat. Altogether, this resulted in the production of gas samples that were composed of between 98 % and 99 % ozone. Additionally, a method based on evaporation-condensation cycles of liquid ozone in the gas phase was developed by Dr S. Lee, KRISS (Republic of Korea), during a three month secondment at the BIPM. This allowed the analysis of non-condensed impurities by mass spectrometry and a more accurate quantification of the oxygen content based on pressure measurements, molecular oxygen being the main impurity observed. With this setup, final measurements of the ozone cross-section at the three wavelengths produced by the laser light source in the BIPM facility have been undertaken. Measurements at two wavelengths were completed, and final measurements at the remaining wavelength will be completed in early 2014. The results obtained have demonstrated good reproducibility (better than 0.3 %) and the overall uncertainty estimation is close to 0.5 %. Final results and their publication are expected in the following months.

5.1.6 BIPM-IAEA workshop on CO_2 isotope ratio standards and preparation for CCQM-K120

Following the signing of the BIPM-IAEA memorandum of understanding in 2012, the BIPM and IAEA organized a workshop, hosted by the VSL, the Netherlands, on 4 June 2013, with the aim of understanding the current status of CO_2 and CH_4 isotope ratio standards and their importance for accurate concentration measurements of these important greenhouse gases. The conclusions of the workshop were presented at the 30th Meeting of the CCQM-GAWG (November 2013), and technical proposals for a key comparison (CCQM-K120) on CO_2 in air standards, to be coordinated by the BIPM and the NIST, were accepted. Initial work to develop measurement methods at the BIPM and validation standards for the comparison has started.

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

5.2.1 Purity methodology and small molecule purity analysis

A paper outlining the BIPM implementation of the mass balance method for determining the mass fraction of the main component of a high purity organic material was published in *Analytical Chemistry*.

A "White Paper" describing an objective approach to the use of this data to 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 was prepared by the BIPM and was discussed at the CCQM Working Group on Organic Analysis (OAWG) meeting which was held at the BIPM in April 2013. As a result of those discussions a revised approach was presented at the OAWG meeting held in Pretoria, South Africa, in November 2013 and which was accepted for implementation.

A proposal to establish a working group for delivery of an International Union of Pure and Applied Chemistry (IUPAC) Technical Report on Organic Purity by drawing on technical expertise recruited from NMIs with active programmes in Organic Analysis was prepared. A suitable group of experts were approached and they agreed to participate and the proposal was reviewed favourably by the IUPAC Analytical Division. The proposal has been submitted to the IUPAC Project Committee for final approval, with a target for commencement in 2014.

Feasibility studies for the implementation of a BIPM capability for quantitative nuclear magnetic resonance (qNMR) assignments of the purity of organic calibrators have continued with the focus on:

- preparation and ampouling of gravimetrically assigned standard solutions of selected organic materials in deuterated NMR solvents;
- methods for the verification of gravimetrically assigned analyte concentration in solution by an independent quantitative chromatographic analysis.

Agreement between gravimetric and analytical values of ampoule-sealed solutions in volatile deuterated solvent at relative uncertainties below 0.1 % when using quantification by GC-FID has been achieved.

The technical capabilities of the BIPM Organic Analysis programme were augmented during 2013. A Karl Fischer titration apparatus and an additional HPLC-UV system were purchased. The Karl Fischer system replaces existing equipment that was nearing the end of its working life and the additional LC-UV capability will allow improved management of the workload arising from the increased requirements in this area of both the Small and Large Organic Purity work programmes.

5.2.2 Organic programme quality system

The Quality System documentation was reviewed and revised in advance of an Internal Audit undertaken in July 2013. Corrective actions identified as a result of the Internal Audit have been implemented and documented.

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

Following on from the initial discussion of results at the November 2012 OAWG meeting in Hong Kong (China) of the CCQM-K55.c [(L)-Valine] key comparison and the parallel CCQM-P117.c pilot study coordinated by the BIPM, a review was undertaken to identify the possible causes of the disparity of results reported using quantitative NMR (qNMR) methods. The result of the review was discussed at the OAWG meeting held at the BIPM in April 2013. Additional and unanticipated studies were required to resolve a claim by one of the key comparison participants regarding the presence of a significant quantity of an unaccounted ammonium impurity in the material. These studies demonstrated clearly that the claim was not justified and it was withdrawn. A proposal for the KCRV was discussed at the April meeting, and draft final reports for both the key comparison and the parallel pilot study were subsequently prepared and circulated to all comparison participants. A slightly revised KCRV for the comparison was agreed after discussion at the OAWG meeting in November 2013. The final report of the comparison will be sent for approval in December 2013.

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

A candidate batch of comparison material for the CCQM-K55.d comparison has been prepared at the BIPM. A bulk source material was sub-divided into more than 250 sealed vials each containing at least 500 mg of folic acid. The impurity profile of the batch is currently under investigation as is the suitability of its homogeneity and stability for the purposes of the comparison. Contingent on a successful outcome to these studies, it is planned that the key comparison and a parallel pilot study will start towards the end of 2014.

5.2.5 Organic large molecule purity – angiotensin I

A range of analytical methods for the purity determination of the intact decapeptide angiotensin I (ANG I) were developed and validated by the BIPM. These activities have received additional support through a collaborative agreement with the NIST. ANG I is a hypertension marker that is frequently monitored and is crucial for clinical chemistry. It provides a model system for developing future large organic molecule purity comparisons for the CCQM. Procedures developed and validated for the identification and quantification of structurally related peptide impurities for use in the characterization of the model peptide ANG I include: LC-hrMS/MS (Orbitrap), LC-MS/MS (Qtrap), and LC-UV-CAD.

External calibration has been used for all three methods for the quantification of six related peptide fragments for which pure calibrator materials could be synthesized commercially, allowing the purity mass fraction value of a pure ANG I material provided by the NIST and the corresponding measurement uncertainty to be evaluated using the mass balance approach.

A quantitative AA analysis method for the mass fraction value assignment of ANG I subsequent to complete microwave-assisted vapour-phase hydrolysis was also developed. The LC-MS/MS (Qtrap) method for AAs has been further developed to serve as the basis of an LC-ID-MS/MS method for the AA analysis of the hydrolyzed peptides. Traceability has been established through in-house purity capabilities for AAs. A peptide impurity corrected amino acid (PICAA) analysis approach, requiring quantification of constituent amino acids following hydrolysis of the material and correction for AAs originating from impurities has been developed and validated as an alternative to the full mass balance approach that could require unviable large quantities of peptide material.

The purity mass fraction value of the pure ANG I material provided by the NIST and the corresponding measurement uncertainty has been evaluated using the PICAA approach. The final result was in agreement with the results obtained using the mass balance approach.

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 BIPM has successfully finalized the cross-validation of different approaches for the purity mass fraction value assignment of the model decapeptide ANG I in collaboration with NIST. The methods developed will be used in the planned CCQM key comparison on peptide purity. External publication of the study results is currently ongoing.

5.2.6 Organic large molecule purity – insulin

Insulin (INS) plays an important role in the treatment and monitoring of diabetes. Pure primary calibrator materials are a fundamental requirement for pharmaceuticals, laboratory medicine and clinical chemistry, and the molecule provides a model system for developing future large organic molecule purity comparisons for the CCQM.

Measurements to assign a mass balance purity value to an INS material have been completed, including different methods for the identification and quantification of structurally related impurities, notably: LC-hrMS/MS (Orbitrap), LC-MS/MS (Qtrap), LC-UV-CAD. NMR spectroscopy has been used to provide data to confirm the characterization of the INS.

A PICAA analysis method, requiring quantification of constituent amino acids following hydrolysis of the material and correction for AAs originating from impurities for the mass fraction value assignment of INS, is being implemented.

5.2.7 Organic large molecule purity – Human C-peptide

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

The assignment of the mass fraction content of high-purity materials will be the subject of the CCQM-K115/P55.2 comparison. C-peptide (hCP) has been proposed and has been accepted as the most appropriate choice for a study material for a first CCQM key comparison and parallel pilot study looking at competencies to perform peptide purity mass fraction assignment. C-peptide (hCP) was chosen with the aim of leveraging the work required for the comparison and thereby minimizing the workload for NMIs while simultaneously focusing on a material directly relevant to existing CMC claims. The BIPM will coordinate this comparison in collaboration with NIM, China, in 2014-2015.

The 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, containing 31 amino acids. It will directly support NMI services and 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 can support a wider range of NMI capabilities was recently presented and approved at the CCQM WG meetings in November 2013.

The comparison hCP material has been synthesized and was provided by the NIM, China. The comparison samples were filled under nitrogen using a glove box to avoid contamination. Homogeneity and stability studies are planned at the BIPM.

Different methods for the identification and quantification of structurally related impurities are currently under development: LC-hrMS/MS (Orbitrap), LC-MS/MS (Qtrap), and LC-UV-CAD.

Further procedures for use in the characterization of the hCP material that are going to be developed or investigated are GC-MS, KFT, TGA as well as supporting data from ion chromatography, CHN/O and NMR measurements.

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

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

The annual joint meeting of the JCTLM Working Groups was held at the BIPM on 3 December 2013. This was followed by a JCTLM Members' and Stakeholders' Meeting on 4-5 December that brought together 70 attendees from the *In Vitro* Diagnostic Industry, as well as from the clinical chemistry and laboratory medicine community. The first session of the meeting was on the 'Impact of Reference Measurement Systems on Clinical Evidence', the second session on "Commutability", and the last session on "JCTLM current and future activities". The 12th meeting of the Executive Committee of the JCTLM was held at the BIPM on 6 December 2013.

The revised text of the Declaration of Cooperation (DoC) between the CIPM, IFCC and ILAC, and its Appendices III and IV has been approved by the three sponsoring organizations and posted on the BIPM JCTLM website. The amendments made to the text were in line with the current review processes used by the JCTLM, as well as the revision in the harmonized standards (ISO 15194 and 151943 related to Certified Reference Materials and Reference Procedures) of European Directive on *In Vitro* Medical Devices. In addition, a statement on the obligations for JCTLM Member Organizations was included in Appendix IV.

In March 2013, the WG1 Cycle 9 reference materials, and measurement methods, and WG2 Cycle 7 reference measurement laboratory services approved by the Executive Committee during its 11th annual meeting in December 2012 were published in the database.

As of December 2013 the JCTLM Database contained:

- 299 available certified reference materials that cover 11 categories of analytes. Of these reference materials, 33 are in List II, which includes reference materials value-assigned using internationally agreed protocols, and three are in List III, which covers reference materials with nominal properties;
- 156 reference measurement methods or procedures that represent about 80 different analytes in eight categories of analytes;
- 92 reference measurement services, delivered by nine reference laboratories and two NMIs in five countries and which cover six 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 January 2013, and email notifications were sent to about 350 potential contributors to the JCTLM. As of July 2013, 58 nominations for materials, 12 nominations for methods, and 12 nominations for services had been received and sent to Review Teams for evaluation.

ISO TC 212 WG2 is currently revising two normative standards of particular importance to the JCTLM processes, notably ISO 17511 and ISO 15195, and the BIPM, as a liaison A organization to ISO TC 212, has been active in this activity.

5.4 Publications

External publications

1. Viallon J., Moussay P., Idrees F., Wielgosz R., Niederhauser B., Final report of the ongoing key comparison BIPM. QM-K1: Ozone at ambient level, comparison with METAS (July 2013), *Metrologia*, 2013, **50**, *Tech. Suppl.*, 08022.
2. Flores E., *et al.*, Final report on Pilot Study CCQM-P110: Study on the accuracy and uncertainty of FT-IR methods calibrated with synthetic spectra for NO2 concentration measurements, *Metrologia*, 2013, **50**, *Tech. Suppl.*, 08011.
3. Norris J.E., Choquette S.J., Viallon J., Moussay P., Wielgosz R., Guenther F.R., 2013, Temperature Measurement and Optical Path-length Bias Improvement Modifications to NIST Ozone Reference Standards, *J. Air & Waste Manage. Assoc.*, 2013, **63**(5), 565-574.
4. Flores E., Viallon J., Moussay P., Wielgosz R.I., Accurate Fourier Transform Infrared (FT-IR) Spectroscopy Measurements of Nitrogen Dioxide and Nitric Acid Calibrated with Synthetic Spectra, *Appl. Spectrosc.*, 2013, **67**, 1171-1178.
5. Westwood S., Josephs R., Choteau T., Daireaux A., Wielgosz R. Mass Balance Method for the SI Value Assignment of the Purity of Organic Compounds, *Anal. Chem.*, 2013, **85**, 3118.
6. Viallon J., Moussay P., Idrees F., Wielgosz R., Botha A., Final report of the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with NMISA (July 2012), *Metrologia*, 2013, **50**, *Tech. Suppl.*, 08014.
7. Viallon J., Moussay P., Idrees F., Wielgosz R., Morillo Gomez P., Sánchez C., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with ISCIII (December 2012), *Metrologia*, 2013, **50**, *Tech. Suppl.*, 08008.
8. Viallon J., Moussay P., Idrees F., Wielgosz R., Novák J., Vokoun M., Final report of the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with CHMI (September 2013), *Metrologia*, 2013, **50**, *Tech. Suppl.*, 08024.

9. Galbally I.E., *et al*., Guidelines for continuous measurements of ozone in the troposphere, GAW Report No. 209, 2013, 76 pp.

10. Stoppacher N., Josephs R.D., Daireaux A., Choteau T., Westwood S.W., Wielgosz R.I. Impurity identification and determination for the peptide hormone angiotensin I by liquid chromatography-high-resolution tandem mass spectrometry and the metrological impact on value assignments by amino acid analysis, *Anal. Bioanal. Chem.* 2013, **405,** 8039–8051.

11. Stoppacher N., Josephs R.D., Daireaux A., Choteau T., Westwood S.W., Wielgosz R.I. Comparative evaluation of measurement uncertainties for impurities in a candidate reference materials for the peptide angiotensin I determined by liquid chromatography coupled to triple quadrupole mass spectrometry and linear ion trap – high resolution mass spectrometry, *in preparation*.

BIPM publications

1. Josephs R.D., Stoppacher N., Li M. Routes to Macromolecular/Biomolecular Purity (CON 3) - Concept Paper on SI Value Assignment of Purity: Model for the classification of peptides for primary structure purity determinations, Input for BAWG Drafting Group.

5.5 Activities related to the work of Consultative Committees

The CCQM held its 19th meeting at the BIPM on 18-19 April 2013, and was preceded by meetings of its working groups.

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

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) and the CCQM Working Group on Organic Analysis (OAWG).

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).

5.6 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 BIPM and CCQM liaison to the ISO-REMCO and is a member of the World Anti-Doping Agency (WADA) Laboratory Committee.

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.

5.7 Travel

R.I. Wielgosz to:

- Atlanta and Gaithersburg (USA), 22-25 January 2013, to participate in revision of standards for ISO TC 212 WG2 (Reference Systems – Laboratory Medicine) and meetings at the NIST;
- Teddington (UK), 28-30 January 2013 and 26-27 June 2013, to participate in the NMS Chem/Bio-metrology advisory working group;
- PTB, Braunschweig (Germany), 7-8 February 2013, to attend the EURAMET Metchem Plenary Session and to give an update on the CCQM Strategy Document;
- Delft (the Netherlands), 4 June 2013, to Chair BIPM-IAEA workshop on CO2 and CH4 isotope ratio standards;
- Rotterdam (the Netherlands), 5-7 June 2013, to Chair Session on Metrology and Standardization at the GAS 2013 conference;
- Greenwich (UK), 2 September 2013, to give invited lecture on 'Linking Essential Climate Variables to SI Traceable Measurement' at the 16th International Conference on the Properties of Water and Steam (ICPWS16);
- Daejeon and Seoul (Republic of Korea), 7-11 October 2013, to give an invited lecture at the 3rd International Conference on the Standardization in Clinical Chemistry and for meetings at the KRISS;
- Pretoria (South Africa), 4-8 November 2013, for the CCQM Working Groups' meetings, Workshop and to visit the NMISA;
- Singapore, 19-21 November, for ISO TC 212 WG2 and plenary session, and for meetings at the HSA.

E. Flores to:

- Rotterdam (the Netherlands), 6-7 June 2013, to present a poster at the GAS 2013 conference;
- Pretoria (South Africa), 4-8 November 2013, to attend the 30th CCQM Working Group on Gas Analysis meeting and visit the NMISA laboratories.

R. Josephs to:

- IAM, Budapest (Hungary), 2 March 2013, to represent the BIPM at the Inter-Agency Meeting of the Codex Alimentarius Commission;
- ISA/CNRS, Lyon (France), 23 May 2013, to attend the ABSciex user workshop for protein quantification by mass spectrometry;
- Capita, London (UK), 19-20 June 2013, to attend a management training course;
- NMISA, Pretoria (South Africa), 4-8 November 2013, to give presentations at the meeting of the CCQM Working Group on Bioanalysis;
- NIST, Gaithersburg (USA), 16-17 December 2013, to give a presentation on the angiotensin project and to discuss future collaboration.

N. Stoppacher to:

- Thermo Fisher Scientific, Courtabœuf (France), 7 February 2013, to attend the user meeting on "Biomolécules: de l'identification des peptides à la caractérisation des protéines thérapeutiques" ;
- NIST, Gaithersburg (USA), 16-17 December 2013, to give a presentation on angiotensin purity determination by mass spectrometry and to discuss future collaboration.

J. Viallon to:

- Vienna (Austria), 8-10 April 2013, to attend the European Geosciences Union general assembly;
- Geneva (Switzerland), 3-5 June 2013, to give a lecture and take part in discussions by the 'Absorption Cross-Section of Ozone' committee;
- Rotterdam (the Netherlands), 6-7 June 2013, to present a poster at the GAS 2013 conference;
- Pretoria (South Africa), 4-8 November 2013, to attend the 30th CCQM Working Group on Gas Analysis meeting and visit the NMISA laboratories;
- San Francisco (USA), 9-13 December 2013, to present a poster at the American Geosciences Union Fall meeting.

S. Westwood to:

- Sydney (Australia), 21-24 March 2013, for the WADA Laboratory Directors Meeting and a WADA Laboratory Expert Group meeting;
- Pretoria (South Africa), 4-7 November 2013, for the CCQM Working Group on Organic Analysis meeting;
- Montreal (Canada), 26-28 November 2013, for a WADA Laboratory Expert Group meeting.

5.8 Visitors

- S. Vaslin-Reimann (LNE) and V. Delatour (LNE), 19 February 2013
- J. Norris (NIST), 25-29 February 2013
- M. Groening (IAEA), 1 March 2013
- H. Schimmel (IRMM), 7 March 2013
- B. Sweeney (NPL), 27-31 May 2013
- B. Niederhauser and H.P. Andres (METAS), 8-12 July 2013
- J. Novak and M. Vokun, 9-13 September 2013
- F. Lager (EC-JRC), 21-25 October 2013.

5.9 Guest workers

- S. Lee (KRISS), 6 March to 5 June 2013
- M. Li (NIM China), since 2 May 2013.