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

Supplement: scientific Departments

(1 July 2010 – 31 December 2011)

February 2012

Bureau International des Poids et Mesures

BIPM Mass Department
Director: A. Picard
(1 July 2010 to 31 December 2011)

1.1 Calibrations

1.1.1 Certificates (P. Barat, H. Fang and A. Picard)

From 1 July 2010 to 31 December 2011, certificates were issued for the following 1 kg prototypes in platinum-iridium: Nos. 4, 20 and 92 (USA), No. 23 (Finland), No. 3 (Norway), No. 58 (Egypt), No. 74 (Canada), No. 95 (Kenya) and No. 96 (Mexico). These were the first calibrations of No. 95 and No. 96, which were newly fabricated. Calibrations were completed for prototypes No. 93 (Pakistan) and No. 97 (BIPM). Calibration of a prototype for Denmark is under way.

Certificates for 1 kg standards in stainless steel were issued: three for NIMT (Thailand), two for NIS (Egypt), one for BIM (Bulgaria), two for VSL (Netherlands), one for MSL (New Zealand), two for JV (Norway), one for LATU (Uruguay) and three for NMC, A*STAR (Singapore). Calibrations are under way for 1 kg standards in stainless steel: one for SMD, SPF Economie (Belgium) and two for VSL (Netherlands).

Determinations of magnetic susceptibility were made for 1 kg standards in stainless steel: one for BIM (Bulgaria), one for LATU (Uruguay), three for NMC, A*STAR (Singapore), one for SMD, SPF Economie (Belgium) and one for CESMEC (Chile).

1.1.2 Mass calibration laboratory (P. Barat and A. Picard)

The previous Director's Report (2010) reported that, a complete renovation of room 104, normally used for 1 kg mass calibrations began in February 2010. The renovation was completed in July 2010. The Metrotec balance, which had been moved to room 105, was reinstalled in room 104 in August 2010 with the help of Mettler-Toledo (Greifensee, Switzerland). The balance has been re-commissioned in its new location: monitoring of masses of BIPM 1 kg prototypes and BIPM working standards in platinum iridium were made before and after the relocation. Results agreed to within 1.3 µg, with a standard uncertainty $u_c = 2$ µg; which indicates, as for the first relocation, that the transfer of the Metrotec balance from room 105 to room 104 was carried out successfully.

To replace the HK1000 MC balance, the BIPM acquired, in 2010, a M-One 6V-LL mass comparator from Mettler-Toledo. This new mass comparator was installed in room 104 in December 2010.

1.1.3 Air density determination (P. Barat and A. Picard)

The previous Director's Report (2010) reported that, following the renovation of room 105 in late 2006, some discrepancies were observed in the air density as determined by an equation of state. Measurement of the air density using artefacts (gravimetric method) and by comparing this result to the CIPM-2007 formula for air density determination, enabled the air density difference between the two methods to be tracked. After renovation of room 104, the same study was carried out, the mean relative difference inside the Metrotec balance was determined as 1.0×10^{-5}, which is negligible. Calibrations requiring significant correction for air buoyancy can be made with confidence in room 104.

1.1.4 Automated 100 g balance to support BIPM mass calibrations (C. Goyon-Taillade)

This facility was introduced in the BIPM Quality Management System in September 2010, following peer review by an expert from the NPL (UK).

Mass calibrations were performed for the two 25 g in copper for the BIPM watt balance project and for a set of masses RD1 (50 g to 10 g) and the set ZW3 (5 g to 1 g). The set ZW3 was especially designed for use in subsequent calibrations, performed manually, using the Mettler-Toledo balance UMT5. With an uncertainty of 2 µg on the 100 g mass reference used, the automated 100 g balance provides calibration uncertainty of 0.4 µg for 1 g mass.

1.1.5 Volume of mass standard above 300 g (C. Goyon-Taillade)

Within the framework of calibration services offered to National Metrology Institutes (NMIs), during the reporting period, densities were determined for one mass standard in stainless steel belonging to LATU (Uruguay) and three mass standards in stainless steel belonging to NMC, A*STAR (Singapore).

To prepare the ensemble of mass standards for the future *mise en pratique* for the new definition of the kilogram, calibrations were performed for Pt/Ir and stainless steel sets constituted by 4 cylinders and one stack of 8 disks for each set.

Fabrication of a new prototype dedicated to a BIPM working standard, is under way in the BIPM workshop. Its density was determined during 2011. Its mass is currently 13 g above 1 kg.

1.1.6 Volume of mass standard less 100 g (C. Goyon-Taillade and F. Idrees)

Volumes were determined for the two masses of 1 g and 95 mg used to determine the sensitivity scale for the new M-One mass comparator from Mettler-Toledo. For the watt balance project, the volumes of two 25 g masses in copper were determined.

1.2 BIPM susceptometer (H. Fang)

The Mass department provided a susceptometer, including three magnets and two calibrated magnetic transfer standards, to INTI (Argentina). The Excel program used for measurement data computing and uncertainty evaluation was revised to improve the understanding of the data evaluation method and to facilitate data storage.

1.3 Pressure (P. Barat, C. Goyon-Taillade)

Calibrations of BIPM manometers, with respect to the pressure balance maintained in the Mass Department, were conducted every three months. Forty-six internal certificates were issued during the period 1 July 2010 to 31 December 2011. In addition, seven study notes were issued during this period.

1.4 Balances to support development programmes (P. Barat and A. Picard)

As mentioned in the previous Director's Report (2010), a new mass comparator has been purchased to replace the HK1000 MC balance which was obsolete. Installation of the new M-One 6V-LL mass comparator from Mettler-Toledo was carried out in December 2010. Testing and characterization of some parameters of the mass comparator (position errors in air and under vacuum, linearity, etc) had to be postponed due to delays in the delivery of certain devices from different suppliers. These have been now installed on the new mass comparator and some measurements have been carried out. The first measurements in air of two mass standards in platinum iridium and two in stainless steel have been undertaken. Air density artefacts have been used to determine the air density inside the enclosure of the mass comparator. The results show that there is no discrepancy between the air density calculated from the CIPM-2007 formula and that determined using the air density artefacts. Comparison of the results obtained between the Metrotec and the M-One mass comparators on Pt-Ir and stainless steel mass standards shows good agreement within 2.1 µg with a standard uncertainty of u_c = 4 µg. This uncertainty is larger than the one usually obtained due to the fact that characterization of the new mass comparator has not yet been carried out.

These initial results indicate that the new mass comparator will be a good replacement for the HK1000 MC balance.

1.5 International Avogadro Coordination project (P. Barat and A. Picard)

Within the framework of the Avogadro project, a special study was conducted to estimate the amount of water adsorbed or desorbed between air-vacuum cycles on a silicon-based material. Physical and chemical water sorption effects occurred on the silicon sphere during air-vacuum cycles. The amount of water on the surface of the mass artefact, due to the physical water sorption, can be removed by placing the mass under vacuum (1 mPa). However, to remove the water due to chemical water sorption, more energy is required. This can be done by baking the artefact under vacuum. PTB provided a 1 kg natural silicon sphere "Silo02" which has been etched and covered by a 0.2 µm thermal oxide layer. The Mass Department is using this sphere to distinguish between chemical and the physical sorption.

Firstly, the physical sorption effect was determined by weighing the sphere in moist air followed by measurements under vacuum (1mPa). From these two weighing conditions it was possible to deduce the physical sorption coefficient, which is about 10 ng cm^{-2}. The next step was to transfer the sphere located in the mass comparator under vacuum to the dry glove box (<0.1 ppm of water and oxygen) without any contact with moist air, by using an automatic loadable container. The sphere was baked at 400 °C for 2 hours in a vacuum oven attached to the glove box. After this thermal treatment the sphere was transferred back (again without contact with moist air) to the mass comparator, remaining under vacuum. Additional weighing under vacuum was carried out to deduce the mass difference of the sphere under vacuum before and after baking, and therefore to determine the chemical sorption coefficient. After baking the sphere became so dry that large electrostatic charges were present which distorted the results. The study is ongoing.

1.6 Study of gravity gradient (P. Barat and A. Picard)

A study was conducted to evaluate the feasibility to deduce the gradient of the local acceleration due to gravity by using a set of four stainless steel artefacts belonging to CENAM (Mexico). The centre of mass of these 1 kg masses are at different heights due to their shape. As a function of the combination of the masses weighed under vacuum (2 mPa) and their orientations (face up or down) it should be possible to determine the gradient of local gravity acceleration. The relative local gravity gradient $(1/g)(\partial g/\partial h)$ measured by using a relative gravimeter is equal to -0.265×10^{-7} m^{-1} i.e. for one kilogram 0.265 µg / mm. The results obtained so far do not agree with the measured gradient and the sources of the discrepancy were investigated. The centre of mass of each artefact was controlled; the results obtained do not explain the discrepancy observed. A customs deadline meant that the artefacts were returned to CENAM before the discrepancy was resolved. Further measurements are required to complete this study.

1.7 Ensemble of mass standards (P. Barat, F. Idrees, E. de Mirandes, and A. Picard)

Considerable progress has been made since the last Director's Report was published towards the establishment of a new ensemble of mass standards, known as "the BIPM ensemble of mass standards" (BEMS). The ensemble will play a crucial role in the dissemination of the mass unit following the forthcoming redefinition of the kilogram. The ensemble will be composed of sixteen 1 kg mass standards of different materials (Pt-Ir, stainless steel and silicon) stored under different conditions (in a pure argon flow, in a pure nitrogen flow, in vacuum and in air). Storage of the BEMS requires an unpolluted environment, which will ensure better long-term stability of the mass of the standards. In the near future, a weighted average mass of the standards will be computed regularly by choosing the statistical weight of each standard to be proportional to the stability of the standard.

At present, the BIPM has fourteen new 1 kg mass standards, which constitute its ensemble of mass standards: four Pt-Ir, four stainless steel, four natural crystal silicon spheres and two surface artefacts (stack of discs in Pt-Ir and in stainless steel). The first characterization measurements of the standards, volume and mass in air, are almost complete. A dedicated room for the storage of the ensemble has been prepared. A thermally isolated cabin has been designed to isolate the ensemble from outside temperature fluctuations. A storage network has been carefully designed. Each mass standard will be stored in an electro-polished stainless steel container. The containers have been manufactured by the BIPM workshop. The argon gas storage network has been completed. The ultrapure argon and nitrogen gases (less than 50 ppb of impurities) are currently supplied from gas bottles. A nitrogen generator has been installed to supply a continuous flow of gas (0.1 l/min) through the containers.

The gas of each container will be continuously analysed to detect changes in the concentration of impurities which could be related to a fluctuation of the mass of the standard stored inside. Analysers have been purchased to measure the oxygen and water content in the argon and nitrogen gases. The first measurements to evaluate the background purity of the gas sources have been made. A preliminary vacuum storage network has been built and has been connected to a mass spectrometer, which will identify and quantify vacuum impurities. First measurements to characterize the vacuum in the network have been carried out.

The Mass Department has developed a mathematical algorithm to compute the weighted average of the mass of the elements of the ensemble in order to optimize the stability and the robustness of the average mass. This algorithm is currently operational. It has been satisfactorily tested using measurements from historical mass comparisons made at the BIPM over a 20 year period.

The next steps in the project will be to complete the nitrogen and vacuum storage networks and fully automate measurement of gas and vacuum impurities of each container.

1.8 Trilateral cooperation among NPL, METAS and BIPM (S. Davidson (NPL), P. Fuch (METAS) and A. Picard)

In the last Director's Report (2010), it was stated that a trilateral cooperation was launched to provide sufficient resources to support the preparation for the *mise en pratique* of the future new definition of the kilogram by the BIPM Mass Department during 2009–2012. Allocation of resources given by physicists from NPL and METAS are unchanged at 60 % and 50 % of a full-time equivalent, respectively. This cooperation covers the following main activities: The methodology of air-vacuum mass comparisons, surface analysis of contamination on the surface of the artefacts, and the effectiveness of the cleaning method employed on the various materials used (Pt-Ir, silicon stainless steel and gold alloy). BIPM provided the Pt-Ir and gold alloy samples, while NPL provided the silicon samples.

METAS has invested in: a XPS X-Ray Photoemission Spectrometer (operational); a UHV Storage chamber for 3 × 8 1 kg standards; a 1 kg vacuum mass comparator; and a Contact Angle Measurement (CAS) system. The CAS system measures surface wettability; hydrophobic properties depend on surface conditions. The CAS is calibrated by XPS and contact angle measurement can be used in parallel with XPS as a "Quick test" of surface quality. The suitability of a quartz crystal microbalance to monitor cleaning (and contamination) processes is being investigated. METAS demonstrated that H_2-plasma removes contaminant carbon leaving only carbides; it is non-abrasive and does not change the mass of an artefact. All storage and cleaning methods are suitable except O_2 plasma cleaning with storage in vacuum. The recontamination after cleaning is apparently not continuous (self-limiting to 1-2 atomic layers). The O_2 plasma oxidation of metal can be removed via H_2 plasma exposure and possible change in morphology with oxidation.

NPL Sorption artefacts of Pt-Ir, stainless steel and silicon were used to evaluate the effect of vacuum pressure between 10^{-3} Pa and 100 Pa. Results identified a hysteresis in the sorption effects, dependent on the pressure history of the artefacts. For all materials sorption effects were consistent for pressures below 0.1 Pa, however sorption characteristics varied between materials with Pt-Ir artefacts giving 0.08 μg/cm^3, stainless steel 0.16 μg/cm^3 and silicon 0.63 μg/cm^3. Additionally, silicon gave unexpected results at vacuum pressures in the region 1 Pa to 100 Pa. Further investigation of the silicon artefacts is planned. A method for evaluating the cleaning of artefacts has been developed which uses reliably deposited hydrocarbon contamination on weights. The method involved the use of a cold cathode vacuum gauge at a pressure of about 4 Pa. A deposition rate of 0.15 nm/h was achieved. The process allowed artificial contamination of weights to a depth of 5 nm to 10 nm (typical build up for carefully stored weights over a period of years) in a few hours and will facilitate further work to evaluate various cleaning procedures.

NPL and METAS evaluated the transfer (to vacuum) and storage of artefacts in argon and air. The results showed that storage and transfer to vacuum under an argon atmosphere significantly reduced the contamination build up on the standards used.

Within the framework of this cooperation, BIPM purchased materials in order to constitute the ensemble of reference mass standards (BEMS) and to develop a storage facility to maintain the ERMS under vacuum or inert gas conditions (see §7).

The BIPM appreciates and thanks METAS and NPL, and other participants in this collaboration, which permitted the BIPM Mass Department to undertake its programme of work, particularly for the forthcoming redefinition of the kilogram. The cooperation will continue in 2012, providing more results for use in the preparation of the *mise en pratique*.

1.9 Humidity generator (C. Goyon-Taillade and F. Idrees)

The development of a humidity generator based on two water vapour saturators was suspended because the resistance bridge used to monitor the temperatures of the saturators, by means of standard platinum resistance thermometers (SPRTs), malfunctioned and was sent for repair. The humidity bench will be dedicated to internal calibration services for secondary instruments that measure the humidity or dew point of ambient air. All other components are ready for the generator when the resistance bridge is repaired.

1.10 Publications

External publications

1. Berry J., Davidson S., Barat P., Davis R., Comparison of UV/ozone cleaning of platinum/iridium kilogram mass standards with nettoyage-lavage cleaning, *Metrologia*, 2011, **48**(3), 181–186.

2. Andreas B., Azuma Y., Bartl G., Becker P., Bettin H., Borys M., Busch I., Gray M., Fuchs P., Fujii K., Fujimoto H., Kessler E., Krumrey M., Kuetgens U., Kuramoto N., Mana G., Manson P., Massa E., Mizushima S., Nicolaus A., Picard A., Pramann A., Rienitz O., Schiel D., Valkiers S., Waseda A., Determination of the Avogadro Constant by Counting the Atoms in a ^{28}Si Crystal, *Phys. Rev. Lett.*, 2011, **106**(3), 030801.

3. Andreas B., Azuma Y., Bartl G., Becker P., Bettin H., Borys M., Busch I., Fuchs P., Fujii K., Fujimoto H., Kessler E., Krumrey M., Kuetgens U., Kuramoto N., Mana G., Massa E., Mizushima S., Nicolaus A., Picard A., Pramann A., Rienitz O., Schiel D., Valkiers S., Waseda A., Zakel S., Counting the atoms in a ^{28}Si crystal for a new kilogram definition, *Metrologia*, 2011, **48**(2), S1–S13.

4. Picard A., Barat P., Borys M., Firlus M., Mizushima S., State-of-the-art mass determination of ^{28}Si spheres for the Avogadro project, *Metrologia*, 2011, **48**(2), S112–S119.

1.11 Activities related to the work of Consultative Committees

- R. Davis was Executive Secretary of the CCM and the CCT and a member of several working groups and task groups of these CCs until end October 2010.
- A. Picard was promoted to Director of the Mass Department on 1 November 2010 and therefore nominated Executive Secretary of the CCM and the CCT. At the same time he became a member of several working groups and task groups of these CCs. In addition A. Picard is coordinator for mass measurements in the former International Avogadro Coordination project/CCM Working Group on the Avogadro Constant.

1.12 Activities related to external organizations

- A Picard acts as the BIPM liaison with IAC, IMEKO TC3 and Euramet TC-M and TC-T.

1.13 Travel (conferences, lectures and presentations, visits)

A. Picard to:

- NPL, Teddington (UK), 27-28 October 2010, to attend to the New Kelvin Dissemination Workshop.
- NPL, Teddington (UK), 29 October 2010, for a meeting of the NPL, BIPM, METAS Trilateral Comparison on the preparation of a *mise en pratique* for the redefined kilogram.
- PTB, Braunschweig (Germany), 3-5 November 2010, to attend an IAC meeting.
- IMEKO 2010, Pattaya (Thailand), 21-25 November 2010, TC3, TC5 & TC22 Joint Conference; to attend meeting as member of the technical committee (TC3) and to give invited key presentation on the redefinition of the kg.
- NMIJ, Tsukuba (Japan), 29-30 November 2010, to give an invited talk on the redefinition of the kg and to visit the laboratories.
- London (UK), 24-25 January 2011, to attend the Royal Society Discussion Meeting on "The new SI: units of measurement based on fundamental constants".
- Euramet TC-M meeting, San Anton (Malta), 2-4 March 2011, to attend the satellite meetings and to give a talk on the new definition of the kg and its *mise en pratique*.
- NIM CCM-WG Force and torque, Beijing (China), 28-31 March 2011, to attend the meeting as Executive Secretary of the CCM, to give a presentation on the forthcoming new definition of the kilogram and to visit the NIM joule balance.
- iMERA-Plus meeting, Prague (Czech Republic), 4-5 July 2011, to participate in the elaboration of the JRP S06 and JRP S07.
- International Congress of Metrology, Paris (France), 4 October 2011, to attend the ICM.
- Euramet TC-T workshop, Brussels (Belgium), 27-28 October; to attend the meeting on the Uncertainties in thermometric fixed points & SPRT calibrations.
- University Paris VII, France, 25 November 2011, *Journée discussion sur le SI*, to give a lecture on « *Vers une nouvelle définition du kilogramme : définition, réalisation et dissémination* ».
- Bureau des Longitudes, Paris (France), 7 December 2011, to attend the conference on: *Le Système International et la nouvelle définition du kilogramme*.

P. Barat to:

- NPL, Teddington (UK), 29 October 2010, for meeting of NPL, BIPM, METAS Trilateral Comparison on the preparation of a *mise en pratique* for the redefined kilogram.

C. Goyon-Taillade to:

- LNE, Paris (France), 7-10 June 2011, to attend a training course on "*Management qualité dans les laboratoires selon la norme 17025 vs 2005*"

E. de Mirandes to :

- London (UK), 24-25 January 2011: to attend the Royal Society Discussion Meeting "The new SI: units of measurement based on fundamental constants".
- Euramet TC-M meeting, San Anton (Malta), 2-4 March 2011, to attend the satellite meetings and give talk on the BIPM ensemble of mass standards.

1.14 Visitors

- Mr J. Soullard, MBraun France (Orsay, France), to replace some components of the glove box, 13 and 19 July 2010;
- Mr J. Soullard, MBraun France (Orsay, France); V. Petitbon-Thévenet and C.-O. Bacri, Institut de Physique Nucléaire d'Orsay, to give a presentation on the BIPM glove box, 23 July 2010;
- Mrs R. Sukhon (NIMT), for technical discussions and to collect three 1 kg mass standards following their calibration, 4-5 and 12 August 2010;
- Mrs J. Pereira, Mettler-Toledo (Viroflay, France), to give a presentation on a new balance and to replace the one used for centre of gravity measurements, 5 August 2010;
- Mr M. Kliebenschädel, Mettler-Toledo (Greifensee, Switzerland), to move the Metrotec balance from room 105 to room 104, 23-26 August 2010;
- Messrs D. Heydenbluth and M. Schreiber, Sartorius AG, to replace some parts of the CCL1007 mass comparator, 30 August and 1-2 September 2010;
- Mr D. Newell (NIST), to deliver prototypes No. 20 and No. 92 for calibration, 12 September 2010;
- Mr S. Davidson (NPL), for an external audit of the mass activities, 23-24 September 2010;
- Mrs D. Heikens (VSL), to collect two 1 kg mass standards following calibration, 1 December 2010;
- Mr M. Kliebenschädel, Mettler-Toledo (Greifensee, Switzerland) and Mr M. Baumeler, Metrotec Engineering AG (Nänikon, Switzerland), to install the new M-One mass comparator, 6-10 December 2010;
- Mr D. Milon, Mettler-Toledo (Viroflay, France), to visit the new mass calibration laboratory following the installation of the new M-One mass comparator, 8 December 2010;
- Mr R. Steiner (NIST), to collect prototypes No. 20 and No. 92 following calibration, 16 December 2010;
- Mr A. Manninen (MIKES), to deliver prototype No. 23 for calibration, 11 January 2011;
- Messrs F. Gauthé and M. Charland, Embassy of Canada in France, to collect prototype No. 74 following calibration, 19 January 2011;
- Mr E. Auvray, Swagelok (Courtaboeuf, France), for technical discussions, 20 January 2011;
- Mr H. Kolbjørnsen (JV), to deliver prototype No. 36 and two 1 kg mass standards for calibration, 25 January 2011;
- Messrs D. Heydenbluth and M. Schreiber, Sartorius AG, to make some adjustments to the CCL1007 mass comparator, 22 February 2011;
- Mrs T. Garberg (JV), to collect prototype No. 36 and two 1 kg mass standards following calibration, 10 March 2011;
- Mr A. Hashadme (NIS), to collect prototype No. 58 following calibration, 17 March 2011;
- Messrs P. Girault and S. Cantelou, Mettler-Toledo (Viroflay, France), to deliver the antistatic device which will be used on the glove box, 8 April 2011;

- Mr T. David (KEBS), to collect the newly made prototype No. 95 following calibration, 2-4 May 2011;
- Mr P. J. Abbott (NIST), to deliver prototype No. 4 for calibration, 8 May 2011;
- Mr Fernando Leyton (CESMEC), to deliver one 1 kg mass standard for calibration, 30 September 2011;
- Mrs B. Goldstein (NIST), to visit the Mass Department, to deliver prototypes No. 79 and No. 85 for calibration and to collect prototype No. 4 following calibration, 2-3 and 6 October 2011;
- Mrs R. Courtland, Associate Editor *IEEE Spectrum*, for an interview on the redefinition of the kilogram, 6-7 October 2011;
- Mr D. Labrousserie, to take pictures in the Mass Department, 7 October 2011;
- Mr Bent Hamer and Mrs Marianne Slot (Norway), to present a film project, 10 October 2011;
- Mr K. Riski (MIKES), to collect prototype No. 23 following calibration, 14 October 2011;
- Mr I. Hernandez (CENAM), to collect prototype No. 96 following calibration, 21 October 2011;
- Mr L. Nielson (DFM), to deliver prototype No. 48 for calibration, 29 November 2011.

BIPM Time Department[1]
Director: E.F. Arias
(1 July 2010 to 31 December 2011)

2.1 International Atomic Time (TAI) and Coordinated Universal Time (UTC) (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*. The *BIPM Annual Report on Time Activities for 2010*, volume 5, complemented by computer-readable files on the BIPM website (www.bipm.org/en/publications/time_activities.html) provides the definitive results for 2010.

2.2 Algorithms for time scales (Z. Jiang, W. Lewandowski, G. Panfilo and G. Petit)

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.

A new prediction algorithm for EAL has been studied, validated and implemented for the monthly calculation of UTC. The new prediction model takes into account the frequency drift which affects most of the participating atomic clocks. The frequency drift of each clock is estimated with respect to the Terrestrial Time (TT) computed at the BIPM and representing the best reference for frequency. Several tests on the past data have shown a reduction of the EAL frequency drift of about 1 order of magnitude with the introduction of the new prediction algorithm. As a consequence, an important improvement in the long-term stability of EAL is expected.

The new algorithm for predicting clock frequency has been implemented in the UTC calculation starting in September 2011 with the agreement of the Consultative Committee for Time and Frequency (CCTF). After few months of having incorporated the new algorithm in the calculation an improvement in the long term performance of EAL is already clear.

2.2.1 EAL stability

Some 88 % of the clocks used in the calculation of time scales are either commercial caesium clocks of the Symmetricom/HP/Agilent 5071A type or active, auto-tuned hydrogen masers. To improve the stability of EAL, a weighting procedure is applied to clocks where the maximum relative weight each month depends on the number of participating clocks. On average during 2010 and 2011, about 15 % of the participating clocks were at the maximum weight. This procedure generates a time scale which relies upon the best clocks.

The stability of EAL, expressed in terms of an Allan deviation, is about 4 parts in 10^{16} for averaging times of one month. Long-term drifts limit the stability to around 2 parts in 10^{15} for averaging times of six months.

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 frequency

[1] Time, Frequency and Gravimetry Department until 31 December 2010, Time Department from 1 January 2011.

standards. Since July 2010, individual measurements of the TAI frequency have been provided by thirteen primary frequency standards, including ten caesium fountains (IT CSF1, LNE-SYRTE FO1, LNE-SYRTE FO2, LNE-SYRTE FOM, NICT CSF1, NIST F1, NMIJ 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*.

As of July 2004, a monthly steering correction of at most 7 parts in 10^{16} is applied as deemed necessary. Since July 2010, 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 $+4.6 \times 10^{-15}$ to $+6.7 \times 10^{-15}$, with a standard uncertainty of less than 1×10^{-15}. From July 2010 to August 2011, fourteen steering corrections have been applied, giving a total correction to $[f(EAL) - f(TAI)]$ of -9.4×10^{-15}. Since the introduction of the new prediction algorithm in September 2011, monthly steering corrections of -5×10^{-16} have been applied.

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. We have provided an updated computation of TT(BIPM), named TT(BIPM10), valid until December 2010, which has an estimated accuracy of about 5 parts in 10^{16}. Moreover we provide each month an extension of TT(BIPM10) based on the most recent TAI computation. Such an extension is useful for pulsar analysis pending the yearly updates of TT(BIPM). Studies aimed at improving the computation of TT(BIPM) are ongoing, in order to keep it in line with improvements in the primary frequency standards.

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

Following a recommendation by the CCTF (2009), the Time Department has implemented the calculation of the differences between the predictions of UTC(USNO) and UTC(SU) (as broadcast by GPS and GLONASS) and UTC. These differences have been published in BIPM *Circular T* since January 2011.

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 Consultative Committee for Length (CCL)/CCTF Frequency Standards Working Group, and the CCTF Primary Frequency Standards Working Group, seeking to encourage comparisons, knowledge-sharing between laboratories, the creation of better documentation, and the use of high-accuracy primary frequency standards (Cs fountains) for TAI.

The CCL/CCTF Frequency Standards Working Group has proposed various other microwave and optical atomic transitions as secondary representations of the second. The latest changes to the list, containing frequency values and uncertainties for transitions in Rb, Hg^+, Yb^+, Sr^+ and Sr, were recommended by the CCTF in June 2009, and no further updates have been produced during the period covered by this report.

Advanced time and frequency transfer

During the past decade very significant advances have been made in the field of optical frequency metrology, concerning both ultra-stable optical frequency standards as well as the means to compare frequencies locally using the optical comb technique. These developments imply strong requirements on time and frequency transfer techniques, which are not satisfied by the methods currently in common use, and it is urgent to focus attention on this aspect.

A workshop arranged at the BIPM in June 2011, had the objectives to survey the current situation of time and frequency transfer, to project future needs and to study the perspectives for satisfying them. The workshop was organized by the CCTF Working Group on Coordination of the Development of Advanced Time and Frequency Transfer Techniques (WGATFT) with the support of the BIPM and served as a basis for further work by the WG in support of preparations for future improvements of the SI second and of time scales. Some 50 participants took part in the workshop.

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

TAI currently relies on data from about 70 participating time laboratories equipped with GNSS receivers and/or operating two-way satellite time and frequency transfer (TWSTFT) stations.

Significant improvements have been made within the Time Department on the time links used for the calculation of TAI; 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, replaced by either multi-channel single- or dual-frequency receivers. Ten TWSTFT links are officially submitted for use in the computation of TAI, representing 15 % of the time links. Additional TW links exist in the Asia-Pacific region but have not yet been officially introduced into the calculation; various other European laboratories are becoming equipped.

The GPS phase and code data provided by time laboratories is processed each month using the Precise Point Positioning (PPP) technique. Following approval by the CCTF at its meeting in June 2009, such PPP links were introduced in the calculation of TAI from September 2009. Currently, more than 30 laboratories participate regularly, close to 20 of which are used as TAI links. Since 2011, the combination of TWSTFT and PPP (so called TWPPP) is used whenever possible, and generally concerns some ten links for which the two techniques are available. Comparisons of the TAIPPP links with others obtained by TWSTFT and P3 are published monthly on the Time Department's ftp server.

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

After the introduction of the first GLONASS common-view civil-code link between PTB and VNIIFTRI into UTC in November 2009, studies proved that time link uncertainty could be improved by a combination with the corresponding GPS link. As a result, two time links have been regularly computed since January 2011 by a combination of GLONASS and GPS.

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

All GNSS links are corrected for satellite positions using IGS and ESA post-processed, precise satellite ephemerides, and those links 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

In addition to GPS and GLONASS code measurements, time and frequency transfer may also be carried out using dual-frequency, carrier-phase measurements. This technique, already widely used by the geodetic community, can be adapted to the needs of time and frequency transfer. A study is being conducted under the framework of the IGS Working Group on Clock Products, of which a physicist from the Time Department is a member.

The method developed to perform the absolute calibration of the Ashtech Z12-T hardware delays allows the BIPM to use this receiver for differential calibrations of similar receivers world-wide, and calibration campaigns began in January 2001. Calibration results have also been issued for other receivers: the Septentrio PolaRx2 since 2006 and the Dicom GTR50 and Javad JPS E-GGD since 2009. Other types of receivers are being investigated in collaboration with laboratories equipped with them. Since 2009, the BIPM travelling receiver for differential calibrations is a GTR50. In all cases, at least two receivers remain at the BIPM to serve as a local reference with 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.

Data from geodetic-type receivers world-wide are collected for TAI computation, using procedures and software developed in collaboration with the Observatoire Royal de Belgique (ORB). These P3 time links are now routinely computed and compared to other available techniques, notably two-way time transfer. After one year of work, the software producing 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 new available data are likely to be used in the frame of multi-GNSS system time links, but further studies on inter-frequency biases have to be carried out.

Geodetic-type receivers also provide raw phase measurements which may be used, along with the code measurements, to compute time links. The BIPM has computed its own solutions for such time links since October 2007, using the GPSPPP software from Natural Resources Canada (NRCan), and these links have been introduced into the TAI regular computation since September 2009. In 2011 a new version of the NRCan PPP software was installed. It is capable of processing both GPS and GLONASS data. Comparisons with other PPP software have been carried out and studies are continuing to improve long-term stability brought about by new processing techniques. Cooperation has started with the Space Research Centre in Poland (SRC) to improve GLONASS time transfer.

2.4.3. Two-way time transfer

Three meetings of the TWSTFT participating stations have been held since July 2010, and the CCTF WG on TWSTFT met at the NIM (Beijing, China) in October 2010, and at NMIJ (Tsukuba, Japan) in September 2011. The TWSTFT technique is currently operational in twelve European, two North American and seven Asia-Pacific time laboratories. Ten TWSTFT links are routinely used in the computation of TAI; four others are in preparation for their introduction or re-introduction into TAI, or for particular studies such as the 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 Uncertainties of TAI time links

The values of the Type A and Type B uncertainties of TAI time links are published in *Circular T*, together with information on the time links used in each monthly calculation. The values of u_A have been individually updated when deemed necessary, depending on the noise level present in the links. Due to upgrading of time transfer equipment at participating laboratories, the Time Department has refined the methods for clock comparison, a recomputation of u_A values, using latest evaluation tools, and has presented the results at a meeting.

2.4.5 Calibration of delays of time-transfer equipment

The BIPM continues to organize and run campaigns for measuring the relative delays of GPS time equipment in time laboratories that contribute to TAI. From July 2010 to December 2011, GPS and GLONASS time equipment for single- and dual-frequency reception was calibrated. The BIPM also supports TWSTFT calibration trips, using a GPS receiver from our time laboratory.

Work on the absolute calibration of GNSS receivers has been carried out by a Ph.D. student through a collaboration co-financed with the CNES, and involving the LNE-SYRTE. The doctoral thesis "Contribution to the absolute calibration of a GNSS reception chain" was defended in November 2011, completing the planned programme of work. It focused on the development and optimization of a method of absolute calibration to independently determine the electrical delay of each element in a GNSS reception chain (time receiver, antenna and antenna cable) with an overall uncertainty of less than one nanosecond. The absolute calibration method can be used to characterize performance and environmental sensitivity of each component of the acquisition system.

Cooperation continued with EURAMET in obtaining regional support for GNSS equipment calibration in contributing laboratories. This action follows the recommendation CCTF (2009) and opens up the possibility of future interaction with other RMOs.

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

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. Guidelines for the characterization of the frequency traceability of local realizations UTC(k) to the SI second have been prepared by staff of the Time Department, as requested by the CCTF WG on the CIPM MRA.

Key comparison of stabilized lasers CCL-K11.UTC

As decided at the 98th meeting of the CIPM in 2009, the BIPM continues to support the CCL-K11 key comparison in terms of participation in measurement campaigns as well as in giving general advice. During the period of this report, staff from the Time Department have been involved only in the reporting of the measurement results and no BIPM presence for measurement campaigns took place.

Key comparison of absolute gravimeters CCM.G-K1

The Gravimetry activity at the BIPM has been closed and the absolute gravimeter has been prepared for transfer to a Member State. The Draft A report of the key comparison CCM.G-K1 that was part of the International Comparison of Absolute Gravimeters ICAG-2009 was prepared by the staff of the Time Department and has been endorsed by the CCL-WG. The Draft B report has been submitted to the Consultative Committee for Mass and Related Quantities (CCM) for approval. A scientific article is being written, which covers the full ICAG-2009 comparison, including the Pilot Study results, for submission to a scientific journal.

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

The publication of the five-day values of [UTC-UTC(k)] in BIPM Circular T gives traceability of the SI second to local realizations of UTC. The participating laboratories make predictions of UTC, which are validated after publication of [UTC-UTC(k)] with a delay that ranges to 10 days after the last day of data. Clearly, a better prediction could be possible with more frequent publication of [UTC-UTC(k)]. Improvement in the prediction of the local time scales will impact on the steering of the various GNSS times, that use values of some UTC(k) as references.

With the aim of providing support to National Metrology Institutes (NMIs) and other participants in this direction, and to improve access to UTC, the Time Department has called for expressions of interest for laboratories to participate in a pilot experiment for producing daily values of the differences on a weekly solution. Laboratories are requested to provide daily time transfer files and clocks. The call has been a success, 74 % of the laboratories have responded positively, representing about 86 % of the total clock weight. The pilot experiment will start at the beginning of 2012, and after some studies a report will be submitted to the CCTF in September 2012.

This new study will be published only on the Time Department's ftp server. Nothing in the procedure applied will change for the monthly calculation of UTC, which remains the only key comparison on time.

2.7 **New proposed definition of UTC** (F. Arias, 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. Some of these actions were promoted through the publication of a *Metrologia* Special Issue on Modern Applications of Time Scale in August 2011 (Guest editors: F. Arias and W. Lewandowski), and via the organization of a discussion meeting at the Royal Society on "UTC for the 21st Century" (Organizers: T. Quinn and F. Arias, 3-4 November 2011). The process will conclude with the vote on the recommendation that will take place in January 2012 at the ITU.

2.8 **Pulsars** (G. Petit)

Some collaboration continues with radioastronomy groups observing pulsars and analyzing pulsar data to study the potential capability 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).

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

The BIPM maintains the web and ftp sites for the *IERS Conventions* (tai.bipm.org/iers/). Updates to the *Conventions* (2003) were posted on the website (tai.bipm.org/iers/convupdt) until the completion of the new reference edition, the *IERS Conventions* (2010) in December 2010. The new edition implements the latest recommendations of scientific unions and the conclusions of the unions' working groups and commissions and describes the latest realizations of the celestial and terrestrial reference frames, and an updated model for the transformation between them. It also describes updated conventional models for the gravitational field and for the effect of ocean tides and complements the models for the displacement of reference points with new models for atmospheric tidal loading and for the oceanic pole tide loading, along with updated or new conventional models for signal propagation in the troposphere and ionosphere. In addition, the *Conventions* now provide a complete set of associated conventional software. These tasks have been carried out with the help of the Advisory Board for the *IERS Conventions* updates, including representatives from all groups involved in the International Earth Rotation and Reference Systems Service (IERS).

Activities related to the realization of reference frames for astronomy and geodesy are being developed in cooperation with the 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.

Some of the activities on international coordination on space-time references that has been the work of staff of the Time Department converged on the approval by the 24th CGPM of Resolution 9 on the adoption of the International Terrestrial Reference System (ITRS), as defined by the International Union of Geodesy and Geophysics (IUGG) and realized by the IERS. This will now be adopted as the unique international reference system for terrestrial reference frames for all metrological applications.

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 sections when needed.

2.11 Publications

External publications

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6. D'Agostino G., Robertsson L., Relative beam misalignment errors in high accuracy displacement interferometers: calculation and detection, *Appl. Phys. B: Lasers Opt.*, 2011, **103**(2), 357–361.
7. Defraigne P., Harmegnies A., Petit G., Time and frequency transfer combining GLONASS and GPS data, *Proc. Joint Meeting of the EFTF and IEEE FCS,* 2011, 676–680.
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40. BIPM Annual Report on Time Activities for 2009, 2010, 4, 104 pp., available only at www.bipm.org/en/publications/time_activities.html.
41. *Circular T* (monthly), 7 pp.
42. Bauch A., Piester D., Fujieda M., Lewandowski W., Directive for operational use and data handling in two-way satellite time and frequency transfer (TWSTFT), *Rapport BIPM*-2011/01.

2.12 Activities related to the work of Consultative Committees

E.F. Arias is Executive Secretary of the CCTF. She is a member of the CCTF WG on TWSTFT, the CCTF WG on Primary Frequency Standards (WGPFS) and the CCTF WG on TAI.

Z. Jiang is a member of the CCTF WG on TWSTFT.

W. Lewandowski is Secretary of the CCTF WG on TWSTFT and Secretary of the CCTF WG on Global Navigation Satellite Systems Time-Transfer Standards (CGGTTS).

G. Panfilo is a member of the CCTF WGPFS and of the Sub-Group on Algorithms of the CCTF WG on TAI and collaborates with the CCTF WGMRA.

G. Petit is a member of the CCTF WG on TAI and its Sub-Group on Algorithms, of the WGPFS, and of the CGGTTS.

L. Robertsson is, since the 1 January 2010, Executive Secretary of the CCL and a member of the CCL WG on strategic planning and of the Discussion group DG-11 (Lasers). He is the BIPM representative on the Working Group on Gravimetry of the CCM.

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 System. She is an associate member of the IERS, a member of the International Celestial Reference System Centre, and of the Conventions Centre of the IERS. She is a member of the International VLBI Service (IVS), and of its Analysis Working Group on the International Celestial Reference Frame. She is the BIPM representative to the Governing Board of the IGS. She is the BIPM representative to the International Committee for GNSS and she is the chairperson of the Task Force on Time References. She is a member of the GGOS Steering Committee representing the BIPM as a scientific service of the IAG. 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. She is the BIPM representative to the Working Party 7A of the Study Group 7 of the 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 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 the Working Party 7A of the Study Group 7 of the ITU-R, and the UN International Committee on GNSS (ICG).

G. Petit is co-director of the Conventions Centre of the IERS. He is president of the IAU Commission 52 'Relativity in Fundamental Astronomy', member of the IAU Working Group on Numerical Standards in Fundamental Astronomy, of the IGS Working Group on Clock Products, of the GNSS Science Advisory Committee of the ESA, and of the Fundamental Physics Group of the CNES.

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:

- Geneva (Switzerland), 4-12 October 2010, for the meetings of the ITU-R Study Group 7 and Working Party 7A;
- Turin (Italy), 18-22 October 2010, for the 5th Meeting of the ICG, acting as Task Force on Time References chairperson and session chairman respectively;
- Turin (Italy) , 30 November to 3 December 2010, for a meeting concerning the CCTF WG on the MRA, for a meeting of the CCTF WG on Strategic Planning and for the meeting on "Optical clocks: a new frontier in high accuracy metrology";
- London (UK), 24-25 January 2011, for the Royal Society discussion meeting "The new SI: units of measurement based on fundamental constants";
- Zürich (Switzerland), 2-4 February 2011, for the meeting of the GGOS strategic planning retreat (invited);

- San Francisco (USA), 2-5 May 2011, for the IFCS/EFTF meeting (with presentations) and for meetings of the CCTF WGs on Strategic Planning, the CGGTTS and the TW participating laboratories;
- Vienna (Austria), 7 June 2011, for the 2nd preparatory meeting on the ICG;
- Sèvres (France), 28-29 June 2011, for the BIPM workshop on Development of advanced time and frequency transfer techniques;
- Tokyo (Japan), 5-9 September 2011, to the 6th Meeting of the ICG;
- Tsukuba (Japan), 12-13 September 2011, to the Meeting of the CCTF TWSTFT WG;
- Beijing (China), 14-16 September 2011, invited to the NIM;
- Brussels (Belgium), 20 September 2011, for a meeting of the Galileo FOC Timing Interface Working Group;
- Paris (France), 21 October 2011, for a round table on Polish metrology, Polish Scientific Centre;
- Chicheley (UK), 3-4 November 2011, to attend a Royal Society meeting on "UTC for the 21st century";
- Toulouse (France), 10 November 2011, for a meeting on GNSS calibration and for a Ph.D. thesis dissertation.

Z. Jiang to:

- St Petersburg (Russian Federation), 21-26 June 2010, to the Conference IAG TG SMM;
- Beijing (China), 16-17 September 2010, to the CCTF TWSTFT WG Meeting;
- China, 13-15 September 2010, to the Forum on modern time transfers at BIRM;
- Beijing (China), 20-21 September 2010, to the NIM, invited to lecture on absolute gravimetry and ICAGs;
- Chinese Taipei, 27 September to 1 October 2010, for an ISO/IEC 17025 audit, invited by the Taiwan Accreditation Foundation to assess the work of National Time and Frequency Laboratories (TL);
- Chinese Taipei, 30 September 2010, to the Industrial Technology Research Institute, invited to lecture on ICAG09;
- San Francisco (USA), 2-5 May 2011, to the Joint Meeting IFC-EFTF 2011;
- Melbourne (Australia), 28 June 2011 to 7 July 2011, to the General Assembly IUGG/IAG 2011;
- Tsukuba (Japan), 12-13 September 2011, to the Meeting of the CCTF TWSTFT WG;
- Long Beach (USA), 14-17 November 2011, PTTI 2011 Conference.

W. Lewandowski to:

- Warsaw (Poland), four trips to the Space Research Centre (SRC) and the Central Office of Measures (GUM), including several lectures;
- Brussels (Belgium), 16 July 2010, to attend a meeting of Galileo FOC Timing Interface Working Group;
- Beijing (China), 7-18 September 2010, for the 18th meeting of the CCTF Working Group on TWSTFT;
- Portland, Oregon, (USA), 19-25 September 2010, to attend the 50th meeting of the Civil GPS Service Interface Committee (CGSIC) and chair its Timing Sub-Committee, and to attend the ION GNSS conference;
- Geneva (Switzerland) 4-12 October 2010, for meetings of the ITU Working Party 7A and Study Group 7 on the Future of the UTC Leap Second;
- Paris (France), 21 October 2011, organization and co-chairing a Round Table on Challenges of Contemporary Metrology;
- Turin (Italy), 18-23 October 2010, to attend the 5th meeting of the UN International Committee on GNSS ICG;
- Turin (Italy), 11-12 November 2010, to attend a meeting of Galileo FOC Timing Interface Working Group;

- Reston, Virginia (USA), 14-18 November 2010, for the 42nd PTTI Systems and Applications Meeting and a meeting of the TWSTFT participating stations;
- Vienna (Austria), 13-14 February 2011, to attend a preparatory meeting of the UN International Committee on GNSS ICG;
- Istanbul (Turkey) , 6-8 April 2011, to attend a EURAMET time meeting;
- Berlin (Germany), 13-14 April 2011, to attend the XV Polish-German Forum;
- Istanbul (Turkey), 15-19 August 2011, to co-chair the GASS 2011 timing session and to attend a special session on "URSI - ITU relations";
- New Delhi (India), 20-23 August 2011, visit to NPL of India;
- Tokyo (Japan), 4-11 September 2011, to attend the 6th meeting of the UN International Committee on GNSS ICG;
- Tsukuba (Japan), 11-14 September 2011, for the 19th meeting of the CCTF Working Group on TWSTFT;
- Portland, Oregon, (USA), 14-24 September 2011, to attend the 51st meeting of the Civil GPS Service Interface Committee (CGSIC) and chair its Timing Sub-Committee, and to attend the ION GNSS conference;
- Geneva (Switzerland), 25-30 October 2011, for a meeting of Working Party 7A;
- Chicheley (UK), 3-4 November 2011, to attend a Royal Society meeting on "UTC for the 21st century" and give a presentation on GNSS Times and UTC;
- Brussels (Belgium), 7-9 November 2011, to attend 4th High-level Conference on European Space Policy;
- Long Beach, California (USA), 14-18 November 2011, for the 43rd PTTI Systems and Applications Meeting and to act as secretary of TWSTFT Participating Stations meeting;
- Noordwijk (the Netherlands), 29 November 2011, to attend a meeting of Galileo FOC Timing Interface Working Group.

G. Panfilo to:

- San Francisco (USA), 1-5 May 2011, to attend the IFCS/EFTF joint conference and to give one oral presentation;
- Chicheley (UK), 3-4 November 2011, to attend a Royal Society meeting on "UTC for the 21st century".

G. Petit to:

- Paris (France), 20-22 September 2010, for the *Journées 2010 SRST*, one invited presentation;
- Marne-la-Vallée (France), 4-8 October 2010; for the REFAG symposium of the IAG, one invited presentation;
- Villafranca (Spain), 3 November 2010, for a meeting of the GNSS Science Advisory Committee of the ESA;
- Paris (France), 7 February and 9 November 2011, for meetings of the Fundamental Physics Group of the CNES;
- Vienna (Austria), 4-8 April 2011, for meetings of the Directing Board of the IERS, the Governing Board of the IGS, and for the General Assembly of the European Geophysical Union, with a presentation;
- San Francisco (USA), 2-6 May 2011, for the IEEE IFCS-EFTF 2011 Joint Conference, with a presentation and a meeting of the CGGTTS working group;
- Sèvres (France), 28-29 June 2011, for the BIPM workshop on Development of advanced time and frequency transfer techniques, one invited presentation and one presentation;
- Istanbul (Turkey), 15-19 August 2011, for the General Assembly of the URSI, with one invited presentation and one presentation;

- Copenhagen (Denmark), 30 August-2 September 2011, for a meeting of the GNSS Science Advisory Committee of the ESA and to attend the 2nd International Colloquium on scientific and fundamental aspects of Galileo, member of the organizing committee with a presentation;
- Geneva (Switzerland), 26-30 September 2011, to attend the meeting of the Working Party 7A of the ITU;
- Toulouse (France), 10 November 2011, for a meeting on GNSS calibration and for a Ph.D. thesis jury;
- Paris (France), 18 November 2011, for a meeting of the GNSS Science Advisory Committee;
- Paris (France), 28 November 2011, for an invited conference at the Paris Observatory.

L. Robertsson to:

- Borås (Sweden), 20-21 September 2010, to the 4th Meeting of the EURAMET TC for Length;
- Sydney (Australia), 19-27 November 2010, for activities related to the calculable capacitor at the NMIA;
- Turin (Italy), 30 November to 3 December 2010, to visit INRIM and for the meeting on "Optical clocks: a new frontier in high accuracy metrology";
- Frankfurt (Germany), 28 February and 1 March 2011, for the Discussion Meeting on the Future International Comparisons of Absolute Gravimeters (ICAGs);
- Sèvres (France), 28-29 June 2011, for the BIPM workshop on Development of advanced time and frequency transfer techniques, acting as local organizer;
- Bern (Switzerland), 3-4 October 2011, to the EURAMET-TC-L meeting;
- Bern (Switzerland), 4-6 October 2011, to the Macroscale conference;
- Bern (Switzerland), 6-7 October 2011, to the Meeting of the CCL-WG-MRA.

2.15 Visitors

- Dr Ismaël Cognard, LPCE, Orléans (France), to discuss pulsar analysis and time scales, 21 December 2010;
- Magnus HSU, NMIJ/AIST (Japan), 20 March 2011;
- Mrs Monludee Ranusawud, NIMT (Thailand), 7 October 2011;
- Mr Franco Cordara, INRIM (Italy), for work related to the CCTF Working Group on the MRA, 6 December 2011.

2.16 Guest workers

- Miss A. Proia (Ph.D. student), to work on her Ph.D. on absolute calibration of GNSS receivers, 11 to 15 October 2010 and 28 February to 11 March 2011.

BIPM Electricity Department

Director: M. Stock

(1 July 2010 to 31 December 2011)

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

Development work focused on final validation of a new automatic system for the calibration of secondary Zener voltage standards, on the resolution of some issues with the new transportable Josephson voltage standard, and on the development of a dedicated Josephson voltage standard for the watt balance. In parallel, the programme of on-site Josephson comparisons and calibrations continued.

The validation process for the new automatic system for the calibration of electronic Zener voltage standards against a Josephson voltage standard at 1.018 V was finalized.

The first step of the evaluation process, involved direct comparison of the SINIS programmable Josephson Voltage Standard (JVS) of the automatic system to the traditional JVS used for on-site comparisons. The two primary standards were found to be in accordance within a total combined uncertainty of 11.7×10^{-10} V (k=1).

The second step compared the calibration results obtained with the two set-ups for five different Zener voltage standards. The calibration results agreed within 15 nV for all five standards. The corresponding Type A uncertainty is lower than the $1/f$ noise floor limit (typically 10 nV at 1 V) of the Zeners under test.

All the results converged and confirmed that the new automated measurement set-up is consistent with the previous set-up and that the traceability of the results to the primary JVS can be guaranteed. The results were published in a BIPM report (*Rapport BIPM*-2011/05). The system is now routinely used for calibrations of BIPM and customers' Zener references at 1.018 V. Extension of the set-up to the 10 V level will be possible as soon as 10 V programmable arrays become available, when only a few modifications of the bias current supply will be required.

The latest results obtained for the evaluation of the new transportable Josephson voltage standard (JVS), based on a conventional SIS array operated at the 10 V level were presented at the CPEM conference (Daejeon, Republic of Korea) in July 2010. Significant progress has been realized on the bias source that demonstrated its efficiency during an on-site BIPM Josephson comparison. However, propagation of the RF signal along the waveguide and the antenna on the chip are still not reliable and lead to intermittent loss of the quantized voltage steps.

Technical work on the development of a dedicated Josephson voltage standard for the watt balance experiment has progressed. The dedicated DC bias source has been assembled and tested in a simulation design where the array of Josephson junctions has been replaced by an array of resistors. The experiment has made it possible to check that the automated switching process from one set of emptied batteries to the charged batteries is effective and does not significantly affect the electronic circuitry.

The operating margins of each of the 13 cells of the NIST SNS programmable array have still to be determined because problems with the array have been identified. Some electrical connections between the array and its support board broke because of the large number of thermal cycles needed between room temperature and liquid helium temperature. Furthermore, current-dependent voltage steps were observed for which no clear explanation has been found. Experiments to explain this behaviour are in progress, in cooperation with NIST. NIST can provide the BIPM with a spare chip should a major failure occur with the existing one.

The Electricity Department participated, as a support laboratory, for the key comparison APMP.EM.BIPM-K11.3. This comparison is piloted by the KRISS (Republic of Korea) and involves ten National Metrology Institutes (NMIs) in the APMP regional metrology organization.

The three travelling standards (solid-state Zener diodes) were calibrated against the BIPM primary voltage standard at the levels of 1.018 V and 10 V during three periods between July 2010 and January 2011. The BIPM measurements will allow a strong link to the ongoing BIPM bilateral comparison of Zener voltage references, BIPM.EM-K11.a and BIPM.EM-K11.b, as it has already been the case with a similar EURAMET comparison in 2000.

An internal audit within the framework of the BIPM Quality Management System was successfully completed in March 2011.

3.2 Electrical impedance (resistance and capacitance)

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

A large part of this activity is dedicated to comparisons and calibrations for NMIs and to the maintenance of the primary references and facilities, which are used both for measurement services and research.

A new technician was employed by the department in August 2010. Considerable progress has since been made on various projects that required development of electronics. The development of electronics is particularly important for the preparation of future on-site comparisons of quantum Hall resistance standards (BIPM.EM-12). In addition to a cryostat, the transportable BIPM facility includes a high-accuracy comparison bridge operated at 1 Hz and a series of thermally stabilized standard resistors. A new version of the 1 Hz bridge has been built with more modern electronics (optimized for transport and ease of servicing). The accuracy of the new bridge was demonstrated by comparison to the existing system (to within a desired accuracy level of around 0.001 ppm). A prototype thermally-stabilized enclosure for resistance standards was successfully developed, and a series of such enclosures for use as transportable standards is planned. The construction of a spare cryogenic current comparator for the regular calibration service was finalized.

The reference resistor included in the watt balance experiment requires periodic calibration. Formerly, this required the reference resistor to be un-mounted and brought close to the calibration facilities in the Electricity Department. A triply shielded 40 m long cable was installed to link the two laboratories, and the first tests demonstrated the feasibility of high-accuracy calibrations over such a distance, avoiding possible perturbations of the standard.

During 2011, the BIPM experienced repeated problems with the supply of liquid helium, due to external factors in the global helium market. So far we have been able to minimize delays and disruption to our external calibration and comparison services, but a reliable supply of liquid helium is essential to all the BIPM's on-going activities in electricity. The Electricity Department is considering options for switching some systems to closed cycle cryo-coolers which would replace traditional liquid cryostats and therefore its reliance on external suppliers. The purchase of a first liquid-free system is planned for 2012.

Following discussions at the CPEM 2010 conference, the BIPM started a collaboration with the NPL (UK) to perform a direct comparison of the quantum Hall resistance (QHR) in graphene and GaAs. Graphene samples available at NPL showed plateaus of sufficient metrological quality to make a universality test of the QHR between these two materials very interesting. It was decided that the most practical way to make a direct comparison was to use the BIPM travelling QHR cryostat in combination with the cryostat and 1:1 ratio cryogenic current comparator (CCC) bridge available at NPL. To this end, R. Goebel and N. Fletcher travelled to NPL with the cryostat, associated equipment, and BIPM GaAs QHR samples in October 2010.

The 1:1 measurement of two QHR samples was not a standard set-up for the NPL CCC bridge, and the measurement system required some optimization. For this reason it was only possible to obtain very preliminary results in the initial 1 week period. It was evident that, with care, a significant result with a relative uncertainty approaching 1 part in 10^{10} would be possible. It was therefore decided to leave the BIPM travelling cryostat on-site to allow extended measurements. At the end of nearly 6 months of measurements and investigations, various systematic effects in the bridge were found and eliminated and the final result showed no difference between the value of the i=2 QHR plateau in graphene and GaAs, to within a relative standard uncertainty of 9×10^{-11}. It should be noted that this uncertainty is an order of magnitude better than the best results obtained with room temperature resistance standards. Some small errors in the CCC bridge were identified that could only be seen when comparing two quantum standards.

The comparison result was published in the *New Journal of Physics* in September 2011, and a more detailed paper on the CCC measurement has since been submitted for publication. The result is interesting from the point of view of physics and fundamental constants, as it strongly suggests that there are no material dependent corrections to the simple relation $R_K=h/e^2$. It also demonstrates that graphene has great potential as a material for QHR standards. Future samples will operate at higher temperature and lower magnetic fields, reducing the cost and complexity of realizing a QHR reference. These advances confirm the role of the QHR as a robust and accessible *mise en pratique* for electrical units within the SI (present and future).

An internal quality audit of the resistance measurement service took place in April 2011.

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

The capacitance reference at 10 pF has been maintained by regular links to the quantum Hall resistance (four times over the reporting period). The working standards were used to disseminate the farad via comparisons and calibrations as listed in sections 4 and 5. During 2011, 33 standards were calibrated for 10 different NMIs. No major development work on the capacitance bridges has been undertaken; instead work has focused on the calculable capacitor. An internal quality audit of the capacitance measurement service took place in April 2011.

The BIPM participated in the EURAMET comparison EM-S31 of 10 pF and 100 pF standards traceable to the QHR; the report is being prepared by the pilot laboratory (PTB).

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

Several significant changes to parts of the mechanical design of the calculable capacitor were made following the visit of John Fiander from NMIA (Australia) in April-May 2010. Three major groups of components were manufactured in the BIPM workshop (following designs produced by NMIA): a new mount for the lower guard electrode, replacement springs for the top mounts of the main electrode bars, and an additional alignment probe to allow direct measurement of the diagonal spacing of the main electrodes.

These parts have since been installed in the BIPM capacitor, and mostly work well. With the new alignment probe, a procedure has been developed that allows the electrode bars to be correctly positioned to the required tolerances of around ±100 nm at their top and bottom mounts. The replacement top springs maintain this alignment during movements of the guard electrode. The tilt adjuster for the lower guard works reliably for obtaining good optical alignment of the interferometer. The remaining problem is the lower mirror mount which is sensitive to external vibration. Different spring designs are now under investigation, and ideas to isolate the instrument from external vibrations are being explored. A factor of 10 or so improvement in the mechanical stability of the interferometer is required to achieve reliable servo-locking to a fringe centre (the mode of operation that will be used during the electrical measurements).

Formal collaboration between the NMIA and the BIPM was completed in 2011 when the last sets of modified mechanical components were produced. Informal collaboration will continue over the next couple of years, while both teams continue to refine their respective instruments, to achieve the best possible measurements of the von Klitzing constant, R_K. The BIPM staff involved in the calculable capacitor project greatly appreciate the dedication of their Australian colleagues over the many years taken to bring this project to fruition. Their unparalleled expertise has resulted in a first class instrument that should serve world metrology well for many years to come. We look forward to comparing measurement results in the near future.

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

Six on-site comparisons of Josephson voltage standards with NMC, A*STAR (Singapore), VNIIM (Russia), CMI (Czech Republic), MSL (New Zealand), CENAM (Mexico) and INTI (Argentina) have been successfully completed. The two first comparison results have been published and show very good agreement between the BIPM and the participants:

at 1.018 V: $(U_{A*STAR} - U_{BIPM}) = +1.8$ nV $u = 0.9$ nV

at 10 V: $(U_{A*STAR} - U_{BIPM}) = +0.4$ nV $u = 1.0$ nV

at 10 V: $(U_{VNIIM} - U_{BIPM}) = -0.1$ nV $u = 2.0$ nV

The reports of the remaining four comparisons are in preparation.

One bilateral voltage comparison using Zener voltage standards as transfer standards was carried out at the level of 10 V with NSAI (Ireland) in March 2011. The comparison results have been published and show very good agreement between the BIPM and NSAI.

at 10 V: $(U_{NSAI} - U_{BIPM}) = 0.16$ µV $u = 1.4$ µV

In the ongoing BIPM key comparison programme for resistance, bilateral comparisons were organized with GUM (Poland), NML (Ireland) and KRISS (Republic of Korea). The results for the GUM have been published:

$(R_{GUM} - R_{BIPM}) / 1\ \Omega = -0.062 \times 10^{-6}$ $u = 0.043 \times 10^{-6}$

$(R_{GUM} - R_{BIPM}) / 10\ \mathrm{k}\Omega = -0.037 \times 10^{-6}$ $u = 0.034 \times 10^{-6}$

The reports for NML and KRISS are in the draft B stage.

In the ongoing BIPM key comparison programme for capacitance, bilateral comparisons were organized with NPLI (India) and NML (Ireland). Both reports are in the draft A stage.

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

During the period from July 2010 to September 2011 the Electricity Department calibrated the following standards:

Two Zener diode voltage standards were calibrated at 1.018 V and 10 V for DMDM (Serbia) and BIM (Bulgaria).

Resistance at 1 Ω, 100 Ω or 10 k Ω was calibrated for: BEV (Austria), CMI (Czech Republic), DFM (Denmark), DMDM (Serbia), EIM (Greece), GUM (Poland), IPQ (Portugal), MKEH (Hungary), MSL (New Zealand), NMC, A*STAR (Singapore), NMIA (Australia), SMU (Slovakia).

1, 10 or 100 pF capacitors were calibrated for: BEV (Austria), BIM-NCM (Bulgaria), CEM (Spain), CENAM (Mexico), CMI (Czech Republic), EIM (Greece), GUM (Poland), INMETRO (Brazil), INTI (Argentina), IPQ (Portugal), MIKES (Finland), NMC, A*STAR (Singapore), SMD (Belgium), UME (Turkey).

During the reporting period (18 months) a total of 78 calibration certificates for 20 NMIs were provided.

3.6 **Publications**

External publications

1. Solve S., Chayramy R., The BIPM Compact Josephson Voltage Standard, *IEEE Trans. Instrum. Meas.,* 2011, **60**(7), 2366–2371.

2. Tang Yi-hua, Solve S., Witt T.J., Allan Variance Analysis of Josephson Voltage Standard Comparison for Data Taken at Unequal Time Intervals, *IEEE Trans. Instrum. Meas.,* 2011, **60**(7), 2248–2254.
3. Power O., Solve S., Chayramy R., Stock M., Bilateral comparison of 1.018 V and 10 V standards between the NSAI (Ireland) and the BIPM, March to April 2010 (part of the ongoing BIPM key comparison BIPM.EM-K11.a and b), *Metrologia*, 2010, **47**, *Tech. Suppl.*, 01017.
4. Goebel R., Fletcher N., Stock M., Dudek E., Domanska-Mysliwiec D., Mosiadz M., Orzepowski M., Bilateral comparison of 1 Ω standards between the GUM (Poland) and the BIPM, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 01001.
5. Goebel R., Fletcher N., Stock M., Dudek E., Domanska-Mysliwiec D., Mosiadz M., Orzepowski M., Bilateral comparison of 10 kΩ standards between the GUM (Poland) and the BIPM, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 01002.
6. Power O., Solve S., Chayramy R., Stock M., Bilateral comparison of 10 V standards between the NSAI (Ireland) and the BIPM, March 2011 (part of the ongoing BIPM key comparison BIPM.EM-K11.b), *Metrologia*, 2011, **48**, *Tech. Suppl.*, 01010.
7. Solve S., Chayramy R., Stock M. and Katkov A., Comparison of the Josephson voltage standards of the VNIIM and the BIPM (part of the ongoing BIPM key comparison BIPM.EM-K10.b, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 01007.
8. Solve S., Chayramy R., Stock M., *et al.*, Comparison of the Josephson voltage standards of the NMC, A*STAR and the BIPM (part of the ongoing BIPM key comparisons BIPM.EM-K10.a and b, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 01006.
9. Witt T.J. and Fletcher N.E., Standard deviation of the mean and other time series properties of voltages measured with a digital lock-in amplifier, *Metrologia*, 2010, 47(5), 616–630.
10. Janssen T.J.B.M., Fletcher N.E., Goebel R., Williams J.M., Tzalenchuk A., Yakimova R., Kubatkin S., Lara-Avila S. and Falko V.I., Graphene, universality of the quantum Hall effect and redefinition of the SI system, *New J. Phys*., 2011, **13** 093026.
11. Stock M., Review article: The watt balance: determination of the Planck constant and redefinition of the kilogram, *Phil. Trans. R. Soc. A*, 2011, **369**, 3936-3953.

BIPM publications

12. Solve S., Chayramy R., Stock M., The BIPM 1.018 V Zener Measurement Set-up, *Rapport BIPM*-2011/05, 32pp

3.7 Activities related to the work of Consultative Committees

M. Stock is the Executive Secretary of the CCEM and the CCPR and a member of several of their working groups. The 26th CCEM meeting was held on 12-13 March 2011 and the next CCPR meeting is being organized for February 2012.

R. Goebel organizes the review of comparison reports and protocols within the CCPR key comparison working group WG-KC.

3.8 Activities related to external organizations

M. Stock is a member of the CPEM Executive Committee. N. Fletcher and M. Stock are members of the Technical Committee of CPEM 2012.

M. Stock is the contact person for the BIPM liaison with the International Commission on Illumination (CIE). The annual coordination meeting was held on 27 October 2011 at the BIPM. The main topic was the planned collaboration between the CCPR and the CIE on the publication of the new *mise en pratique* for the photometric units.

3.9 Travel (conferences, lectures and presentations, visits)

M. Stock to:

- Bergen (Norway), 1 July 2010, to chair a session on QA4EO (Quality Assurance for Earth Observation) at the ESA Living Planet Symposium;
- NPL, Teddington (UK), 5-7 July 2010, to participate in CCPR working group meetings and in a workshop on comparison analysis;
- MIKES, Espoo (Finland), 28-29 October 2010, to participate at the EURAMET TCEM meeting;
- Oslo (Norway), 8-9 March 2011, to participate in the EURAMET TCPR meeting;
- Kobe (Japan), 5-6 December 2011, to participate in the APMP TCEM meeting;
- Four additional trips related to the watt balance.

S. Solve to:

- Leiden (the Netherlands), 22-23 March 2011, to attend the EURAMET Power and Energy Workshop;
- Berlin (Germany), 18-20 May 2011, to attend the EURAMET quantum experts meeting;
- CENAM, Quéretaro (Mexico), 26-28 September 2011, to perform a peer review of the service "Calibration of Solid-state DC Voltage Standards of CENAM".

S. Solve and R. Chayramy to:

- NMC, A*STAR, Singapore (Singapore), 21 September to 1 October 2010, to carry out a direct on-site BIPM Josephson voltage standard comparison;
- CMI, Brno (Czech Republic), 24 February to 4 March 2011, to carry out a direct on-site BIPM Josephson voltage standard comparison;
- MSL, Lower Hutt (New Zealand), 25 April to 5 May 2011, to carry out a direct on-site BIPM Josephson voltage standard comparison;
- CENAM, Quéretaro (Mexico), 19-25 September 2011, to carry out a direct on-site BIPM Josephson voltage standard comparison;
- INTI, Buenos Aires (Argentina), 26 November to 3 December 2011, to carry out a direct on-site BIPM Josephson voltage standard comparison.

R. Goebel to:

- NPL, Teddington (UK), 1-9 October 2010, for a collaboration on measurements of the QHR in graphene.

N. Fletcher to:

- NPL, Teddington (UK), 1-9 October 2010, 22-24 November 2010, 26 January 2011, 21 March 2011, for a collaboration on measurements of the QHR in graphene;
- London (UK), 24-25 January 2011, to attend the discussion meeting 'The new SI - Units of measurement based on fundamental constants' at the Royal Society;
- PTB, Braunschweig and Berlin (Germany), 16-20 May 2011, to transport capacitance standards for a comparison and to attend the EURAMET TC-EM quantum experts meeting;
- London (UK), 2-3 June 2011, to attend a 'Topical research meeting on graphene and related two-dimensional materials' at the Institute of Physics;
- PTB, Braunschweig (Germany), 29-31 August 2011, for discussions on precision comparisons of the fractional quantum Hall effect.

B. Rolland to:

- PTB, Braunschweig and Berlin (Germany), 16-20 May 2011, to transport capacitance standards for a comparison and to attend the EURAMET TC-EM quantum experts meeting.

3.10 Visitors

- L. Callegaro and V. D'Elia, INRIM (Italy), for an informal comparison of 1000 pF standards, 19-21 October 2010;
- Delegation from Kuwait on 22 October 2010;
- A. Katkov, VNIIM (Russian Federation), to carry out a direct Josephson comparison with the VNIIM transportable JVS, 8-12 November 2010;
- 15 science councillors from embassies in Paris on 15 February 2011;
- Delegation from Luxembourg on 16 February 2011;
- 9 groups of visitors during the meeting of Representatives of States Parties to the Metre Convention on 26 May 2011;
- B. Goldstein, senior scientific advisor to the director of the Physical Measurement Laboratory, NIST (USA), 3 October 2011;
- R. Courtland, associate editor *IEEE Spectrum*, 7 October 2011;
- V. Villière, general manager for legal metrology, NMIA (Australia), 7 October 2011;
- M. Ranusawud and three colleagues from NIMT (Thailand), 7 October 2011;
- 9 groups of visitors during the 24th CGPM meeting, 19 October 2011;
- P. Blattner, METAS (Switzerland), CIE Division 2 Director, and M. Paul, CIE General Secretary, for the annual coordination meeting between the BIPM and the CIE, 27 October 2011;
- 17 visitors during the visit organized by the Japanese Chamber of Commerce in Paris, 17 November 2011.

BIPM watt balance
(1 July 2010 to 31 December 2011)

4.1 Watt balance (M.P. Bradley[1], R. Chayramy, A. Dupire, H. Fang, A. Kiss, E. de Mirandés, A. Picard, L. Robertsson, J. Sanjaime, S. Solve, M. Stock, S. Amenuvora[2], A. Zeggagh[3])

Between 1 July 2010 to 31 December 2011, development work for the BIPM watt balance focused on improved velocity measurements and on preparations for transfer of the instrument into a dedicated laboratory, where the balance will be installed inside a vacuum enclosure. In parallel, a feasibility study for a future cryogenic watt balance was pursued.

Until recently, the coil velocity had been measured with a one-axis interferometer. This involved a moveable mirror placed 40 cm above the centre of the coil, within the suspension. In these circumstances, the measured velocity was not exactly that of the coil because the suspension was not perfectly rigid. The velocity measurement has recently been refined by using a three-axis interferometer, consisting of three single-beam Michelson interferometers, made at the BIPM. Corner cubes are employed as retro-reflectors; these are insensitive to tilt and thus measure the proper vertical velocity component of the moving coil. The retro-reflectors are fixed directly onto the moving coil support for a better correlation between the measured velocity and induced voltage. Calculations show that both Gouy phase shift and diffraction error due to truncation of the laser beam introduce a relative error less than 10^{-8}. So far, an improvement of the standard deviation of the residuals (after fitting the magnetic profile) of a factor of ten has been achieved on the voltage-velocity ratio with the new interferometer. The voltage-velocity ratio now has a relative standard deviation comparable to that of the force-current ratio, with a relative standard deviation of a few parts in 10^4. Moreover, the new data acquisition scheme allows position and time data to be sampled at high frequency in order to reduce the periodical non-linearity effect of the interferometric measurements.

Several sets of measurements of the Planck constant were carried out using the new interferometer from May to July 2011. Every set consisted of at least five measurements, each of which took approximately one night. Results showed improved repeatability and reproducibility of the voltage-velocity ratio by a factor of five. The relative reproducibility of the Planck constant was consequently reduced to about 1×10^{-6}.

The optical systems used to determine undesirable deviations from a vertical trajectory of the moving coil have been redesigned to be much more compact. In particular, a small corner cube, placed directly on the moving coil, serves as a probe for horizontal translations in both directions. A new device to detect the absolute vertical position of the moving coil inside the magnetic field is under development.

Various studies were carried out to evaluate parasitic effects related to high voltages, the vertical rotation of the coil suspension and decentring of the test mass on the weighing pan. In particular, an experiment was carried out to investigate the possible influence of the coil-current on the magnetic properties of the magnetic circuit. For this, a coil with two separate windings on the same support was used. A current was driven through one winding while the dual-coil travelled inside the air gap. Possible current effects on the magnetic field can be observed in the voltage-velocity ratio measured with the second winding. The dual-coil experiment showed that the coil current of 1 mA changed the magnetic field of the magnet by about 5×10^{-5}. According to our present understanding, this effect should not have any consequences to the simultaneous measuring scheme, and for separate weighing and moving measurements the effect should be cancelled out when combining results with opposite current polarities. We predict that the definitive magnetic circuit will be less sensitive to the coil current.

[1] Research Fellow in the Electricity Department, September 2009 – August 2011
[2] Student from Institut Universitaire de Technologie d'Evry (France), April – July 2011
[3] Student from Ecole des Mines, Douai (France), May 2011 – May 2012

An interesting new approach is being investigated which should allow the separation of the induced voltage from the resistive voltage drop of the coil in the simultaneous measurement approach. When using a coil with two separate windings, the first winding carries the current needed for the weighing measurements while the second winding is used to sense the induced voltage, and vice versa, and thus compensates for small differences between the windings. Values for the Planck constant can be obtained in three ways: from the combination of both windings and from each individual winding. This technique should allow the Planck constant to be determined by the simultaneous measuring technique, without superimposing the resistive voltage drop and the induced voltage on the same coil.

Work on the development of a dedicated Josephson voltage standard has progressed and is described in the section on the Electricity Department.

An aluminium vacuum chamber (1 m diameter, 2 m high) has been designed and will be installed in the new dedicated watt balance laboratory at the end of 2011. Working under vacuum (1 mPa) avoids air buoyancy corrections, corrections for the index of refraction of air (for the velocity measurements) and air convection generating undesirable forces on the elements hung from the balance. The vacuum chamber is composed of 4 parts: one fixed part to receive the electrical and mechanical connections and three mobile parts to permit easy access to the different parts of the experiment. To reduce the transmission of seismic and acoustic vibrations into the experiment, the vacuum chamber is decoupled from the set-up using flexible connections and by inserting dampers between the chamber and the 64 tonne concrete support block. An inner support structure has been designed to minimize horizontal tilts and displacements of the suspension with respect to the magnetic circuit. A new mass exchanger and a device to automatically determine the sensitivity of the weighing cell have been developed and will be integrated into the suspension. To improve the control of the coil alignment, a dynamic alignment system based on piezo actuators will also be integrated. These changes require the fabrication of a significant number of mechanical pieces by the BIPM workshop.

It has taken much longer than expected to find a company capable of carrying out the final high-precision machining of the parts needed for the yoke of the definitive magnetic circuit. This specialist work incorporates very tight mechanical tolerances, large dimensions and the ability to work with unusual materials (FeNi 50:50) in the components. At present the contractual arrangements for the fabrication are being negotiated. All parts of the yoke have been pre-machined by the BIPM workshop. The Sm_2Co_{17} magnets, mounted between FeNi plates, have been fabricated to BIPM specifications. The system for the later assembly of the complete system is almost finished.

In parallel to the work on the room temperature watt balance, much progress was made on work to assess the feasibility of a future cryogenic version of the experiment during the period of this report. A study has been carried out on the properties of trapped magnetic flux (and related magnetic forces) in the superconducting wire of the coil. The Bean model predicts a strong increase of the magnetic moment – and the forces – of a monofilament superconducting wire with the wire diameter. Small wire diameters are best suited for a cryogenic watt balance. Measurements were carried out at NIST, Boulder, Colorado, on wires of different diameter (15 µm to 49 µm) to verify the predictions of the Bean model. The results obtained confirmed the overall trend of strong scaling of the magnetic moment with filament diameter.

Magnetization hysteresis curves of each of the wires were determined. For watt balance operation, the major concern are the so-called "minor hysteresis loops", which the superconducting wire undergoes while it travels through the slightly varying magnetic field within the air gap. Measurements showed that after an excursion around the hysteresis loop the magnetization value does not return exactly to its previous value; this leads to a change of the force detected by the weighing cell. Variation in the force due to this hysteresis effect was found to be at the nanonewton level or below. This effect should not compromise the ultimate accuracy of the cryogenic BIPM watt balance at the 10^{-8} level.

In parallel, a small-scale apparatus has been built to carry out the moving phase of the watt balance with a superconducting coil. The purpose of the experiment is to verify if the superconducting and normal coil, under equivalent conditions, show the same behaviour in a magnetic field, as far as relevant for watt balance operation.

A NbTi superconducting wire and a Cu non-superconducting wire have been wound together in a coil of 8 cm radius and with 506 turns. Both wire diameters are close to 230 µm. The coil has been placed in a cryostat filled with liquid helium. Two external field coils generated a radial magnetic field of several mT. These field coils are placed outside the cryostat and moved at a constant vertical velocity of about 8 mm s^{-1}. Care has been taken to make the translation system as rigid as possible to avoid undesirable lateral displacements and tilts in the moving coils. Excellent repeatability of the trajectory of the external coils has been achieved. The voltages induced in the superconducting and non-superconducting coils inside the cryostat are measured separately by two well-synchronized digital voltmeters.

At present, the experiment is fully operational. Measurements of the ratio between the induced voltages in both coils have been taken at temperatures ranging from room temperature (where both wires are normal conductors) to liquid helium temperature. At present, the measured ratio between the voltages induced in both coils shows a sudden change at the critical NbTi temperature (9.3 K). This result is surprising and needs further investigation to understand its origin.

4.2 Publications

External publications

1. Mirandés E. d., Fang H., Kiss A., Solve S., Stock M., Picard A., Alignment procedure used in the BIPM watt balance, *IEEE Trans. Instrum. Meas*., **60** (7), 2011, 2415–2421.

2. Picard A., Bradley M.P., Fang H., Kiss A., Mirandés E. d., Parker B., Solve S., Stock M., The BIPM watt balance: Improvements and developments, *IEEE Trans. Instrum. Meas.*, **60** (7), 2011, 2378–2386.

3. Stock M., Review article: The watt balance: determination of the Planck constant and redefinition of the kilogram, *Phil. Trans. R. Soc. A*, 2011, **369**, 3936–3953.

4.3 Travel (conferences, lectures and presentations, visits)

M. Stock and A. Picard to:

- RWTH, Aachen (Germany), 17 September 2010, to discuss the fabrication of the watt balance magnet;
- Fraunhofer Institute for Production Technology, Aachen (Germany), 1 June 2011, to discuss the fabrication strategy for the watt balance magnet.

A. Picard to:

- 6Tec, Grenoble (France), 18-19 January 2011, for discussion on the vacuum chamber and the integration of the watt balance components.

A. Picard, E. d. Mirandés, M.P. Bradley and M. Stock to:

- London (UK), 24-25 January 2011, to attend the Royal Society discussion meeting 'The new SI - Units of measurement based on fundamental constants'. M. Stock gave an invited lecture on watt balances and the determination of the Planck constant.

M.P. Bradley, H. Fang, A. Kiss, E. d. Mirandés, A. Picard, M. Stock to:

- METAS, Bern (Switzerland), 22-23 June 2011, to attend the watt balances technical meeting and to give a series of presentations on the progress of the BIPM experiment.

M.P. Bradley to:

- Washington (USA), 1-6 August 2010, to attend the Applied Superconductivity Conference ASC 2010;
- NIST, Gaithersburg (USA), 9-10 August 2010, to visit the NIST watt balance;
- NIST, Boulder (USA), 12-18 August 2010, to work on the properties of superconducting wires with the NIST magnetics group.

H. Fang, A. Kiss, E. d. Mirandés, A. Picard to:

- Paris (France), 4 October 2011, to present three posters at the *Congrès International de Métrologie*.

4.4 Visitors

- D. Wayner, Vice-President NRC Physical Sciences, 16 July 2010;
- NCSLI Executive Committee: D. Porter (Boeing), G. Harris (NIST), M. Smith (Wescan Cal Service), 2 September 2010;
- B. Anderson and J. Olthoff (NIST), 16 November 2010;
- S. Schlamminger (NIST), to discuss the future NIST watt balance, 6-7 December 2010;
- R. Steiner (NIST), 9, 13-16 December 2010;
- J. Kim, K.-C. Lee, B.-C. Woo, to discuss the possible future KRISS watt balance, 10-11 January 2011;
- M. Hsu (NMIA), 20 May 2011;
- B. Goldstein, senior scientific advisor to the director of the Physical Measurement Laboratory, NIST (USA), 3 October 2011;
- M. Ranusawud and three colleagues (NIMT), 7 October 2011;
- R. Courtland, Associate Editor *IEEE Spectrum*, 7 October 2011;
- N. J. Moreau, President IUPAC, 28 October 2011;
- F. Fihmann from 6Tec (Grenoble) for discussion on the vacuum chamber and the integration of the watt balance components, 5-7 October 2010, 25 October 2010, 5-7 December 2010 and 16 May 2011.

BIPM Ionizing Radiation Department

Director: P.J. Allisy-Roberts

(1 July 2010 to 31 December 2011)

5.1 X- and γ-rays (P.J. Allisy-Roberts, D.T. Burns, C. Kessler, S. Picard, P. Roger)

5.1.1 Dosimetry standards and equipment

Work on the development of cavity ionization chambers and in particular on the determination of air volumes has continued. Measurements with a second, automated 3D coordinate measuring machine (CMM) have shown that, under certain conditions, measurements of the thickness of graphite plates made using the manual CMM can be subject to a systematic underestimation of 4 µm to 5 µm. Although the effect of this on the air-volume determination for a typical BIPM cavity chamber is around 1.5 parts in 10^3, the best estimate derived from the ensemble of chambers measured to date does not differ from the present estimate for the ^{60}Co reference standard by more than the standard uncertainty of 8 parts in 10^4.

New transfer chambers have been constructed for the calorimeter dose conversion and a new design of waterproof envelope was tested. Following the supply of a graphite-walled chamber to the ARPANSA (Australia) in 2010, a chamber was constructed for the ININ (Mexico) for use as a primary air-kerma standard. Although dimensional measurements were made at the BIPM to assure the quality of the components, the ININ will be responsible for their own determination of the air volume and characterization of the standard.

The BIPM calorimeter for absorbed dose to water has been used at regular intervals in the BIPM reference ^{60}Co beam; the statistical standard uncertainty in the determination of the reference absorbed-dose rate is now around 4 parts in 10^4. The calorimetric determination of absorbed dose to water is 2.0 parts in 10^3 higher than the reference ionometric determination, which is well within the combined standard uncertainty. This result was presented to the CCRI(I) at its meeting in May 2011.

At the request of the BIPM, the LNE-LNHB (France) kindly offered accelerator time for BIPM staff to make saturation measurements for the parallel-plate transfer chambers used in accelerator photon beams. This resulted in an accurate determination of the ion recombination correction and the results were published in a BIPM report. A second calorimeter core and jacket and replacement transfer chambers are under development, to serve both as independent verifications and as replacements in the event of failure. This turned out to be timely, as the most recent series of stability measurements, after three series of off-site comparisons at National Metrology Institutes (NMIs), showed the calorimeter response to have changed. This is currently under investigation, but as a consequence the comparison at the NPL (UK), scheduled for September 2011, was postponed.

Monte Carlo calculations for the absorbed-dose conversion from graphite to water have continued, with calculations being made for the NIST (USA) comparison using photon spectra supplied by the NIST. With the introduction of a new design of waterproof envelope, repeat calculations in water were made for all beams at the NRC (Canada), PTB (Germany) and the NIST. A comprehensive analysis of the uncertainties was made, which necessitated additional work measuring depth-ionization profiles in water and graphite and making the corresponding Monte Carlo calculations. The level of agreement between the measurements and calculations was used to derive a standard uncertainty for the ratio of photon attenuation coefficients in graphite and water of around 1.5 parts in 10^3. The combined standard uncertainty of the calculated dose conversion is estimated to be around 2.5 parts in 10^3. A draft paper has been prepared and a presentation of the dose conversion was given at the IAEA IDOS symposium in November 2010.

Before the removal of the Picker ^{60}Co source in 2011, measurements were made in both the Picker and CISBio beams of the ratio of ionization currents at pairs of depths, and Monte Carlo calculations were made of these arrangements. The aim is to find a measured parameter that is proportional to the scatter component of the photon spectrum, which can subsequently be used in characterizing the new ^{60}Co beam. In view of this and other additional work that arose during the period of this report, the plan to compare the low- and medium-energy x-ray standards using Shonka and free-air transfer chambers was postponed.

In preparation for the installation of a new source to replace the Picker ^{60}Co source that was removed in July 2011, new fire doors were fitted, requiring modifications to the safety interlock systems, and a new external shielding wall was designed and constructed. The new irradiator, without the source, was installed in November 2011 and mechanical measurements were made to determine the reference plane.

The project to develop an absorbed-dose standard for medium-energy x-rays has progressed more slowly than anticipated, but nevertheless shows promise. Measurements with a thin-walled graphite cavity standard showed a decrease in response by one third when reducing the radiation quality from 250 kV to 100 kV. Encouragingly, initial Monte Carlo calculations have reproduced this large change within the statistical standard uncertainty of 7 parts in 10^3 and work will continue to reduce this uncertainty. It is interesting that the chamber of C552 air-equivalent plastic, constructed with the aim of reducing the uncertainties, showed a change in response that was not reproduced in the corresponding calculations and it is concluded that C552 is therefore not suitable for this purpose. In absolute terms, the air-kerma rate determined using the graphite-walled chamber and calculated correction factors was within 2 parts in 10^2 of the reference air-kerma rate (as determined by the existing free-air chamber standard) even at 100 kV where this represents a real challenge. The difference might be related to the ratio of photon interaction coefficients used in the calculations and experimental work is in progress to obtain a better estimate for this ratio. There is good reason to be optimistic that the target standard uncertainty of 1 part in 10^2 can be achieved; the present reference being 3 parts in 10^2.

Work continued on evaluating best estimates for the W_a-value for air and the I_c-value for graphite. The BIPM calorimeter, graphite-walled cavity chamber and Monte Carlo calculations were used to determine the product of W_a and the graphite-to-air stopping power ratio, $s_{c,a}$. The result of this work is $W_a s_{c,a} = 33.84$ J C^{-1} with a standard uncertainty of 1.8 parts in 10^3. This result was included in an analysis of the existing data in the literature using a novel minimization process, from which the result is $W_a s_{c,a} = 33.72$ J C^{-1} with standard uncertainty 1 part in 10^3. Expressed in terms of W_a and I_c, the conclusion is to make a change in the recommended value for I_c from 78 eV to 82 eV (with standard uncertainty 2 eV) with no evidence for a need to change the present recommendation for W_a. However, the uncertainty of W_a should be increased from 1.5 parts to 3.5 parts in 10^3. This work was presented to the ICRU Report Committee on Key Data at a meeting in April 2011 and to the CCRI(I) in May 2011.

Primary measurements and reference chamber calibrations have continued in all of the reference x- and gamma-ray beams, including the mammographic radiation qualities. The mammography facility was presented as a poster at the IAEA IDOS Symposium. Comparisons and calibrations are underpinned by a significant effort in equipment calibration and maintenance, as required by the BIPM Quality Management System (QMS), and audited in August 2010. Procedures, technical instructions, forms and laboratory records were subsequently modified to include BIPM comparisons for ionizing radiation in the QMS. This was followed by a successful internal audit of the quality system for calibrations and comparisons in November 2011.

The laboratory visits associated with the CGPM and with the meeting of the NMI Directors and government representatives required a significant effort in preparing posters and presentations to explain the work.

5.1.2 Dosimetry comparisons

Five comparisons in terms of air kerma in gamma radiation were carried out, in the ^{60}Co beam with the KRISS (Republic of Korea) and the NIST, and in the ^{137}Cs beam with the KRISS, NIST and the ENEA (Italy). The KRISS comparison reports have been published; the NIST reports have been drafted and issued for comment; unfortunately, the ENEA instruments were not working correctly and the comparison will need to be repeated.

Eight air-kerma comparisons were carried out in x-ray beams, with the ENEA, MKEH (Hungary) and the VNIIM (Russian Federation) at low energies; with the VNIIM, ENEA and the MKEH at medium energies and with the PTB and the ENEA in the mammography beams. The ENEA low-energy report has been published as well as the VNIIM and MKEH medium-energy reports; the ENEA comparison for medium energies will be repeated as the transfer standard was not working properly, as will the mammography comparison because of the different calibration conditions used at the ENEA. The PTB mammography report has been published.

Eight reports of previous comparisons were published in the *Metrologia Technical Supplement*, two reports each for the NMIJ (Japan), ARPANSA and the GUM (Poland), and one each for the VNIIM and the NRC.

Following successful key comparisons in the accelerator photon beams at the NRC and the PTB, both published since last year's Director's report, measurements were made in the NIST accelerator and the results are currently being analysed. These comparisons are technically challenging and illustrate the importance of stable beam monitoring and beam radial uniformity measurements to obtain viable results. The comparison programme had included the METAS (Switzerland) and the NPL but unfortunately both had to be postponed, the former by the METAS. The comparison protocol was revised in the light of experience gained in the most recent comparison.

At the request of the LNE-LNHB, an indirect bilateral comparison in terms of graphite absorbed dose in ^{60}Co was made in 2011. The reference beams at both laboratories were used, in combination with the graphite phantoms of each laboratory. The analysis of the result is in progress.

Regarding the high-dose comparison piloted by the BIPM in 2009 and using the NIST and NPL alanine dosimeters, discussions with the participants resulted in a consensus on how to present the observed dose-rate effect and the report was published in *Metrologia*. At the request of the PTB, a recent series of irradiations was also made of the PTB alanine dosimeter in the range from 10 Gy to 20 Gy in the BIPM reference ^{60}Co beam for absorbed dose to water. The results are under analysis.

Periodic calibrations continued for the brachytherapy transfer chamber in terms of air kerma in the ^{60}Co beam and in the 250 kV x-ray quality; this chamber is used together with a well-type ionization chamber in the BIPM comparison of brachytherapy dosimetry for ^{192}Ir sources. The well-type chamber is calibrated periodically using two sources, a low dose rate source of ^{166m}Ho and a high dose rate source of ^{137}Cs. Dr José Alvarez Romero, on an IAEA Fellowship from the ININ (Mexico), worked on this project until 12 July 2010 followed by Dr Jacco de Pooter, on secondment to the BIPM from the VSL for 4 weeks during the summer of 2010. One new comparison, with the PTB, was carried out in 2011. All the results from the four comparisons to date are being evaluated to determine a comparison reference value. Unfortunately, a lack of manpower has slowed this work. The second type of brachytherapy comparison proposed, for the measurement of ^{125}I brachytherapy seed sources, as used for the treatment of prostate cancer, has not yet been launched but may benefit from collaboration with the LNE-LNHB.

5.1.3 Characterizations of national standards for dosimetry

Seven series of characterizations of national standards were made in the low-energy, medium-energy and mammography x-ray beams, for the IAEA, HIRCL (Greece) and the ITN (Portugal), and a further eighteen in the BIPM gamma-ray beams in terms of air kerma, ambient dose equivalent and absorbed dose to water, as requested by the IAEA, CIEMAT (Spain), METAS, HIRCL, ITN, CRRD (Argentina) and the BARC (India). The BIPM report on the measuring conditions used for these characterizations was updated and published.

The IAEA/WHO dosimetry assurance programme continues to be supported by biannual reference irradiations in the ^{60}Co beam.

5.2 Radionuclides (P.J. Allisy-Roberts, S. Courte, C. Michotte, M. Nonis and G. Ratel)

5.2.1 International Reference System (SIR) for gamma-ray emitting radionuclides

5.2.1.1 SIR submissions in 2010

During 2010, the BIPM received 13 ampoules filled with 11 different radionuclides from 4 laboratories (i.e. one ampoule each containing ^{18}F (LNE-LNHB), ^{57}Co (NIST), ^{64}Cu (LNE-LNHB), ^{67}Ga (NIST and PTB), ^{113}Sn (LNE-LNHB and PTB), ^{123}I (LNE-LNHB), ^{125}Sb (PTB), ^{134}Cs and ^{137}Cs (NMISA), ^{207}Bi (LNE-LNHB) and

^{228}Th (PTB). The radionuclide ^{125}Sb was measured for the first time in the SIR. All the submissions had been made to generate equivalence values in the associated ongoing BIPM key comparisons BIPM.RI(II)-K1.

Four radionuclides with short half lives ^{18}F ($T_{1/2}$ = 1.8290 (5) h), ^{64}Cu ($T_{1/2}$ = 12.701 (4) h), ^{123}I ($T_{1/2}$ = 13.21 (3) h), and ^{67}Ga ($T_{1/2}$ = 3.2590 (10) d) were measured, demonstrating the NMIs' requirements in this domain. There are now 4 results for ^{64}Cu which has enabled a more robust evaluation of the KCRV.

The report submitted by the IRMM in 2009 for a diluted aliquot of ^{177}Lu distributed for the CCRI(II)-K2.Lu-177 comparison enabled the equivalent activity to be evaluated and entered in the SIR database. The ^{203}Hg (LNE-LNHB) 2009 result was provided and is now registered. It is worth noting that the density of the NMI solutions ranged from 1.000 g cm^{-3} to 1.098 g cm^{-3}, even for some medium atomic mass radionuclides which requires a correction to the SIR measurements.

Unfortunately, due to a gas filling system failure, it has not proved possible for the LNE-LNHB to submit definitive values for the activities of the gas ampoules filled with ^{85}Kr at different pressures in 2006 which would have provided the SIR with a set of comparative data.

A final value for the ampoule of ^{177}Lu sent by the IRMM for the SIR has been submitted so this, together with the value entered in the database for the NPL last year, will provide a robust link for the international comparison to be linked to the SIR for this radionuclide. The Draft B report of this comparison piloted by the NIST is in circulation.

Except for an ampoule of ^{134}Cs submitted by the NPL in 2008, for which final results are expected early in 2012, all submissions prior to 2011 have been evaluated and their results entered in the SIR database.

5.2.1.2 SIR Submissions in 2011

During 2011, the BIPM received 11 ampoules filled with 10 different radionuclides from 6 laboratories (i.e. one ampoule each containing ^{60}Co (CNEA), ^{64}Cu (ENEA), ^{111}Ag (NPL) – for a first measurement in the SIR, ^{125}Sb (LNE-LNHB), ^{137}Cs (BEV), ^{152}Eu (CNEA), ^{201}Tl (NIST) and two containing ^{241}Am (CNEA and the LNE-LNHB). Finally, an ampoule of the short half-life positron emitter ^{11}C ($T_{1/2}$ = 20.370 (29) min) was delivered by the LNE-LNHB, which will provide the first SIR entry for this medical imaging radionuclide. All the submissions had been made to generate equivalence values in the associated key comparisons.

The cumulative number of ampoules measured since the beginning of the SIR, in 1976, is now 955, corresponding to a total of 710 independent results for 66 different radionuclides. In addition, 41 results have been withdrawn since the beginning of the SIR, a number which has not increased in recent years and represents about 5.8 % of the registered results.

5.2.1.3 SIR Reports and quality assurance

Updated reports of fifteen comparisons were published in the *Metrologia Technical Supplements* covering ^{22}Na, ^{56}Co, ^{60}Co, ^{99m}Tc and ^{111}In in 2010 and ^{75}Se, ^{88}Y, ^{124}Sb and ^{139}Ce in 2011. Each result prior to 2006 has now been published in the *Metrologia Technical Supplements* except for one which required a recent decision of the KCWG(II) and is now in preparation. There are two outstanding results from 2007 pending publication, one of which is actually in press. To date, all the Draft A reports have been submitted except for 3 results that are still awaited from the NMIs concerned.

There are 33 results awaiting publication in the KCDB and, to speed up the reporting process, the KCWG(II) recently decided to stop including pair-wise degrees of equivalence both in the comparison reports and in the KCDB. Every effort will be made to ensure that reports are published as quickly as possible, particularly when NMIs make submissions that are to replace out-dated results already removed from the KCDB.

The KCWG(II) is discussing the future use of a partially weighted mean (Mandel-Paule mean) rather than an arithmetic mean to evaluate KCRVs. Validation of the proposed method using SIR data was carried out at the BIPM using software developed at the IRMM.

The linearity of the updated SIR electronics has been evaluated using ^{99m}Tc and ^{64}Cu sources and at 10^{-5} is an order of magnitude improvement over the original SIR. A BIPM report of this result is close to publication.

Successful internal audits of the SIR within the BIPM Quality System were carried out in October 2010 and November 2011.

5.2.2 Gamma spectrometry

Routine measurements of potential impurities in SIR ampoules are made using the Ge(Li) and HPGe spectrometers. No impurity was detected in the ^{99}Mo and ^{18}F solutions submitted to the SIR by the LNE-LNHB. The presence of ^{121}Te and ^{110m}Ag has been identified in solutions of ^{123}I and ^{113}Sn, respectively, from the LNE-LNHB. One impurity was identified in a solution of ^{201}Tl from the NIST and several impurities were identified in solutions of ^{64}Cu and ^{111}Ag from the ENEA and the NPL, respectively. Measurements of several swabs for BIPM sealed source leakage tests were carried out and certificates issued.

Work is well in hand to calibrate the high-purity germanium spectrometer (HPGe). The efficiency measurements at 3 different source positions are almost complete.

5.2.3 Extension of the SIR to short-lived radionuclides

The BIPM.RI(II)-K4.Tc-99m key comparison using the SIR Transfer Instrument is now running smoothly. The results of the first ^{99m}Tc comparison, at the NIST, show agreement with the KCRV within one standard uncertainty and have been published. The results of the second comparison, which took place at the KRISS, also agreed with the KCRV within one standard uncertainty and were presented at the International Conference on Radionuclide Metrology 2011 in Tsukuba, Japan. A third comparison took place at the NMIJ after a postponement because of the earthquake in March 2011, and the results are being analysed. The NIM (China), LNMRI (Brazil), CNEA (Argentina), IFIN-HH (Romania) and the VNIIM (Russian Federation) are the next planned participants. The difficulties encountered in transporting the SIRTI (including the niobium reference source) to the NMIs and back to the BIPM demonstrate that no more than two comparisons a year can be organized.

The extension of the SIRTI for measuring ^{18}F is in development and Monte-Carlo simulations were carried out to study the response of the SIRTI for this pure β^+ emitter that is widely used in medical imaging using positron emission tomography (PET).

5.2.4 Extension of the SIR to pure beta emitters

In preparation for extending the SIR to the measurement of pure beta emitters, in autumn 2010 the ESWG(II) proposed a pilot comparison to compare the suitability of two measurement methods, one from the CIEMAT (Spain) based on the use of universal efficiency curves (UEC) using commercial liquid-scintillation (LS) spectrometers, the other proposed by the NMISA (South Africa) using TDCR spectrometers.

Previous attempts to use the CIEMAT/NIST method had been abandoned as this requires a comparison of the absolute activity of the solutions as determined by the BIPM and the NMI, which is a labour-intensive method requiring mathematical models to evaluate the tracer and the radionuclide efficiencies. Consequently, the new proposal relies only on the relative experimental determination of the efficiency of an appropriate tracer obtained with a set of quenched tracer samples, and on the measurements of the radionuclide by the NMI, and the quenching index of the LS spectrometer being used to evaluate the radionuclide efficiency from the tracer efficiency. This method is fast, independent of any theoretical models and is similar to the present methodology of the SIR.

The radionuclide chosen was ^{63}Ni, a comparatively simple to measure pure β emitter. The ENEA (Italy), IRMM (Geel), LNE-LNHB (France), NIST, NMISA, PTB and the POLATOM (Poland) each sent an ampoule containing a solution of ^{63}Ni that they had previously standardized using their own techniques, to both the CIEMAT and the BIPM. In parallel the LNE-LNHB provided the BIPM with an ampoule of ^{3}H from the same batch as that used for the 2009 ^{3}H comparison to serve as a tracer. Measurements were carried out at the same time at the CIEMAT and at the BIPM.

The BIPM used three different commercial liquid scintillators and prepared three sets of five samples for each of the seven ^{63}Ni solutions and in parallel three sets of ^{3}H standards quenched by addition of an increasing number of drops of nitromethane. All these samples were measured with the BIPM Beckman LS spectrometer and also with the BIPM TDCR spectrometer. With the collaboration of the LNE-LNHB, three sets of five samples were measured in two other LNE-LNHB-owned commercial LS spectrometers, and with a LNE-LNHB TDCR spectrometer to ensure the robustness of the measurement methods.

The measurements have shown that, even though one of the scintillators is less efficient than the two others, the quenching index, the composition of the scintillator, or type of spectrometer has no significant influence on the outcome of the comparison, with all the results agreeing at a 2 % to 3 % level. However, this spread could actually reflect discrepancies in the different primary activity determinations by the participating laboratories rather than the parameters for the relative measurements. This outcome is confirmed by the similar results obtained at the CIEMAT using the same solutions. Consequently, the use of the Universal Efficiency Curves method remains a possibility to extend the SIR to pure β emitters but further work is needed to decrease the spread in the results and improve the uncertainties. The analyses of the parallel TDCR measurements are pending.

5.2.5 CCRI activity comparison of ^{241}Pu

The CCRI(II)-K2.Pu-241 activity comparison was organized and piloted by the NPL at the end of 2009. Although the BIPM did not participate in the activity comparison of this alpha emitter, the new Excel-based reporting forms for comparisons produced by the BIPM were used by the participants. Consequently, the pilot laboratory requested in early 2011 that the BIPM develop an Excel application with macros to read the NMI comparison forms containing all the measurement details and so produce tables summarizing the data. The objective is to automate and speed up the production of comparison reports. The ^{241}Pu comparison has been used to test the process and a Draft A report including 10 tables was produced by the BIPM. However, it should be noted that finalizing the layout of the tables into the report in Word format and circulating the draft several times to the participants for comment and amendments is time consuming and difficult to accelerate. Nevertheless, the report was started in January 2011 and is now in an advanced Draft B stage with proposals for the KCRV and degrees of equivalence.

5.2.6 Other CCRI activity comparisons with BIPM involvement

The Draft A comparison reports for the ^{85}Kr comparison of 2009 and the ^{3}H comparison of 2009 have been circulated to the participants. The latter comparison includes a result from the BIPM. The Draft B report for the earlier ^{89}Sr comparison is in preparation.

The results of the comparison of radionuclide activity uncertainty evaluation, piloted by the IRA (Switzerland) and the NPL (UK), were presented at the ICRM conference in Tsukuba, Japan, (September 2011) and a provisional Draft B report of the comparison was issued by the organizing laboratories and circulated to the participants for comment. The BIPM values are consistent with the comparison reference evaluation. A revised version of the report was presented to the KCWG(II) in November 2011. The lessons learned from this comparison will be used in the development of the KCWG(II) planned special issue of *Metrologia* on the subject of radionuclide measurement uncertainties.

5.3 Thermometry (P.J. Allisy-Roberts, S. Picard, M. Nonis)

The draft B report of the CCT-K3.1 comparison, carried out in 2009 between the BIPM and the LNE-INM, was approved by the Consultative Committee for Thermometry (CCT) and published. Internal audits took place in August 2010 and June 2011.

Two newly-purchased water triple point cells of well-known isotopic content and a new gallium cell have been included as fixed points with the existing standards. Fifteen SPRTs and ten commercial laboratory thermometers belonging to the BIPM Mass, Electricity, Time and IR departments were calibrated.

5.4 Publications

External publications

1. Allisy-Roberts P.J., Kessler C., Burns D.T., Derlaciński M., Kokociński J., Comparisons of the standards for air kerma of the GUM and the BIPM for ^{60}Co and ^{137}Cs gamma radiation, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06015.
2. Burns D.T., Lye J.E., Kessler C., Roger P., Butler D.J., Key comparison BIPM.RI(I)-K2 of the air-kerma standards of the ARPANSA and the BIPM in low-energy x-rays, *Metrologia*, 2010, **47**, *Tech. Suppl.*, 06023.
3. Burns D.T., Allisy-Roberts P.J., Desrosiers M.F., Sharpe P.H.G., Pimpinella M., Lourenço V., Zhang Y.L., Miller A., Generalova V., Sochor V., Supplementary comparison CCRI(I)-S2 of standards for absorbed dose to water in ^{60}Co gamma radiation at radiation processing dose levels, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06009.
4. Burns D.T., Csete I., Roger P., Key comparison BIPM.RI(I)-K3 of the air-kerma standards of the MKEH, Hungary and the BIPM in medium-energy x-rays, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06017 .
5. Burns D.T., Kessler C., McCaffrey J.P., Key comparison BIPM.RI(I)-K2 of the air-kerma standards of the NRC, Canada and the BIPM in low-energy x-rays, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06002 .
6. Burns D.T., Kessler C., Roger P., Toni M.P., Pinto M., Bovi M., Cappadozzi G., Silvestri C., Key comparison BIPM.RI(I)-K2 of the air-kerma standards of the ENEA-INMRI, Italy and the BIPM in low-energy x-rays, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06010 .
7. Burns D.T., Kessler C., Villevalde A.Y., Oborin A.V., Key comparison BIPM.RI(I)-K3 of the air-kerma standards of the VNIIM, Russian Federation and the BIPM in medium-energy x-rays, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06004 .
8. Burns D.T., Roger P., Denozière M., Leroy E., Key comparison BIPM.RI(I)-K2 of the air-kerma standards of the LNE-LNHB, France and the BIPM in low-energy x-rays, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06013 .
9. Burns D.T., Roger P., Saito N., Kurosawa T., Morishita Y., Key comparison BIPM.RI(I)-K3 of the air-kerma standards of the NMIJ, Japan and the BIPM in medium-energy x-rays, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06012.
10. Kessler C., Roger P., Allisy-Roberts P.J., Yi C.-Y., Comparison of the standards for air kerma of the KRISS and the BIPM for ^{137}Cs gamma radiation, *Metrologia*, 2010, **47**, *Tech. Suppl.*, 06022.
11. Kessler C., Yi C-Y., Chung J-P., Roger P., Allisy-Roberts P.J., Comparison of the standards for air kerma of the KRISS and the BIPM for ^{60}Co gamma radiation, *Metrologia*, 2010, **47**, *Tech. Suppl.*, 06021.
12. Kessler C., Allisy-Roberts P.J., Lye J., Oliver C., Comparison of the standards for air kerma of the ARPANSA and the BIPM for ^{60}Co gamma radiation, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06016 .
13. Kessler C., Allisy-Roberts P.J., Morishita Y., Kato M., Takata N., Kurosawa T., Tanaka T., Saito N., Comparison of the standards for absorbed dose to water of the NMIJ and the BIPM for ^{60}Co γ-ray beams, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06008 .
14. Kessler C., Allisy-Roberts P.J., Oborin A.V., Villevalde A.Y., Comparison of the standards for air kerma of the VNIIM and the BIPM for ^{60}Co gamma radiation, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 06001.

15. Kessler C., Allisy-Roberts P.J., Oborin A.V., Villevalde A.Y., Comparison of the standards for air kerma of the VNIIM and the BIPM for ^{137}Cs gamma radiation, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06003.
16. Kessler C., Burns D.T., Büermann L., Key comparison BIPM.RI(I)-K7 of the air-kerma standards of the PTB, Germany and the BIPM in mammography x-rays, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06011.
17. Kessler C., Burns D.T., O'Brien M., Key comparison BIPM.RI(I)-K7 of the air-kerma standards of the NIST, USA and the BIPM in mammography x-rays, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06014.
18. Kessler C., Burns D.T., McCaffrey J.P., Key comparison BIPM.RI(I)-K7 of the air-kerma standards of the NRC, Canada and the BIPM in mammography x-rays, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06022.
19. Michotte C., Courte S., Ratel G., Kossert K., Nähle O., Update of the ongoing comparison BIPM.RI(II)-K1.Y-88 to include recent activity measurements of the radionuclide ^{88}Y by the PTB, Germany, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06006.
20. Michotte C., Ratel G., Kossert K., Nähle O., Maringer F.J., Update of the BIPM comparison BIPM.RI(II)-K1.Ce-139 of activity measurements of the radionuclide ^{139}Ce to include the 2008 results of the PTB, Germany and the BEV, Austria, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06019.
21. Michotte C., Ratel G., Moune M., Bobin C., Activity measurements of the radionuclide ^{124}Sb by the LNE-LNHB, France for the ongoing comparison BIPM.RI(II)-K1.Sb-124, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06021.
22. Michotte C., Courte S., Ratel G., Moune M., Bobin C., Update of the ongoing comparison BIPM.RI(II)-K1.Se-75 to include recent activity measurements of the radionuclide ^{75}Se by the LNE-LNHB (France), *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06007.
23. Michotte C., Ratel G., Courte S., Garcia-Toraño E., Kossert K., Nähle O., van Wyngaardt W.M., Simpson B.R.S., Update report of the BIPM comparison BIPM.RI(II)-K1.Na-22 of activity measurements of the radionuclide ^{22}Na to include the CIEMAT, PTB and the NMISA, *Metrologia,* 2010, **47**, *Tech. Suppl.,* 06001.
24. Michotte C., Courte S., Ratel G., Sahagia M., Wätjen A.C., Fitzgerald R., Maringer F-J., Update of the ongoing comparison BIPM.RI(II)-K1.Co-60 including activity measurements of the radionuclide ^{60}Co for the IFIN-HH (Romania), NIST (USA) and the BEV (Austria), *Metrologia,* 2010, **47**, *Tech. Suppl.,* 06010.
25. Michotte C., Courte S., Ratel G., Sochorová J., Update of the comparison BIPM.RI(II)-K1.Co-56 of activity measurements of the radionuclide ^{56}Co to include the result of the CMI-IIR, *Metrologia,* 2010, **47**, *Tech. Suppl.,* 06011.
26. Michotte C., Ratel G., Courte S., Verdeau E., Amiot M-N., Activity measurements of the radionuclide ^{111}In for the LNE-LNHB, France in the ongoing comparison BIPM.RI(II)-K1.In-111, *Metrologia,* 2010, **47**, *Tech. Suppl.,* 06019.
27. Michotte C., Courte S., Ratel G., Moune M., Johansson L., Keightley J., Update of the BIPM.RI(II)-K1.Tc-99m comparison of activity measurements for the radionuclide ^{99m}Tc to include new results for the LNE-LNHB and the NPL, *Metrologia,* 2010, **47**, *Tech. Suppl.,* 06026.
28. Picard S., Burns D.T. , Roger P., Allisy-Roberts P.J., McEwen M.R., Cojocaru C.D., Ross C.K., Comparison of the standards for absorbed dose to water of the NRC and the BIPM for accelerator photon beams, *Metrologia,* 2010, **47**, *Tech. Suppl.,* 06025.
29. Picard S., Burns D.T., Roger P., Allisy-Roberts P.J., Kapsch R.P., Krauss A., Key comparison BIPM.RI(I)-K6 of the standards for absorbed dose to water of the PTB, Germany and the BIPM in accelerator photon beams, *Metrologia,* 2011, **48**, *Tech. Suppl.,* 06020.
30. Picard S., Nonis M., Solve S., Allisy-Roberts P. J., Renaot E., Martin C., Subsequent Bilateral Comparison to CCT-K3; CIPM Key comparison CCT-K3.1: Comparison of Standard Platinum Resistance Thermometers at the Triple Point of Water (T = 273.16 K) and at the Melting Point of Gallium (T = 302.9146 K), *Metrologia,* 2011, **48**, *Tech. Suppl.,* 03001.

BIPM reports

31. Allisy-Roberts P.J., Burns D.T., Kessler C., Measuring conditions and uncertainties for the comparison and calibration of national dosimetric standards at the BIPM, ***Rapport BIPM*-2011/04**, 21 pp.
32. Picard S., Burns D.T., Ostrowsky A., Determination of the recombination correction for the BIPM parallel-plate ionization chamber type in a pulsed photon beam, ***Rapport BIPM*-2011/06**, 9 pp.
33. Roger P., High-voltage measurement for the BIPM x-ray generators, ***Rapport BIPM*-2011/07**, 9 pp.

Internal seminars

- Radiation protection for the Ionizing Radiation Department, P.J. Allisy-Roberts, September 2010
- The BIPM mammography dosimetry programme, C. Kessler, December 2010
- Application of the Mandel-Paule method to the computation of key comparison reference values, C. Michotte, December 2011

5.5 Activities related to the work of Consultative Committees

P.J. Allisy-Roberts is Executive Secretary of the CCRI and its three Sections, the CCRI(III) in March 2011, CCRI(I) in May 2011, CCRI(II) and the CCRI itself in June 2011. In addition there have been eleven Working Group meetings during the last 18 months including the RMO WG in May 2011.

P.J. Allisy-Roberts and D.T. Burns are members of the KCWG(I), ADWG(I) and BSWG(I). The KCWG(I) and the ADWG(I) met together in May 2011 and C. Kessler and S. Picard also participated. D.T. Burns is also member of an *ad hoc* group evaluating the effect of excess charge on the value for W_{air}.

C. Michotte is the coordinator of the CCRI(II) Working Group on the SIR Transfer Instrument and a member of the KCWG(II) which met in November 2010, June and November 2011. She is also the contact person at the BIPM and *rapporteur* for the JCGM/WG1 that met in November 2010, May and November/December 2011.

G. Ratel is a member of the CCRI(II) working group on the extension of the SIR to beta emitters, which met on 5 November 2010 and 16 November 2011, the KCWG(II) which met on 4 November 2010, in June and November 2011, the UCWG(II), which met on 3 November 2010 prior to its merger with the KCWG(II) in June 2011, and the BqWG(II) which met on 2 November 2010, 18 April 2011 and 16 November 2011.

S. Picard is Executive Secretary of the Consultative Committee for Acoustics, Ultrasound and Vibration (CCAUV).

5.6 Activities related to external organizations

P.J. Allisy-Roberts is the BIPM representative on the IAEA SSDL Scientific Committee which she currently chairs. She is a member of the Working Group for the UK NMS programme for ionizing radiation and acoustics and of the *Comité scientifique rayonnements ionisants* (LNE, France). She is a member of the editorial board of the *Journal of Radiological Protection* and of the *Revue Française de Métrologie*. She was elected to the Board of the European Federation of Medical Physicists where she currently serves as the European Matters Committee Chairman.

D.T. Burns is the BIPM representative at the ICRU, a member of the ICRU Committee on Fundamental Quantities and Units and a member of two ICRU Report Committees, on Key Data for Dosimetry and on Operational Quantities for Radiation Protection. He is the BIPM contact person for the EURAMET-TC for ionizing radiation. He was elected to Fellowship of the Institute of Physics (UK) in 2011.

C. Kessler acted as the external peer reviewer for the dosimetry services at the CNEA, Argentina in January 2011.

G. Ratel is the BIPM representative on the International Committee for Radionuclide Metrology (ICRM) and is the President of the ICRM Nominating Committee. He also reviews papers for *Metrologia*.

5.7 Travel (conferences, lectures and presentations, visits)

P.J. Allisy-Roberts to:

- London (UK), 9 July, 6 October 2010, 28 January, 31 March and 21 July 2011, for meetings of the editorial board of *Journal of Radiological Protection*; 12 July 2010 to participate in a discussion group at the Institute of Physics;
- Udine (Italy), 24 September 2010 for an EFOMP Board meeting;
- Vienna (Austria) 9-12 November 2010, to chair some scientific sessions and to make a presentation on international ionizing radiation metrology comparisons at the International Symposium on Standards, Applications and Quality Assurance in Medical Radiation Dosimetry (IDOS) at the IAEA; 19-21 September 2011, to attend the IAEA General Conference;
- Brussels, (Belgium), 19 January and 3 August 2011, to attend the EU Training and Education in Radiation Protection Board meeting on behalf of the EFOMP;
- Manchester (UK), 14 June 2011, to attend an Update meeting for Radiation Protection Advisers on developments in radiation protection standards;
- Strasbourg (France), 26 July 2011, to discuss the scientific programme for an EFOMP sponsored conference to be held there in 2012;
- Dublin (Ireland), 2 September 2011, to attend the International Medical Physics and Engineering Conference and to chair a session;
- Saclay (France) 8 September 2011, together with D.T. Burns and C. Kessler for the presentation of the thesis of M. Le Roy on radiation dosimetry;
- Braunschweig (Germany), 28-30 September 2011, with C. Kessler for an ^{192}Ir brachytherapy dosimetry comparison at the PTB;
- Paris (France), 24 November 2011, for a meeting on radiation protection at the ASN and to participate in the *Comité scientifique rayonnements ionisants* at the LNE.

D.T. Burns to:

- Gaithersburg (MD, USA), 22 September to 1 October 2010, for a comparison of absorbed-dose standards in the NIST linear accelerator beams;
- Vienna (Austria) 9-12 November 2010, to chair a session and to make a presentation at the International Symposium on Standards, Applications and Quality Assurance in Medical Radiation Dosimetry (IDOS) at the IAEA;
- Essen (Germany), 15-19 November 2010, to attend a meeting of the Main Commission of the ICRU;
- Barcelona (Spain), 14-15 April 2011, to attend a meeting of the ICRU Report Committee on Key Data for Dosimetry;
- Saclay (France), 18-21 April 2011, for a comparison of graphite absorbed-dose standards for ^{60}Co radiation with the LNE-LNHB and for ion recombination measurements in the accelerator beam at the LNE-LNHB.

S. Picard to:

- Gaithersburg (MD, USA), 22 September to 6 October 2010, with P. Roger, for a comparison of absorbed dose standards in the NIST linear accelerator beams;
- Vienna (Austria), 8-12 November 2010, to present the poster entitled "The BIPM Graphite Calorimeter Standard for Absorbed Dose to Water" and participate in the International Symposium on Standards, Applications and Quality Assurance in Medical Radiation Dosimetry (IDOS) at the IAEA;

- Trappes (France), 27 January 2011, to visit the acoustic and vibration section of the LNE;
- Saclay (France), 18-21 April 2011, for a comparison of graphite absorbed-dose standards for ^{60}Co radiation with the LNE-LNHB and for ion recombination measurements in the accelerator beam at the LNE-LNHB;
- Paris (France), 21-22 June 2011, to participate in a recruitment panel of the LNE-INM/CNAM;
- La Defense (France), 27-29 June 2011, to participate in a course on Intercultural Team Management;
- Villejuif (France), 1 July 2011, to visit the radiotherapy unit of the Institut Gustave Roussy.

G. Ratel to:

- Saclay (France) 7-9 March 2011, to measure the ^{63}Ni samples for the trial comparison;
- Tsukuba (Japan), 19-23 September 2011, to attend the 18th ICRM Conference and then the ICRM Executive Board as Chairman of the ICRM nominating Committee. He chaired the session on International comparisons, refereed 7 articles to be published in the proceedings of the conference; he also gave a talk entitled "Pilot comparison to mimic the operation of the extended SIR for measurements of pure β emitters";
- Caen (France), 28-29 November 2011, to attend the "*Colloque national de radioprotection sur le zonage radiologique*";
- Roissy (France), 30 November 2011 and 1 December 2011, to attend with S. Courte an APAVE course to obtain the aptitude certificate for the transport of dangerous goods;
- Saclay (France), 8 December 2011, to give a talk on the SIR and its present status.

C. Michotte to:

- Daejeon (Republic of Korea), 25 September to 2 October 2010, to make an activity comparison of ^{99m}Tc (BIPM.RI(II)-K4.Tc-99m) at the KRISS using the SIR Transfer Instrument;
- Tsukuba (Japan), 18-28 September 2011, to make an activity comparison of ^{99m}Tc (BIPM.RI(II)-K4.Tc-99m) at the NMIJ using the SIR Transfer Instrument and to make an oral communication at the 18th ICRM on the results of the ^{99m}Tc comparison at the KRISS.

C. Kessler to:

- Vienna (Austria) 9-12 November 2010, to present a poster at the International Symposium on Standards, Applications and Quality Assurance in Medical Radiation Dosimetry (IDOS) at the IAEA;
- Braunschweig (Germany), 28-30 September 2011, for a brachytherapy comparison at the PTB.

5.8 Visitors

- Dr Steffen Groth (WHO), 2 July 2010
- Dr Uwe Wätjen, Gabriel Suliman and Jan Paepen (IRMM), 20 July 2010
- Mr Sandor Vörös (METAS), 24 August 2010
- Mrs Maria Paz Aviles (CIEMAT), 22 November 2010
- Mr Frank Delaunay, Jean-Marc Bordy and François Damoy (LNE-LNHB), 13 January 2011
- Dr Philippe Cassette (LNE-LNHB), 16 February 2011
- Le Directeur de Cabinet du Préfet, 8 April 2011
- Mr Thierry Branger, Mrs Carole Fréchou and Mr Mathieu Rozenzweig (LNE-LNHB), 29 April 2011
- CCRI(I) participants, 4 May 2011
- Dr Margarita Saravi (CRRD), 9 May 2011
- NMI directors and government representatives, 27 May 2011
- Delegation from SASO, Saudi Arabia, 27 May 2011

- Mr Thierry Branger , Mrs Valérie Lourenzo and Mrs Carole Fréchou (LNE-LNHB), 9 June 2011
- Mr Vladimir Sochor (CMI), 22 to 24 June 2011
- Mr Thierry Branger (LNE-LNHB), 5 July 2011
- Prof. Chary Rangacharyulu (University of Saskatchewan, Canada), 8 August 2011
- Dr Shingo Ichimura (Vice President, AIST) and Dr Toshiyuki Fujimoto (Deputy Director, NMIJ), 19 September 2011
- Dr Guiseppe Felici (Sordina, Italy), 4 October 2011
- Delegation from Japanese Chamber of Commerce and Industry in France (CCIJF), 17 November 2011

5.9 Secondees and guest workers

- Dr José Alvarez Romero (ININ) on an IAEA Fellowship until 12 July 2010
- Dr Jacco de Pooter (VSL), 19 July to 12 August 2010
- Mr Chul-Young Yi and Mr Hyum-Moon Kim (KRISS), 2 to 6 August 2010
- Mr Gabor Machula (MKEH), 13 to 17 September 2010
- Mrs Anna Villevalde (VNIIM), 25 to 29 October 2010 and 28 November to 2 December 2011
- Dr Maria Pia Toni and Mr Massimo Pinto (ENEA), 17 to 28 January 2011
- Mr Marc Donois and Aimé Ostrowsky (LNE-LNHB) 1 to 4 March 2011
- Mr Ladislav Czap (IAEA), 23 to 27 May 2011
- Mr João Cardoso (ITN), 7 to 11 March 2011
- Dr Istvan Csete (MKEH), 5 to 9 September 2011
- Mr Ronnie Minniti (NIST), 12 to 16 September 2011

BIPM Chemistry Department

Director: R.I Wielgosz

(1 July 2010 to 31 December 2011)

6.1 Gas metrology programme (J. Viallon, E. Flores, M. Petersen, P. Moussay, F. Idrees, R.I. Wielgosz)

6.1.1 Ozone photometer comparison and calibration programme

In September 2010, the last report of a comparison performed during the first cycle of the key comparison BIPM.QM-K1 (comparison performed with VSL (the Netherlands) in September 2008) was reviewed by the Gas Analysis Working Group (GAWG) and published in *Metrologia Technical Supplement*.

The reports of the two first comparisons performed during the second cycle of the key comparison BIPM.QM-K1 which started in May 2009, i.e. with NIST (USA) in June 2009 and CHMI (Czech Republic) in September 2009 were reviewed and published this year.

Between July 2010 and September 2011, six additional laboratories brought or sent their ozone national standard to the BIPM for a comparison with the BIPM-SRP27 reference standard as part of the key comparison BIPM.QM-K1: NMISA (South Africa) in August 2010; CENICA (Mexico) in October 2010; VSL, NMC, A*STAR (Singapore) and ISCIII (Spain) in December 2010; and EAA (Austria) in September 2011. All the reports have been reviewed and published.

In December 2010, a comparison using the BIPM.QM-K1 protocol was performed with the Department of Environment, Climate Change and Water (DECCW), New South Wales, (Australia), which has not yet been nominated as a designated institute in the CIPM MRA. The report of this comparison was published as a BIPM report (*Rapport BIPM*-2011/03).

Two institutes have brought or sent an ozone analyser to the BIPM for a calibration: NMISA in August 2010 and GUM (Poland) in September 2011.

6.1.2 Comparisons using the gas phase titration facility

Further validations concerning potential losses of reactant in the molbloc units have been performed. The purity of reactants and inexistence of parasitic reactions have been confirmed by FTIR (40 m cell). The flow measurement elements have been calibrated. The titration can be linked to primary standards of NO or NO_2. Efforts continue to resolve the inconsistency between the results linked to NO standards and the results linked to NO_2 standards.

6.1.3 NO gas standard comparison facility

The BIPM continues to maintain its nitric oxide comparison facility. The internal procedure on the value assignment of secondary gas standards for internal use is under review.

6.1.4 Maintenance of the NO_2 facility and CCQM-K74, CCQM-P110, CCQM-P120 coordination

During a workshop at the 24th meeting of the CCQM GAWG in November 2010 the BIPM, in its role as coordinating laboratory of the key comparison CCQM-K74, was asked to investigate additional sources of uncertainty in its measurement results which had been proposed as reference values for the key comparison. The additional sources of uncertainty investigated were: the impurity analysis uncertainties, the reaction of NO_2 to

HNO_3 in the BIPM permeation facility, the stability of the gas concentration of the transfer standards (cylinders), and the contributions from flow measurements.

In response in April 2011, a report that summarized the results of the series of new investigations entitled "*Proposed u(KCRV) for the Draft B report of CCQM-K74: Nitrogen dioxide, 10 µmol/mol*" was distributed and presented during the 25th meeting of the CCQM GAWG. A revised version of this report (0.2) was distributed in July 2011 and, after being approved, the first version of the Draft B CCQM-K74 report was submitted to the CCQM GAWG. Comments were received from reviewers in September 2011 and the final report is being finalized by the BIPM.

The Draft B reports of pilot studies CCQM-P110 protocols B1 and B2 were distributed to participating laboratories in September 2011. The reports had been presented during the 26th Meeting of the CCQM GAWG in Boulder, Colorado, USA, and due to the potential impact of both, the BIPM was asked to present revised versions of the reports, including new features and a new title for the CCQM-P110 protocol B1 study. New versions of both reports are being drafted by the BIPM.

6.1.5 Key comparison on methane standards

The gas chromatography (GC-FID) facility for methane measurements was installed at the BIPM in December 2010. A method validation programme has been undertaken. It required the installation of a new version of the GC-FID facility control software and an update of the system configuration. System validation activities continued in September 2011, using ten primary methane standards provided by NIST in two different air matrices. The measurement protocol is currently being finalized and the comparison protocol drafted.

The cavity ring-down spectroscopy (CRDS) methane instrument was sent to the USA in July 2011 for repair. It was returned to the BIPM in November 2011. The CRDS facility was successfully validated using the NIST primary methane standards.

6.1.6 Formaldehyde

Validation studies of the facility for the generation of formaldehyde (HCHO) in nitrogen have continued. The influence of the carrier gas flow rate and the gas chamber temperature have been studied to find the optimum values for the stable generation of formaldehyde in the desired range of concentrations. Impurities in the output gas mixture were studied by FTIR spectrometry. In high concentration mixtures, water was detected and quantified. Water was found to represent about 4 % of the mass lost by the paraformaldehyde permeation tube. The water loss from the formaldehyde permeation tubes will require constant monitoring with a trace water analyser, which will be permanently installed on the diluted gas stream to better quantify this impurity, hence keeping a reasonable uncertainty on the formaldehyde concentration determination.

In parallel, a series of measurements to study the stability of potential transfer standards for the planned key comparison CCQM-K90 have been performed. While National Metrology Institutes (NMIs) are developing their own gas cylinder standards, commercial cylinders were tested during the last seven months and were found to be insufficiently stable for use in a key comparison. Cylinders of formaldehyde in nitrogen produced and/or certified by NMIs will be tested in 2012, with the aim of starting the key comparison CCQM-K90 in 2013.

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

An important step has been reached in this project, with the completion of the laser ozone photometer, which has been used to perform new relative measurements of the ozone cross-section at three different wavelengths in the Hartley band: 244.06 nm, 248.32 nm and 257.34 nm. To obtain these results, the performance of the laser ozone photometer has been studied in detail. Linearity of the instrument has been demonstrated, including the influence of the light power on ozone concentrations. The uncertainty budget for the instrument has been completely reviewed, focusing on the laser light path length inside the instrument's cells. A system of centering irises was developed to insure that the path length is equal to the cell length. These tests in conjunction with the accurate length measurements already performed, and the tilted windows installed on the cells, provides a reduction in this uncertainty, which is the second major uncertainty component of Standard Reference Photometers (SRPs) after the ozone absorption cross-section.

Finally, relative measurements of the ozone cross-section have been performed at the three available wavelengths, using the procedure for ozone photometer comparisons. The measured values are in agreement with other published values, when using the same reference value of the ozone absorption cross-section at the mercury line wavelength (253.65 nm). These results have been submitted for publication in the *Journal of Geophysical Research*.

In parallel, all parts of the facility for (absolute) measurements of the ozone absorption cross-section on pure ozone have been received, including parts for the pure ozone generator. The experiment has been assembled and the first validation studies performed. In particular, the performance of the mass spectrum analyser has been validated on samples of oxygen in nitrogen. A home-made discharge generator to produce ozone from pure oxygen has been successfully tested on air samples. The first tests of ozone production are to be performed before the end of 2011.

6.2 **Organic analysis programme** (S. Westwood, R. Josephs, A. Daireaux, T. Choteau, R.I. Wielgosz)

6.2.1 Primary calibrator (chloramphenicol) purity

Preliminary studies were undertaken on the suitability of chloramphenicol for selection as the measurand in the CCQM-K55.c comparison. Source materials from several suppliers were investigated by standard characterization techniques but all were found to be of too high a level of purity to be suitable for the intended purposes of the CCQM-K55 series of key comparisons. After discussion at the April 2011 meeting of the CCQM Organic Analysis Working Group (OAWG), it was agreed to halt the work on chloramphenicol and investigate (L)-valine as an alternative.

6.2.2 Primary calibrator (L-Valine) purity

The development and validation of analytical methods for use in the production and characterization of the CCQM-K55.c [(L)-Valine] comparison material has been undertaken.

Procedures developed for the CCQM-K55.c production study included:

- LC-MS/MS methods for confirmation of the identity and quantification of the related substance impurity content of the CCQM-K55.c comparison material;
- LC-CAD methods for quantification of the related substance impurity content of the CCQM-K55.c comparison material;
- GC-MS and GC-FID methods for the identification and relative quantification of amino acid impurities in (L)-Valine;
- GC-FID methods for the detection of the potential impurity (D)-Valine and estimation of the enantiomeric purity of the (L)-Valine material;
- Protocols based on LC-MS/MS, LC-CAD and GC-MS analysis for testing the stability and homogeneity of the related substance impurity content of the L-Valine candidate material

- Analysis of NMR spectroscopic data obtained by an external collaborator to confirm the impurity profile of the CCQM-K55.c material and to obtain an independent assessment of its mass fraction valine content;
- Application of GC-MS methods for detection of residual organic solvent in the CCQM-K55.c candidate material and its application in assessing the stability and homogeneity of the residual solvent content of the candidate material;
- Development of Karl Fischer titration conditions for the assignment of the water content of the candidate material;
- Application of thermogravimetric analysis to provide confirmatory data for the estimates of residual solvent and water content obtained by other techniques;
- Trace metal analysis to confirm the absence of significant levels of metals;
- Elemental microanalysis of the percentage carbon, nitrogen and hydrogen content to provide supporting data for the BIPM characterization of the candidate material.

Homogeneity studies of the candidate material analysed by LC-MS/MS demonstrated a sufficient degree of homogeneity. Stability studies employing the LC-UV-CAD are ongoing.

6.2.3 Organic large molecule purity analysis – establishment study

Pure material characterization methods for analytes of higher molecular weight and complexity that are of relevance to the CCQM have been investigated at the BIPM. Study strategies for the model systems angiotensin I and insulin were developed after consultation with the NIST and the NIBSC (UK). Pure amino acids, isotopically labelled amino acids, angiotensin I, and insulin have been purchased. The specific laboratory equipment required (e.g. hydrolysis instrumentation, rotary vacuum evaporator, high resolution mass spectrometry system) has been purchased, installed and validated. Two laboratories have been rebuilt to provide sample preparation facilities and to accommodate the high resolution mass spectrometry system that has been connected to an existing liquid chromatography system. A new compressor and nitrogen generator system has been purchased and was installed in a dedicated plant room to supply the mass spectrometer facility.

In addition, a Research Fellow working in the field of larger molecule purity analysis has been recruited for a period of two years.

6.2.4 Organic large molecule purity analysis – angiotensin I

The BIPM has developed and validated analytical methods for amino acids (AAs), for use in the characterization of both angiotensin I (ANG I) and insulin (INS). Identification and quantification of major impurities present in a set of selected AAs is of utmost relevance for peptide/protein value assignment based on AA analysis.

Procedures were developed and validated for the determination of structurally related and other impurities in a set of six selected pure AAs (isoleucine, leucine, phenylalanine, proline, tyrosine and valine materials). The procedures were as follows:

- LC-UV-CAD method for the identification and quantification by external calibration of the selected AAs and related compounds;
- LC-MS/MS (Qtrap) method using chromatography with a reverse-phase analytical column with embedded acidic ion-pairing groups and electrospray ionization for the identification and quantification of the selected AAs and related compounds;
- LC-hrMS (Orbitrap) for the identification of the selected AAs and related compounds;
- GC-MS methods for determination of volatile organic impurities of the selected AA materials;

- Karl Fischer titration method for the determination of the water content of the selected AA materials;
- Thermogravimetric analysis as a supporting method to estimate the total volatiles, water content and residues;
- NMR spectroscopy and elemental microanalysis to provide confirmatory data for the characterization of the selected AA materials.

The purity of the six selected AAs and the corresponding measurement uncertainties were evaluated using a mass balance purity approach.

The value-assigned AAs will be used to perform quantitative AA analysis for the mass fraction value assignment of ANG I after complete hydrolysis. The LC-MS/MS (Qtrap) method for AAs has been further developed to serve as an LC-ID-MS/MS method for the AA analysis of hydrolyzed peptides/proteins. Method optimization and validation is in progress.

Method development studies for characterization of intact peptide candidate material provided by the NIST have started. Procedures developed or investigated to date for the characterization of model peptide ANG I include:

- LC-UV-CAD method for the identification and quantification by external calibration of ANG I and related compounds;
- LC-MS/MS (Qtrap) method for the identification and quantification of the selected amino acids and related compounds (validated using decomposed ANG I);
- LC-hrMS (Orbitrap) for the identification and quantification of ANG I and related compounds;
- GC-MS methods for determination of volatile organic impurities;
- Karl Fischer titration method for the determination of the water content;
- Thermogravimetric analysis as a supporting method to estimate the total volatiles, water content and residues;
- NMR spectroscopy and elemental microanalysis to provide confirmatory data for the characterization of the ANG I.

6.2.5 Organic large molecule purity analysis – insulin

Value-assigned AAs from the ANG I study will also be used for quantitative AA analysis for mass fraction value assignment of INS after complete hydrolysis. The LC-MS/MS (Qtrap) method for AAs has been further developed to serve as an LC-ID-MS/MS method for the AA analysis of hydrolyzed INS. Method optimization and validation is in progress.

Method development studies for the characterization of intact INS provided by the USP have started. Procedures being developed or investigated to date for use in the INS characterization include:

- LC-UV-CAD method for the identification and quantification by external calibration of INS and related compounds;
- LC-MS/MS (Qtrap) method for the identification and quantification of selected amino acids and related compounds;
- GC-MS methods for determination of volatile organic impurities;
- Karl Fischer titration method for the determination of the water content;
- Thermogravimetric analysis as a supporting method to estimate total volatiles, water content and residues;

- NMR spectroscopy and elemental microanalysis to provide confirmatory data for the characterization of INS.

6.2.6 Purity methodology and small molecule purity analysis

A comprehensive compilation has been undertaken of all data reported by component and by participant for the four organic purity comparisons coordinated by the BIPM to date (CCQM-P20.e, CCQM-P20.f, CCQM-K55.a and CCQM-K55.b). The aim of the review was to develop a proposal for the assessment of the ongoing performance of an NMI in this area which could also be used for the technical review of Calibration and Measurement Capability (CMC) claims by the CCQM Key Comparison Working Group (KCWG).

An overview of the results and a preliminary approach for its use to link comparison results to CMC claims was reported to the CCQM OAWG in April 2011. This approach has been revised and an expanded version of the proposal was discussed further at the November 2011 OAWG meeting. As a result of this proposal, individual "report cards" summarizing the performance of each NMI have been incorporated into the Draft B reports for CCQM-K55.a and CCQM-K55.b and will be included in all future purity comparison reports.

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 is being prepared for distribution and discussion within the OAWG.

6.2.7 Organic programme quality system

A Quality System has been implemented within the Chemistry Department that will ensure all aspects of the technical work within the BIPM Organic Analysis work programme, related to key comparisons, complies with relevant BIPM technical and quality system requirements.

A BIPM internal audit of the Organic Programme Quality System was undertaken in December 2010 and was followed by an external Peer Review in June 2011. Dr Byungjoo Kim from KRISS (Republic of Korea) was the technical assessor for the Peer Review.

The Peer Review found that the BIPM operates its Organic Analysis programme to provide purity analysis comparisons for the CCQM in a competent manner and has sufficient capabilities to provide the related services. It concluded that the BIPM:

- has a documented a technical management system based on the requirements of ISO Guide 34 and ISO/IEC 17025, and has properly implemented it,
- has staff members and equipment to conduct the services,
- has management and technical capabilities for the services.

6.2.8 Purity comparison CCQM-K55.a (Estradiol)

The Draft B Report for the CCQM-K55.a (Estradiol) comparison has been accepted in principle by the OAWG members. After final comments are received, the Final Key Comparison Report should be circulated in early 2012, initially within the OAWG and subsequently to the Chairs of the other CCQM WGs for final approval prior to publication in KCDB Appendix B. A draft final report for the parallel pilot study, CCQM-P117.a (Estradiol) has been prepared and circulated to pilot study participants for comment.

6.2.9 Purity comparison CCQM-K55.b (Aldrin)

In September 2010, results were received from all participants (19 for CCQM-K55.b and 5 for the parallel pilot study CCQM-P117.b). An initial summary was circulated to all participants prior to a detailed initial discussion at the CCQM Organic Analysis Working Group meeting in Singapore in November 2010. There was a difference of approximately 10 mg/g between the higher mass fraction assignments reported by the majority of laboratories that used a mass balance approach to assign the aldrin content of the comparison material and a smaller set of laboratories that assigned a lower value using techniques that included an assessment by quantitative NMR (qNMR).

Follow-up studies discussed at the April 2011 OAWG meeting demonstrated conclusively that the difference arose from the presence of a significant non-volatile organic impurity that had not been detected using standard mass balance techniques applicable to this class of impurity. The discrepancy was not due to an inherent bias in the qNMR techniques or an inhomogeneity that was not accounted for in the comparison material.

As requested at the April 2011 meeting of the OAWG, the BIPM proposed Key Comparison Reference Values (KCRVs) for the main component and also for the major classes of impurities present in the material. A Draft B report based on these KCRVs and their associated measurement uncertainties was distributed prior to the WG meeting in November 2011. The reference value for the aldrin content of the comparison was based on a consensus estimate mass balance approach, appropriately taking into account the non-volatile organic residue content, and was similar in approach to that used for the CCQM-K55.a comparison.

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

The CCQM-K55.c [(L)-Valine] comparison material has been prepared at the BIPM. The bulk source material was sub-divided into units of 500 mg. The impurity profile of the candidate material batch is being assigned and the suitability of the homogeneity and stability of the batch for the purposes of the comparison are under investigation. If these studies are completed satisfactorily, a call for participation will be circulated in early 2012 with a target sample distribution in May 2012.

6.3 **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 is coordinating the development of the JCTLM Database.

The annual JCTLM Working Group 1 and 2 joint meetings, and *Ad Hoc* Working Group 3 meetings were held in conjunction with the American Association for Clinical Chemistry (AACC) meetings in Anaheim, USA, in July 2010, and in Atlanta, USA, in July 2011. For the two annual review cycles (cycle 7 (2010) and cycle 8 (2011)), the JCTLM review teams used the newly-implemented nomination and review process. This process was modified to ensure consistency with the revised harmonized standards EN/ISO 15194:2009 and 15193:2009 published in the *Official Journal of the European Community*.

The 9th and 10th meetings of the Executive Committee of the JCTLM were held at the BIPM headquarters on 2–3 December 2010, and 8–9 December 2011, respectively. The Declaration of Cooperation between the International Committee for Weights and Measures (CIPM), International Federation of Clinical Chemistry and Laboratory Medicine (IFCC) and International Laboratory Accreditation Cooperation (ILAC) was revised to be consistent with current JCTLM processes and approved. Appendix III was modified to provide references to the dated international standards used by the Working Groups to evaluate compliance of the nominations, and a statement for the obligations of Member Status was added to Appendix IV.

The list of JCTLM review teams in Working Group 1 was updated to include the review team member appointed for the review of nominations for Nucleic Acids. The document for the terms of reference for each review team was revised for harmonization by the Quality Review Team Leader.

WG2 procedures have been updated to include extended criteria for reference measurement service providers regarding their regular participation in the EQAS Scheme for the listed measurands for which they offer a service.

The JCTLM Database was updated in March 2011 to include WG1 Cycle 7 reference materials, and measurement methods, and WG2 Cycle 5 reference measurement laboratory services approved by the Executive Committee during its 9th annual meeting.

As of December 2011 the JCTLM Database contains:

- 247 available certified reference materials covering 12 categories of analytes. Of these reference materials, 33 are in List II, which includes reference materials value-assigned using internationally agreed protocols, and 3 are in List III, which covers reference materials with nominal properties;
- 152 reference measurement methods or procedures that represent about 80 different analytes in eight categories of analytes;
- 86 reference measurement services, delivered by 10 reference laboratories in 6 countries and which cover six categories of analytes.

The WG1 Cycle 8 call for nominations of higher order reference materials and reference measurement methods or procedures, and the WG2 Cycle 6 call for nominations of reference measurement laboratory services were announced on the JCTLM website in January 2011, and email notifications were sent to about 300 JCTLM potential contributors. As of July 2011, 40 nominations for materials, 7 nominations for procedures, and 5 nominations for services had been received and sent to Review Teams for evaluation.

6.4 Metrology in biosciences and biotechnology activities

The BIPM commissioned study on 'Measurement Service and Comparison Needs for an International Measurement Infrastructure for the Biosciences and Biotechnology: Input for the BIPM Work Programme' was completed and published in March 2011 and is available at

http://www.bipm.org/utils/common/pdf/rapportBIPM/2011/02.pdf .

6.5 Publications

External publications

1. Viallon J., Moussay P., Idrees F., Wielgosz R.I., Rakowska A., Final report on the on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with VSL, 2008, *Metrologia*, 2010, **47**, *Tech. Suppl.*, 08024.
2. Viallon J., Moussay P., Idrees F., Wielgosz R., Novak J. and Vokoun M., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with CHMI, 2009, *Metrologia*, 2011, **48**, *Tech. Suppl.*, 08001.
3. Viallon J., Moussay P., Idrees F., Wielgosz R. and Fentanes O., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with CENICA (October 2010), *Metrologia*, 2011, **48**, *Tech. Suppl.*, 08003.
4. Viallon J., Moussay P., Idrees F., Wielgosz R., Gomez P.M., Sanchez C., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with ISCIII (December 2010), *Metrologia*, 2011, **48**, *Tech. Suppl.*, 08005.

5. Viallon J., Moussay P., Idrees F., Wielgosz R., Norris J.E. and Guenther F.R., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with NIST (June 2009), *Metrologia*, 2011, **48**, *Tech. Suppl.*, 08006.
6. Viallon J., Moussay P., Idrees F., Wielgosz R., Botha A., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with NMISA (August 2010), *Metrologia*, 2011, **48**, *Tech. Suppl.*, 08007.
7. Viallon J., Moussay P., Idrees F., Wielgosz R., Heikens D., Wessel R., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with VSL (December 2010), *Metrologia*, 2011, **48**, Tech. Suppl., 08008.
8. Viallon J., Moussay P., Idrees F., Wielgosz R., Rakowska A., Chin-Chye T., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with NMC, A*STAR (December 2010), *Metrologia*, 2011, **48**, *Tech. Suppl.*, 08017.
9. Viallon J., Moussay P., Idrees F., Wielgosz R., Froehlich M., Wolf A., Final report on the ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with EAA (September 2011), *Metrologia*, 2011, **48**, *Tech. Suppl.*, 08018.
10. Petersen M., Viallon J., Moussay P., Wielgosz R.I., Relative measurements of ozone absorption cross-sections at three wavelengths in the Hartley band using a well-defined UV laser beam, 2011, *submitted to Journal of Geophysical Research*
11. Westwood S., Josephs R., Choteau T., Mesquida C., Daireaux A., Wielgosz R., Davies S., Windust A., Kang M., Ting H., Kato K., Frias E., Pérez M., Apps P., Fernandes-Whaley M., Wiangnon K., Ruangrittinon N., Wood S., LeGoff T., Duewer D., Schantz M., Siekmann L., Esker J., An international comparison of mass fraction purity assignment of digoxin: CCQM Pilot Study CCQM-P20.f (Digoxin), *Metrologia Technical Supplement*, in press.
12. Josephs R.D., Daireaux A., Westwood S., Wielgosz R.I., Simultaneous determination of various estrogens by normal phase – liquid chromatography – tandem mass spectrometry with atmospheric pressure photoionization for the purity assessment of the monitored drug ß-estradiol, *Anal. Bioanal. Chem.* (in preparation).

BIPM publications

13. Viallon J., Moussay P., Idrees F., Wielgosz R.I. and Ross G. 2011 Comparison of Ozone Reference Standards of the DECCW and the BIPM, December 2010 *Rapport BIPM*-2011/03, 18 pp.

6.6 Activities related to the work of Consultative Committees

R.I. Wielgosz is the Executive Secretary of the CCQM. The CCQM held its 17th meeting at the BIPM (14–15 April 2011), and was preceded by meetings of its working groups. CCQM workshops on 'Metrology and the need for reliable microbial measurement/testing results' and 'Relative molecular mass measurements for the identification of peptides, proteins and other molecules' and were held at the BIPM on 6–7 and 13 April 2010 respectively.

S. Westwood is a member of the CCQM Organic Analysis Working Group and the CCQM Organic Analysis Working Group Taskforce on Core Key Competencies.

R. Josephs is a member of the CCQM Bioanalysis and Organic Analysis Working Groups.

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

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

S. Maniguet is a member of the CCQM Organic Analysis Working Group and Key Comparison Working Group.

6.7 Activities related to external organizations

R.I. Wielgosz is a BIPM representative to the 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 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.

6.8 Travel

R.I. Wielgosz to:

- Novo Nordisk, Copenhagen (Denmark), 7–8 October 2010;
- NIST, Gaithersburg (USA), 26–27 October 2010, to attend the AACC Harmonization meeting;
- Singapore (Singapore), 1–5 November 2010, to attend the 24th CCQM Gas Analysis Working Group meeting;
- Helsinki (Finland), 3–4, February 2011, to attend the EURAMET Metchem Plenary Session;
- Warsaw (Poland), 20 May 2011, for a presentation at the GUM on World Metrology Day;
- Teddington (UK), 7–8 June 2011, to participate in the NMS Chem/Bio-metrology advisory working group;
- Atlanta (USA), 23 July 2011, to attend and chair the JCTLM Working Groups Meeting;
- San Juan (Puerto Rico), 31 July to 1 August 2011, to attend the IUPAC ICTNS meeting;
- Boulder (USA), 27–29 September 2011, to attend the 26th CCQM Gas Analysis Working Group meeting;
- Geneva (Switzerland), 25–26 October 2011, for a presentation and participation in the ISO Workshop on International Standards for Biotechnology.

J. Viallon to:

- Singapore (Singapore), 1–5 November 2010, to attend the 24th CCQM Gas Analysis Working Group meeting;
- Rotterdam (the Netherlands), 9–11 February 2011, to give a lecture on "Dynamic generation of formaldehyde standards by permeation tubes: performance evaluation using FTIR and Cavity-Ring Down Spectroscopy techniques" during the conference GAS 2011;
- NPL, Teddington (UK), 27 June 2011, to visit the gas metrology laboratories and discuss formaldehyde in nitrogen standards;
- Boulder (USA), 27-29 September 2011, to attend the 26th CCQM Gas Analysis Working Group meeting.

E. Flores to:

- Singapore (Singapore), 1–5 November 2010, to attend the 24th CCQM Gas Analysis Working Group meeting;
- Rotterdam (the Netherlands), 9–11 February 2011 to attend GAS 2011 Parallel session Metrology, accreditation and chemometrics and present the lecture: Accurate measurements of nitrogen dioxide and nitric acid mole fraction by FT-IR spectroscopy calibrated by gas standards and synthetic spectra;
- Boulder (USA), 27–29 September 2011, to attend the 26th CCQM Gas Analysis Working Group meeting.

S. Westwood to:

- Rockville, MD (USA), 13–14 September 2010 for the 10th International Reference Standard Symposium;

- Copenhagen (Denmark), 8 October 2010; to visit Novo-Nordisk;
- Singapore, 3–5 November 2010, for the CCQM-OAWG meeting;
- Barcelona (Spain), 9–11 December 2010, for a meeting of the WADA Laboratory Committee;
- Cologne (Germany), 15 February 2011, as an invited speaker at the Manfred Donike Workshop on Doping Analysis;
- Dresden (Germany), 19–22 February 2011, for the WADA Laboratory Directors Meeting and a WADA Laboratory Committee meeting;
- Montreal (Canada), 20–22 June 2011, for a WADA Laboratory Committee meeting;
- Delft (the Netherlands), 11–15 July 2011, for the 34th ISO-REMCO meeting;
- Sydney (Australia), 1–4 November 2011, for the CCQM-OAWG meeting;
- Brussels (Belgium), 8–9 November 2011, for an ISO-REMCO workshop.

R. Josephs to:

- United States Pharmacopoeia (USP), Rockville (USA), 13-14 September 2010, to attend the International Symposium on Pharmaceutical Reference Standards;
- NIST, Gaithersburg (USA), 15 September 2010, to discuss the Angiotensin project;
- Novo Nordisk, Copenhagen (Denmark), 7–8 October 2010, to give a presentation on the Organic Analysis Work programme for Larger Molecules;
- NMC, A*STAR/HSA, Singapore (Singapore), 1–5 November 2010, for the CCQM-OAWG/BAWG meetings;
- École Nationale Supérieure de Paris, Paris (France), 25 November 2010, for Orbitrap (Thermo) user meeting;
- CCMAS, IAM and Workshop, Budapest (Hungary), 4–9 March 2011, to represent the BIPM at the Inter-Agency Meeting, Codex Alimentarius CCMAS meetings and at the Joint AOCS/ BIPM/ ICC/ IUPAC/ NMKL Workshop on Methods for Food Identification and Authenticity – Characterizing the Unknown;
- CENAM, Querataro (Mexico), 3–6 October 2011, to give a presentation at the CCQM-BAWG meeting;
- British Mass Spectrometry Society, Dublin (Ireland), 8–9 November 2011, to present a poster at the Mass Spec Europe 2011 conference.

N. Stoppacher to:

- British Mass Spectrometry Society, Dublin (Ireland), 8–9 November 2011, to present a poster at the Mass Spec Europe 2011 conference.

S. Maniguet to:

Anaheim (USA), 23 July 2010, to attend the JCTLM Working Groups Meeting and AACC Meetings.

6.9 Visitors

- O. Fentanes (CENICA), 4–8 October 2010
- D. Heinkens (VSL), 29 November to 3 December 2010
- A. Rakowska and T. Chin Chye (NMC-A*Star), 13–16 December 2010
- P. Kolasiński (GUM), 5–9 September 2011
- M. Fröhlich and A. Wolf (EEA), 19–23 September 2011
- J. Walden and P. Kuronen (FMI), 7–8 November 2011
- O. Barosso (WADA), 25 November 2011

6.10 Guest workers

- P. Mitchell (NMIA), 1 July to 30 September 2011