Calibration campaign against the international prototype of the kilogram in anticipation of the redefinition of the kilogram part I: comparison of the international prototype with its official copies

Michael Stock, Pauline Barat, Richard S Davis, Alain Picard and Martin J T Milton

Bureau International des Poids et Mesures (BIPM), Pavillon de Breteuil, F-92312 Sèvres Cedex, France

E-mail: mstock@bipm.org

Received 22 January 2015, revised 11 February 2015
Accepted for publication 12 February 2015
Published 24 March 2015

Abstract
This report presents the results of the first phase of the campaign of calibration carried out with respect to the international prototype of the kilogram (IPK) in anticipation of the redefinition of the kilogram (Extraordinary Calibrations). The definition of the kilogram was realized according to the procedure outlined in the 8th Edition of the SI Brochure. Thus the IPK and its six official copies have been cleaned and washed following the BIPM procedure.

The mass comparisons carried out during this campaign showed a very good repeatability. The pooled standard deviation of repeated weighings of the prototypes was 0.4 µg. The effect of cleaning and washing of the IPK was to remove a mass of 16.8 µg. The effect of cleaning and washing of the six official copies was found to be very similar, giving an average mass removed from the seven prototypes of 15 µg with a standard deviation of 2 µg.

The differences in mass between the IPK and the official copies have changed by an average of 1 µg since the 3rd Periodic Verification of National Prototypes of the Kilogram (1988–1992). These results do not confirm the trend for the masses of the six official copies to diverge from the mass of the IPK that was observed during the 2nd and 3rd Periodic Verifications.

All BIPM working standards and the prototypes reserved for special use have been calibrated with respect to the IPK as part of this campaign. All of them were found to have lower masses than when they were calibrated during the 3rd Periodic Verification. As a consequence, the BIPM ‘as-maintained’ mass unit in 2014 has been found to be offset by 35 µg with respect to the IPK. This result will be analyzed in a further publication.

Keywords: kilogram, IPK, international prototype, mass unit, redefinition of the SI

(Some figures may appear in colour only in the online journal)
the ampere, the kelvin and the mole, will be redefined [1]. In the last two years, significant progress has been made towards establishing the necessary experimental link between the IPK and a fundamental or atomic constant [2].

The final step in the chain of traceability to the IPK can only be performed by the BIPM, which, under supervision of the International Committee for Weights and Measures (CIPM), is responsible for its maintenance and storage. The IPK was last used during the Third Periodic Verification (3rd PV) of National Prototypes of the Kilogram [3] which was carried out between 1988 and 1992. Since then the IPK and its six official copies have been stored in a safe and have not been used. Mass calibrations provided by the BIPM for the National Metrology Institutes (NMIs) are made using a set of working standards and two prototypes reserved for ‘special use’, all in Pt-Ir. At the end of the 3rd PV, the set of working standards consisted of the standards nos. 9, 31, 42, 63, 67, 77 and 650. Two other standards, nos. 25 and 73, were reserved for ‘special use’. These standards were calibrated with respect to the IPK in 1992, at the end of the 3rd PV. Two additional working standards, nos. 88 and 91, were added to the set later. Prototype no. 67 no longer belongs to the BIPM. Table 1 shows an overview of all standards mentioned in this article.

After the 3rd PV no direct link with the IPK has been possible and the working standards have been used to form the BIPM ‘as-maintained’ mass unit. The calibration uncertainty with respect to the IPK calculated at the end of the 3rd PV was 2.3 µg. Subsequently this has been increased to take into account the imperfect knowledge of mass changes of the working standards and was estimated to be 7 µg (Type B) in 2013.

In order to ensure continuity of the kilogram derived from its present definition to its future definition, the CCM has recommended that the traceability to the IPK should be established by a new calibration campaign [4]. This would link all recent and future determinations of the Planck constant \(h\), either by electro-mechanical means or through a determination of the Avogadro constant \(N_A\), which will contribute to the redefinition of the unit of mass. This programme requires that mass standards from those NMIs involved in such measurements be recalibrated as directly as possible at the BIPM against the IPK. This calibration campaign was given the name ‘Extraordinary Calibrations’. This distinguishes it from the ‘periodic verifications’ carried out from 1939 to 1946 and from 1988 to 1992 that included the re-calibration of prototypes held by the Member States.

### 2. Organization of the calibration campaign

The calibration campaign is planned to be carried out in two phases, the first of which is reported here. This first phase only involves BIPM mass standards. Its objectives are:

- to calibrate a set of eight BIPM working standards and two prototypes reserved for special use with respect to the IPK,
- to investigate the effects of cleaning and washing on the IPK, its six official copies and the two prototypes for special use,
- to select two reference standards (from the eight working standards) to be used in the second phase,
- to investigate the long-term effects of cleaning and washing on the IPK, the six official copies and the two prototypes reserved for special use over a period of several months, (as was done during the 3rd PV [3]).

| Standard | Role | Date of first use at the BIPM | Date of last cleaning and washing prior to this work |
|----------|------|-----------------------------|-----------------------------------------------------|
| IPK      | International prototype of the Kilogram (IPK) | 1889 | 1992 |
| 9        | Working standards | 1889 | 2003a |
| 31       | Working standards | 1889 | 2003 |
| 42       | Working standards | 1953 | 1976 |
| 63       | Working standards | 1974 | 1982 |
| 77       | Working standards | 1992 | 2004 |
| 88       | Working standards | 2004 | 2003 |
| 91       | Working standards | 2004 | 2004 |
| 650      | Working standards | 1979 | 2001 |

Note: All of these standards are made from Pt-Ir (90% to 10%). Further details on the history of these standards are given in [3].

*a The base of prototype no. 9 was cleaned in 2010 with a mixture of equal parts of ethanol and diethyl ether.

Note: All of these standards are made from Pt-Ir (90% to 10%). Further details on the history of these standards are given in [3].
The second phase of the calibration campaign will consist of a series of calibrations of mass standards from the NMIs with respect to the two reference standards selected in the work reported here. It will be reported in a future publication.

3. Measurement process

All mass comparisons were carried out with an M_one mass comparator (Mettler Toledo), equipped with a six-place mass exchanger and an airtight enclosure. All measurements were made in air. For each set of measurements, the positions of the masses were changed once, in order to determine and eliminate any possible influence due to the different positions on the mass exchanger. In November 2013 a thorough study of the influence of the mass handler position did not detect any significant effect.

In each weighing set all pairwise mass differences between the standards in the comparator were determined. In this way 15 mass differences were obtained between the six standards in every set. Each mass difference was obtained from an ABABABA measurement sequence. This sequence of determinations of the 15 mass differences was repeated once. Then the positions of the six standards on the mass exchanger were changed by one position and the above sequence was repeated. In this way a total of 60 mass differences were determined for each set of measurements.

Since there were more mass standards involved in this study than positions available in the mass exchanger, two BIPM working standards, nos. 650 and 91, were selected to be included in every weighing set. By this means all mass values included in the different weighing sets can be linked and compared. These standards did not undergo any cleaning-washing operation during the campaign reported here. (The last cleaning-washing operations for these working standards were in 2001 and 2004, respectively, see Table 1).

The mass stability of working standards nos. 650 and 91 during the calibration campaign was verified by a comparison with respect to working standards nos. 9 and 31 at the beginning of the campaign (December 2013), in July 2014, and at the end of the long-term recontamination study (November 2014). Standards nos. 9 and 31 were not used between these dates. With respect to nos. 9 and 31, the working standards nos. 650 and 91 were found to have changed by 0.4 µg and 0.5 µg, respectively, during the period from December 2013 to July 2014. The application of a correction corresponding to this drift would only have a negligible effect on the results of the calibration campaign. The reference standards have therefore been assumed to be stable during this period. Between July 2014 and November 2014, nos. 650 and 91 have changed with respect to nos. 9 and 31 by 1.4 µg and 0.8 µg, respectively. The results of the long-term study have been corrected for these drifts.

The numerical results presented in the following sections have been obtained from a least-squares adjustment. This uses as input data the mass differences from all weighing sets (in total 840 equations) and determines the set of masses which minimizes the sum of the squared differences between the calculated and the experimental mass differences. Since the linear equations are not all independent (the matrix is not of full rank) an additional constraint is needed to define a unique solution to the problem. The constraint used to calculate the absolute mass values from the measured mass differences is that the mass of the IPK after the second cleaning and washing is 1 kg exactly. The reference masses nos. 650 and 91 are assumed to be stable, as explained above. The same mass standard before and after a cleaning and washing operation is treated mathematically as two different standards, with two different masses. This allows the mass loss due to cleaning and washing to be determined.

Between 11 December and 27 December 2013 five preliminary sets of measurements involving the IPK, the six official copies (nos. K1, 7, 8(41), 32, 43 and 47) and the two prototypes for special use (nos. 25 and 73) were carried out, to give an initial set of mass values and to determine the repeatability of the measurements. As described above, working standards nos. 650 and 91 were included in each weighing set to link the results. All prototypes have been measured two or three times. None of the prototypes had been cleaned or washed at this stage. The mass values of all prototypes were determined with respect to the working standards nos. 650 and 91, in terms of the BIPM ‘as-maintained’ mass unit. The pooled standard deviation for the whole data set is 0.4 µg.

4. Cleaning and washing of the IPK, its six official copies and prototypes nos. 25 and 73

Prior to the work reported here, the last cleaning-washing operation on the IPK and its official copies was performed in 1992, towards the end of the 3rd PV. Prototypes nos. 25 and 73 were cleaned and washed for the last time in 2008 (see Table 1).

In this campaign, the prototypes were cleaned and washed at different times in three groups as indicated in Tables 2 to 4. The cleaning and washing was performed according to the BIPM procedure, which consists of a solvent cleaning and steam washing [5]. The standards in the first group were each cleaned and washed three times; all others were cleaned...
IPK and the six official copies is a mass loss of 15 consistent. On average, the effect of cleaning and washing on the results for the IPK and its six official copies are very consistent when cleaning and washing all prototypes. We note that operation alone cannot always be predicted with accuracy. Sufficient to clean a prototype, although the effect of the first operations and not an intrinsic property of the prototype. This is related to the reproducibility of the cleaning-washing operation, as for example for nos. 25 and 73. We believe that this washing operation to the total mass loss varies between prototypes, as for example for nos. 25 and 73. For the IPK and its six official copies the previous cleaning and washing had been in 1992, for nos. 25 and 73 in 2008.

The mass lost in each cleaning and washing reduces in successive operations. The third operation has no significant effect which confirms previous observations at the BIPM that two cleaning-washing operations are sufficient. The total effect was a mass reduction of 15 µg for official copy no. 7 and of 13 µg for official copy no. 32.

Table 3 shows the results of cleaning and washing of the prototypes of the second group, which included the four remaining official copies.

As for the first group (table 2), the reduction in mass during the second cleaning-washing operation is much smaller than during the first operation. The total is very similar to that observed for the first group.

Table 4 shows the results of cleaning and washing on the three remaining prototypes, including the IPK.

The relative contribution of each individual cleaning-washing operation to the total mass loss varies between prototypes, as for example for nos. 25 and 73. We believe that this is related to the reproducibility of the cleaning-washing operations and not an intrinsic property of the prototype. According to our observations, two cleaning-washing operations are sufficient to clean a prototype, although the effect of the first operation alone cannot always be predicted with accuracy.

Table 5 and figure 1 summarize all the mass changes measured when cleaning and washing all prototypes. We note that the results for the IPK and its six official copies are very consistent. On average, the effect of cleaning and washing on the IPK and the six official copies is a mass loss of 15 µg.

We can use these results to estimate the rate at which these standards have accumulated contamination. Under the assumption that the accumulation of contamination has been linear over the 22 years since the last cleaning and washing, they correspond to contamination rates in the range 0.6–0.8 µg yr⁻¹. For comparison, the range of contamination rates observed at the 3rd PV was 0.6 µg yr⁻¹ to 1.3 µg yr⁻¹ for the official copies and 1.5 µg yr⁻¹ for the IPK. It should be pointed out that the IPK which showed the largest contamination at that time, was the only prototype that had not been cleaned and washed since the previous PV in 1946.

The range of contamination rates observed here is somewhat less than the typical contamination rate observed for national prototypes of 1 µg yr⁻¹. This value was observed during the 3rd PV [3] and is typical of the value observed by NMIIs. This might be explained by the fact that, contrary to most national prototypes, the IPK and its official copies are stored in a very stable environment and only used very rarely. If we take into account that the initial recontamination during the first months after cleaning and washing occurs at a faster rate (0.037 µg d⁻¹) over 120 d was reported from the 3rd...
Periodic Verification), the long-term contamination rate of the IPK and its copies becomes even smaller.

The working standards reserved for special use, nos. 25 and 73, show a significantly higher contamination rate (their last cleaning and washing was in 2008) than the IPK and its official copies. This is not surprising because contrary to the latter, they have been used in the laboratory since the last cleaning and washing.

There is no explanation available for the differences in mass change after cleaning and washing between the IPK and its official copies, or between nos. 25 and 73. These might depend on the detailed unpredictable interactions between each prototype and its environment and are not necessarily a property of the prototype itself.

5. Results of mass comparisons of the six official copies and prototypes nos. 25 and 73 with respect to the IPK

The different weighing sets including the IPK and the six official copies, after cleaning and washing, all included the BIPM working standards nos. 650 and 91, as described in section 3. This allows the weighing sets to be linked and to derive the masses of the six official copies with respect to the IPK. The results are given in table 6. The mass values of the prototypes obtained during the 3rd PV [3] are shown in the second column. The third column gives the masses of the prototypes with respect to the IPK, obtained during the present campaign. All masses are shown as deviations from 1 kg. The fourth column shows the mass changes between the 3rd PV and the present campaign.

The IPK (year) is the mass of a prototype determined with respect to the IPK in the indicated year. The BIPM ‘as-maintained’ mass unit were 35 µg higher than those based on the IPK. This is a consequence of the working standards being found to have lower masses than when they were calibrated during the 3rd Periodic Verification (e.g. nos. 25 and 73 in table 6). The results of the recalibration of the working standards and their change of mass will be examined in detail in a further publication.

With respect to the IPK the official copies have changed on average by only 1 µg since the 3rd PV. This result differs from the observation made at the 2nd and 3rd PVs, that many of the official copies had increased in mass with respect to the IPK (figure 2). A drift rate of 50 µg/century would have led to a relative drift of the official copies with respect to the

![Figure 1. Mass losses of the IPK and its six official copies after cleaning and washing.](image)

| Prototype | $m_{IPK}(1991)/mg$ | $m_{IPK}(2014)/mg$ | $m_{IPK}(2014) - m_{IPK}(1991)/mg$ |
|-----------|--------------------|--------------------|----------------------------------|
| IPK       | 0                  | 0                  | 0                                |
| K1        | 0.135              | 0.134              | −0.001                           |
| 7         | −0.481             | −0.478             | 0.003                            |
| 8(41)     | 0.321              | 0.321              | 0.000                            |
| 32        | 0.139              | 0.133              | −0.006                           |
| 43        | 0.330              | 0.330              | 0.000                            |
| 47        | 0.403              | 0.401              | −0.002                           |
| 25        | 0.158              | 0.140              | −0.018                           |
| 73        | 0.428              | 0.395              | −0.033                           |

Note: The second column shows the masses of the prototypes obtained during the 3rd PV. The third column gives the masses of the prototypes with respect to the IPK, obtained during the present campaign. All masses are shown as deviations from 1 kg. The fourth column shows the mass changes between the 3rd PV and the present campaign. The mean mass change is $-0.001$ µg with a standard deviation of 0.003 µg.
IPK of 10µg since 1991, which was not observed. The data presented here suggest that the IPK and the six official copies have behaved over the period since the 3rd PV as a consistent set of mass standards.

In November 2014 the prototype no. 34 of the French Academy of Sciences was compared with working standards nos. 91 and 650. This prototype had participated in the 3rd PV and had since then been stored at the Academy in Paris, without being used. The total mass removed during two cleaning and washing operations from no. 34 was 19.6 µg. After cleaning and washing, its mass with respect to the IPK has been found 1 µg lower than its mass observed during the 3rd PV. This result suggests that the different storage environments of the IPK and of no. 34 have had no significant influence on their mass difference.

In contrast, the prototypes reserved for special use (nos. 25 and 73) are found at lower mass values than at the end of the 3rd PV. The mass loss is 18µg for no. 25 and 33µg for no. 73.

The uncertainty of the results presented in table 6 is estimated to be 3 µg. It is dominated by the contribution related to the choice of the reference for mass stability (2 µg) and the statistical uncertainty of the general least squares fit (0.7 µg).

6. Study of the initial mass increase after cleaning and washing

The cleaning and washing of the IPK and its official copies and the mass comparisons to determine the masses of the official copies with respect to the IPK were finished by the end of February 2014. This was followed by a study of the mass increase of the prototypes after cleaning and washing over a period of about 10 months. A similar study was done during the 3rd PV.

The results are shown in figure 3. Working standards nos. 650 and 91 were again used as references for mass stability. The measurements on the IPK were limited, in order...
to minimize the risk of subjecting it to mechanical wear. All prototypes show an initial rapid increase of mass, which then decreases. The initial slope for the first 70d is in a range from 0.01\( \mu \text{g d}^{-1} \) (for no. 32) to 0.03\( \mu \text{g d}^{-1} \) (for nos. 7, 43 and 47). A significant spread of the mass increases was also observed at the 3rd PV [3]. The initial slope for the IPK is 0.02\( \mu \text{g d}^{-1} \), which is about half the value of 0.037\( \mu \text{g d}^{-1} \) observed at the 3rd PV. Only two prototypes show a significant mass increase after 70d: K1 and no. 7.

7. Summary and conclusions

During phase 1 of the Extraordinary Calibrations the IPK and its six official copies have been cleaned and washed and their masses have been compared. BIPM working standards and the prototypes for special use have been recalibrated with respect to the IPK.

In summary, we report that:

- The repeatability of weighings of the prototypes is typically below 0.5\( \mu \text{g} \).
- The IPK and its six official copies have behaved in a consistent way during cleaning and washing: the change of mass was on average −15\( \mu \text{g} \), with a standard deviation of 2\( \mu \text{g} \).
- The masses of the six official copies have changed on average by only −1\( \mu \text{g} \) (with standard deviation of 3\( \mu \text{g} \)) with respect to the IPK since the 3rd Periodic Verification (1988–1992).
- Previous studies have observed a long-term trend of increasing mass of the official copies with respect to the IPK. This trend is not consistent with our results. The official copies and the IPK have behaved over the last two decades as a consistent set of mass standards.
- The slopes of initial mass gain after cleaning and washing are in general smaller than those observed during the 3rd PV. For example, the slope of mass gain for the IPK was 0.02\( \mu \text{g d}^{-1} \), although the official copies showed a significant spread of slopes.

These observations lead us to conclude that the IPK and its six official copies have behaved as a consistent set. The divergence in their masses observed at the time of the 3rd PV has not been repeated. However, comparison of the IPK versus the BIPM working standards shows that they have lost mass since the 3rd PV. Consequently, the BIPM ‘as-maintained’ mass unit in 2014 is offset from the IPK by 35\( \mu \text{g} \). This will be the subject of a more detailed report.

References

[1] Resolution 1 of the CGPM 2011 On the possible future revision of the International System of Units, the SI (www.bipm.org/en/CGPM/db/24/1/)
[2] Milton M J T, Davis R and Fletcher N 2014 Towards a new SI: a review of progress made since 2011 Metrologia 51 R21–30
[3] Girard G 1994 The third periodic verification of national prototypes of the kilogram (1988–1992) Metrologia 31 317–36
[4] Recommendation CCM G1 2010 Considerations on a new definition of the kilogram (www.bipm.org/utils/common/pdf/CC/CCM/CCM12.pdf)
[5] Girard G 1990 The washing and cleaning of kilogram prototypes at the BIPM BIPM Monographie 1990/1 (www.bipm.org/utils/en/pdf/Monographic1990-1-EN.pdf)