

The SI unit of mass

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Abstract

The present definition of the unit of mass in the International System (SI) is based on the international prototype of the kilogram, an artefact dating back to the 1880s. At present there is considerable effort worldwide aimed at replacing this artefact definition by one based on physical constants. This paper gives a brief history of the SI unit and how it is currently realized. The focus is on historical information, often forgotten, which has current relevance.

1. Introduction

It is well known that the kilogram is the last of the base units of the International System (SI) to be defined by an artefact [1]: ‘The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram’. Three other base units are affected by this definition: the ampere, whose definition refers to the newton; the mole, whose definition refers to 0.012 kg of carbon-12 and the candela, whose definition refers to the watt.

The international prototype, designated as \mathfrak{K} , was officially sanctioned in 1889. Its form is a cylinder with diameter and height roughly 39 mm (figure 1), made of an alloy of 90% platinum and 10% iridium by mass. Stored at the Bureau International des Poids et Mesures (BIPM), it is accessible only with the permission of the International

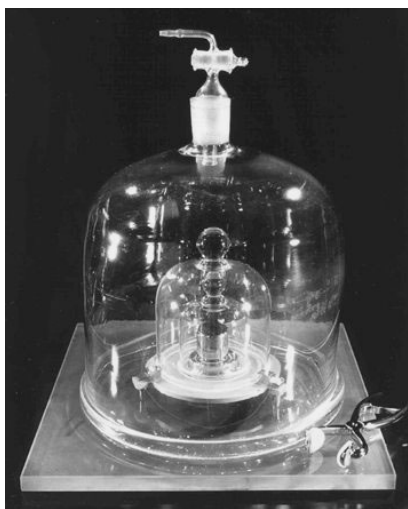


Figure 1. Facsimile of the international prototype under three glass bells. The facsimile is made of Pt/Ir.

Committee for Weights and Measures (CIPM). The unit of mass is disseminated throughout the world by comparisons with \mathfrak{K} , made indirectly through a hierarchical system. The first echelon of these comparisons is normally with a subset of the ‘official copies’ of \mathfrak{K} , followed by calibrations of additional copies known as the ‘national prototypes’. In this way, each nation state can ensure that the mass of its prototype and all measurements that derive from it are traceable to \mathfrak{K} . As we shall see, the need for strict ‘traceability’ to the base units was of primary importance in 1889, even if the word is of more recent coinage. In the vocabulary of the *GUM* [2], we might say that Type A uncertainties were well understood and carefully calculated but that Type B uncertainties were generally omitted from uncertainty budgets.

Other base units of the SI were once defined through artefacts but these have been replaced by definitions based on the fundamental physical constants [1, 3]. Compared to the alternatives, the fundamental physical constants have the obvious advantages of stability and universality. It is not surprising that non-artefact routes to the kilogram are under active investigation [4–6]. While much interest is justifiably focused on these investigations, it is useful to understand the present unit of mass that has served us for well over a century and continues to serve us today.

The purpose of this review is to outline the present system for realizing the unit of mass and to place the issues confronting us today in historical context.

2. \mathfrak{K} , its official copies and the national prototypes

The Metre Convention was signed in 1875, creating the BIPM and giving to it the task of providing member states with standards of mass and length. For the sake of continuity, the mass of the new kilogram was to be consistent with the mass of the so-called *Kilogramme des Archives* [7]. The latter, a cylinder of platinum, was fabricated at the close of

the 18th century and supposedly represented the mass of one litre of water at its maximum density. The BIPM was further charged with conserving the new international prototype of the kilogram as well as with organizing periodic comparisons and verifications of the national and international prototypes.

A basic consideration in 1875 was the choice of material for both the kilogram and metre artefacts. The old platinum standards had been forged from platinum sponge. Advice was taken from the French Section of the *Commission Internationale du Mètre* (CIM), which had been created in 1867 and which was dissolved following the adoption of the Metre Convention. By 1875, Sainte-Claire Deville and Debray had succeeded in melting a mixture of platinum and iridium to form an alloy that was harder than pure platinum but retained its other desirable qualities (resistance to corrosion, high density, good electrical and thermal conductivities, low magnetic susceptibility). In an early example of technology transfer, the Johnson–Matthey company succeeded in reproducing Sainte-Claire Deville’s process on an industrial scale [8]. One need only read the description given in [8] of the multiple chemical operations required to purify iridium to appreciate how formidable this task was. The resulting ingot was forged and sent to the mint in Paris for further compression. After machining, the final finish was produced by polishing with emery.

The first three prototypes were made from a preliminary batch of material provided by Johnson–Matthey. In 1880, these artefacts were referred to as KI, KII and KIII. As a first step, they were compared at the Paris Observatory with the *Kilogramme des Archives*. A report of these measurements may be found in [9], where the *Kilogramme des Archives* is given the symbol *A*. Since the density of *A* is almost 5% less than that of the ‘new’ Pt/Ir prototypes, a buoyancy correction of about 2.7 mg was applied. By a curious omission, the volume of *A* had not been determined by hydrostatic weighing at any point during its manufacture. Therefore, the volume was inferred from a combination of dimensional and ‘stereometer’ measurements made in about 1850 [10]. When the correction for air buoyancy was applied, it was noted that the masses of KIII and *A* were identical. For this reason, KIII was chosen as the international prototype of the kilogram. The CIPM formally adopted this decision in 1883. Unlike all other prototypes, \mathfrak{K} has no mark engraved on its surface.

(It is ironic that such great effort was expended to ensure that \mathfrak{K} and *A* had identical mass, for it was later discovered that the mass of *A* diminishes with time. In 1939, measurements at the BIPM indicated that *A* had lost some 0.43 mg during the preceding 58 years. This loss rate is qualitatively similar to that observed for several other platinum standards of similar manufacture to *A* [11, 12] and begs the question of how much the mass of *A* had already changed between 1799 and 1880.)

A second order was placed with Johnson–Matthey, this time for 40 cylinders from which to manufacture what were to become the national prototypes and additional official copies (*témoins*). The density of each prototype was determined by hydrostatic weighing, as discussed below, and then each artefact was adjusted to a tolerance of ± 1 mg with respect to the international prototype. A tighter manufacturing tolerance had been considered but was ultimately rejected as impractical. The 40 prototypes were numbered consecutively and each was

lightly engraved on the side with its number¹. About 30 of these were selected by lot in 1889 and distributed to member countries of the Metre Convention.

The international prototype was stored at the BIPM along with two official copies. Over the years, one official copy was replaced and four have been added. Access to \mathfrak{K} and its official copies is under the strict supervision of the CIPM. Three keys are required to enter the storage vault: one of these is kept by the Director of the BIPM, one is in the possession of the President of the CIPM and the third is held by the Archives de France. In 1889, the BIPM was allocated two prototypes for use as working standards. This number has also increased over the years. Among the present set of BIPM prototypes and other standards is prototype No 25, which is reserved for exceptional use.

Figure 1 shows the international prototype under three glass bells, the largest of which has a valve at the top and a base that reposes on a glass flat. The official copies have only two bells (figures 2 and 3). In fact, the third bell was used to subject \mathfrak{K} to a partial vacuum when the international prototype was first stored in the vault [13]. It was later supposed that equilibrium with the ambient air was re-established rather quickly [11]. In any case, the attempt at vacuum storage was never repeated and the valve is now left in the open position.

Calibration certificates for the first 40 prototypes report the mass measured with respect to \mathfrak{K} and give a ‘probable error’ of 0.002 mg. The calculation is given in [14]. Since probable error is the standard uncertainty multiplied by 0.6745, this represents a Type A standard uncertainty of 0.003 mg. Measurements were made using three different balances, each of which has a standard deviation of roughly 0.006 mg for a single comparison weighing [14].

2.1. Volume determinations

Also listed on the certificate are the volume and density of the prototype at 0 °C (determined by hydrostatic weighing), the probable error of the volume, the mean temperature of the hydrostatic bath and the volumetric thermal expansion in two different temperature scales, including the *Echelle Normale* [15]. An additional datum is the mass of the ingot at the time of hydrostatic weighing, which in all cases was within a gram of the final adjustment.

It is reasonable to suppose that two surprises during the density determination of KIII influenced subsequent work. Was the density of the ingot homogeneous? The density of KIII was determined early in its adjustment, when the ingot had a mass of about 1147 g. The ingot was then machined and polished to its final mass, its volume at 0 °C being calculated on the assumption that the density was unchanged by the removal of material. A majority of those overseeing this work thought it prudent to confirm the assumption and so the density of KIII was redetermined after final adjustment, despite the risk involved. The new measurements revealed a relative increase in density of ‘only’ 1.25×10^{-4} [16] but, in fact, this finding must have been extremely vexing and may explain why the density of the succeeding 40 prototypes was determined when

¹ There is one exception. Prototype No 8 was mistakenly engraved ‘41’. It is now referred to as prototype No 8(41) and remains at the BIPM as an official copy of the international prototype.



Figure 2. The international prototype of the kilogram and its six official copies. This safe was used until the end of the third periodic verification. The original international prototype of the metre is stored in the black tube on the upper shelf.



Figure 3. The international prototype and its six official copies in the safe used since the end of the third periodic verification.

the ingots were much closer to their final mass. Was the mass of KIII affected by the second hydrostatic weighing? In fact, the mass appeared to increase by some 0.040 mg. After various cleaning procedures failed to change this result, washing with vapours of ethanol and water finally returned the mass of KIII to its expected value. Not surprisingly, the same washing procedure was later adopted for the final calibration of the national prototypes [9, 17].

Determination of density by means of hydrostatic weighing relied on an accepted formula for the thermal expansion of distilled water [18]. It was, of course, further assumed that the maximum density of distilled water is exactly 1 kg l^{-1} , for the *Kilogramme des Archives* was supposed to represent the mass of 1 litre of water at its maximum density under atmospheric pressure. The accepted thermal expansion of water was checked by Thiesen at the BIPM and was found to be in error [19]. Nevertheless, the suspect formula was employed pending a definitive study of water density. The work of Chappuis and others finally established that the maximum density of doubly distilled tap-water used at the BIPM was $999.972 \text{ kg m}^{-3}$ [20]. It is both remarkable and satisfying to note that essentially the same value is found today, based on modern tables [21] for the density of Standard Mean Ocean Water and corrections for the isotopic abundances of BIPM tap water. The volumes at 0°C of all the early prototypes have now been corrected upwards² by 28×10^{-6} .

The thermal expansion of water found by Chappuis [22] and others [21] also disagrees significantly with the formula used to establish the volumes of the early prototypes. The relative magnitude of the error depends on the temperature of the hydrostatic bath, reaching 12×10^{-6} at 20°C (almost exactly what Thiesen had suspected). Since laboratories were not air conditioned, the bath temperatures had large seasonal differences [19]. The volumes of the first prototypes have never been corrected for this error, which may be substantial compared to the probable errors reported on the certificate. It should be noted, however, that a relative uncertainty of less than 18×10^{-6} of the volume is all that is required to make an air buoyancy correction accurate to 0.001 mg.

The remaining information on the certificate is the coefficient of volumetric thermal expansion for Pt/10%Ir. Here, one may take advantage of the fact that both the metre and kilogram prototypes were made of the same alloy. The

² Since 1964, the litre has been defined as 0.001 m^3 . It is recommended that the results of accurate volume measurements not be expressed in litres [1].

linear thermal expansion coefficient is an essential parameter when using the metre prototypes and its cube is assumed to be the coefficient of volumetric thermal expansion. In an extensive study of the linear thermal expansion of prototypes of the metre, Péard documents the variability among samples of Pt/10%Ir and recommends a best value for the linear coefficient [23]. The uncertainty is small and has no consequences for mass metrology. In terms of temperatures defined by the ITS-90 [15], the volumetric thermal expansion α for all prototypes and other standards made of Pt/10%Ir is taken to be

$$\alpha/(10^{-6} \text{ } ^\circ\text{C}^{-1}) = 25.869 + 0.005\,65t,$$

where t is the temperature in $^\circ\text{C}$. When this coefficient is used to correct the volume of a prototype from 0°C to 20°C , the result differs by a negligible 2×10^{-7} from the value derived from the estimated expansion coefficient given in the initial certificates.

2.2. Additional investigations

2.2.1. Partial vacuum. The Bunge balance of the BIPM was used in the calibration of the first prototypes. An unusual feature of this balance was its ability to operate under reduced pressure (of the order of 10 kPa). Indeed, the CIM had envisaged that all prototypes would be calibrated in vacuum as well as in air; however, this idea was abandoned as impractical. Nevertheless, the difference in mass between two prototypes was measured both in air and in vacuum with no significant discrepancies. However, the dispersion in the measurements is relatively large [14].

2.2.2. Transport. In a second test, a prototype was packed in its travelling container and taken to Marseille and back with negligible consequences to its mass. Again, the measurement dispersion is considerable. We point out that the surfaces of the prototype were protected from the clamping mechanism by clean chamois leather only, whereas modern practice is to insert lens tissue between the leather and the surface of the prototype.

2.2.3. First periodic verification of national prototypes. Ten years after the distribution of the national prototypes, member states were invited to send their prototypes back to the BIPM to check on their stability. Measurements were carried out during various periods from 1899 to 1911 [11, 24], eventually involving 25 numbered prototypes, some not yet attributed, and including an official copy. The international prototype was not used. This was a true ‘verification’ because no new certificate was issued unless the mass value calculated at the end of the verification changed by more than 0.05 mg from the value certified in 1889. One of the national prototypes was found to be so badly damaged that its mass was no longer within the accepted tolerance of ± 1 mg. Of the remaining prototypes, only two had changed by as much as 0.05 mg. The standard used in these measurements was the average mass (from the 1889 certificates) of an ensemble of self-consistent prototypes. An interesting remark at the conclusion of the report [24] is that the final uncertainty is of the order of 0.01 mg and, therefore, changes of this magnitude are not significant.

In a history of the BIPM during its first 50 years, Maudet [25] remarks that some prototypes become scratched from use but that this does not seem to have a significant effect on their mass. In the same monograph, Guillaume extrapolates the results in hand to conclude that the kilogram definition will be stable to 1×10^{-8} for 10 000 years [26].

3. Second periodic verification of national prototypes

With the authorization of the CIPM, a comparison among \mathfrak{K} and its six official copies was begun in 1939. The 1939 study is notable for the first mention of a hypothesis that \mathfrak{K} may have lost some tens of micrograms since 1889. Although this study was interrupted by war, it was already clear that a method for cleaning the prototypes reproducibly would be essential in order to progress. Work during the war years resulted in the development of the BIPM method of cleaning and washing [27], which involves rubbing the artefact with a chamois soaked in solvent followed by steam washing.

The comparisons of \mathfrak{K} and its official copies were taken up again in 1946 and all prototypes were cleaned and washed. Unfortunately, the effect of cleaning/washing was not determined. Based on these comparisons, it is not as apparent that \mathfrak{K} has lost mass compared to the official copies, although the author says that this is still a possibility. He then poses the question as to whether the third bell jar and the initial storage under vacuum might be responsible for the mass of \mathfrak{K} evolving differently from the official copies.

When these comparisons were completed, the CIPM called for the second periodic verification. Although the word ‘verification’ is still used, this exercise resulted in new certificates being issued for each participating prototype. The invitation to participate was issued in 1947 and the measurements were completed in 1954. Additional national prototypes had been manufactured since the original 40 (see below) and these were included. Four of the prototypes that had been certified in 1889 seemed to have gained more than 0.03 mg, for no apparent reason. The author concludes by saying that the way mass standards are currently realized, as well as how they are used and stored, preclude any better agreement between measurements made at widely spaced intervals of time and, of necessity, by different observers [11]. The remark highlights virtually all the shortcomings of a mass unit based on an artefact. No uncertainty statement is included either in the certificates resulting from the second verification or in the written reports of this work.

4. Third verification of national prototypes

Work on the third verification began in 1988. The new verification was motivated in large part by the passage of time, the relative ease of overseas travel and, above all, the appearance of a new generation of mass comparators having a standard deviation of the order of 0.001 mg. It is not necessary to go into the many interesting details of the third verification because a full report has already been published in *Metrologia* [28]. It is, nevertheless, interesting to contrast this work with that described earlier.

First, the issue of cleaning and washing of prototypes was addressed in a more searching way than had been done previously. The effect of cleaning on all prototypes was measured for the first time. The availability of a high-precision mass comparator made it possible to carry out preliminary studies on the effects of cleaning/washing [28, 29]. It was thus seen that, for many if not most prototypes, the recontamination rate is about 0.001–0.002 mg per month for several months, followed by a contamination rate that is an order of magnitude less. Similarly, it was possible to study the effect of repeated cleaning/washing procedures on the same prototype. These studies show that the mass loss due to successive cleaning/washing operations becomes negligible after at most two such operations. This means that: (a) two cleaning/washing operations are sufficient (though perhaps not necessary); and (b) the BIPM method of cleaning/washing does not damage the prototype.

Based on these studies, the CIPM decided that the definition of the kilogram should be interpreted as referring to the mass of the international prototype just after cleaning and washing using the BIPM procedure and to deduce this mass by an extrapolation coefficient that had been recommended by the BIPM.

The CIPM had created the Consultative Committee for Mass and Related Quantities (CCM) in 1980 and now asked its Working Group on Mass Standards to consider the BIPM proposal that all prototypes participating in the third verification should themselves be cleaned and washed. The Working Group agreed to the proposal and the CIPM gave its assent. (Since all the prototypes in a comparison were cleaned and washed within a few days of each other, there would be no

significant corrections to make.) The BIPM was further asked to document its method of cleaning and washing, resulting in the publication of [29].

By the time of the third verification, computers were available for handling the analysis of large data sets, allowing various mathematical models to be considered. Certificates issued following the third verification gave the combined standard uncertainty ($k = 1$) for the mass of each national prototype as 0.0023 mg, with 12 degrees of freedom. The effect of cleaning and washing of each prototype was also noted in the certificate. It was a remarkable achievement.

In 1991, Quinn [30] briefly reviewed the inferences that could already be drawn from the third verification, focusing on the stability of the unit of mass as it is defined in the SI. Figure 8 from his review (also appearing as figure 5 in Girard's report [28]), has served as a spur to researchers working on linking the present artefact definition to physical constants. The same figure is reproduced here as figure 4. The graph shows changes as a function of time in the mass of the six official copies (K1 and Nos 7, 8(41), 32, 43 and 47) with respect to the mass of \mathfrak{K} . Prototype No 25 is also included in the graph because it is kept by the Mass Section of the BIPM and reserved for special use. For a given prototype i , each point on the graph is $m_{t,i} - m_{0,i}$ where $m_{t,i}$ is the mass of i found on date t and $m_{0,i}$ is the mass of i when initially calibrated. In keeping with the SI definition, $m_{t,\mathfrak{K}} = m_{0,\mathfrak{K}} \equiv 1$ kg. Recall that the six official copies and \mathfrak{K} are stored together so that stability during transport to and from the BIPM is not an issue (the period 1939–1945 being an exception [11]). Of the seven prototypes shown in the figure, the mass of six has increased with respect to \mathfrak{K} since their initial calibration, most by about 0.05 mg (5×10^{-8}) in

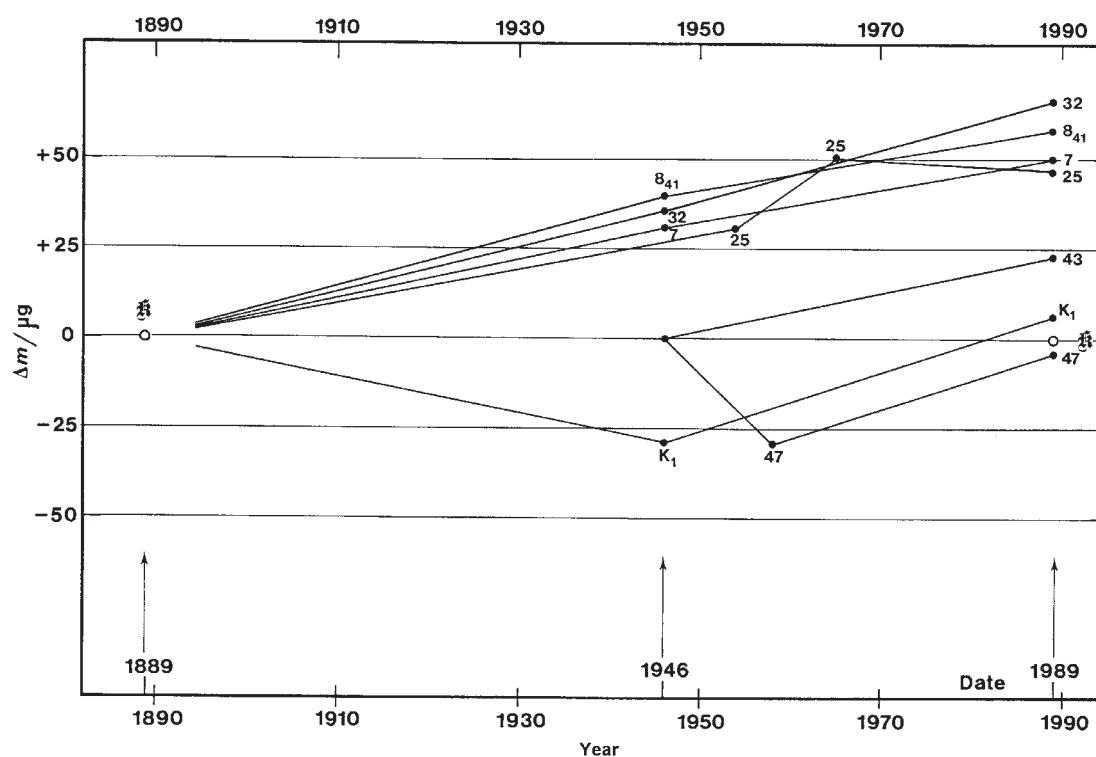


Figure 4. Relative changes in mass of the six official copies with respect to the mass of the international prototype.

100 years. Although there is a maximum of only three data points for each of the official copies, and each point save that of 1989 has a combined standard uncertainty that is difficult to assess, the trend is nevertheless suspicious. This trend is even more evident for remaining prototypes included in the third verification: the mass of 22 out of 27 of them appears to have increased since their initial calibration, a handful at rates that exceed those seen in figure 4 [28]. Of the five prototypes whose mass has decreased with respect to the mass of \mathcal{K} , two had obviously been damaged.

What are we to make of this trend? Because no plausible mechanism has been proposed to explain either a steady increase in mass of the official copies and national prototypes, or a decrease in mass of \mathcal{K} , one is left in doubt. In addition, the possibility that the entire ensemble of prototypes is drifting with respect to the physical constants cannot be excluded; but at least one can say that this effect has not yet been observed [31] (although published in 1989, the conclusion of [31] remains valid). Success in the watt balance or Avogadro experiments ultimately will decide this question and lead the way to a less problematic definition of the kilogram.

5. BIPM calibrations since the third verification

The BIPM continues to calibrate national prototypes upon request and to provide new prototypes (see section 6 and table 1). The balances used are servo-controlled and fully automated. They have a standard deviation of 0.001 mg or less and have been closely studied to minimize known sources of systematic error, principally thermal currents [32], scale non-linearity and adjustment of the automatic weight exchanging mechanism.

Among the calibrations that have been carried out, 18 are of prototypes that were included in the third verification. The present policy of the BIPM is to clean and wash each prototype only if requested to do so. Thus, only seven of the 18 were cleaned and washed as part of their calibration. The standards used are the working standards of the BIPM, the masses of which are traceable to prototype No 25, reserved for exceptional use. We assume that after cleaning and washing, the mass of prototype No 25 recovers the value assigned after the third verification. A check standard, prototype No 63, is also reserved for exceptional use [33, 34].

Table 1. 1 kg prototypes in platinum–iridium distributed since 1993.

78	Has belonged to CMS-ITRI (Chinese Taipei) since 1995 (PV ^a 1995, p 164)
79	Allocated to the United States of America in 1996 (PV 1996, p 171)
80	Allocated to Thailand in 1996 (PV 1996, p 171)
81	Has belonged to the National Physical Laboratory (United Kingdom) since 1997 (PV 1997, p 298)
82	Has belonged to the National Physical Laboratory (United Kingdom) since 1997 (PV 1997, p 298)
67	Allocated to the Czech Republic in 1999 (PV 1999, p 246). Previously this prototype had belonged to the BIPM
83	Allocated to Singapore in 2003 (PV 2003, to be published)
84	Allocated to the Republic of Korea in 2003 (PV 2003, to be published)

^a PV: Procès-Verbaux du Comité International des Poids et Mesures.

In analysing this data set, we find that, before cleaning and washing, the mass of the 18 prototypes had increased by a median rate of $1.9 \mu\text{g year}^{-1}$, but with significant dispersion about the median. For the seven prototypes that were cleaned and washed, the median value of their final mass is only $1 \mu\text{g}$ higher than that found in the third verification. Again, and significantly, there is considerable scatter about the median.

6. Additional prototypes

Additional prototypes were required following the distribution of the first 40 prototypes. The first two of these were made from material recovered from scrap. The material for prototypes Nos 43–50 was supplied by Lyon–Alemant, and Johnson–Matthey has furnished the material for all subsequent prototypes. As of today, the series extends to No 84, with four more in the final stages of calibration. The original lime furnace used by Johnson–Matthey to melt the alloy [8] was replaced by an induction furnace and then by electron-beam melting. The fabrication process used in the mid-20th century is described by Bonhoure [11]. Subsequently, single-point diamond turning was used, which replaced polishing [35]. In order to create a fine crystal structure, the ingot received from Johnson–Matthey was softened by heat and then extruded through a die at the National Physical Laboratory (Teddington). Most recently, new prototypes have been finished by polishing with diamond paste, and Pt/10%Ir ingots are now simply forged rather than extruded.

An annotated list of the prototypes distributed as of the end of the third periodic verification is given in appendix 4 of Girard's report [28]. This list is brought up to date in table 1. Table IV of [28] shows the chemical compositions for material obtained used to fabricate prototype Nos 62–80 and table V lists their densities at 0 °C. Two points are remarkable: (a) the densities of prototypes from the same ingot have a homogeneity that has not been equalled before or since; and (b) density variation between ingots is strongly correlated with iridium content. Although such correlation is expected, it is more usually obscured by other, unknown sources of density variability within and between the ingots.

A joint programme between the BIPM and the AIST/NMIJ (Japan) seeks to identify the process parameters that lead to a homogeneous alloy with optimized physical properties.

7. Other materials

The optimism expressed in the BIPM's semicentennial monograph [26] (see conclusion of section 2) is tempered by the next sentence, which introduces the possibility of manufacturing 1 kg prototypes from improved materials: either more stable or less costly. Subsequent work at the BIPM, through 1950, is summarized in [36]. Of course special alloys of stainless steel are now commonly used as secondary standards and in legal metrology [37]. Were the kilogram to be redefined in terms of a physical constant, a 20-year stability of secondary artefact standards would seem to be sufficient for the needs of mass metrology.

8. Conclusion

A brief history of the SI unit of mass has been presented. Particular attention has been paid to the way uncertainties have been handled (or ignored). An inescapable conclusion, already suspected in 1939 and confirmed in 1992, is that the mass of the national prototypes and official copies tends to increase over time with respect to the mass of the international prototype. The experience of all metrologists involved in these studies is that, even though the average or median behaviour of the prototypes is predictable (e.g. short-term and long-term recontamination rates after cleaning and washing), there is considerable dispersion about the average. It is also clear, nevertheless, that the combined standard uncertainty of 0.0023 mg for the calibration of all prototypes involved in the third verification is justified.

The present review confirms Quinn's suggestion [30] that a definition of the kilogram based on physical constants should be realized to a relative uncertainty of about 10^{-8} in order to remove doubts about the present artefact-based system.

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