

## Effects of Cleaning on the US Prototype Kilograms

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### Abstract

This paper discusses the stability of national prototype kilograms No. 4 and No. 20, belonging to the United States. Calibration history, changes in mass with respect to time, and effects on mass and surface profiles due to cleaning and washing are described.

### 1. Introduction

The definition of the unit of mass in the International System of Units (SI) simply states: “the unit of mass is the kilogram; it is equal to the mass of the international prototype of the kilogram.” The International Prototype of the Kilogram,  $\mathcal{K}$ , is stored in ambient air and is subject to contamination; therefore, its surface must be cleaned in order to restore its mass to a “perfect” kilogram, as per the definition. In 1989, the Comité International des Poids et Mesures (CIPM) recognized this problem and specified the conditions under which the definition applies.

According to this specification, the unit of mass is defined as the mass of  $\mathcal{K}$ , one kilogram, immediately after cleaning and washing using the method specified by the Bureau International des Poids et Mesures

(BIPM). Therefore, cleaning is inherent to the present realization of the unit of mass. \* However, owing to the nature of an artifact definition and the problems associated with it (such as contamination, wear, and damage), it is difficult to quantify the results of cleaning. The effect of cleaning on platinum-iridium prototype kilograms has been a topic of concern for mass metrologists and the subject of many studies for a long time [1]. This paper briefly describes the properties of the U.S. prototypes including their density, calibration history, and surface profiles before and after cleaning.

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\* To be precise, the CIPM recommendation was limited to the analysis of results of the third verification of national prototypes (1988-1992) and was not intended as a redefinition of the kilogram.

## 2. Density of the Pt-Ir Prototype Kilograms

The densities and volumes of prototypes No. 1 through No. 40 were reported at 0 °C in the original certificates. However, the uncertainty is not given for these numbers or for the thermal expansion of the prototypes, which is assumed to be the same for all. As air conditioning was not available in the 1880s, the hydrostatic determinations of volume were made at different temperatures for different prototypes. As reported on the certificate and in [2], the density of prototype No. 4 was determined at 9.8 °C and that of No. 20 at 17.9 °C. The certificates were issued in 1889 and, therefore, it is worth re-examining the uncertainty of the density measurements.

Hydrostatic measurements of the volume were reported in great detail by Thiesen [2]. The relative standard deviation of the volume measurements is  $9 \times 10^{-6}$  ( $0.4 \text{ mm}^3$ ) for No. 4 and  $3 \times 10^{-6}$  for No. 20. It was common practice at the time to report "probable error" instead of standard deviation. We have divided probable errors by 0.6745 in order to recover the corresponding standard deviation. In addition, we have used the raw data to correct what appears to be a small error in the reported uncertainty of the volume of No. 20. Thiesen's results are relative to the maximum density of water. The thermal expansion of water was taken from Broch's table [3]. Thiesen suspected that the tabulated thermal expansion of water was in error but he supplied sufficient information so that a recalculation could be

made, if necessary. He used a value for the coefficient of volumetric thermal expansion of Pt/10%Ir supplied to him by Broch.

The maximum density of de-aerated tap water at the BIPM was later taken to be  $999.972 \text{ kg/m}^3$  [4], essentially identical to the modern result. The volumes of all national prototypes have been based on an assumption of this value since the early 20th century. Additional work by Chappuis at the BIPM, using the same temperature scale as Thiesen, demonstrated that relative errors in the thermal expansion of water reach approximately  $12 \times 10^{-6}$  at 20 °C [5] (in excellent accord with Thiesen's early estimate). Errors in the thermal expansion were never corrected and so the reported volumes of the first 40 national prototypes may be biased low by as much as  $0.6 \text{ mm}^3$ . This error is essentially negligible for mass metrology and probably explains why corrections were never made.

The volumetric coefficient for the thermal expansion of Pt/10%Ir alloy was extensively studied [6] because the same alloy, from the same source, was used to fabricate prototypes of the meter. The value of the coefficient now used by the BIPM [7] is based on this work but is similar to the original estimate. The difference in old and new coefficients leads to a relative difference in inferred volume of less than  $2 \times 10^{-6}$  between 0 °C and 20 °C.

Year	K20	K4	Uncertainty	Cleaning State
1889	1 kg -0.039 mg	1 kg -0.075 mg	3 µg	cleaned, alcohol and water vapors
1937	1 kg -0.021 mg		<20 µg	cleaned, wiped with cloth
1948	1 kg -0.019 mg		Not available	as received
1984	1 kg -0.001 mg	1 kg - 0.075 mg	8 µg	as received
1984	1 kg - 0.022 mg	1 kg - 0.106 mg	8 µg	cleaned, BIPM method
1992	1 kg - 0.013 mg		2.3 µg	as received
1992	1 kg - 0.021 mg		2.3 µg	cleaned, BIPM method
1999	1 kg - 0.019 mg	1 kg -- 0.098 mg	4 µg	as received
1999	1 kg - 0.039 mg	1 kg - 0.116 mg	4 µg	cleaned, BIPM method

**Table 1.** Results of calibration of prototypes No. 20 and No. 4 by the BIPM.

We conclude that both the volumes at 0 °C and the coefficient of volumetric expansion of Pt/10%Ir alloy are sufficiently well known for the first 40 national prototypes to permit the effect of a change in air density of 1.2 kg/m<sup>3</sup> (going from air to vacuum) to be corrected to a standard uncertainty of less than 0.001 mg.

### 3. Calibration History and Mass Values

The US prototype kilograms No. 20 and No. 4 have been re-calibrated by the BIPM several times since the original calibration of 1889. Table 1 shows the results of these measurements; the uncertainties reported in this table correspond to a combined standard uncertainty ( $k=1$ ). Table 1 includes the pre-cleaning measurement results when available. For each calibration, direct comparisons were made with the BIPM working standards. The original calibration of 1889 as well as that of 1938 were done after cleaning using the methods specified in Table 1. For the 1948

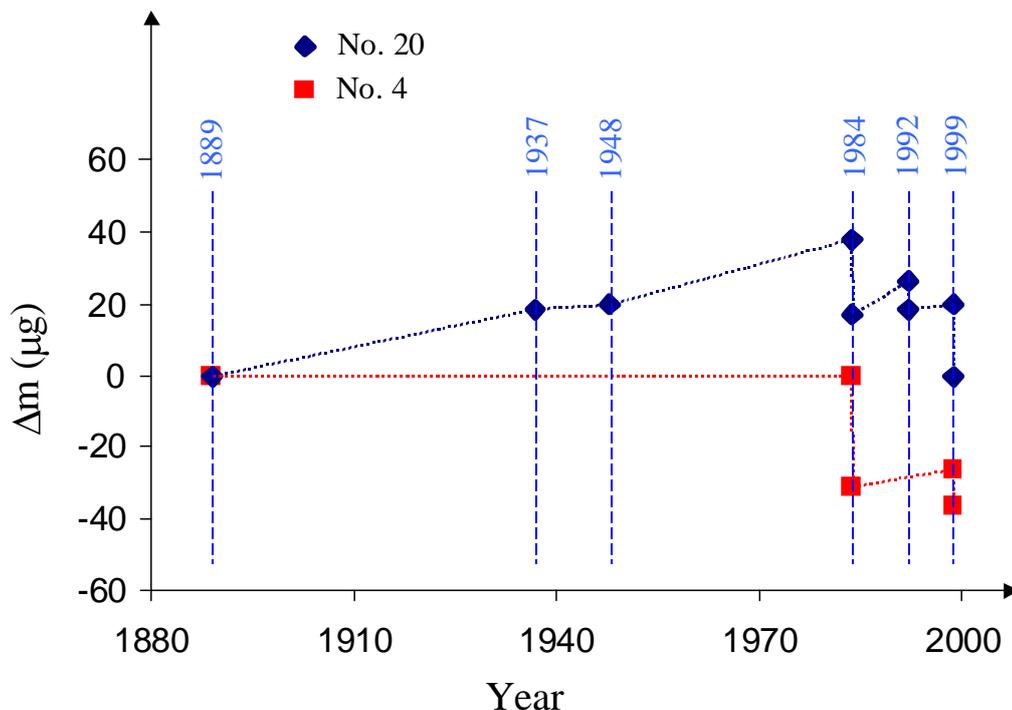
calibration, which took place during the course of the second verification of national prototypes, No. 20 was cleaned by ordinary wiping ("simple nettoyage par essuyage" [7]). The 1948 calibration certificate does not report an uncertainty. For the 1984, 1992 and 1999 calibrations, the mass was determined before and after cleaning, therefore allowing for a quantitative measure of the effects of cleaning on the mass of the prototypes; in all these cases, the BIPM method was used to clean the prototypes. No. 20 clearly exhibits a peculiar behavior with its 1999 mass being exactly that of 1889 while No. 4 lost 41 µg in the same period of time. However, while No. 20 actually shows a gain in mass relative to 1889 over the years, except for 1999, the losses since 1984 for both No. 20 and No. 4 are more consistent.

The mass of a prototype kilogram as given on the BIPM calibration certificate is only true at the time of calibration by the BIPM or subsequently after the prototype is cleaned

using the BIPM method. When the prototype is put in use, a correction must be applied. This correction is based on a model developed by the BIPM that predicts the gain in mass as a function of time after cleaning and washing using the BIPM method [8]. According to this model, a Pt-Ir kilogram gains 1.11  $\mu\text{g}/\text{month}$  for the first three months after cleaning followed by a decrease in the rate of gain in mass to 1  $\mu\text{g}/\text{year}$ . The combined standard uncertainty assigned by the BIPM to its own standards during the slow-growth regime is about 0.3  $\mu\text{g}$  per year for a maximum of five years (i.e. 1.5  $\mu\text{g}$  per 5 years). It is obvious from Figure 9 of [9], however, that the dispersion in this model is very large. This is true even for prototypes maintained at the BIPM. When this model was applied after cleaning of No. 20 at the NIST in 1995, it resulted in an after-cleaning correction of 7  $\mu\text{g}$

with a combined standard uncertainty of 1.2  $\mu\text{g}$  at the time of travel to the BIPM in 1999. However, the “as received” calibration by the BIPM revealed a mass of (1 kg – 0.019 mg) and therefore an after-cleaning correction of only 2  $\mu\text{g}$  that indicates a slower than predicted rate of mass gain.

Figure 1 gives a graphical history of the mass calibration of the US prototypes and the effects of cleaning on Pt-Ir mass standards. While pre- and post-cleaning data are only available for the 1984, 1992, and 1999 calibrations, it is interesting to point out that the resulting change in mass varied significantly between these three instances. As can be seen from the data presented in Figure 1, the loss in mass due to cleaning ranged between 8  $\mu\text{g}$  and 31  $\mu\text{g}$  with most measurements resulting in a mass loss of



**Figure 1.** Change in mass relative to the 1889 calibration. Data points on the same vertical line represent pre- and post-cleaning values where the largest value is the pre-cleaning mass.

approximately 20  $\mu\text{g}$ . It is worth noting that the US prototype kilograms have been kept in a clean room class 1000 environment since 1997 except for the time when No. 4 was temporarily moved to the microscopy laboratory to perform the studies mentioned below and during transportation to the BIPM for calibration.

#### 4. Surface Profiles before and after Cleaning

It is believed that kilograms No. 20 and

they were manufactured using the same method and alloy, and they were maintained and used under similar conditions. Therefore, it was assumed that the surface of No. 4 is a good representative of that of No. 20 as well as those of other prototypes manufactured at the same time. In addition, this assumption allowed us to spare No. 20, the official US national standard, from additional handling and therefore eliminated added risks of damage.

Using optical microscopy, the surface

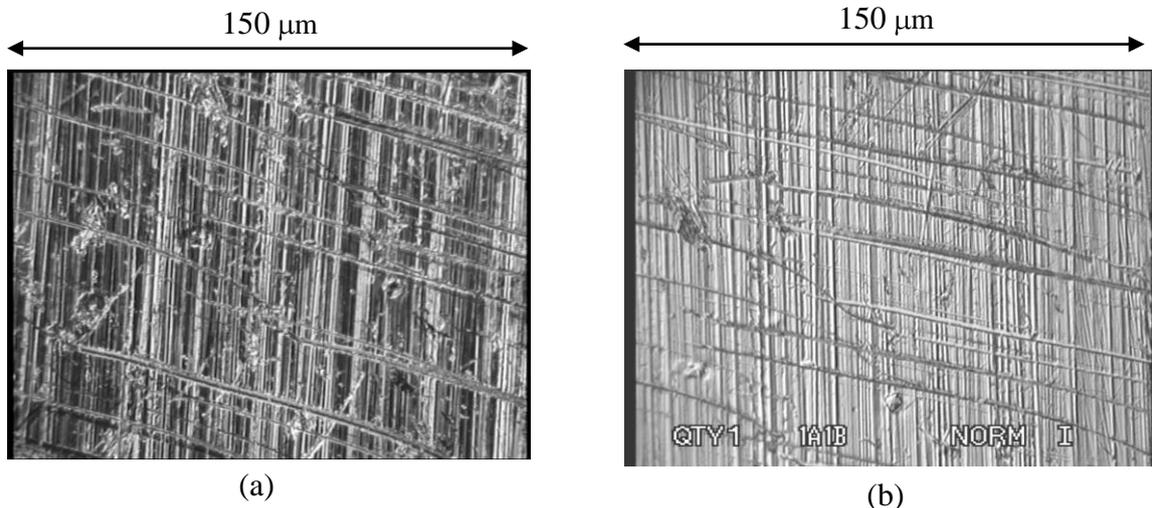


Fig. 2. Bottom surface of No. 4: (a) before cleaning; (b) after cleaning.

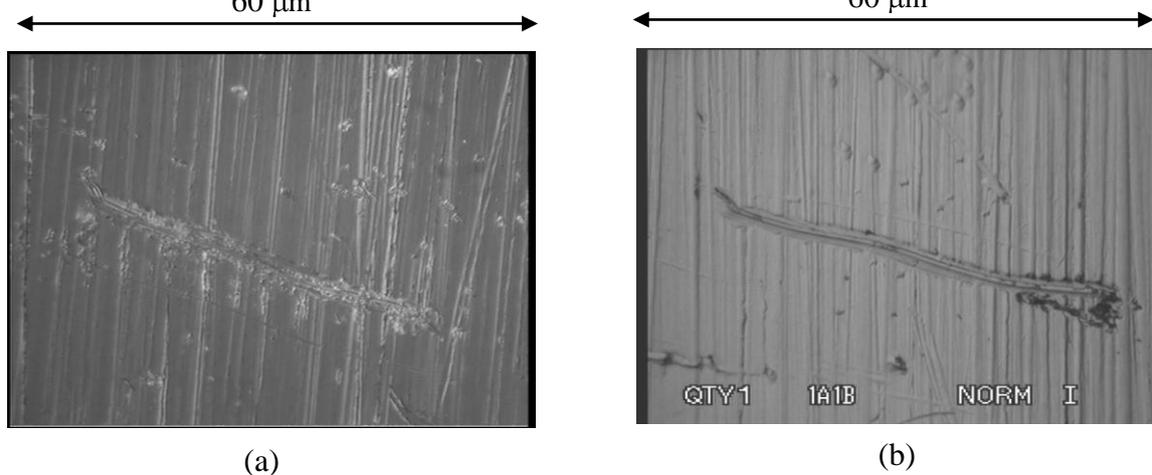


Fig. 3. Wear mark on bottom surface of No. 4: (a) before cleaning; (b) after cleaning.

No. 4 have similar surface characteristics since

profiles of prototype No. 4 were monitored

before and after cleaning and washing using the BIPM method in order to assess the qualitative effects of cleaning. Figures 2(a) and 2(b) show the surface profiles of the bottom surface of No. 4 before and after cleaning. Figures 3(a) and 3(b) illustrate the profile of one of the wear marks from each of the areas depicted in Fig. 2(a) and Fig. 2(b), respectively. It is clear from the pre-cleaning data that there is either a chipping of material around the wear marks or the wear marks had rough edges that caused contamination particles to adhere to them. Based on this study, it is not possible to identify clearly the nature of the structure found around the edges of the wear marks before cleaning. The post-cleaning profiles clearly show a change. The structure around the edges of the wear marks disappeared leaving a much cleaner-looking surface. It is interesting to point out that even with this drastic change in the surface profiles between the pre- and post-cleaning process, the mass only changed by 18 µg.

## 5. Conclusions

Until such time as the definition of the kilogram can be replaced by a definition based on fundamental constants, the problems of surface contamination of the national prototypes will remain of primary importance for mass metrology. This article has focused on the practical problems and considerations of realizing the present definition of mass in national laboratories.

## 6. References

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