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C. Goyon, R.S. Davis
BIPM

H. Bettin, H. Toth
PTB

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Pavillon de Breteuil, F-92312 SEVRES cedex

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C. Goyon, R.S. Davis
Bureau International des Poids et Mesures, F-92312 Sèvres cedex

H. Bettin, H. Toth
Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

Abstract

A comparison of density measurements made at the PTB and the BIPM was carried out in 2009. A 1.02 kg platinum-iridium cylinder was provided by the BIPM and used as a travelling standard. The cylinder was in the final phases of becoming a 1 kg national prototype. The results of the participants differ by only 5×10^{-6} relatively, which is small compared to the combined standard uncertainty. The BIPM relative combined standard uncertainty (k=1) is estimated to be 6.4×10^{-6} at 20 °C and 6.5×10^{-6} at 0 °C. The PTB relative combined standard uncertainty (k=1) is estimated to be 2.7×10^{-6} at 20 °C and 2.9×10^{-6} at 0 °C.

1. Introduction

A traditional role of the BIPM is to provide copies of the international prototype of the kilogram to Member States for use as national prototypes. Prototypes are made of an alloy, Pt/10%Ir. Their densities are determined by hydrostatic weighing during the manufacturing process. At the end of 2008, the PTB proposed a bilateral comparison with the BIPM in order to check that the measurements of this metrologically important parameter (the density of a 1 kg prototype of Pt/Ir) are equivalent.

2. Travelling standard

The travelling standard, with BIPM control code JM57, was cut from an ingot produced by Johnson-Matthey plc (United Kingdom) and delivered to the BIPM on the 18 September 2008. In January 2009, the BIPM workshop had produced the rough-cut stage of the normal manufacturing process for prototypes: a cylinder of height 39 mm, approximately equal to diameter, and a mass about 16 g in excess of 1 kg. The position of the centre of gravity is taken as half the height. The density is determined at a temperature t and is calculated at a reference temperature θ.

$$\rho(\theta) = \rho(t)(1 + \alpha_\theta (t - \theta)) \qquad (1)$$

where all temperatures are in °C, traceable to the ITS-90 scale.

Ever since the first 1 kg prototypes were allocated in 1889, the reference temperature for the density of these Pt/Ir artefacts has been taken to be 0 °C. The volumetric thermal expansion coefficient is inferred from linear expansion measurements of the same alloy performed at the BIPM during the first half of the 20th century [1], and subsequently corrected for changes to the contemporary temperature scale.
The volumetric thermal expansion coefficient (mean coefficient between 0 °C and t_{90}) is

$$\alpha_0 = (A_0 + B_0 \times (t_{90}\text{-}\theta_{90})) \times 10^{-6}\ °C^{-1}$$

where $A_0 = 25.869$,
$B_0 = 0.005\ 65\ °C^{-1}$,
$\theta_{90} = 0$ °C.
The subscript "90" refers to the temperature traceable to the ITS-90 scale.

If θ_{90} is taken to be 20 °C, this coefficient becomes

$$\alpha_{20} = (A_{20} + B_{20} \times (t_{90}\text{-}\theta_{90})) \times 10^{-6}\ °C^{-1}$$

where $A_{20} = 26.081$,
$B_{20} = 0.005\ 65\ °C^{-1}$,
$\theta_{90} = 20$ °C.

The range of linear expansion results reported in [1], including those derived by two independent methods from three different batches of alloy, leads to a range of mean volumetric coefficients of volumetric thermal expansion that is within $\pm 1 \times 10^{-7}\ °C^{-1}$ of the assumed value. The standard uncertainty ($k = 1$) is estimated to be $6 \times 10^{-8}\ °C^{-1}$.

Since BIPM and PTB both measure the density near 20 °C, the uncertainty of α can be neglected for the comparison of the measurement results.

The density of JM57 was determined at the BIPM in February 2009. It was carried by hand to the PTB on 3 March. The PTB determined its density in April 2009. The travelling standard was returned to the BIPM on 27 April.

3. BIPM density measurement

3.1. Hydrostatic weighing device

Density calibrations are made with doubly distilled tap water as the standard for which we assume that the maximum density at 4 °C is 999.972 $kg \cdot m^{-3}$. This is based on the CIPM-2001 formula [2] corrected for the isotopic abundance of BIPM doubly distilled tap water, and is, remarkably, the same density that was measured directly at the BIPM in 1907 [3]. The thermal expansion of doubly distilled water is calculated with the CIPM-2001 formula. Corrections for the compressibility of water and for air dissolved in the water have been considered [2].

The balance is a commercial electronic comparator (Mettler-Toledo AT1005) which has a capacity of 1.109 kg, an electronic scale of 109 g and a resolution of 10 µg [4]. Upper and lower horizontal mass exchangers are suspended from the weighing pan, and these can be controlled so that objects on any of four positions can be selected for weighing. The lower mass exchanger is submerged in the hydrostatic bath. The suspension wire at the air/water interface is made of Ni/Cr alloy with a diameter of 0.25 mm. It is treated to reduce the influence of surface tension using the method developed by the NBS (now NIST) [5].

The objects on the lower exchanger are completely immersed in a vessel that contains 18 dm^3 of liquid. A commercial thermo-regulated bath (Lauda RK 20KS) is used to circulate

water inside the double wall of the vessel in order to stabilize the temperature of the doubly distilled water during measurements. The temperature is set to the approximate ambient temperature of the laboratory.

Air temperature at the level of the upper mass exchanger and water temperature close to the unknown artefact are measured with two standard platinum resistance thermometers connected to a voltmeter (Hart Scientific model 1590) by means of a multiplexer from the same company (model 2590). The ratio of the thermometer resistance to an external, calibrated 100 Ω resistor is measured. Pressure is measured with a manometer (Paroscientific model 745-16B) and relative humidity with a capacitive transducer (Rotronic model BT-RS1).

3.2. Uncertainties

The uncertainty has been calculated in conformity with guidelines established in the *Guide to the Expression of Uncertainty in Measurement* [6].

Table 1 lists the major sources of uncertainty for the density measurement of Pt/Ir mass standards at 20 °C.

The reproducibility component comes from the comparison between the BIPM former hydrostatic weighing apparatus and this one for two mass standards in Pt/Ir. Measurements were carried out on the prototype n° 83 (code JM38) when its mass was 1 kg + 71 g in 1995 on the former apparatus and when its mass was 1 kg + 9.7 g in 2001 on the present apparatus. The second is mass standard n° 841 (code JM37). The density calibration was performed when its mass was 1 kg + 62.8 g in 1995 and when its mass was 1 kg + 0.2 g successively in 2002 and 2003. The relative difference between the two series in 2002 and 2003 is 3×10^{-6} the relative density difference with the present apparatus and the former one is 10^{-5}.

The relative combined standard uncertainty ($k = 1$) is estimated to be 6.4×10^{-6}. One can see that the largest component of this uncertainty is due to differences in results between our old apparatus (which no longer exists) and our new apparatus. We thus chose to be conservative in our uncertainty estimate. The present comparison with the PTB is therefore useful to assess the performance of our present apparatus.

Table 1. Major uncertainty sources of density determination of Pt/Ir mass standard at 20 °C at BIPM.

Uncertainty sources	Standard uncertainty	Relative standard uncertainty in density ($\times 10^{-6}$)
Type A		
Reproducibility	$5 \times 10^{-6} \times \rho$	5.0
Experimental standard deviation of the mean	$1 \times 10^{-6} \times \rho$	1.0
Repeatability weighing in water	30 µg	0.7
Repeatability weighing in air	30 µg	0.7
Type B		
Density of water		
Dissolved air	$50\% \times 2.5 \times 10^{-3}$ kg·m^{-3}	1.2
Isotopic composition	1×10^{-3} kg·m^{-3}	1.0
Temperature	4.2 mK	0.8
Formula	0.4×10^{-3} kg·m^{-3}	0.4
Balance nonlinearity	0.13 mg	2.8
Mass standard weighing in water	50 µg	1.1
Mass standard weighing in air	50 µg	1.1
Air density	1.8×10^{-4} kg·m^{-3}	0.2
Height dependence of gravitational acceleration	1×10^{-8} m^{-1}	0.1

3.3. Measurement

After its fabrication and before weighing, JM57 was first cleaned with a detergent. The artefact was then rubbed with a chamois-leather soaked with a mixture of 50% ethanol /50% diethyl ether. Finally, the artefact was cleaned for six hours in an ultrasonic bath filled with doubly distilled water.

The mass, 1015.874 12(6) g, was determined by comparison with a platinum-iridium mass standard in air, carried out on the upper mass exchanger of the hydrostatic device, before weighing in water.

The density of JM57 was determined by four series of weighings at a temperature of 19.5 °C between the 5 and 13 February 2009.

The mean of results leads to the values of:

density at 20 °C : 21 539.22 $kg \cdot m^{-3}$ with u_c (k = 1) = 0.14 $kg \cdot m^{-3}$

volume at 20 °C : 47.163 9 cm^3 with u_c (k = 1) = 0.000 3 cm^3.

With the thermal expansion coefficient of equation (1) the following values are calculated:

density at 0 °C : 21 550.41 $kg \cdot m^{-3}$ with u_c (k = 1) = 0.14 $kg \cdot m^{-3}$

volume at 0 °C : 47.139 4 cm^3 with u_c (k = 1) = 0.000 3 cm^3.

4. PTB density measurement

4.1. Hydrostatic weighing device

The hydrostatic weighing apparatus of the PTB WG 3.23 “Thermal State Behaviour and Density” is equipped with a 1200 g comparator balance (special AX1006 of Mettler-Toledo) that has an electronic range of 10 g and a resolution of 1 µg. A weight handler for up to four mass standards is integrated in the balance [7].

The sample is placed between two density standards in a vertical arrangement [8], thus reducing the movement of the bodies in the liquid during the measurements to a minimum. The liquid is pure pentadecane with a density of about 769 kg/m^3. Due to its low and stable surface tension no measurable meniscus error occurs, even without special treatment of the Pt/10%Ir wire (0.25 mm in diameter). The density standards, Si1PTB and Si2PTB, are used to determine the density of the liquid at the positions of the standards. The liquid density at the sample’s position is calculated by a linear interpolation and a correction due to a possible non-linear height dependence of the liquid temperature [7]. The temperature distribution is measured by thermistors and a digital multimeter Agilent 2001, while the absolute temperature near the sample is determined with a 25 Ω standard platinum resistance thermometer, a calibrated 25 Ω standard resistor and an ac resistance ratio bridge ASL F18.

The vessel with the pentadecane is placed in a water thermostat that is regulated to a temperature stability of about 20 µK [9].

In the measurement procedure, the empty suspension and the suspension with one of the standards or the sample are weighed subsequently by the balance. Mass standards (in air) are used to substitute the apparent weights. The air density in the balance is calculated from measured values of temperature, pressure and humidity using the CIPM-2007 formula [10]. The air temperature is measured using thermocouples, a nanovoltmeter (Keithley model 181) and a scanner (Keithley model 705). The air pressure is measured with a manometer (Druck DPI141) and the humidity with a capacitive transducer (Vaisala HMI37 / HMP 35B).

4.2. Uncertainties

Table 2 contains the main uncertainty contributions to the density determination of the Pt/Ir sample JM57 at 20 °C at PTB. Due to the small volume of the sample, the uncertainties of the density standards are not important. The largest contributions stem from the mass of the sample, the standard deviation of the measurements, the mass of the substitution weights, the air density and the height dependence of the gravitational acceleration. The contributions due to the volume determination of the substitution weights are negligible.

An additional uncertainty is due to the fact that a small difference in the balance reading may occur since the substitution weight is on the balance whereas the standards and samples are below and the weight forces do not act at the same position of the balance pan. This represents an off-centring error. A maximal error of 100 µg for a 1000 g weight is estimated.

Table 2: Main uncertainty contributions of the density determination of the Pt/Ir sample JM57 at 20 °C at PTB.

Uncertainty sources	Standard uncertainty	Relative standard uncertainty in density ($\times 10^{-6}$)
Type A		
Experimental standard deviation of the mean	$0.16 \times 10^{-6}\ \rho$	0.16
Type B		
Mass of Pt/Ir sample JM57	75 µg	2.00
Mass of density standard Si1PTB	21 µg	0.04
Mass of density standard Si2 PTB	21 µg	0.03
Volume of density standard Si1PTB	0.036 mm^3	0.05
Volume of density standard Si2PTB	0.036 mm^3	0.05
Height dependence of gravitational acceleration	$17 \times 10^{-9}\ m^{-1}$	0.51
Non-linearity of the liquid density	0.000020 kg/m^3	0.03
Mass of substitution weight T1 (700 g)	15 µg	0.05
Mass of substitution weight T2 (117 g)	6 µg	0.02
Mass of substitution weight T3 (20.2 g)	1 µg	0.03
Mass of substitution weight T4 (1000 g)	15 µg	0.41
Balance reading (empty suspension)	10 µg	0.27
Balance reading (sample)	10 µg	0.27
Air density	0.000125 kg/m^3	0.43
Liquid temperature	3 mK	0.08
Off-centring	0.67×10^{-7}	1.50
Combined standard uncertainty		2.66

4.3. Measurements

Before the measurements, the sample JM57 was cleaned with ethanol. Then, the mass, 1015.874 063(75) g, was determined with the mass comparison apparatus of the WG 3.23 [7, 11] in comparison to calibrated stainless steel mass standards.

The density of the sample JM57 was determined at 20 °C in four series of five measurements from 2 to 3 April 2009. The results are:

density at 20 °C : 21 539.33 $kg \cdot m^{-3}$ with $u_c(k = 1) = 0.06\ kg \cdot m^{-3}$

volume at 20 °C : 47.163 69 cm^3 with $u_c(k = 1) = 0.000\ 13\ cm^3$.

With the thermal expansion coefficient of equation (1) the following values are calculated:

density at 0 °C : 21 550.52 $kg \cdot m^{-3}$ with $u_c(k = 1) = 0.06\ kg \cdot m^{-3}$

volume at 0 °C : 47.139 19 cm^3 with $u_c(k = 1) = 0.000\ 14\ cm^3$.

5. Conclusion

This was the first time to our knowledge that an inter-laboratory density comparison of a 1 kg Pt/Ir artefact has been made. The relative difference of 5×10^{-6} between the participating laboratories is consistent at the 95 % level of confidence with their claimed uncertainties. This difference corresponds to a difference of about 0.3 µg in the air buoyancy correction between ambient atmospheric conditions and vacuum, which is the worst case normally encountered.

In the manufacturing process, after the density determination, a prototype is adjusted to a tolerance of 1 kg ± 1 mg in mass. Its mass is decreased by about 15 g. A volume of only 0.7 cm^3 is removed. The measured density at 1 kg +15 g is used to determine the final volume of the prototype. It is assumed that the change in density during its final adjustment is insignificant. This assumption has been tested by density measurements carried out on two prototypes with successively smaller mass: prototype n° 84 at 1 kg + 14 g and 1 kg + 5 g (relative difference of 1.1×10^{-6}) and prototype n° 85 at 1 kg + 19 g and 1 kg + 5 g (relative difference of 4×10^{-7}). These tests were made with the BIPM apparatus, in 2003.

6. References

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