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Comparison of Solid Density Standards Between IMGC and NBS

Anna Peuto
Istituto di Metrologia "G. Colonnetti," Strada delle Cacce 73, 10135 Turin, Italy
and
Richard S. Davis
National Bureau of Standards, Gaithersburg, MD 20899

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Solid-object density standards developed independently by the Istituto di Metrologia "G. Colonnetti" (IMGC) and NBS, and traceable to SI units of length and mass, have been compared using a silicon transfer standard. Results agree to approximately 1×10^{-6}, which is conistent with the uncertainties assigned by the two laboratories.

Key words: density standards; hydrostatic weighing; international comparison; International System of Units; silicon; volume standards.

1. Introduction

The commonly adopted density standard is water. The main drawback of water as a reference standard is its reproducibility, which is difficult to check. The last international comparison of density measurement, involving eight major metrological laboratories [1][1], gave results which differed by as much as 13 parts per million (ppm) on the measurement of a stainless steel kilogram volume by hydrostatic weighing.

In classical hydrostatic weighing many sources contribute to the final uncertainty aside from the density of the reference liquid. Nevertheless, the adoption of a solid density standard allows the metrologist to overcome the problem of water reproducibility and to diminish the effect of other sources of error.

NBS began a program to establish a solid density standard in 1965 [2] and, more than 10 years ago, became the first laboratory to succeed in doing so [3]. The Istituto di Metrologia "G. Colonnetti" (IMGC) is among the laboratories which have later developed solid standards [4], following slightly different procedures but coming to the same result: a number of solid objects whose mass and volume are directly traceable to the SI mass and length standards.

No matter which procedure is adopted, measurement of the mass and of the linear dimensions, from which volume is computed, is a complex process, involving sophisticated techniques and accurate measurement of many influencing quantities.

Solid density standards can then be compared to liquid or solid samples through hydrostatic weighing, which again requires a fair deal of attention to sources of

About the Authors: Anna Peuto is with IMGC's mass and volume unit (Sezione Masse-Volumi) while Richard S. Davis serves with the NBS Length and Mass Division.

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[1] Numbers in brackets indicate literature references.

error [5,6]. The best way of assessing the estimate of the uncertainty of both the standards and the procedure used is to have a comparison of standards through hydrostatic weighing.

We have completed such a comparison between IMGC and NBS using silicon crystals as transfer standards.

1.1 Plan of the Comparison

The NBS working standards of density are four 200-g silicon crystals, while IMGC's are three 1-kg spheres of glass-ceramic ($\rho \sim 2.5$ g/cm^3). A compromise had to be reached on the optimum size for the transfer standards and their number. We ultimately decided for maximum convenience of both laboratories to use two cylindrical silicon crystals of approximately 800 g each.

The silicon cylinders were fabricated at NBS from a single rod of commercially-grown, semiconductor-grade material. The rod had previously been ground to a diameter of approximately 7.5 cm. It was sawn twice to produce two cylinders of approximately 810 g. All edges of the cylinders were then bevelled. The cylinders were marked for easy identification by grinding one flat spot into the edge of the crystal henceforth referred to as X1 and producing two such flats in the second crystal, X2. Work damage was removed by etching the crystals in a bath of nitric and hydrofluoric acids [7]. The crystals were further etched to bring their masses to approximately 800.3 g (i.e., apparent mass against stainless steel of 8 g/cm^3 density$=$800.0 g).

The transfer standards were to be compared by hydrostatic weighing to the solid density standards first at NBS, then at IMGC, and finally at NBS again.

We agreed on having each institute follow its own procedures for both the experimental process and the treatment of data. The comparison was meant to be a comparison of density measurements performed on the same basic principles but carried out in thoroughly independent ways, each result affected by the laboratory's own data analysis and by possibly different systematic influences.

The goal of the project was of course to verify the agreement of the final density values, the uncertainty estimate of both institutes being at the 1 ppm level. A strong motivation for such a verification is that the NBS density work has been used to help provide a measurement of N_A, the Avogadro constant. The density measurements, in fact, were the dominant uncertainty in the reported error budget. When that work was done, which was about 15 years ago, it was found that the measured volumes of steel spheres used to establish a working volume standard depended systematically on which of two methods had been used in their cleaning. The two results differed by about 2 ppm. No satisfactory explanation for the discrepancy having been found, it was decided to average the two results and assign an expanded uncertainty of 1 ppm [8]. This is a strategy often imposed upon metrologists because of practical constraints but it is, nonetheless, a solution which begs further study. The work reported here provides an independent check of the density scale used in the NBS determination of N_A.

2. IMGC Standards

The IMGC project for the realization of solid density standards started in 1978. The choice of shape and material, influenced by previous work at NBS, fell on spheres made of Zerodur[2], a glass-ceramic of very low thermal expansion coefficient ($\alpha \approx 10^{-8}$/K). The artifacts, produced for IMGC by an Italian optical firm, have masses slightly below 1 kg and diameters of about 90 mm. The material being inert in air and water, the spheres can be used in hydrostatic weighing. Three such spheres became IMGC's working density standard after measurement of their average diameter. The latter was obtained, for each sphere, by measuring the absolute value of two diameters at 90° and the diametral variations, for a family of nine planes 20° apart passing through each measured diameter [4,9].

To date, mass and volume measurements have been completed on three spheres, which are referred to as SP, S2 and S4. They are of different geometrical quality; SP and S4 have diameter variations not exceeding 0.2 μm and S2 has a maximum variation of 0.8 μm. Uncertainties of volume values are nonetheless estimated to be all within 0.7 ppm (this represents one standard deviation of the mean, 1 s_m).

Average diameter values are traceable to the length standard realized by means of an iodine ($^{127}I_2$) stabilized He-Ne laser, while mass values are traceable to the International Prototype Kilogram through stainless steel mass standards.

2.1 Plan of Comparison

Since the purpose of the project was the determination of the density of the two 800-g crystals by comparison with the three IMGC solid density standards, the five objects were weighed together in air and water cycles involving three objects at a time. From the weighings in air we obtained the mass difference between each pair of objects and between each object and a 1-kg stainless steel standard. Least-squares adjustment

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[2] Brand names are given to specify experimental conditions. This identification does not imply either endorsement by the National Bureau of Standards or assurance that the equipment used is the best available.

of data yielded the masses of the three spheres and the two silicon cylinders.

From the weighings in bi-distilled water of known isotopic composition we obtained two types of results: first the values of all possible (10) volume ratios between the five objects; second, as an interesting check, the volume of the two crystals referred to water as a standard.

The original plan of the experiment, which provided for an equal number of measurements of all volume ratios, could not be carried out because of other commitments. Since IMGC standards were involved in many other density determinations during this comparison period, we obtained a very large amount of data on the mass and volume ratios of our own standards, but with smaller and unequal amounts of data on the crystals.

Rather than further delay the project's conclusion, we kept the data as they were and treated them by taking into account their different values of s_m.

2.2 Apparatus and Procedure

Both air and water weighings were performed with the same single-pan balance of 1-kg capacity and 10 div/mg sensitivity. All weighings were performed by comparison with calibrated stainless steel standards: the same 1-kg standard in the air weighings and the same 500 g and 100 g in the hydrostatic weighings were used for all the five objects, with additional masses to equalize loads.

An air buoyancy correction was applied to all weighings by calculating the air density through the formula recommended by International Committee for Weights and Measures (CIPM) [10], using measurements of atmospheric pressure, dew point, temperature, and estimate of CO_2 content from previous measurements in the lab; all instruments were calibrated against IMGC standards.

Hydrostatic measurements were performed using a loading mechanism quite similar to that of NBS; the suspension wire was of stainless steel (0.25 mm dia.) covered with platinum black. The vessel filled with bidistilled water was placed in an insulated bath controlled by a circulation thermostat. The temperature was measured, via an AC double bridge, by two 25 Ω SPRT's, placed at the lower left and upper right of the artifact under test.

The water, of known isotopic composition [11], was not degassed: a series of tests carried out with an industrial dissolved-oxygen meter confirmed that at the moment of the weighings, some 48 hours after bidistillation, the water can be assumed in equilibrium with atmosphere, i.e., saturated with gases.

Air weighings were double-substitution weighings, following a 5-reading format with two sensitivity determinations.

Hydrostatic weighings were performed in a slightly different way, following a 13-reading format, starting and ending with mass standards on the pan with and without the 500 mg sensitivity weight. Three observations were taken of the apparent mass of each of the objects involved, one reading taken with a smaller sensitivity weight, the three observations then being averaged to give a single value.

Smaller masses were added to the pan so that the readings relative to the three objects fall all within 1/4 of the optical scale.

From a 13-readings series two volume ratios (the third possible one being not independent) were obtained. During one series, temperature drift was usually kept within a few millikelvin and vertical gradient within 2 mK/10 cm.

All data were corrected for temperature drift and the crystal volumes were also corrected to a to 20 °C reference temperature (the water temperature was always kept within 0.2 K of 20 °C). The very different coefficient of thermal expansion of Zerodur and silicon is the only feature that has some influence, differences in compressibility, etc. being negligible.

3. Results

The whole experiment was meant to provide:

- the mass values of the two crystals, X1 and X2;
- the volume ratios of the two crystals to each of the IMGC standards and hence a final value of the crystal volumes; and
- the volume of the two crystals referred to water as a standard.

From the above one can compute the density of the crystals referred to IMGC standards (and compare it to NBS's value) and also referred to water, just as a check.

Let us examine the mass and volume ratios first.

3.1 Mass and Volume Referred to IMGC Solid Standards

The weighings in air of the five objects against the 1-kg standard and against each other provide 15 experimental equations that have been solved by the usual least-squares method.

From the hydrostatic weighings we obtained all 10 possible volume ratios as independent measurements and, again, least-squares adjusted values through a Connor-Youden procedure [12].

For both the mass and volume ratio measurements, we had sets with different numbers of measurements and different standard deviations. We then attributed to each *equation a weight inversely proportional to the variance* of the mean of the corresponding experimental data, s_m^2.

Tables 1 and 2 give experimental results of the mass measurements and volume ratios, the number of measurements, standard deviation of the mean and least-squares adjusted values of the five masses and of the 10 volume ratios, together with the standard deviation of the fit and of the adjusted values.

Final uncertainties were estimated, following BIPM recommendations [13], as the combined uncertainties from type A and type B components.

Tables 3 and 4 list all sources of uncertainty and their influence on mass and volume ratio measurements together with the resulting combined uncertainty. The volumes of the three spheres, as computed from the interferometric measurement of their diameters, were not considered in the least-squares adjustment of volume ratios.

Since small discrepancies exist between hydrostatic and interferometric values of volume ratios for the IMGC standards, slightly different volume and density values for the silicon crystals can be computed, referred to each of the standards. These latter values are given in table 5, together with the average values and the combined uncertainty, where the uncertainty of the standards has been estimated as 0.7 ppm.

3.2 Water as a Reference

When water is taken as a reference a different philosophy must be adopted. Volume ratios are independent of the liquid used in the hydrostatic weighing, as long as

Table 1. Mass measurements (IMGC).

Object	Measured Values (g)	n	s_m (mg)	l.s. adjusted mass (g)	s_m of l.s. adjusted mass (mg)
X1	800.33240	13	0.04	800.33225	0.05
X2	800.30064	3	0.08	800.30070	0.07
S4	967.95836	13	0.03	967.95837	0.04
S2	979.68247	14	0.03	979.68249	0.04
SP	958.56833	30	0.03	958.56837	0.04

s of the fit = 0.08 mg

Table 2. Volume ratios (IMGC).

R	Measured Ratio	n	s_m (10^{-6})	l.s. adjusted ratio	s_m of l.s. adjusted ratio
S4/SP	1.01232589	46	0.12	1.01232588	0.14
S4/X1	1.11341445	6	0.40	1.11341383	0.19
S4/X2	1.11345775	6	0.14	1.11345768	0.15
S2/S4	1.01065800	13	0.30	1.01065732	0.21
S2/SP	1.02311459	27	0.22	1.02311456	0.17
S2/X1	1.12527956	20	0.25	1.12527984	0.21
S2/X2	1.12532385	8	0.26	1.12532416	0.20
SP/X1	1.00985702	12	0.18	1.09985712	0.17
SP/X2	1.09990061	8	0.19	1.09990045	0.15
X1/X2	1.00003929	16	0.17	1.00003939	0.17

s of the fit $= 0.3 \times 10^{-6}$

Table 3. Uncertainty of mass measurements (IMGC).

Source of Uncertainty	Magnitude	Influence on Mass
1 kg standard	50 μg	50 μg
Other mass standard	*70 μg*	*70 μg*
Density of Air	0.28 μg/cm³	68 μg
coming from:		
Pressure	16 Pa	
Dew point	0.3 K	
Temperature	25 mK	
CO_2 content	1×10^{-4}	
Formula	0.08 μg/cm³	
Volume of unknown	0.4 mm³	0.5 μg
Volume of 1 kg standard	0.9 mm³	1 μg
Volume of other mass standards	30 mm³	35 μg
Sensitivity reading	1 div	20 μg
	RSS	0.12 mg
	s_m	X1: 0.05 mg X2: 0.07 mg
Combined Uncertainty		0.14 mg

Table 4. Uncertainty of volume ratio measurements (IMGC).

Source of Uncertainty	Magnitude	Influence on Ratio Measurement (10^{-6})
Mass standard	195 μg	0.2
Volume of mass standards	90 mm³	0.1
Density of air	0.28 μg/cm³	0.03
Coefficient of thermal dilation of silicon	5×10^{-8}/K	0.01
Temperature drift	1 mK	0.2
Absolute temperature	1 mK	0.001
	RSS	0.3×10^{-6}
	s_m	0.2×10^{-6}
Combined Uncertainty		0.4×10^{-6}

Table 5. Density and volume of X1 and X2 referred to IMGC standards.

	Density (20 °C)		Volume (20 °C)	
Standard	X1 (g/cm^3)	X2 (g/cm^3)	X1 (cm^3)	X2 (cm^3)
S2	2.3290763	2.3290763	343.62646	343.61292
S4	2.3290783	2.3290782	343.62617	343.61264
SP	2.3290789	2.3290789	343.62608	343.61254
Average	2.3290778	2.3290778	343.62624	343.61270
s_m	0.0000008	0.0000008	0.00011	0.00011

	Uncertainty of density measurements	
Source of Uncertainty	Magnitude	Influence on Radio Measurement
Volume ratio	0.4×10^{-6}	0.9×10^{-6} g/cm^3
Mass	0.14 mg	0.4×10^{-6} g/cm^3
Density standard	0.7 ppm	1.6×10^{-6} g/cm^3
	RSS	1.9×10^{-6} g/cm^3 (0.8 ppm)
	s_m	0.8×10^{-6} g/cm^3
Combined Uncertainty		2.0×10^{-6} g/cm^3 (0.9 ppm)

its density can be considered near constant during weighings. Gas content, purity and absolute temperature of the water are not a problem when measuring volume ratios but are of the highest importance when water becomes the reference standard.

When doubts about water conditions arise, the weighings must be disregarded: thus some of the observations which could be considered when comparing volumes were disregarded when measuring volumes referred to water. We nonetheless came out with a fair amount of data on X1 and X2 volumes, measured in different samples of water.

Once again the number of measurements and the number of water samples are not the same for the two crystals, but the information is sufficient to check both crystals and confirm the tentative conclusion we have drawn on water, as prepared and analyzed at IMGC.

The volumes of X1 and X2 referred to water are given in table 6, as average results of weighings in the same water sample, together with the number of measurements and standard deviation of the mean. The temperature of the water was between 19.8 °C and 20.0 °C. The data were corrected for thermal expansion of silicon (ref. temp. 20 °C), isotopic composition [14], and gas content of water (-2.5×10^{-6} [15]).

Averaging all observations, as they can be considered to belong to the same set, we obtain a final value in very good agreement with those referred to solid density standards.

The final uncertainty, given in table 7, is only slightly larger than in the case of the solid reference standards. However, there are influencing quantities (gas content, isotopic variations, contamination, etc.) for which either a rough estimate or no estimate at all can be made.

Only after a considerable number of hydrostatic weighings of the solid density standards were we able to assess our water reproducibility; the results on X1 and X2 provide a further check. We have found, in other experiments, maximum discrepancies of 3 ppm.

4. NBS Standards

The fundamental density work at NBS was carried out more than 10 years ago and has been well summarized in review papers [8,16]. Briefly, the volume of highly spherical steel balls was determined by interferometric measurements of ball diameter. Measurement of the mass of each ball then determined its density. It was assumed that the stability in density of the balls would be inferior to that of single-crystal silicon. Therefore, soon after the ball densities were determined, the balls were used to determine the density of four 200 g discs of single-crystal silicon. The transfer was made hydrostatically in a bath of fluorocarbon. Water could

Table 6. Volume of X1 and X2 referred to water (IMGC).

Water Sample	Volume of X1 (cm^3)	n	s_m (mm^3)	Volume of X2 (cm^3)	n	s_m (mm^3)
1 (19.8 °C)	343.62620	5	0.17			
2 (19.8 °C)	343.62600	5	0.08			
3 (19.9 °C)	343.62632	5	0.13			
4 (19.8 °C)				343.61332	5	0.13
5 (20.0 °C)	343.62638	8	0.07			
6 (19.9 °C)	343.62610	8	0.03	343.61268	8	0.06
7 (19.9 °C)	343.62628	7	0.08	343.61270	7	0.06
Average	343.62622	38	0.04	343.61285	20	0.08
Density	*2.3290779 g/cm^3*			*2.3290768 g/cm^3*		
Difference from density referred to solid standards	$+0.1\times10^{-6}$ g/cm^3			-0.9×10^{-6} g/cm^3		

not be used as the transfer fluid because it would have attacked the surface of the steel balls. The fluorocarbon fluid turned out to have many desirable properties compared with water—lower surface tension, higher density, larger appetite for gases. Its chief drawbacks are its higher thermal expansion coefficient and its poorer thermal conductivity.

This work was completed by 1972. The four silicon discs remain the NBS working standards of density.

4.1 Plan of Comparison

The objective of our measurements was the determination of the density of X1 and X2, using our four 200-g silicon discs as working standards. Similar to the measurements at IMGC, we measured the mass of the six objects by weighings in air after which the hydrostatic weighings were carried out.

The hydrostatic weighing and analysis were done as described in reference [5] using fluorocarbon as the transfer fluid. As a check, we also made several measurements using water as the transfer fluid. The water density was not known *a priori* to useful levels of accuracy because it was singly-distilled tap water of unknown isotopic composition.

In all the measurements, the volume ratios of four objects were determined in all six possible pairings. These data were collected in about three hours and constitute one "run." The four objects used were: X1, X2, and two groups of two discs each. The data from each run were analyzed by non-linear least-squares fitting using the total volume of the four discs as a restraint. The computed difference of the two disc-summations and the standard deviation of the least-squares fit were used as process controls.

Seven runs were carried out prior to sending X1 and X2 to IMGC. Four of these used fluorocarbon as a transfer fluid and three used water. Two additional runs in fluorocarbon were made after the crystals returned to NBS.

Table 7. Uncertainty of measurements referred to water (IMGC).

Source of Uncertainty	Uncertainty	Influence on Volume Measurement (mm^3)
Mass of crystal	0.13 mg	0.13
Mass of standards in hydro weigh.	0.17 mg	0.17
Volume of mass standards	84 mm^3	0.10
Sensitivity reading	1 div	0.02
Height difference	0.1 m	0.01
Thermal dilation of silicon (α)	5×10^{-8}/K	0.00
Temp. difference from 20 °C	1 mK	0.00
Density of air	0.28 μg/cm^3	0.08
Density of water coming from:	7.3×10^{-7} g/cm^3	0.25
Temperature	1 mK	
Gas content	20%	
Isotopic abundance	2×10^{-6}	
Pressure	16 Pa	
Depth	*1 cm*	
	RSS	0.35
s_m		X1: 0.04 X2: 0.08
Combined Uncertainty		0.36 mm^3 (1 ppm)

4.2 Apparatus and Procedure

The mass of each 200-g disc was determined by double substitution against a 200-g stainless steel working standard. Measurements were made on a modified single-pan balance having a standard deviation of 12 μg. The two 800-g crystals, X1 and X2, were weighed on a single-pan kilogram balance having a standard deviation of 25 μg. Calibrated stainless steel weights were added to the silicon crystals until their apparent mass equalled that of two of our stainless steel 1-kg standards. The four objects of nearly-equal apparent mass were then intercompared by double-substitution, weighing in all six possible pairings. Standard least squares techniques were used to assign mass values to the unknown objects.

Buoyancy corrections were made using the same equation for the density of moist air as was used at IMGC [10]. Inputs to the equation were obtained from a thermometer and hygrometer mounted in the balance case and from an aneroid barometer placed on an adjacent bench. The ambient level of carbon dioxide was assumed to be that measured previously during surveys of our laboratory.

All hydrostatic measurements were as described in [5]. Our bath chamber below the balance was enlarged slightly to accommodate X1 and X2, since their volumes are larger than any object we have previously measured.

The hydrostatic weighings were analyzed in a slightly different way than in previous work. A hydrostatic weighing of an object, A, proceeds as follows:

I_1: balance pan unloaded
I_2: A on pan in fluid
I_3: A on pan in fluid, S on pan in air
I_4: S on pan in air
I_5: balance pan unloaded,

where S is a 20 mg sensitivity weight of known mass. The set I_1 to I_5 are balance indications. The balance used is a single-pan device with calibrated built-in weights and a 100 mg optical scale that can be read to the nearest 20 μg. Thus each I_i is the sum D_i+O_i where D_i is the combination of calibrated built-in weights used and O_i is the reading on the optical scale. Tare weights are used to ensure that $D_1=D_4$, $D_2=D_3$, and O_1 and O_2 are within one half of the optical scale range.

In the past, we have estimated the contribution of the optical readings to the apparent mass of A in the bath fluid as

$$\frac{M_s'}{2}\left(\frac{O_2-O_1}{O_3-O_2}+\frac{O_3-O_4}{O_4-O_5}\right) \qquad (1)$$

where M_s' is the mass of S reduced by the buoyant effect of air. The drift during the five observations is estimated by

$$\frac{M_s'}{2}\left(\frac{O_2-O_1}{O_3-O_2}-\frac{O_3-O_4}{O_4-O_5}\right) \qquad (2)$$

In this work, we replace eqs (1) and (2) with

$$\frac{M_s'}{2}\left(\frac{O_2-O_1+\frac{1}{4}(O_1-O_5)}{O_4-O_5-\frac{1}{4}(O_1-O_5)}+\frac{O_3-O_4-\frac{1}{4}(O_1-O_5)}{O_4-O_5-\frac{1}{4}(O_1-O_5)}\right) \qquad (1a)$$

and

$$\frac{M_s'}{2}\left(\frac{O_2-O_1+\frac{1}{4}(O_1-O_5)}{O_4-O_5-\frac{1}{4}(O_1-O_5)}+\frac{O_3-O_4-\frac{1}{4}(O_1-O_5)}{O_4-O_5-\frac{1}{4}(O_1-O_5)}\right). \qquad (1b)$$

Equations (1a) and (1b) differ most from (1) and (2) when $V_A\dot{\rho}_L$ is a large number, where V_A is the volume of A and $\dot{\rho}_L$ is the time derivative of the density of the bath fluid. Generally, $\dot{\rho}_L=(\partial\rho_L/\partial T)\dot{T}$. We also assume a linear drift in T, the bath temperature. In (1) and (2), the quantity $(M_s'/2)\cdot(1/(O_3-O_2))$, which is supposed to be an estimate of balance sensitivity, will contain a significant error if $V_A\dot{\rho}_L$ is large. The penalty for this error falls heaviest on those measurements for which (O_2-O_1) is the largest percentage of full-scale. Equations (1a) and (1b), on the other hand, estimate balance sensitivity independent of the volume of the object being weighed. The quantity $(1/4)(O_1-O_5)$ is used to eliminate the small effect of $\dot{\rho}_L$ on the volume of the submerged balance pan. Drift in the fluid density is still measured by comparing the magnitude of (1b) with zero. We may note that the quantity (1a), in addition to random errors, will now be systematically biased by the amount ϵV_A, where ϵ is the increase in bath density between successive measurements. The effect of this bias can be made negligible by establishing a maximum drift criterion and monitoring the quantity (1b) for each group of measurements.

The use of (1a) also means that non-linearities in the optical scale readings are not accounted for, but experience has shown that the non-linearities are small compared with the effects of temperature drift during a reading.

It is worth noting that in analyzing a large quantity of data using both schemes for data reduction, virtually identical final results for every run were obtained. The difference is that the computed standard deviations of the least squares fits were, on occasion, significantly less using the modified scheme.

5. Results

The results of the NBS measurements are shown in tables 8–11. In table 8, the "first set" of measurements was made at NBS prior to sending X1 and X2 to IMGC. The "second set" of measurements was made after the

Table 8. Mass measurements (NBS).

Object	Measured Mass, 1st Set (g)	Measured Mass, 2nd Set (g)	Estimated s_m (μg)	No. of Deg. of Freedom
X1	800.331922	800.331839	35	9
X2	800.300387	800.300375	35	9
Disc 1	200.420702		22	2
Disc 2	199.763720		22	2
Disc 3	200.006331		22	2
Disc 4	199.426629		22	2

Table 9. Uncertainty in mass measurements (NBS).

Source of Uncertainty	Magnitude	Influence on Unknowns (μg)	Influence on Standard Discs (μg)
1 kg standard (stainless steel)	50 μg	40	20
200 g standard	23 μg	23	23
Density of air coming from:	0.40 μg/cm^3	97	49
Pressure	13 Pa		
Relative humidity	3%		
Temperature	50 mK		
CO_2 content	1×10^{-4}		
Formula	0.08 μg/cm^3		
Volume of unknowns	1 ppm	0.4	0.2
Volume of 1 kg standard	1.3 mm^3	1.2	0.6
Volume of 200 g mass standard	1.3 mm^3	1.5	1.5
Sensitivity reading	1 div	20	20
	RSS	109	61
	s_m	35	22
	Total Uncertainty	115 μg	65 μg

return of the transfer standards from IMGC. It is possible that X1 has lost mass during its use although the difference is just at the level of significance (see table 9) even accounting for uncertainties which are common to both sets of measurements. The masses of the four discs have been stable for a number of years. An accident in 1978 involving Disc 4 caused the last change in any of the measured masses.

In table 10, runs 8 and 9 were made subsequent to the return of X1 and X2 to NBS. The masses obtained in the second set of table 8 were used for these two runs. No obvious systematic behavior was observed so the results were pooled with equal weight assigned to each run.

In table 10, it is worth noting the differences in propagated error as a function of transfer fluid. The temperature of the bath need not be known because X1, X2 and the four standard discs have identical temperature coefficients. The other zeros in table 10 are a result of the standards and unknowns being almost identical in density. That is, any type B error which has the effect of changing I_x and I_s (see below) to KI_x and KI_s (where $K\approx 1$) propagates as an error in V_x or D_x which is pro-

Table 10. Results of nine runs (NBS).

Run No.	Transfer Fluid	Grouping of Standard Discs	Fitted Volumes (cm^3) X1	Fitted Volumes (cm^3) X2	Estimated s_m, 3 Deg. of Freedom (mm^3)	Computed Densities (g/cm^3) @ 20 °C X1	Computed Densities (g/cm^3) @ 20 °C X2
1	Fluorocarbon	2+4, 3+5	343.625187	343.611593	0.113	2.3290835	2.3290839
2	Fluorocarbon	2+3, 4+5	343.625692	343.612283	0.090	2.3290801	2.3290792
3	Fluorocarbon	2+3, 4+5	343.625710	343.612123	0.054	2.3290799	2.3290803
4	Fluorocarbon	2+3, 4+5	343.625490	343.612017	0.051	2.3290814	2.3290810
5	Water	2+4, 3+5	343.626419	343.612648	0.143	2.3290754	2.3290770
6	Water	2+3, 4+5	343.625750	343.612266	0.041	2.3290800	2.3290796
7	Water	2+3, 4+5	343.625753	343.612298	0.076	2.3290800	2.3290794
8	Fluorocarbon	2+4, 3+5	343.625693	343.612234	0.112	2.3290803	2.3290800
9	Fluorocarbon	3+5, 2+4	343.625792	343.612358	0.078	2.3290796	2.3290791
		Average	343.625721	343.612202		2.3290800	2.3290799
		s_m	0.000108	0.000095		0.0000007	0.0000006

Table 11. Uncertainties in hydrostatic measurements (NBS).

Source of Uncertainty	Magnitude	Influence on V_x Fluorocarbon (mm^3)	Influence on V_x Water (mm^3)	Influence on D_x Fluorocarbon (μg/cm^3)	Influence on D_x Water (μg/cm^3)
Mass of two standard discs	65 μg	0.018	0.074	0.10	0.50
Density of two standard discs (Ds)	2.21 μg/cm^3	0.326	0.326	2.21	2.21
Calibration of of built-in weights on hydrostatic balance (Type B)	15 μg/100g	~0	~0	~0	~0
Mass of unknowns, X1 and X2	115 μg	0.065	0.115	0.11	0.44
Sensitivity of hydrostatic balance	20 μg	0.016	0.028	0.11	0.19
Bath temperature	2 mK	~0	~0	~0	~0
Density of air	0.40 μg/cm^3	~0	~0	~0	~0
	RSS	0.333	0.355	2.22	2.32
	s_m	0.107	0.107	0.72	0.72
	Total Uncertainty	0.350 mm^3 (1.02 ppm)	0.370 mm^3 (1.09 ppm)	2.33 μg/cm^3 (1.00 ppm)	2.43 μg/cm^3 (1.04 ppm)

portional to $(D_x - D_s)/\rho_L$, where ρ_L is the density of the bath fluid. In fact, calibration of the built-in weights was a major contribution to the error budget reported in [3] because in that work the volume standards were made of density 7.8 g/cm^3 material and the unknowns were silicon. Note also that we are treating uncertainty in the air density during mass measurements and hydrostatic measurements as uncorrelated. This is because the measurements were made on different balances in different rooms with different thermometers, barometers, etc. This choice has little effect on the final uncertainty assignment, although the method used is the more conservative because an error in air density systematic to all mass measurements would have no effect on the resulting assignment of density.

6. Discussion

In comparing results between NBS and IMGC, one must look at the starting premises of the two laboratories. NBS assumes that the *densities* of its four silicon discs are known whereas IMGC assumes that the *volumes* of its three Zerodur spheres are known (or that the density of water is known when water is the standard). This leads to the following schematic equations for obtaining final results:

	NBS	IMGC	
STANDARD:	discs	spheres	water
$V_x=$:	$\frac{M_s}{D_s}\frac{M_x-I_x}{M_s-I_s}$	$V_s\frac{M_x-I_x}{M_s-I_s}$	$\frac{M_x-I_x}{\rho_W}$
$D_x=$:	$D_s\frac{M_s-I_s}{M_s}\frac{M_x}{M_x-I_x}$	$\frac{M_x}{V_s}\frac{M_s-I_s}{M_x-I_x}$	$\frac{M_x}{M_x-I_x}\rho_W$

where the symbols have the following meanings:

V_x: volume of unknown
V_s: volume of standard
M_x: mass of unknown
M_s: mass of standard

D_x: density of unknown
D_s: density of standard
ρ_W: density of water
I_x: $M_x - \rho_L V_x$ (apparent mass of unknown in fluid)
I_s: $M_s - \rho_L V_s$ (apparent mass of standard in fluid)
ρ_L: density of transfer fluid

D_s(NBS) and V_s(IMGC) are assumed known prior to the measurements reported here (we will defer discussion of the IMGC measurements based on water). Thus, for instance, while D_x(NBS) and V_x(IMGC, V_s) are measured independent of the SI unit of mass, V_x(NBS) and D_x(IMGC, V_s) do depend on the SI mass unit as presently realized in each laboratory. Other dependencies differ among the various measurement schemes as will be discussed presently.

Before examining possible discrepancies further, it is useful to compare those results of the two laboratories which should be almost independent of the mass, volume, or density scales used but, rather, depend only on experimental procedures. Such a measure is provided by a comparison of the ratio V_{X1}/V_{X2} measured by the two laboratories:

	V_{X1}/V_{X2}	s_m
IMGC:	1.00003939	0.00000017
NBS:	1.00003940	0.00000014

Based on the mean standard deviations we would expect agreement to about 0.2 ppm. The observed agreement of 0.01 ppm is well within these limits.

The densities reported by IMGC are, however, systematically lower than those of NBS by about 1.0 ppm. The volumes reported by IMGC for X1 and X2 are systematically higher by 1.4 ppm than those reported by NBS.

Although these discrepancies are by no means serious, given the claimed accuracies of the two laboratories at the estimated one standard deviation (1σ) level of accuracy, it is nevertheless useful to examine the possible sources for the slight offsets. In fact, one immediately notices that the masses of X1 and X2 reported by the two laboratories are discrepant by an average of 0.34 mg (0.43 ppm). Assuming the IMGC values to be correct, the NBS values for D_x and V_x would shift toward the IMGC values by 0.3 ppm and 0.8 ppm respectively if "corrected" for the mass error. On the other hand, if the NBS values were correct, the IMGC values for D_x and V_x would shift toward the NBS values by 0.6 ppm and 1.1 ppm for both types of measurements (i.e., spheres or water used as standards). The difference in shifts is due to the heavy reliance on fluorocarbon ($\rho \sim 1.8$ g/cm^3) as transfer fluid at NBS compared with the exclusive reliance at IMGC on water ($\rho \sim 1.0$ g/cm^3) as either transfer fluid or standard[3].

It might be tempting, then, to attribute most of the observed discrepancies in V_x and D_x to the mismeasurement of the mass of X1 and X2 at one of the laboratories were it not for the fact that the Zerodur spheres and/or the silicon discs used as standards in the two laboratories would almost certainly be subject to the same systematic error. Such an error could arise from mass standards or from faulty evaluation of the density of air. If the standards and unknowns were both subject to the same systematic error, a "correction" at NBS would leave the values of D_x unchanged but would shift V_x closer to the IMGC value by 0.5 ppm. A similar "correction" at IMGC would move results *farther* from NBS by 0.6 ppm and 0.1 ppm for the case of Zerodur spheres used as standards; the results using water as standard would shift closer to NBS values by 0.6 ppm and 1.1 ppm. All these shifts can be estimated by propagating changes through the schematic equations given above.

Aside from the discrepant mass values, the systematic difference in density measurements might of course be due to the volume/density standards. In fact, among IMGC density measurements those referred to one of the spheres (S2) are lower than the others by about 1 ppm. S4 and SP are in much better agreement with NBS values (0.6 ppm). Discrepancies are still not significant compared to the uncertainties attributed to the standards, so that we considered all IMGC measurements in the final computation. Besides, IMGC standards were recently involved in a comparison with PTB sponsored by the European Economic Community (EEC): the results are still to be published but it might be useful here to note that the best agreement was obtained for S2, so that there is no evidence of this standard being mismeasured.

As for now, density measurements of 1 ppm uncertainty agreeing within 1 ppm are a satisfactory result. Separate inquiries should be carried out on each single cause of discrepancy to obtain both a better agreement and a smaller uncertainty.

7. Conclusions

The mass and volume assignments to the transfer standards, X1 and X2, made by IMGC and NBS agree to at worst 1.5 ppm, average density values agreeing to 0.9 ppm. Each laboratory assigns an uncertainty of about 1

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[3] In fact, the measurements made at NBS which used water as the transfer fluid would shift by 0.6 ppm and 1.1 ppm while those using fluorocarbon would shift by 0.2 ppm and 0.6 ppm. It is interesting to note that no systematic differences in the water and fluorocarbon measurements at NBS were observed.

ppm so that the observed agreement is good. We note a larger than expected discrepancy in the assignment of mass to X1 and X2. Resolution of this discrepancy might improve volume agreement by as much as 1.1 ppm or worsen agreement by as much as 0.6 ppm.

While we cannot resolve the cleaning anomaly which was observed during the NBS work which established its volume standard, we can at least confirm that the uncertainty which NBS ultimately placed on its measurements is a reasonable one. Thus the uncertainty which these measurements brought to the measurement of the Avogadro constant by Deslattes et al. is also confirmed.

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