Measurement of the volume of a Zerodur sphere of nominal mass 1 kg by comparison hydrostatic weighing with Zerodur and silica standards of similar nominal mass

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ABSTRACT

This report describes a method for measuring the volume of a Zerodur sphere of nominal mass 1 kg by making comparison hydrostatic weighings with two calibrated volume reference standards of similar nominal mass manufactured from Zerodur and silica respectively. The result obtained was in good agreement with a values previously determined by the Physikalisch-Technische Bundesanstalt (PTB) and a UKAS accredited UK Laboratory.

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1 INTRODUCTION

The National Physical Laboratory recently took part in a volume comparison of a Zerodur spherical volume standard of nominal mass 1 kg. The other participants were H & D Fitzgerald Ltd, a UK laboratory accredited by UKAS for density measurement, and the Physikalisch-Technische Bundesanstalt (PTB).

This comparison gave NPL the opportunity to test the feasibility and methodology of measuring the volume of the sphere by hydrostatic weighings against NPL's own calibrated Zerodur[1] and silica[2] spherical volume standards (identified as 'NPLW S01' and 'NPLW S02' respectively) of similar nominal mass.

For the purpose of this investigation, the sphere being tested was allocated the identity 'SF'.

2 EXPERIMENTAL METHOD

The experimental set up and procedure was broadly similar to that described in NPL Report CMAM 66 [1] which describes traceability through volume reference standards. However, the method used in this investigation was to compare the apparent mass[3] in water of the test sphere with the apparent mass in water of a reference standard sphere. From Archimedes hypothesis, the difference between the true mass and the apparent mass of a sphere in water is equal to the mass of water displaced by the sphere. Using the formula given by Patterson and Morris [2] to calculate the water density, the volume of water displaced by the sphere can therefore be determined. Applying this method to both the test and reference spheres, their volume difference can be measured, and as the volume of the reference sphere is known the volume of the test sphere can be calculated.

The conventional hydrostatic weighing method of measuring the volume of an artefact relies on calculating the volume of a liquid of known density that is displaced by the artefact (see

[1] Calibrated for mass and volume by the Instituto di Metrologia "G. Colonnetti", Turino, Italy in March 2001

[2] Calibrated for mass and volume by the Physikalisch-Technische Bundesanstalt, Braunschweig, Germany in January 2001

[3] The apparent mass of an artefact is its true mass less the upthrust (or buoyant force) acting upon it from the medium in which it is weighed.

NPL Report MOT3 [3]). The advantage of the method described in this report is that because the volume difference between the test and reference artefact is small, a slight error in the calculated liquid density will not significantly affect the overall uncertainty of the measurement. This advantage diminishes as the volume difference between the test and the reference artefact increases. For example, in a comparison of a stainless steel 1 kg weight against a 1 kg Zerodur sphere the uncertainties achieved using the method described in this report would be approximately twice that obtainable by the conventional method.

3 MASS MEASUREMENT

The mass value of sphere SF was determined at NPL on a Mettler AT 10005 comparator by making comparison weighings against two NPL stainless steel Reference Standards and applying corrections for air buoyancy.

4 VOLUME OF SPHERE

4.1 Weighing procedure

The experimental set up and weighing closely followed the procedure described in NPL Report CMAM 66 [1]. Initially, the test sphere SF was loaded in the lower station of the exchanger and reference sphere NPLW S01 in the upper station. A series of measurement runs were performed exchanging and weighing each sphere alternately. To reduce the possibility of station dependent systematic errors, the positions of the spheres on the exchanger were then reversed (i.e. sphere SF was loaded in the upper station and NPLW S01 in the lower) and the experiment repeated. Finally, the whole experiment was repeated using reference sphere NPLW S02 in place of NPLW S01.

4.2 Calculation of volume

Let W_1 be equal to the apparent mass in water of the test sphere (TS) and the apparent mass in air of the makeweights (S1) (kg)

W_2 be equal to the apparent mass in water of the reference sphere (RS) and the apparent mass in air of the makeweights (S2) (kg)

M_{TS} be the mass of the test sphere (kg)

V_{TS} be the volume of the test sphere (m^3)

M_{RS} be the mass of the reference sphere (kg)

V_{RS} be the volume of reference sphere (m^3)

M_{S1} be the mass of the makeweights S1 (kg)

V_{S1} be the volume of the makeweights S1 (m^3)

M_{S2} be the mass of the makeweights S2 (kg)

V_{S2} be the volume the makeweights S2 (m^3)

ρ_A be the air density at the time of weighing the test and reference spheres (kg m^{-3})

$\rho_{W(TS)}$ be the water density at the time of weighing the test sphere (kg m^{-3})

$\rho_{W(RS)}$ be the water density at the time of weighing the reference sphere (kg m^{-3})

then $$W_1 = (M_{TS} - \rho_{W(TS)}.V_{TS}) + (M_{S1} - \rho_A.V_{S1}) \quad \text{(kg)} \tag{1}$$

and $$W_2 = (M_{RS} - \rho_{W(RS)}.V_{RS}) + (M_{S2} - \rho_A.V_{S2}) \quad \text{(kg)} \tag{2}$$

The contributions due to the apparent masses of the cradle and suspension are the same in both weighing configurations. They therefore cancel out and are omitted from equations (1) and (2).

Let ΔW be equal to the difference in balance readings for the two weighing configurations.

Then $$\Delta W = W_1 - W_2 \quad \text{(kg)} \tag{3}$$

substituting equations (1) and (2) in (3)

$$\Delta W = \left[(M_{TS} - \rho_{W(TS)}.V_{TS}) + (M_{S1} - \rho_A.V_{S1})\right] - \left[(M_{RS} - \rho_{W(RS)}.V_{RS}) + (M_{S2} - \rho_A.V_{S2})\right]$$

rearranging

$$\rho_{W(TS)}.V_{TS} = (M_{TS} - M_{RS}) + (M_{S1} - M_{S2}) + \rho_A(V_{S2} - V_{S1}) + \rho_{W(RS)}.V_{RS} - \Delta W$$

therefore $$V_{TS} = \frac{(M_{TS} - M_{RS}) + (M_{S1} - M_{S2}) + \rho_A(V_{S2} - V_{S1}) + \rho_{W(RS)}.V_{RS} - \Delta W}{\rho_{W(TS)}} \quad (m^3) \tag{4}$$

5 CORRECTIONS TO THE CALCULATED VOLUME

5.1 Thermal expansion

Equation (4) assumes that the test sphere and the reference sphere are at the same temperature. In practice, the spheres will be at the ambient temperature of the water at the time the measurement is made. Since the formula requires a value for the volume of the test sphere at the measurement temperature (T °C), a correction must be applied to the calibrated volume of the silica sphere to compensate for its thermal expansion. A correction is not required for the Zerodur reference sphere because its cubic coefficient of thermal expansion at 20 °C is $< 0.30 \times 10^{-6}$, which is not significant for this investigation. Similarly, no correction is required to convert the test sphere volume at the measurement temperature to the volume at 20 °C.

Thus, if $V_{(T)}$ is the volume of the silica sphere at T °C (m^3)

$V_{(20)}$ is the volume of the silica sphere at 20 °C (m^3)

α is the volume thermal expansivity of silica (°C^{-1})

then

$$V_{(T)} = V_{(20)}\left[1 + \alpha\left(T - 20\right)\right] \quad (m^3) \qquad (5)$$

5.2 Water density

The values for the density of air-free water obtained using the formula given by Patterson and Morris [2] require corrections for the following:

- The effect of air saturation
- The difference in isotopic composition between Standard Mean Ocean Water (SMOW) and local NPL water
- The compressibility of water due to the depth of immersion of the spheres

More detailed explanations and methods of calculating these corrections are given in NPL Report CMAM 66 [1].

5.3 Gravitational gradient

A correction to the difference in apparent mass between the spheres and the makeweights is required to compensate for the variation in gravitational force with height. This is also described more fully in NPL Report CMAM 66 [1].

6 EVALUATION OF UNCERTAINTIES

6.1 Mass value

The uncertainty in the determination by NPL of the mass value of the test sphere has been calculated using the methodology described in NPL Report CMAM 22 (in preparation).

6.2 Volume of sphere

MEASUREMENT CONTRIBUTIONS

The measured volume of the test sphere at temperature T (°C) is given by equation (4):

$$V_{TS} = \frac{(M_{TS} - M_{RS}) + (M_{S1} - M_{S2}) + \rho_A (V_{S2} - V_{S1}) + \rho_{W(RS)} . V_{RS} - \Delta W}{\rho_{W(TS)}} \quad (m^3)$$

If Δ_{ST} is the uncertainty contribution of the surface tension force acting on the suspension (obtained by direct measurement)

then $$V_{TS} = \frac{(M_{TS} - M_{RS}) + (M_{S1} - M_{S2}) + \rho_A (V_{S2} - V_{S1}) + \rho_{W(RS)} . V_{RS} - \Delta W + \Delta_{ST}}{\rho_{W(TS)}} \quad (m^3) \quad (6)$$

Partial differentiation of this expression with respect to the density of water at the time of measurement of the reference and test spheres, gives sensitivity coefficients ($c_{\rho W(RS)}$ and $c_{\rho W(TS)}$) each containing a term which includes the total volume of the reference sphere.

i.e.

$$c_{\rho W(RS)} = \left(\frac{\partial V_{TS}}{\partial \rho_{W(RS)}} \right) = \frac{V_{RS}}{\rho_{W(TS)}}$$

and

$$c_{\rho W(TS)} = \left(\frac{\partial V_{TS}}{\partial \rho_{W(TS)}} \right) = -\left[\frac{(M_{TS} - M_{RS}) + (M_{S1} - M_{S2}) + \rho_A (V_{S2} - V_{S1}) + \rho_{W(RS)} . V_{RS} - \Delta W + \Delta_{ST}}{\rho_{W(TS)}{}^2} \right]$$

But the actual uncertainty related to the water density contribution is dependent on the volume difference between the test and reference spheres (because the experimental basis for the measurement is the difference in the volume of water displaced by the two spheres), so partial differentiation of equation (6) results in a high and fallacious sensitivity coefficient. However, over the relatively small water temperature difference (<20 mK) between the two spheres, the water density can be considered a linear function of the water temperature. Therefore, provided that this difference in the ambient water temperatures is within the temperature gradient contribution of the water density uncertainty, equation (6) can be simplified to an expression for the volume difference between the test and reference spheres.

i.e. $$V_{TS} = V_{RS} + \left[\frac{(M_{TS} - M_{RS}) + (M_{S1} - M_{S2}) + \rho_A (V_{S2} - V_{S1}) - \Delta W + \Delta_{ST}}{\rho_W} \right] \quad (m^3) \qquad \textbf{(7)}$$

where ρ_W is the mean of the water densities $\rho_{W(RS)}$ and $\rho_{W(TS)}$.

The uncertainty in the measured volume may then be expressed as follows

$$u_c(V_{TS})^2 = c_1{}^2 u(V_{RS})^2 + c_2{}^2 u(M_{TS})^2 + c_3{}^2 u(M_{RS})^2 + c_4{}^2 u(M_{S1})^2 + c_5{}^2 u(M_{S2})^2 + c_6{}^2 u(\rho_A)^2 + c_7{}^2 u(V_{S2})^2 + c_8{}^2 u(V_{S1})^2 + c_9{}^2 u(\Delta W)^2 + c_{10}{}^2 u(\Delta_{ST})^2 + c_{11}{}^2 u(\rho_W)^2$$

where u_c is the combined standard uncertainty of the input standard uncertainties
$u(x)$ is the input standard uncertainty of quantity x
c_1, c_2, c_3……cn are the sensitivity coefficients of the input uncertainties

Then by partial differentiation

$$c_1 = \left(\frac{\partial V_{TS}}{\partial V_{RS}} \right) = 1$$

$$c_2 = \left(\frac{\partial V_{TS}}{\partial M_{TS}} \right) = \frac{1}{\rho_W}$$

$$c_3 = \left(\frac{\partial V_{TS}}{\partial M_{RS}} \right) = -\frac{1}{\rho_W}$$

$$c_4 = \left(\frac{\partial V_{TS}}{\partial M_{S1}} \right) = \frac{1}{\rho_W}$$

$$c_5 = \left(\frac{\partial V_{TS}}{\partial M_{S2}} \right) = -\frac{1}{\rho_W}$$

$$c_6 = \left(\frac{\partial V_{TS}}{\partial \rho_A} \right) = \frac{(V_{S2} - V_{S1})}{\rho_W}$$

$$c_7 = \left(\frac{\partial V_{TS}}{\partial V_{S2}} \right) = \frac{\rho_A}{\rho_W}$$

$$c_8 = \left(\frac{\partial V_{TS}}{\partial V_{S1}} \right) = -\frac{\rho_A}{\rho_W}$$

$$c_9 = \left(\frac{\partial V_{TS}}{\partial \Delta W} \right) = -\frac{1}{\rho_W}$$

$$c_{10} = \left(\frac{\partial V_{TS}}{\partial \Delta_{ST}} \right) = \frac{1}{\rho_W}$$

$$c_{11} = \left(\frac{\partial V_{TS}}{\partial \rho_W} \right) = -\left[\frac{(M_{TS} - M_{RS}) + (M_{S1} - M_{S2}) + \rho_A (V_{S2} - V_{S1}) - \Delta W + \Delta_{ST}}{\rho_W{}^2} \right]$$

WATER DENSITY CONTRIBUTIONS

Equation

The combined standard uncertainty associated with the water density equation over the temperature range 15 °C to 25 °C is taken from Patterson and Morris[2] and is given by:

$$u_C(\rho_{W(TS)}, \rho_{W(RS)}) = <0.001 \quad (\text{kg m}^{-3})$$

Therefore

$$c_{12} = \left(\frac{\partial \rho_{W(TS)}, \partial \rho_{W(RS)}}{\partial 0.001} \right) = 1$$

Expansivity

As demonstrated in Appendix 4 of NPL Report CMAM 66 [1], over the limited temperature range in which this work was carried out (19.8 °C to 20.1 °C) the volume expansivity of water can be assumed to be linear with a value of 0.206 636 x 10^{-3} °C^{-1} and with a maximum error of ± 0.01%.

Temperature

The contributions to the measurement uncertainty of the water temperature comprise the maximum measured difference in water temperatures adjacent to the spheres during a comparison (i.e. the temperature gradient), together with the calibration uncertainty and stability of the PRT.

Therefore if

> ρ_W is the water density calculated from the measured temperature (kg m^{-3})
> ΔT is the water temperature measurement uncertainty (°C)
> α is the volume thermal expansivity of water (°C^{-1})

then the change in ρ_W with temperature ΔT is given by:

$$\Delta\rho_W = \alpha \,.\Delta T.\, \rho_W \ (\text{kg m}^{-3})$$

and the uncertainty due to temperature contributions in ρ_W may be evaluated as follows:

$$u_C(\rho_W)^2 = c_{13}{}^2 u(\alpha)^2 + c_{14}{}^2 u(T)^2$$

Therefore

$$c_{13} = \left(\frac{\partial \rho_W}{\partial \alpha}\right) = \rho_W .\Delta T$$

$$c_{14} = \left(\frac{\partial \rho_W}{\partial \Delta T}\right) = \rho_W .\alpha$$

AIR DENSITY CONTRIBUTIONS

The dependence of the uncertainty in air density on the parameters that are measured to calculate it, i.e. temperature, pressure, dew point and carbon dioxide concentration, are taken from Giacomo [4] and can be expressed:

$$u_C(\rho_A)^2 = c_{15}{}^2 u(\rho_{A(p)})^2 + c_{16}{}^2 u(\rho_{A(T)})^2 + c_{17}{}^2 u(\rho_{A(d)})^2 + c_{18}{}^2 u(\rho_{A(CO_2)})^2$$

therefore

$$c15 = \left(\frac{\partial \rho_A}{\partial \rho_{A(p)}} \right) = +1 \times 10^{-5} \text{ Pa}$$

$$c16 = \left(\frac{\partial \rho_A}{\partial \rho_{A(t)}} \right) = -4 \times 10^{-3} \text{ °C}^{-1}$$

$$c17 = \left(\frac{\partial \rho_A}{\partial \rho_{A(d)}} \right) = -3 \times 10^{-4} \text{ °C}^{-1}$$

$$c18 = \left(\frac{\partial \rho_A}{\partial \rho_{A(x_{CO2})}} \right) = +0.4 \quad \partial x_{CO2}$$

7 RESULTS

The summary tables (Figure 1 and 2) and graph (Figure 3) give the values of the measured mass and volume obtained from this investigation together with their combined uncertainties quoted at a confidence level of approximately 95% (k=2). The mass and volume values obtained by PTB, and the volume calculated from information supplied by H & D Fitzgerald are also included.

	Mass (g)	**Mass uncertainty (k=2) (± g)**
NPL	978.007 06	0.000 26
PTB	978.006 94	0.000 25

Figure 1. Mass of test sphere SF

	Volume at 20 °C (cm^3)	**Volume uncertainty (k=2) (± cm^3)**
NPL (using Zerodur sphere)	386.277 12	0.000 86
NPL (using silica sphere)	386.277 28	0.000 74
H & D Fitzgerald[4]	386.276 93	0.000 80
PTB	386.276 73	0.000 80

[4] The volume was calculated by NPL using NPL's mass value and a density value supplied by H & D Fitzgerald. An uncertainty similar to that obtained by PTB and NPL has been assumed.

Figure 2. Reported values for the volume of test sphere SF

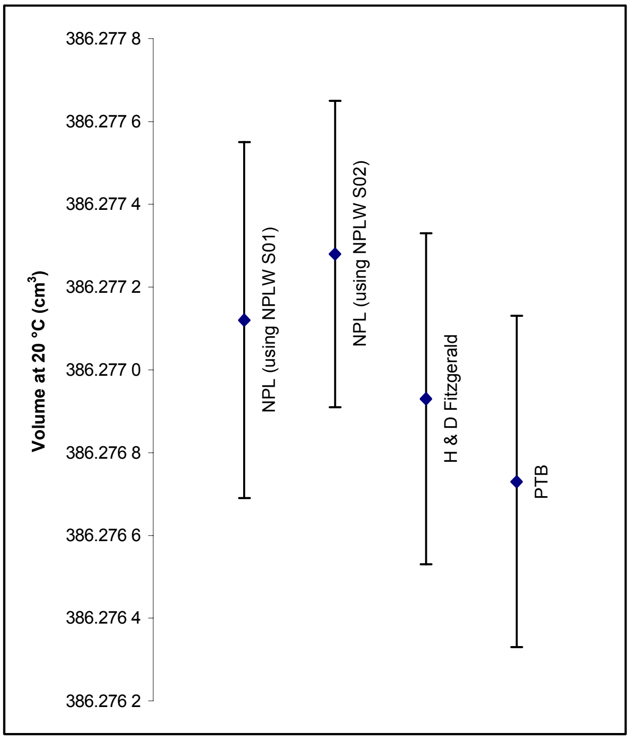

Figure 3. Volume of test sphere SF

The error bars represent the combined uncertainties at k=2

NPL's calculations of the volume and uncertainties of the test sphere using the Zerodur reference sphere are shown in Appendices 1.1 and 2.1 respectively; the calculations using the silica reference sphere are shown in Appendices 1.2 and 2.2. The NPL volume values shown in Figure 2 were calculated using NPL's determination for the mass value of the test sphere. If PTB's mass value (0.12 mg less than NPL's) were substituted, NPL's values for the volume would be 0.000 12 cm^3 lower in both cases, bringing them in closer agreement with the PTB value.

8 CONCLUSIONS

The mass values of the test sphere obtained by NPL and PTB were in agreement with each other and within their calculated uncertainties.

The values obtained by NPL of the volume of the test sphere, using the two reference spheres, were within 0.000 16 cm^3 of each other and are in agreement with the volumes obtained by PTB and H & D Fitzgerald. The NPL uncertainties have been estimated as ± 0.000 86 cm^3 using the Zerodur reference sphere and ± 0.000 74 cm^3 using the silica reference sphere.

The uncertainties achieved for both the mass and volume determinations were similar to those given by PTB. However, it is anticipated that when NPL's new precision 1 kg balance and 1 kg hydrostatic weighing apparatus are fully operational, NPL will be able to improve further on the uncertainties achieved.

9 ACKNOWLEDGEMENTS

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APPENDIX 1.1

CALCULATION OF THE VOLUME OF SPHERE SF
Using Zerodur reference sphere NPLW S01

Parameters	Mass (g)	Volume cm^3	Coefficient of expansion
Zerodur (SF)	978.007 060	-	0.00E+00
Zerodur (S01)	1005.731 786	395.998 635 0	0.00E+00
Standards (S1)*	020.020 073	2.547 9	-
Makeweights (S2)	002.000 021	0.254 6	-

* 0.000 003 g added to S1 to compensate for gravitational gradient

Run	ΔW	Air density	SF			S01			SF
	g	kg m^{-3}	Water temp. °C	Water density kg m^{-3}	Corr. Density* kg m^{-3}	Water temp. °C	Water density kg m^{-3}	Corr. Density* kg m^{-3}	Volume at 20 °C cm^3
1	-0.003 03	1.195 1	19.836	998.239 4	998.240 0	19.840	998.238 6	998.238 8	386.276 63
2	-0.002 90	1.194 7	19.838	998.239 0	998.239 6	19.842	998.238 2	998.238 3	386.276 50
3	-0.003 83	1.194 6	19.841	998.238 4	998.239 0	19.848	998.237 0	998.237 1	386.277 18
4	-0.004 11	1.194 2	19.844	998.237 8	998.238 4	19.854	998.235 7	998.235 9	386.277 21
5	-0.003 73	1.197 6	19.961	998.213 7	998.214 4	19.960	998.213 9	998.214 1	386.277 48
6	-0.003 91	1.195 6	19.962	998.213 5	998.214 2	19.964	998.213 1	998.213 3	386.277 42
7	-0.003 66	1.195 7	19.986	998.208 6	998.209 2	19.991	998.207 6	998.207 7	386.276 88
8	-0.004 32	1.194 7	19.978	998.210 2	998.210 9	19.989	998.208 0	998.208 1	386.277 06
9	-0.005 48	1.193 1	19.968	998.212 3	998.212 9	19.988	998.208 2	998.208 3	386.277 51
10	-0.005 76	1.192 6	19.964	998.213 1	998.213 8	19.988	998.208 2	998.208 3	386.277 48
11	-0.003 29	1.200 2	20.088	998.187 5	998.187 7	20.088	998.187 5	998.188 1	386.277 07
12	-0.003 15	1.200 0	20.084	998.188 3	998.188 5	20.080	998.189 1	998.189 8	386.277 26
13	-0.003 84	1.199 6	20.090	998.187 1	998.187 2	20.086	998.187 9	998.188 5	386.277 94
14	-0.002 74	1.198 9	20.086	998.187 9	998.188 1	20.084	998.188 3	998.189 0	386.276 69
15	-0.003 00	1.198 2	20.082	998.188 7	998.188 9	20.079	998.189 3	998.190 0	386.277 04
16	-0.002 67	1.198 0	20.078	998.189 6	998.189 7	20.078	998.189 6	998.190 2	386.276 47
17	-0.002 88	1.200 2	19.873	998.231 8	998.232 0	19.878	998.230 8	998.231 4	386.276 68
18	-0.002 55	1.199 9	19.884	998.229 6	998.229 7	19.878	998.230 8	998.231 4	386.277 22
19	-0.002 54	1.199 7	19.886	998.229 2	998.229 3	19.881	998.230 2	998.230 8	386.277 13
20	-0.002 58	1.199 6	19.893	998.227 7	998.227 9	19.883	998.229 8	998.230 4	386.277 56
								Average (cm^3):	**386.277 12**
								σ (±cm^3):	**0.000 39**

*Formula includes corrections for air saturation (Bignell), immersion depth and isotopic ratio

APPENDIX 1.2

CALCULATION OF THE VOLUME OF SPHERE SF
Using silica reference sphere NPLW S02

Parameters	Mass (g)	Volume cm^3	Coefficient of expansion
Zerodur (SF)	978.007 060	-	0.00E+00
Silica (S02)	1011.755 310	459.718 750 0	1.40E-06
Standards (S1)	010.500 016	1.335 3	-
Makeweights (S2)	050.070 222	6.403 3	-

* 0.000 002 g added to S1 and 0.000 009 g added to S2 to compensate for gravitational gradient

			SF			S02				SF
Run	ΔW g	Air density kg m^{-3}	Water temp. °C	Water density kg m^{-3}	Corr. Density* kg m^{-3}	Water temp. °C	Water density kg m^{-3}	Corr. Density* kg m^{-3}	Volume at T°C cm^3	Volume at 20 °C cm^3
1	-0.000 98	1.179 8	19.920	998.222 2	998.222 3	19.918	998.222 6	998.223 2	459.718 697 2	386.277 05
2	-0.000 98	1.179 1	19.924	998.221 4	998.221 5	19.919	998.222 4	998.223 0	459.718 697 9	386.277 27
3	-0.001 31	1.181 9	19.937	998.218 7	998.218 8	19.932	998.219 7	998.220 3	459.718 706 2	386.277 43
4	-0.001 21	1.180 4	19.940	998.218 1	998.218 2	19.934	998.219 3	998.219 9	459.718 707 5	386.277 37
5	-0.000 89	1.180 1	19.949	998.216 2	998.216 4	19.940	998.218 1	998.218 7	459.718 711 4	386.277 20
6	-0.000 84	1.179 8	19.954	998.215 2	998.215 3	19.940	998.218 1	998.218 7	459.718 711 4	386.277 55
7	-0.002 11	1.190 7	20.018	998.202 0	998.202 1	20.012	998.203 2	998.203 9	459.718 757 7	386.277 19
8	-0.002 22	1.187 8	20.032	998.199 1	998.199 2	20.024	998.200 7	998.201 4	459.718 765 4	386.277 28
9	-0.001 90	1.186 7	20.040	998.197 4	998.197 6	20.030	998.199 5	998.200 1	459.718 769 3	386.277 02
10	-0.002 03	1.185 9	20.050	998.195 4	998.195 5	20.036	998.198 3	998.198 9	459.718 773 2	386.277 38
11	-0.003 80	1.196 0	20.027	998.200 1	998.200 8	20.028	998.199 9	998.200 1	459.718 768 0	386.277 72
12	-0.003 68	1.194 8	20.030	998.199 5	998.200 1	20.034	998.198 7	998.198 8	459.718 771 9	386.277 27
13	-0.003 74	1.193 9	20.036	998.198 3	998.198 9	20.042	998.197 0	998.197 2	459.718 777 0	386.277 05
14	-0.004 31	1.193 3	20.040	998.197 4	998.198 1	20.048	998.195 8	998.195 9	459.718 780 9	386.277 37
15	-0.004 60	1.192 6	20.107	998.183 5	998.184 2	20.108	998.183 3	998.183 5	459.718 819 5	386.277 34
16	-0.004 52	1.191 5	20.108	998.183 3	998.184 0	20.110	998.182 9	998.183 1	459.718 820 8	386.277 14
17	-0.002 67	1.197 9	19.948	998.216 4	998.217 1	19.954	998.215 2	998.215 3	459.718 720 4	386.277 28
18	-0.002 72	1.196 2	19.953	998.215 4	998.216 0	19.960	998.213 9	998.214 1	459.718 724 3	386.277 15
19	-0.003 17	1.194 5	19.961	998.213 7	998.214 4	19.972	998.211 5	998.211 6	459.718 732 0	386.277 10
20	-0.003 69	1.193 2	19.967	998.212 5	998.213 1	19.980	998.209 8	998.210 0	459.718 737 1	386.277 34
									Average (cm^3):	**386.277 28**
									σ (±m^3):	**0.000 17**

*Formula includes corrections for air saturation (Bignell), immersion depth and isotopic ratio

APPENDIX 2.1

CALCULATION OF THE MEASUREMENT UNCERTAINTY OF THE VOLUME OF SPHERE SF
Using Zerodur reference sphere NPLW S01

All uncertainties calculated at k=1

Table A - contributions to air density uncertainty

Parameter	Symbol	Nominal value	Uncertainty Contribution	Value	Divisor	Standard uncertainty (u) (source unit)	Sensitivity coefficient (c_x)		Standard uncertainty (u) ±(kg m^{-3})
Pressure	$\rho_{A(p)}$	1 020 hPa	Stability	20.000 00 Pa	√3	11.547 01 Pa	c_{15}	0.000 01	0.000 12
			Calibration	6.000 00 Pa	2	3.000 00 Pa		0.000 01	0.000 03
Temperature	$\rho_{A(T)}$	20 °C	Stability	0.050 00 °C	√3	0.028 87 °C	c_{16}	0.004 00	0.000 12
			Gradient	0.200 00 °C	√3	0.115 47 °C		0.004 00	0.000 46
			Calibration	0.030 00 °C	2	0.015 00 °C		0.004 00	0.000 06
Dew point	$\rho_{A(d)}$	7 °C	Stability	2.000 00 °C	√3	1.154 70 °C	c_{17}	0.000 30	0.000 35
			Gradient	2.000 00 °C	√3	1.154 70 °C		0.000 30	0.000 35
			Calibration	0.200 00 °C	2	0.100 00 °C		0.000 30	0.000 03
Carbon dioxide	$\rho_{A(CO2)}$	400 ppm		0.000 04 kg m^{-3}	√3	0.000 02 kg m^{-3}	c_{18}	0.400 00	0.000 01
CIPM equation				0.000 12 kg m^{-3}	1	0.000 12 kg m^{-3}		1.000 00	0.000 12
						Combined air density uncertainty:			**0.000 71**

Table B - contributions to water density

Parameter	Symbol	Nominal value	Uncertainty Contribution	Value	Divisor	Standard uncertainty (u) (source unit)	Sensitivity coefficient (c_x)		Standard uncertainty (u) ±(kg m^{-3})
Water density equation	$\rho_{W(T)}$	0.998 g cm^{-3}	*P & M**	0.001 00 kg m^{-3}	1	0.001 00 kg m-3	c_{12}	1.000 00	0.001 00
Expansivity	α	0.000 207 °C^{-1}		0.000 00 °C^{-1}	1	0.000 00 °C^{-1}	c_{13}	0.023 95	0.000 00
Water temperature	ΔT	0.024 °C	Stability	0.005 00 °C	√3	0.002 89 °C	c_{14}	0.000 21	0.000 60
			Gradient	0.030 00 °C	√3	0.017 32 °C		0.000 21	0.003 58
			Calibration	0.001 00 °C	2	0.000 50 °C		0.000 21	0.000 10
						Combined water density uncertainty:			**0.003 76**

Table C - contributions to volume of artefact at T °C

Parameter	Symbol	Nominal value	Uncertainty Contribution	Value	Divisor	Standard uncertainty (u) (source unit)	Sensitivity coefficient (c_x)		Standard uncertainty (u) ±(cm^3)
Volume of reference sphere	V_{RS}	396 cm^3	Calibration	0.000 06 cm^3	2	0.000 03 cm^3	c_1	0.002 53	0.000 00
Mass of test sphere TS	M_{TS}	978 g	Calibration	0.000 13 g	2	0.000 07 g	c_2	1.002 00	0.000 07
Mass of reference sphere RS	M_{RS}	1 006 g	Calibration	0.000 06 g	2	0.000 03 g	c_3	-1.002 00	-0.000 03
Mass of makeweights (S1)	M_{S1}	20 g	Calibration	0.000 02 g	2	0.000 01 g	c_4	1.002 00	0.000 01
Mass of makeweights (S2)	M_{S2}	2 g	Calibration	0.000 00 g	2	0.000 00 g	c_5	-1.002 00	0.000 00
Air density	ρ_A	0.001 2 g cm^{-3}	*From table A*	0.000 71 kg m^{-3}	1	0.000 71 kg m^{-3}	c_6	-2.297 90	0.000 00
Volume of makeweights (S2)	V_{S2}	0.255 cm^3	Calibration	0.000 00 cm^3	2	0.000 00 cm^3	c_7	0.001 20	0.000 00
Volume of makeweights (S1)	V_{S1}	2.548 cm^3	Calibration	0.010 00 cm^3	2	0.005 00 cm^3	c_8	-0.001 20	-0.000 01
Balance difference	ΔW	0.002 g	Calibration	0.000 19 g	2	0.000 10 g	c_9	1.002 00	0.000 10
Surface tension	Δ_{ST}	0.000 2 g	Repeatability	0.000 21 g	√3	0.000 12 g	c_{10}	1.002 00	0.000 12
Density of water	ρ_w	0.998 g cm^{-3}	*From table B*	0.003 76 kg m^{-3}	1	0.003 76 kg m^{-3}	c_{11}	-10.004 55	-0.000 04
Standard deviation	σ		Repeatability	0.000 39 kg m^{-3}	1	0.000 39 cm^3		1.000 00	0.000 39
						Combined volume uncertainty :			**0.000 43**

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APPENDIX 2.2

CALCULATION OF THE MEASUREMENT UNCERTAINTY OF THE VOLUME OF SPHERE SF
Using silica reference sphere NPLW S02

All uncertainties calculated at k=1

Table A - contributions to air density uncertainty

Parameter	Symbol	Nominal value	Uncertainty Contribution	Value	Divisor	Standard uncertainty (u) (source unit)		Sensitivity coefficient (c_x)	Standard uncertainty (u) ±(kg m^{-3})
Pressure	$\rho_{A(p)}$	1 020 hPa	Stability	20.000 00 Pa	√3	11.547 01 Pa	c_{15}	0.000 01	0.000 12
			Calibration	6.000 00 Pa	2	3.000 00 Pa		0.000 01	0.000 03
Temperature	$\rho_{A(T)}$	20 °C	Stability	0.050 00 °C	√3	0.028 87 °C	c_{16}	0.004 00	0.000 12
			Gradient	0.200 00 °C	√3	0.115 47 °C		0.004 00	0.000 46
			Calibration	0.030 00 °C	2	0.015 00 °C		0.004 00	0.000 06
Dew point	$\rho_{A(d)}$	7 °C	Stability	2.000 00 °C	√3	1.154 70 °C	c_{17}	0.000 30	0.000 35
			Gradient	2.000 00 °C	√3	1.154 70 °C		0.000 30	0.000 35
			Calibration	0.200 00 °C	2	0.100 00 °C		0.000 30	0.000 03
Carbon dioxide	$\rho_{A(CO2)}$	400 ppm		0.000 04 kg m^{-3}	√3	0.000 02 kg m^{-3}	c_{18}	0.400 00	0.000 01
CIPM equation				0.000 12 kg m^{-3}	1	0.000 12 kg m^{-3}		1.000 00	0.000 12
								Combined air density uncertainty:	**0.000 71**

Table B - contributions to water density

Parameter	Symbol	Nominal value	Uncertainty Contribution	Value	Divisor	Standard uncertainty (u) (source unit)		Sensitivity coefficient (c_x)	Standard uncertainty (u) ±(kg m^{-3})
Water density equation	$\rho_{W(T)}$	0.998 g cm^{-3}	*P & M**	0.001 00 kg m^{-3}	1	0.001 00 kg m-3	c_{12}	1.000 00	0.001 00
Expansivity	α	0.000 207 °C^{-1}		0.000 00 °C^{-1}	1	0.000 00 °C^{-1}	c_{13}	0.013 97	0.000 00
Water temperature	ΔT	0.014 °C	Stability	0.005 00 °C	√3	0.002 89 °C	c_{14}	0.000 21	0.000 60
			Gradient	0.030 00 °C	√3	0.017 32 °C		0.000 21	0.003 58
			Calibration	0.001 00 °C	2	0.000 50 °C		0.000 21	0.000 10
								Combined water density uncertainty:	**0.003 76**

Table C - contributions to volume of artefact at T °C

Parameter	Symbol	Nominal value	Uncertainty Contribution	Value	Divisor	Standard uncertainty (u) (source unit)		Sensitivity coefficient (c_x)	Standard uncertainty (u) ±(cm^3)
Volume of reference sphere	V_{RS}	460 cm^3	Calibration	0.000 40 cm^3	2	0.000 20 cm^3	c_1	0.002 17	0.000 00
Mass of test sphere TS	M_{TS}	978 g	Calibration	0.000 13 g	2	0.000 07 g	c_2	1.002 00	0.000 07
Mass of reference sphere RS	M_{RS}	1 012 g	Calibration	0.000 06 g	2	0.000 03 g	c_3	-1.002 00	-0.000 03
Mass of makeweights (S1)	M_{S1}	11 g	Calibration	0.000 02 g	2	0.000 01 g	c_4	1.002 00	0.000 01
Mass of makeweights (S2)	M_{S2}	50 g	Calibration	0.000 00 g	2	0.000 00 g	c_5	-1.002 00	0.000 00
Air density	ρ_A	0.001 2 g cm^{-3}	*From table A*	0.000 71 kg m^{-3}	1	0.000 71 kg m^{-3}	c_6	5.078 16	0.000 00
Volume of makeweights (S2)	V_{S2}	6.403 cm^3	Calibration	0.000 00 cm^3	2	0.000 00 cm^3	c_7	0.001 20	0.000 00
Volume of makeweights (S1)	V_{S1}	1.335 cm^3	Calibration	0.010 00 cm^3	2	0.005 00 cm^3	c_8	-0.001 20	-0.000 01
Balance difference	ΔW	0.002 g	Calibration	0.000 19 g	2	0.000 10 g	c_9	1.002 00	0.000 10
Surface tension	Δ_{ST}	0.000 2 g	Repeatability	0.000 21 g	√3	0.000 12 g	c_{10}	1.002 00	0.000 12
Density of water	ρ_w	0.998 g cm^{-3}	*From table B*	0.003 76 kg m^{-3}	1	0.003 76 kg m^{-3}	c_{11}	-72.995 72	-0.000 27
Standard deviation	σ		Repeatability	0.000 17 kg m^{-3}	1	0.000 17 cm^3		1.000 00	0.000 17
								Combined volume uncertainty :	**0.000 37**

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