

# SOP 13

## Gravimetric calibration of volume contained using water

### 1. Scope and field of application

This procedure describes how to calibrate the volume of solution contained by a volumetric flask or other container capable of being filled to a reproducible mark. This is expressed as the volume contained at a standard temperature (20.0°C). This procedure is capable of achieving a reproducibility of better than 0.01% (1 relative standard deviation).

### 2. Principle

The mass of water contained by the flask at a measured calibration temperature is used to compute the volume of water contained at that temperature. The volume that would be contained at the standard temperature (20°C) can be calculated by taking account of the volumetric expansion of the flask. The volume of liquid contained at any desired temperature can be calculated in a similar fashion.

### 3. Apparatus

- Analytical balance capable of weighing the quantity of water contained with a sensitivity of 1 part in  $10^5$  while having the capacity to weigh the water together with the container being calibrated,
- Thermometer accurate to  $\pm 0.1^\circ\text{C}$ .

### 4. Reagents

- Deionized water.

### 5. Procedure

- 5.1 Weigh the clean dry empty container together with the associated closure.
- 5.2 Fill the container being calibrated to the mark with deionized water, allowing the temperature of the container and contained water to reach an equilibrium value. Note this temperature.
- 5.3 Close the container and reweigh it.

## 6. Calculation and expression of results

### 6.1 Volume of the water contained at the calibration temperature

Compute the weight of the water contained from the difference between weights of the filled and empty container:

$$w(\text{H}_2\text{O}) = w(\text{filled container}) - w(\text{empty container}). \quad (1)$$

Compute the mass of water contained, correcting for air buoyancy (see SOP 21):

$$m(\text{H}_2\text{O}) = w(\text{H}_2\text{O}) \left( \frac{1 - \rho(\text{air})/\rho(\text{weights})}{1 - \rho(\text{air})/\rho(\text{sample})} \right). \quad (2)$$

The volume contained at the noted temperature ( $t$ ) is

$$V(t) = m(\text{H}_2\text{O})/\rho(\text{H}_2\text{O}, t). \quad (3)$$

The density of air-saturated water in the temperature range 5 to 40°C is given by the expression (Jones and Harris, 1992)

$$\begin{aligned} \rho_w / (\text{kg m}^{-3}) = & 999.84847 + 6.337563 \times 10^{-2} (t/^\circ\text{C}) \\ & - 8.523829 \times 10^{-3} (t/^\circ\text{C})^2 + 6.943248 \times 10^{-5} (t/^\circ\text{C})^3 \\ & - 3.821216 \times 10^{-7} (t/^\circ\text{C})^4 \end{aligned} \quad (4)$$

where  $t$  is the temperature on ITS 90<sup>1</sup>. To achieve an accuracy of 1 part in 10<sup>4</sup>,  $t$  must be known to within 0.5°C.

### 6.2 Volume that would be contained at an alternate temperature

To convert the volume contained at one temperature ( $t_1$ ) to a standard or alternate temperature ( $t_2$ ), we need to take account of the thermal expansion of the container being used. For Pyrex-like glasses (Corning 7740, Kimble KG-33, Schott Duran, Wheaton 200, *etc.*) the coefficient of linear expansion  $\alpha_l$  is  $32.5 \times 10^{-7} \text{ K}^{-1}$ ; for glasses such as Kimble KG-35,  $\alpha_l$  is about  $55 \times 10^{-7} \text{ K}^{-1}$ .

The coefficient of volumetric expansion,

$$\alpha_v = (1 + \alpha_l)^3 - 1 \approx 3\alpha_l, \quad (5)$$

is used to calculate the corrected volume at the alternate temperature,

$$V(t_2) = V(t_1)[1 + \alpha_v(t_2 - t_1)]. \quad (6)$$

This correction is negligible for all except the most precise work; unless  $t_2 - t_1$  exceeds 10°C or if plastic ware is used.

<sup>1</sup> The International Practical Temperature Scale of 1968 (IPTS 68) has been superceded by the International Temperature Scale of 1990 (ITS 90). A simple equation can be used to relate the two over the oceanographic temperature range 0 to 40°C (Jones and Harris, 1992):

$$t_{90} = 0.0002 + 0.99975 t_{68}.$$

The small difference in temperature scales is typically not important to the calibration of glassware for the procedures in this Guide.

### 6.3 Example calculation

6.3.1 The following data were used for this calculation:

$$\begin{aligned} w(\text{H}_2\text{O}) &= 996.55 \text{ g,} \\ \text{calibration temperature} &= 23.0^\circ\text{C,} \\ \rho(\text{H}_2\text{O}, 23.0^\circ\text{C}) &= 0.997535 \text{ g cm}^{-3}, \\ \alpha_l &= 32.5 \times 10^{-7} \text{ K}^{-1}, \end{aligned}$$

weighing conditions:

$$\begin{aligned} \rho(\text{air}) &= 0.0012 \text{ g cm}^{-3},^2 \\ \rho(\text{weights}) &= 8.0 \text{ g cm}^{-3}. \end{aligned}$$

6.3.2 Correct weight of water to mass:

$$\begin{aligned} m(\text{H}_2\text{O}) &= 996.55 \times \frac{1 - 0.0012/8.0}{1 - 0.0012/0.997535} \\ &= 997.60 \text{ g.} \end{aligned}$$

6.3.3 Compute volume of water contained at the calibration temperature of 23.0°C:

$$\begin{aligned} V(23.0^\circ\text{C}) &= 997.60/0.997535 \\ &= 1000.07 \text{ cm}^3. \end{aligned}$$

6.3.4 Compute volume that would be contained at the standard temperature of 20.0°C, *i.e.*, the standard calibrated volume:

$$\begin{aligned} V(20.0^\circ\text{C}) &= 1000.07 [1 + 3(32.5 \times 10^{-7})(20.0 - 23.0)] \\ &= 1000.04 \text{ cm}^3. \end{aligned}$$

6.3.5 Compute volume that would be contained at 25°C.

$$\begin{aligned} V(25.0^\circ\text{C}) &= 1000.04 [1 + 3(32.5 \times 10^{-7})(25.0 - 20.0)] \\ &= 1000.09 \text{ cm}^3. \end{aligned}$$

## 7. Quality assurance

To ensure that the volume contained is in control, the amount contained should be measured regularly and a property control chart maintained of the volume corrected to 20°C (see SOP 22).

## 8. Bibliography

Jones, F.E. and Harris, G.L. 1992. ITS-90 density of water formulation for volumetric standards calibration. *J. Res. Natl. Inst. Stand. Technol.* **97**: 335–340.

<sup>2</sup> This value is appropriate to measurements of moderate accuracy made at sea level pressure (1 atm) and at normal laboratory temperatures (~ 20°C). For a more accurate value see SOP 21, Equation (1).