SOP 12

Gravimetric calibration of volume delivered using water

1. Scope and field of application

This procedure describes how to calibrate the volume of water delivered by a volumetric pipette—or similar device such as a Knudsen style pipette, a syringe or a piston burette. This is expressed as the volume delivered 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 delivered by the device at a measured calibration temperature is used to compute the volume of water delivered at that temperature. The volume that would be delivered at the standard temperature (20 °C) can be calculated by taking account of the volumetric expansion of the dispenser. The volume of liquid delivered at any desired temperature can be calculated in a similar fashion.

3. Apparatus

3.1 Analytical balance capable of weighing the quantity of water delivered with a resolution of 1 part in 10^5 while having sufficient capacity to weigh the water together with the glass container used to collect it.

3.2 Clean dry glass containers with suitable closures (Note 1)

3.3 Thermometer accurate to ± 0.1 °C

3.4 Timer

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1 If the container and water will be weighed shortly after delivery then an ungreased ground glass stopper, or even a screw cap, is suitable. If it will be some time before the water delivered is weighed, as when samples are delivered on board ship, it is essential that the closure chosen be both air and water-tight.

4. Reagents

4.1 Deionized water

5. Procedure

5.1 Weigh the clean, dry, empty container together with the associated closure.

5.2 Fill the clean pipette or other apparatus being calibrated with deionized water. Allow the temperature of the pipette and water to reach an equilibrium value. Note this temperature.

5.3 Allow the water to drain into the pre-weighed container for a controlled time (60 seconds).

5.4 Close the container and reweigh it.

6. Calculation and expression of results

6.1 Volume of water delivered at the calibration temperature

Compute the weight of the water delivered from the difference between the filled and empty container volumes:

$$w(\mathrm{H_2O}) = w(\text{filled container}) - w(\text{empty container})\ . \qquad (1)$$

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

$$m(\mathrm{H_2O}) = w(\mathrm{H_2O})\left(\frac{1-\rho(\text{air})/\rho(\text{weights})}{1-\rho(\text{air})/\rho(\text{sample})}\right)\ . \qquad (2)$$

The volume dispensed at the temperature noted (t) is

$$V(t) = m(\mathrm{H_2O}) / \rho(\mathrm{H_2O}, t)\ . \qquad (3)$$

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

$$\begin{aligned}\rho_{\mathrm{W}} / (\mathrm{kg{\cdot}m^{-3}}) = {} & 999.84847 + 6.337563 \times 10^{-2}\,(t/°\mathrm{C}) \\ & - 8.523829 \times 10^{-3}\,(t/°\mathrm{C})^2 + 6.943248 \times 10^{-5}\,(t/°\mathrm{C})^3 \\ & - 3.821216 \times 10^{-7}\,(t/°\mathrm{C})^4\ , \qquad (4)\end{aligned}$$

where t is the temperature on ITS 90 (Note 2). To achieve an accuracy of 1 part in 10^4, t must be known to within 0.5 °C.

6.2 Volume that would be delivered at an alternate temperature

To convert the volume dispensed at one temperature (t_1) to the volume that would be delivered at a standard or alternate temperature (t_2), we need to take account of the thermal expansion of the dispenser being used. For pyrex-like glasses (Corning 7740, Kimble KG-33, Schott Duran, Wheaton 200, *etc.*) the coefficient of linear expansion α_l is 32.5×10^{-7} K^{-1}; for glasses such as Kimble KG-35, α_l is about 55×10^{-7} K^{-1}. The coefficient of volumetric expansion,

$$\alpha_V = (1 + \alpha_l)^3 - 1 \approx 3\,\alpha_l \,, \tag{5}$$

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

$$V(t_2) = V(t_1)\,\{1 + \alpha_V\,(t_2 - t_1)\} \,. \tag{6}$$

This correction is negligible for all except the most precise work unless $(t_2 - t_1)$ exceeds 10 °C.

6.3 Example calculation

6.3.1 The following data were used for this calculation:

$w(H_2O) = 30.0000$ g ,
calibration temperature = 23.0 °C ,
$\rho(H_2O, 23.0\ °C) = 0.997535$ g·cm^{-3} ,
$\alpha_l = 32.5 \times 10^{-7}$ K^{-1} ,
weighing conditions
ρ(air) = 0.0012 g·cm^{-3} (Note 3) ,
ρ(weights) = 8.0 g·cm^{-3} .

6.3.2 Correct weight of water to mass:

$$m(H_2O) = 30.0000 \times \frac{1 - 0.0012/8.0}{1 - 0.0012/0.997541}$$
$$= 30.0316 \text{ g} .$$

[2] The International Practical Temperature Scale of 1968 (IPTS 68) has recently 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 & 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 Handbook.

[3] 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).

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

$$V(23.0\ ^\circ\text{C}) = 30.0316 / 0.997535 = 30.1058\ \text{cm}^3\ .$$

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

$$V(20.0\ ^\circ\text{C}) = 30.1058\ \{1 + 3\,(32.5 \times 10^{-7})(20.0 - 23.0)\} = 30.1049\ \text{cm}^3\ .$$

6.3.5 Compute volume that is dispensed at 25 °C.

$$V(25.0\ ^\circ\text{C}) = 30.1049\ \{1 + 3\,(32.5 \times 10^{-7})(25.0 - 20.0)\} = 30.1064\ \text{cm}^3\ .$$

7. Quality assurance

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

References

Jones F. E. & G. L. Harris (1992) ITS-90 density of water formulation for volumetric standards calibration. *Journal of Research of the National Institute of Standards and Technology* **97**, 335–340.