MSL Technical Guide 17

Measuring Volume by Weighing Water

Introduction

A convenient method for measuring the volume of a vessel is to weigh the water it can contain (or deliver). This method, which is also known as the gravimetric method, can be used for calibrating burettes, pipettes, graduated tubes, one-mark flasks, pyknometers and other volumetric vessels with volumes from a few millilitres to thousands of litres. The method can also be used to calibrate water flowmeters. A typical standard volume vessel is shown in Figure 1. This is a 5 L contained volume standard that is calibrated using the gravimetric method described here and used to check other 5 L standards by volume comparison.

This technical guide describes the gravimetric method for measuring volume and explains how the volume is calculated from the weighing data. Key parameters such as air density, water density, water temperature, water impurity and repeatability are covered, along with their contribution to the uncertainty in the value of the measured volume [1]. Some practical details of the method are discussed, including the choice of a suitable balance and thermometer, and an example calculation is given.

Specific applications of this method are not covered in detail in this technical guide. There are many documentary standards and other publications that describe the application of this method to different types of volume or flow measuring equipment [2-10]. For example:

- ISO 4787 [2] provides a method for measuring the capacity of volumetric glassware such as burettes, pipettes and one-mark flasks; and
- OIML R 49-1 [3] gives a test procedure for water meters that is referenced in the New Zealand Water & Wastes Association Water Meter Code of Practice [4].

The weighing device used for the volume determination is most likely to be an electronic balance. It is recommended that this technical guide is used in conjunction with an earlier MSL technical guide on assuring the quality of weighing results from electronic balances [11].

Principle of the Method

There are two forms of the method, one for determining the contained volume of a vessel and the other for measuring the delivered volume.

For a contained volume, the vessel is weighed empty and dry, giving balance reading r_1. It is then filled (usually to a mark) and re-weighed, giving balance reading r_2.

Figure 1. A 5 L contained volume standard.

The equation relating the measured volume of the vessel V to the balance readings is

$$V = (r_2 - r_1)\left(\frac{1}{f.dw - da}\right)\left(1 - \frac{da}{ds}\right), \qquad (1)$$

where V and dw are the measured vessel volume and the density of distilled water at temperature t respectively, f is a water density correction factor ($f = 1$ for distilled water), da is the air density, and ds is normally 8000 kg/m^3. This value is used for density ds because electronic balances are normally set up to correctly measure the mass of objects with a density of 8000 kg/m^3.

For a delivered volume, (1) also applies, but in this case a second vessel is weighed before and after the delivered volume has been added to it, giving balance readings r_1 and r_2 respectively.

Usually the aim of the measurement is to determine the volume of the vessel at a reference temperature t_0 (typically 20 °C). This volume $V(t_0)$ is calculated from V using the equation

$$V(t_0) = V\left[1 + \gamma_V (t_0 - t)\right] \qquad (2)$$

where γ_V is the thermal coefficient of cubic expansion of the material of the vessel. Values for γ_V are given in

Table 5 of [2], for example γ_V is 10×10^{-6} °C^{-1} for borosilicate glass.

Key Parameters

There are several key parameters to consider in measuring volume by weighing water. These are air density, water density, water temperature, water impurity, and repeatability. The effect of other factors on the measurement uncertainty associated with $V(t_0)$, such as weighing accuracy, can usually be kept to an insignificant level by design.

Air Density

For most volume measurements, the air density da can be assumed to be 1.2 kg/m^3. This assumption avoids the need to measure ambient pressure, temperature and humidity, greatly simplifying the measurement. A measurement of the actual air density is usually only required when measuring a volume with a relative expanded uncertainty (see [1]) of less than 0.0001 (0.01 %), which is generally only the case for some pyknometers. If you need to measure volumes with a relative expanded uncertainty of less than 0.0001, contact MSL (see below) to get advice on the best approach to determining the air density.

The relative standard uncertainty in V due to assuming da = 1.2 kg/m^3 is

$$u_{(da=1.2)}(V)/V = 0.016 \text{ mL/L} . \qquad (3)$$

This value assumes that the volume measurement is performed at an altitude below 100 m, with an ambient temperature in the range 15 °C to 25 °C, and with ambient pressure variations at sea level typical of New Zealand (990 hPa to 1040 hPa).

When the volume measurement is performed at an altitude up to about 1000 m, and the desired relative expanded uncertainty is 0.0001 or greater, an assumed air density can be calculated using

$$da = (1.2 - 0.00014h) \text{ kg/m}^3 . \qquad (4)$$

This correction for altitude h in metres is only necessary for altitudes above about 100 m and allows for the decrease in air pressure (and hence air density) with altitude.

Water Density

The density of pure water in kg/m^3 as a function of temperature t for the range 15 °C to 25 °C can be calculated from

$$dw = 1000.2075 + 0.005398t - 0.005278t^2 . \qquad (5)$$

This approximate equation follows [12] and gives density values that agree with measurements on locally distilled water to within 0.01 kg/m^3.

Water Temperature

The density of water decreases by about 0.206 kg/m^3 per °C in the temperature range 15 °C to 25 °C. Hence, water temperature t must be measured to calculate a value for the water density dw. The relative standard uncertainty in V due to standard uncertainty $u(t)$ in the measurement of t is given by

$$u_t(V)/V(t) = 0.0002u(t) . \qquad (6)$$

For example, if $u(t) = 5$ °C, $u_t(V)/V(t) = 0.001$. The vessel is assumed to be at the same temperature as the water.

Water Impurity

Water impurity is an issue when using tap water as a practical alternative to distilled water, for example when measuring larger volumes or calibrating water flowmeters. The impurities in tap water increase the density significantly. The density of the tap water must be measured and a correction applied (via f in (1)) if the desired relative expanded uncertainty of the volume measurement is less than 0.0003.

The density of the tap water can be measured by comparison with distilled water using a pyknometer or equivalent. Figure 2 shows a 50 mL Gay-Lussac pyknometer. A larger variant of this has been developed by MSL to measure the ratio of the density of tap water to distilled water with a relative standard uncertainty of 0.00002.

A measurement of the water density involves two steps. The first step is to determine the volume of the pyknometer using distilled water and the method outlined in this technical guide. This volume measurement is performed several times (typically five or more) because repeatability is usually a major source of uncertainty. The second step is to perform a similar set of measurements using tap water and, for each measurement, to calculate the density of the water dw_{T} from the equation

$$dw_{\mathrm{T}} = \frac{(r_{2\mathrm{T}} - r_1)}{\bar{V}(t_0)}\left(1 - \frac{da}{ds}\right)\left[1 + \gamma_{\mathrm{V}}(t_0 - t)\right] + da , \qquad (7)$$

Figure 2. A 50 mL pyknometer.

where r_1 and $r_{2\mathrm{T}}$ are the balance readings for the dry and tap-water filled pyknometer respectively, and $\bar{V}(t_0)$ is the average value of $V(t_0)$ from the first step.

An average water impurity correction factor is then calculated using

$$f = \overline{dw_\mathrm{T} / dw}, \tag{8}$$

where $\overline{dw_\mathrm{T} / dw}$ is the average of the ratios dw_T / dw calculated from the measurements in the second set. As previously, dw is the density of distilled water at temperature t.

Contact MSL if you would like help with this procedure for measuring the density of tap water. An example calculation of the water purity correction factor is available on request.

Repeatability

The volume measurement is performed n times because repeatability is usually a major source of uncertainty. Typically n is five or more. The standard uncertainty $u_\mathrm{R}(V)$ due to repeatability is the sample standard deviation of these n measurements, that is

$$u_\mathrm{R}(V) = \sqrt{\sum_{i=1}^{n}\left(V_i(t_0) - \bar{V}(t_0)\right)^2 \Big/ (n-1)}, \tag{9}$$

where $V_i(t_0)$ is the i^{th} measured value of $V(t_0)$ and $\bar{V}(t_0)$ is the average of the n volume measurement results. When $n = 5$, $u_\mathrm{R}(V)$ has $\nu = 4$ degrees of freedom and an associated coverage factor $k = 2.78$ (see Table G.2 in [1]). In some cases, more than five measurements may be necessary, either to reduce the expanded uncertainty or to meet the requirements of a standard. For example BS EN ISO 8655-6 [7] specifies 10 measurements for each test volume.

Repeat measurements can be very time consuming, particularly when measuring large volumes such as the 220 L vessel shown in Figure 3.

A pooled variance approach to assessing the repeatability is worth considering if previous measurement results are available for the same vessel type and volume. For example, the results of N prior volume determinations may be pooled to estimate $u_\mathrm{Rp}(V)$. Following H.3.6 of [1], the pooled standard deviation due to repeatability u_Rp is

$$u_\mathrm{Rp}^2 = \sum_{i=1}^{N} \nu_i u_{\mathrm{R}i}^2(V) \Big/ \sum_{i=1}^{N} \nu_i, \tag{10}$$

where $u_{\mathrm{R}i}(V)$ and ν_i are the repeatability and degrees of freedom respectively for the i^{th} volume determination.

A practical minimum for the number of volume measurements in a volume determination is two (that is, $n = 2$). In this case, (10) reduces to

$$u_\mathrm{Rp}^2 = 0.5\sum_{i=1}^{N}\left(V_1(t_0) - V_2(t_0)\right)_i^2, \tag{11}$$

where $\left(V_1(t_0) - V_2(t_0)\right)_i$ is the difference between the two volume measurement results for the i^{th} volume determination and u_Rp has N degrees of freedom. A suggested value for N is 9.

Figure 3. A 220 L reference standard volume. The vessel is on a 1 m wide platform scale.

A quality check on the acceptability of each two-measurement volume determination is that the difference between the two volume values does not exceed $3.2u_\mathrm{Rp}$. This is an F-test at a 5 % level of significance based on estimating $u_\mathrm{Rp}(V)$ from 9 prior two-measurement volume determinations.

Other Factors

The effect of other factors on the measurement uncertainty associated with $V(t_0)$ can usually be kept to an insignificant level. For example, the weighing accuracy can be kept insignificant by a suitable choice of balance.

The Method in Practice

Apparatus

The apparatus required for volume measurement by weighing water is covered in several of the standards (for example [2, 5 & 7]). Most important are an electronic balance (or other weighing device) for weighing the water and a thermometer for measuring the water temperature.

For the weighing uncertainty to be insignificant, the best accuracy of the balance (as reported in a balance calibration certificate from a laboratory accredited to calibrate balances [11]) should be no more than one-third of the accuracy with which the vessel is to be measured. This is usually equivalent to a balance best accuracy of no more than one-tenth of the tolerance or MPE (maximum permissible error) of the vessel to be tested.

Modern electronic balances can easily meet this requirement. Consider, for example, the measurement of the volume of a Class A 2 L one-mark volumetric flask. The expanded uncertainty in the volume measurement of this flask would need to be 0.2 mL (or less) to confirm that the flask complies with the 0.6 mL MPE given in BS EN ISO 1042 [13]. Hence the best accuracy of the balance used for the volume measurement must be no more than one-third of this, that is 0.07 mL of water or

0.07 g. Normally the best accuracy of a balance is about three times its resolution. Hence a suitable balance would have a resolution of 0.01 g and a capacity of 5 kg (or more).

A suitable thermometer would have a resolution of 0.1 °C, an accuracy (expanded uncertainty) of about 0.2 °C, and a temperature sensor in a stainless steel sheath suitable for immersing in water. Hand-held thermometers that meet these requirements are commonly available.

Water

The water to be used for the volume measurement should be at the same temperature as the room in which the volume measurement is to be performed. This normally requires the water to have been in the room for at least 12 hours. This may not always be possible when measuring large volumes using tap water. Measure the temperature of the water before and after it is used for the volume measurement. When calibrating water flowmeters, monitor the temperature of the water as it exits the flowmeter and use an average over the calibration time in the calculation of dw.

Vessel Cleaning

The vessel under test is normally cleaned with detergent and water, and then thoroughly rinsed with some of the water that will be used for the volume measurement. If this cleaning is not sufficient, refer to the cleaning methods given in [2] and [5]. A test for the cleanliness of a glass vessel is to observe the shape of the water meniscus as the water level is raised or lowered. If the glass is clean, the meniscus shape will not change as the water level is altered.

A vessel designed to contain is dried after cleaning, for example by rinsing with ethanol and ventilating with warm dry air. After this treatment, the state of dryness can be checked by monitoring the weight of the vessel. It is best to leave the vessel for 15 to 30 minutes after drying.

Volume Measurement

Follow an appropriate standard, such as ISO 4787 [2] for volumetric glassware. Make sure that the electronic balance is mounted on a sturdy table, has had time to completely warm up, is free from drafts and gives a stable reading with the empty vessel. The room temperature should be stable to within 1 °C/h and preferably in the range 15 °C to 25 °C.

For a vessel designed to contain, record the balance reading r_1 for the dry weight once and use this value in (1) with each of the n filled-vessel readings. It is not practical to re-measure a dry weight with each repeat filled-vessel weighing because the drying time is too long.

For a vessel designed to deliver, wait the appropriate delivery time (see for example [14] or [15]), both when pre-conditioning the vessel and for each volume measurement. Take precautions to avoid errors due to evaporation, for example by putting a cap on the vessel used to collect and weigh the delivered volume.

For both types of vessel, make sure that you know exactly how the volume is defined. For example, the capacity of a vessel with a graduation line is defined as the volume of water at 20 °C contained by the vessel at 20 °C when filled so that the lowest point of the meniscus is horizontally tangent to the plane of the top edge of the graduation line (see Section 7 of [2]). An optical aid for determining the setting is described in 5.4 of [5].

Example Calculation

The example calculation given in Table 1 below is for the measurement of the volume of a burette between the zero and 5 mL graduations. Each value of $V(20)$, the measured volume corrected to 20 °C, was calculated using (1) and (2). The delivered distilled water was weighed using a 200 g capacity balance with a resolution of 0.1 mg and a best accuracy of 0.4 mg. The water temperature was measured with a standard uncertainty of 0.2 °C. Water density dw was calculated using (5) and air density da was taken as 1.2 kg/m^3.

In this case (1) reduces to

$$V = 0.99985\frac{(r_2 - r_1)}{(dw - da)}. \tag{1}$$

Table 1. Calculation for two measurements of a 5 mL volume by weighing the delivered water.

$r_2 - r_1$ /g	t /°C	dw /(kg/m^3)	V(20) /mL
4.9911	21.2	997.950	5.0066
4.9888	21.3	997.928	5.0043
		Average	5.0055

The standard uncertainties for this example burette measurement are summarised in Table 2. A pooled repeatability uncertainty $u_{\mathrm{Rp}} =$ 0.0016 mL was calculated from 9 previous measurements on the same type of burette with $\nu = 9$ degrees of freedom. The weighing uncertainty is taken as the best accuracy of the balance, divided by $k = 2$ to give a standard uncertainty and converted to a volume assuming 1 g is equivalent to 1 mL of water. Following (6), the 0.2 °C standard uncertainty in temperature is equivalent to a 0.0002 mL standard uncertainty in the 5 mL volume.

From Table 2, the overall combined standard uncertainty is $u_{\mathrm{c}}\left[V(20)\right] =$ 0.0016 mL, calculated as the quadrature sum of the components (see 5.1 in [1]). This uncertainty is completely dominated by repeatability. Using a Welch-Satterthwaite calculation (G.4 in [1]), the effective degrees of freedom $\nu_{\mathrm{eff}} =$ 10. Hence, the coverage factor $k = 2.23$ and the overall expanded uncertainty $U\left[V(20)\right] =$ 0.0036 mL.

Table 2. Standard uncertainties for the 5 mL burette measurement example.

Source	Standard uncertainty	$u_i[V(20)]$ /mL
Repeatability	0.0016 mL	0.0016
Weighing	0.0002 g	0.0002
Water temperature	0.2 °C	0.0002
Air density	0.016 mL/L	0.0001
	$U_{\mathrm{c}}[V(20)]$	0.0016

Acknowledgement

The pictures of the 5 L and 220 L standard volumes are included with the kind permission of the Measurement and Product Safety Service of the Ministry of Consumer Affairs.

References and Bibliography

[1] The treatment of measurement uncertainties in this technical guide is in accordance with the following ISO Guide:
ISO, 1995, *Guide to the Expression of Uncertainty in Measurement* 2nd ed. (Geneva: International Organisation for Standardization).

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[3] OIML R 49-2: 2004 (E), Water meters intended for the metering of cold potable water, Part 2: Test methods, Organisation Internationale de Métrologie Légale.

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[9] M Dell'Isola, A Frattolillo, G Ardimento and R Gaudiosi, 2007, Problems in calibrating standard capacity measures for liquids other than water, OIML Bulletin, volume XLV111, number 2, 5-14.

[10] ISO 4064-3: 2005 (E), Measurement of water flow in fully charged closed conduits – Meters for cold potable water and hot water – Part 3: Test methods and equipment, (Geneva: International Organisation for Standardization).

[11] C M Sutton, 2006, *Assuring the Quality of Weighing Results*, MSL Technical Guide 12, http://msl.irl.cri.nz/training_&_resources.

[12] M Tanaka, G Girard, R Davis, A Peuto and N Bignell, 2001, *Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports*, *Metrologia* **38** 301-309.

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[14] BS EN ISO 385: 2005, Laboratory glassware – Burettes, (British, European and ISO Standard).

[15] ISO 648: 1977 (E), Laboratory glassware – One-mark pipettes, (Geneva: International Organisation for Standardization).

Further Information

If you want to know more about volume measurement, density measurement, balances or weighing, contact MSL at msl@irl.cri.nz or see the MSL website http://msl.irl.cri.nz/ for other technical guides and information on training courses.

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