SOP No. 14

Recommended Standard Operations Procedure for Gravimetric Calibration of Volumetric Ware Using an Electronic Balance

1 Introduction

1.1 Purpose of Test

This procedure describes the calibration of either the "to deliver" or "to contain" volume of measuring containers that may be used as volumetric measuring standards. The procedure uses gravimetric calibration principles to minimize calibration uncertainties. Accordingly, the procedure is especially useful for high accuracy calibrations. The procedure does not incorporate measurement control steps to ensure the validity of the standards and the measurement process; additional precautions must be taken. The procedure makes use of an electronic balance and is suitable for all sizes of gravimetric calibrations only limited by the capacity and resolution of the balance.

1.2 Prerequisites

1.2.1 Verify that valid calibration certificates are available for the standards used in the test.

1.2.2 Verify that the standards to be used have sufficiently small standard uncertainties for the level of calibration. Reference standards should not be used for gravimetric calibration.

1.2.3 Verify that the balance used is in good operating condition with sufficiently small process standard deviation, as verified by a valid control chart or preliminary experiments, to ascertain its performance quality when a new balance is put into service. The accuracy of the balance and weighing procedures should be evaluated to minimize potential bias in the measurement process.

1.2.4 Verify that the operator is experienced in precision weighing techniques and has had specific training in SOP 2, SOP 4, SOP 29, GMP 3, GMP 10, and gravimetric calibrations.

1.2.5 Verify that an adequate supply of distilled or deionized water (see GLP 10) is available.

1.2.6 Verify that the laboratory facilities meet the following minimum conditions to enable meeting the expected uncertainty that is achievable with this procedure:

Table 1. Laboratory environmental conditions

Procedure	Temperature	Relative Humidity
Gravimetric	20 °C to 23 °C, a set point ± 2 °C, maximum change 1 °C/h	40 % to 60 % ± 10 % max change / 4 h

2 Methodology

2.1 Scope, Precision, Accuracy

The procedure is applicable for the calibration of any size of measuring container that, when filled with water, will not overload the electronic balance used. Typical containers range in capacity from 1 mL to 20 L; however, this procedure is also applicable for larger provers provided that facility, equipment and standards meet the requirements in this SOP. When larger provers (e.g., 100 gal or more) are tested, also see the Test Notes in SOP 15. The precision of calibration will depend on the care exercised in adjusting the various volumes and strict adherence to the various steps of the procedure. The accuracy attainable will depend on the uncertainties of the standard weights and the air buoyancy and thermal expansion corrections that are made.

2.2 Summary

The electronic balance used is first calibrated by weighing a standard mass. The volumetric vessel to be calibrated is then weighed dry or “wetted down,” depending on whether the calibration is to be made on a “to contain” or “to deliver” basis. The container is filled with pure water of known temperature and re-weighed. The difference in mass is used to calculate the capacity of the container at various neck graduations. The processes of this section and section 3 should be repeated as required to verify all neck graduations for which a calibrated volume is desired.

2.3 Equipment and Standards

2.3.1 Electronic balance having sufficient capacity to weigh the loaded vessel. The sensitivity of the balance will be a limiting factor in the accuracy of the measurement. The resolution and repeatability should be smaller than the accepted uncertainty of the calibration.

2.3.2 Calibrated mass standards with adequate accuracy and traceable to NIST. Ordinarily, standards of ASTM Class 2 or 3 weight specifications are required.

2.3.3 Calibrated thermometer accurate to ± 0.1 °C with recent calibration values that are traceable to NIST to determine water temperature.

2.3.4 Calibrated thermometer accurate to ± 0.5 °C with recent calibration values that are traceable to NIST to determine air temperature.[1]

2.3.5 Calibrated barometer accurate to ±135 Pa (1 mm Hg) with recent calibration values that are traceable to NIST to determine the air pressure.[1]

2.3.6 Calibrated hygrometer accurate to ± 10 % with recent calibration values that are traceable to NIST to determine relative humidity.[1]

[1] Values from the thermometer, barometer and hygrometer are used to calculate the air density at the time of the measurement. The air density is used to make an air buoyancy correction. The accuracies specified are recommended for high precision calibration. Less accurate equipment can be used with only a small degradation in the overall accuracy of the measurement.

2.3.7 Distilled or deionized water (See GLP 10).

2.3.8 Stopwatch or other suitable timing device (does not need to be calibrated.)

2.4 Procedure

2.4.1 Cleanliness check

Verify that all containers to be calibrated are clean as evidenced by uniform drainage of water. No water droplets should remain on any interior surface as the water drains from the container. A reproducible "wet-down" weight is evidence for cleanliness in cases where it is not possible to visually check for uniform drainage. Use GMP 6 or 7 to clean vessels as necessary.

2.4.2 Drying procedure

Use GLP 13 as the procedure to dry any container to be calibrated on a "to contain" basis.

2.4.3 Wet down

Fill the container to capacity with distilled or deionized water, then empty over a 30 s period while avoiding splashing. Drain for 10 s unless another drain time is specified. (This is commonly called a "30 s pour, 10 s drain" emptying procedure.) A 30 s (± 5 s) pour followed by a 10 s drain, with the measure held between a 10 degree and 15 degree angle from vertical, is required during calibration and use for glass flasks. A wet-down is not required if a transfer vessel is used to weigh a delivered volume of water.

2.4.4 Weighings (Option A)

2.4.4.1 Zero the balance and record reading as O_1. Place a standard mass, M_S, on the balance platform (where possible, M_S should be slightly larger than the mass of the filled vessel.) Record reading as O_2.

2.4.4.2 Zero the balance. Place dry or "wet-down" container on balance platform, as appropriate, and record reading as O_3.[2] Caution: all containers must be dry on the outside for all weighings.

2.4.4.3 Fill container to its reference mark. Read and record the temperature of the water used to fill the container. Carefully adjusting the meniscus (if present) to minimize filling error (see GMP No. 3). Zero the balance. Weigh the filled vessel and record reading as O_4.

2.4.4.4 Immediately after weighing, check the temperature of the water in the filled container. If the temperature differs by more than 0.2 °C from that of 2.4.4.3, refill and reweigh as described in 2.4.4.3.

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[2] When calibrating "to deliver" vessels, O4 may be measured before O3. If a transfer vessel is used, the drained mass or empty mass is usually measured before the filled mass.

2.4.4.5 Record air temperature, barometric pressure, and relative humidity at the time of the above measurements.

2.4.4.6 Make a duplicate determination (Run 2).

2.4.5 Weighings (Option B)

2.4.5.1 Zero the balance and record reading as O_1. Place a standard mass, M_{S1}, on the balance platform (where possible M_{S1} should be slightly larger than the mass of the drained or dry vessel.) Record reading as O_2.

2.4.5.2 Zero the balance. Place dry or "wet-down" container on balance platform, as appropriate, and record reading as O_3. Caution: all containers must be dry on the outside for all weighings.

2.4.5.3 After removing empty vessel, zero the balance and record reading as O_4. Place a standard mass, M_{S2}, on the balance platform (where possible M_{S2} should be slightly larger than the mass of the filled vessel.) Record reading as O_5.

2.4.5.4 Fill container to its reference mark. Read and record the temperature of the water used to fill the container. Carefully adjusting the meniscus (if present) to minimize filling error (see GMP 3). Zero the balance. Weigh the filled vessel and record reading as O_6.

2.4.5.5 Immediately after weighing, check the temperature of the water in the filled container. If the temperature differs by more than 0.2 °C from that of 2.4.5.4, refill and reweigh as described in 2.4.5.4.

2.4.5.6 Record air temperature, barometric pressure, and relative humidity at the time of the above measurements.

2.4.5.7 Make a duplicate determination (Run 2).

3 Calculations

3.1 Compute the volume, V_t, for each determination using the equation:

Option A

$$V_t = \left(O_4 - O_3\right)\left(\frac{M_s}{O_2 - O_1}\right)\left(1 - \frac{\rho_a}{\rho_s}\right)\left(\frac{1}{\rho_w - \rho_a}\right) \qquad \text{Eqn. 3.1}$$

Option B

$$V_t = \left[O_{6(filled)} \frac{M_{s2}\left(1 - \frac{\rho_a}{\rho_s}\right)}{(O_5 - O_4)} - O_{3(drained)} \frac{M_{s1}\left(1 - \frac{\rho_a}{\rho_s}\right)}{(O_2 - O_1)} \right] \left(\frac{1}{\rho_w - \rho_a} \right) \quad \text{Eqn. 3.2}$$

Table 2. Variables for volume equations

Variable	Description
M_s, M_{s1}, M_{s2}	mass of standards (i.e., true mass, vacuum mass) (g)
ρ_s	density of M_S (g/cm^3)
ρ_w	density of water at the temperature of measurement (g/cm^3)
ρ_a	density of air at the conditions of calibration (g/cm^3)
V_t	represents either the “to contain” or “to deliver” volume (depending on whether O_3 or O_6 represent a dry or a “wet down” container at the temperature of the measurement) (cm^3 or mL)

3.2 Glassware is typically calibrated to 20 °C. Compute V_{20}, the volume at 20 °C, for each run, using the expression:

$$V_{20} = V_t \left[1 - \alpha \left(t - 20 \right) \right]$$

where α is the cubical coefficient of expansion of the container being calibrated, (see NISTIR 6969, Table 9.10), and, t, is the temperature (ºC) of the water.

3.3 Compute the mean V_{20} for the duplicate measurements.

3.4 Alternative Reference Temperatures

3.4.1 Reference temperatures other than 20 °C (glassware) or 60 ºF (15.56 ºC) (metal test measures and provers used for petroleum products) may occasionally be used. Common reference temperatures for other liquids follow:

Commodity	Reference Temperature
Frozen food labeled by volume (e.g., fruit juice)	-18 ºC (0 ºF)
Beer	3.9 ºC (39.1 ºF)
Food that must be kept refrigerated (e.g., milk)	4.4 ºC (40 ºF)
Distilled spirits or petroleum	15.56 ºC (60 ºF)
Petroleum (International Reference)	15 ºC (59 ºF)
Wine	20 ºC (68 ºF)
Unrefrigerated liquids (e.g., sold unchilled, like soft drinks)	20 ºC (68 ºF)
Petroleum (Hawaii)	26.67 ºC (80 ºF)

3.4.2 If using a different reference temperature, use the following equation and take care to match the cubical coefficient of expansion units with the units of temperature:

$$V_{\mathrm{ref}} = V_t \left[1 - \alpha \left(t - \mathrm{t}_{\mathrm{ref}} \right) \right]$$

4 Measurement Assurance

4.1 Duplicate the process with a suitable check standard (See GLP 1, SOP 30, and NISTIR 6969, Sec. 7.4)

4.2 Plot the check standard value and verify it is within established limits OR a t-test may be incorporated to check the observed value against an accepted value.

4.3 The mean of the check standard is used to evaluate bias and drift over time.

4.4 Check standard observations are used to calculate the standard deviation of the measurement process, s_p.

5 Assignment of Uncertainties

The limits of expanded uncertainty, U, include estimates of the standard uncertainty of the mass standards used, u_c, plus the uncertainty of measurement, s_p, at the 95 percent level of confidence. See SOP 29 for the complete standard operating procedure for calculating the uncertainty.

5.1 The standard uncertainty for the standard, u_s, is obtained from the calibration report. The combined standard uncertainty, u_c, is used and not the expanded uncertainty, U, therefore the reported uncertainty for the standard will usually need to be divided by the coverage factor k. When multiple mass standards are used, see SOP 29 for treatment of dependencies.

5.2 Standard deviation of the measurement process from control chart performance (See SOP No. 17 or 20.)

The value for s_p is obtained from the control chart data for check standards or estimated based on the range of duplicate measurements over time. This value will incorporate a repeatability factor related to the precision of the weighings and the setting of the meniscus, but not related to the errors in reading the meniscus.

5.3 Other standard uncertainties usually included at this calibration level include uncertainties associated with water temperature measurements, thermometer accuracy, calculation of air density, standard uncertainties associated with the density of the standards used, coefficients of expansion, viscosity or surface effects on the volume of liquid clinging to vessel walls after draining, improper observance of drainage times, and the lack of internal cleanliness.

Additional References:

Bean, V. E., Espina, P. I., Wright, J. D., Houser, J. F., Sheckels, S. D., and Johnson, A. N., NIST Calibration Services for Liquid Volume, NIST Special Publication 250-72, National Institute of Standards and Technology, Gaithersburg, MD, (2006)

Appendix A

Gravimetric Calibration Data Sheet (Option A)

Laboratory data and conditions:

Vessel ID		Date	
Material		Operator	
Expansion Coefficient		Air Temperature	
Balance		Pressure	
Load		Relative Humidity	
Process standard deviation from control chart, s_p			

Mass standard(s) data:

ID	Nominal	Mass Correction	Density g/cm^3	ID	Nominal	Mass Correction	Density g/cm^3
M_s – filled weight				M_s – empty weight	Not used for Option A.		
u_s, and k factor				u_s, and k factor			

Observations:

Run 1	Weights	Balance Observations, Units______	
1	Zeroed Balance	O_1	0.00
2	M_S	O_2	
3	Empty or Drained	O_3	
4	Filled	O_4	
	t_w:		
Run 2	Weights	Balance Observations, Units______	
1	Zeroed Balance	O_1	0.00
2	M_S	O_2	
3	Empty or Drained	O_3	
4	Filled	O_4	
	t_w:		

Note: dotted line represents decimal point.

Example
Gravimetric Calibration Data Sheet (Option A)

Laboratory data and conditions:

Vessel ID	321	Date	10/1/99
Material	Soda-lime glass	Operator	GH
Expansion Coefficient	0.000025 / °C	Air Temperature	22.5 °C
Balance	LC 5100	Pressure	747.8 mm Hg
Load	2 L	Relative Humidity	45 %
Process standard deviation from control chart, s_p			0.042 mL

Mass standard(s) data:

ID	Weights	Mass Correction	Density g/cm^3	ID	Nominal	Mass Correction	Density g/cm^3
M_s – filled weight	2 kg	0.000123 g	7.95	M_s – empty weight	Not used for Option A.		
u_s, and k factor		2 mg, k = 2		u_s, and k factor			

Observations:

Run 1	Weights	Balance Observations, Units___g__	
1	Zeroed Balance	O_1	0.000
2	M_s	O_2	2000.003
3	Empty or Drained	O_3	654.729
4	Filled	O_4	2648.747
	t_w: 22.8 °C		
Run 2	**Weights**	**Balance Observations, Units______**	
1	Zeroed Balance	O_1	0.00
2	M_s	O_2	1999.998
3	Empty or Drained	O_3	667.351
4	Filled	O_4	2661.365
	t_w: 22.6 °C		

Note: dotted line represents decimal point.

Calculate the air density (SOP 2) ρ_a:

$$\rho_a = 1.169\,625\ \text{mg/cm}^3 = 0.001\,169\,625\ \text{g/cm}^3$$

Round the results to 9 digits.

Calculate (or look up) the density of the water, ρ_w:

$$22.8\ ^\circ\text{C} = 0.997\,586\,95\ \text{g/cm}^3$$

$$22.6\ ^\circ\text{C} = 0.997\,633\,78\ \text{g/cm}^3$$

Round the results to 8 digits.

Compute the volume, V_t, for each determination using the equation:

$$V_t = (O_4 - O_3)\left(\frac{M_s}{O_2 - O_1}\right)\left(1 - \frac{\rho_a}{\rho_s}\right)\left(\frac{1}{\rho_w - \rho_a}\right)$$

Run 1:

$$V_t = (2\,648.747 - 654.729)\left(\frac{2\,000.000\,123}{2\,000.003 - 0}\right)\left(1 - \frac{0.001\,169\,625}{7.95}\right)\left(\frac{1}{0.997\,586\,95 - 0.001\,169\,625}\right)$$

$$V_t = (1994.018)(0.999\,998\,562)(0.999\,852\,877)(1.003\,446\,462)$$

$$V_t = (1994.018)(1.003\,446\,462) = 2\,000.890\,307\ \text{mL}$$

Compute V_{20}, the volume at 20 °C, for Run 1 using the expression:

$$V_{20} = V_t\left[1 - \alpha\,(t - 20)\right]$$

$$V_{20} = 2\,000.890\,307\left[1 - 0.000\,025\,(22.8 - 20)\right] = 2\,000.750\,244\ \text{mL}$$

Run 2:

$$V_t = (2\,661.365 - 667.351)\left(\frac{2\,000.000\,123}{1999.998 - 0}\right)\left(1 - \frac{0.001\,169\,625}{7.95}\right)\left(\frac{1}{0.997\,633\,78 - 0.001\,169\,625}\right)$$

$$V_t = (1994.014)(1.000\,001\,062)(0.999\,852\,877)(1.003\,548\,392)$$

$$V_t = (1994.014)(1.003\,401\,812) = 2000.797261\ \text{mL}$$

Compute V_{20}, the volume at 20 °C, for Run 2 using the expression:

$$V_{20} = V_t \left[1 - \alpha \left(t - 20\right)\right]$$

$$V_{20} = 2000.797\,261\ [\ 1 - 0.000025\ (\ 22.6 - 20\ )\ ] = 2000.667209\ \text{mL}$$

Calculate the mean V_{20} :

$$\overline{V}_{20} = \frac{(\ 2\,000.750\,244 + 2\,000.667\,209\ )}{2} = 2\,000.708\,727\ \text{mL}$$

Calculate the uncertainty for the calibration:

$$U = u_c * 2$$

$$u_c = \sqrt{u_s^{\,2} + s_p^{\,2} + u_o^{\,2}}$$

The uncertainty for the standard must be divided by the k factor for the standard, u_s. All values must be represented in like units.

$$U_s = 2\ \text{mg},\ k = 2 \qquad u_s = 2\ \text{mg} / 2 = 1\ \text{mg} \qquad \approx 1\ \text{mL}$$

$$s_p = 0.042\ \text{mL}$$

$$u_o = 0.000\,18\ \text{mL}$$

$$u_c = \sqrt{(\ 0.001\ )^2 + (\ 0.042\ )^2 + (\ 0.000\,18\ )^2}$$

$$u_c = 0.042\,012\ \text{mL}$$

$$U = 0.042\,012 * 2 = 0.084\,024\ \text{mL}$$

The volume correction and uncertainty are reported as follows when rounded to two significant digits according to NISTIR 6969, GMP 9:

$$V_{20} = 2000.709\ \text{mL} \pm 0.084\ \text{mL}$$

Appendix B

Gravimetric Calibration Data Sheet (Option B)

Laboratory data and conditions:

Vessel ID		Date	
Material		Operator	
Expansion Coefficient		Air Temperature	
Balance		Pressure	
Load		Relative Humidity	
Process standard deviation from control chart, s_p			

Mass standard(s) data:

ID	Nominal	Mass Correction	Density g/cm^3	ID	Nominal	Mass Correction	Density g/cm^3
M_{s1} – empty weight				M_{s2} – filled weight			
u_s, and k factor				u_s, and k factor			

Observations:

Run 1	Weights	Balance Observations, Units______	
1	Zeroed Balance	O_1	0.000
2	M_{s1}	O_2	
3	Empty or Drained	O_3	
4	Zeroed Balance	O_4	0.000
5	M_{S2}	O_5	
6	Filled	O_6	
	t_w:		
Run 2	**Weights**	**Balance Observations, Units______**	
1	Zeroed Balance	O_1	0.000
2	Zeroed Balance	O_2	
3	M_{s1}	O_3	
4	Empty or Drained	O_4	0.000
5	Zeroed Balance	O_5	
6	M_{S2}	O_6	
	t_w:		

Note: dotted line represents decimal point.