

SOP No. 14

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

1 Introduction

1.1 Purpose of Test

This procedure is a precision mass calibration converting mass values to volumetric values using pure water as a standard reference material. The results provide 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 references measurement control standards to ensure the validity of the standards and the measurement process; however, 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. This procedure calculates the average volume based on two runs. NOTE: NIST calibrations generally make use of the average of five replicates.

1.2 Prerequisites

- 1.2.1 Verify that valid calibration certificates are available for all of the standards used in the calibration.
- 1.2.2 Verify that the mass standards to be used have sufficiently small standard uncertainties for the level of calibration. Reference standards should not be used for gravimetric calibration. Weights of ASTM Class 2 or 3 or OIML Class F₁ or F₂ are needed for this procedure.
- 1.2.3 Verify that the balance used is in good operating condition with sufficiently small resolution and 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. NOTE: standard deviations obtained from mass calibrations will generally not reflect the process repeatability of this procedure.
- 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, maximum change of 1 °C/h during the calibration.	40 % to 60 % ± 10 % stability / 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 the Appendix. 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. Transfer vessels may be used for all procedures except for flasks and containers marked “To Contain” (TC).

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 must be smaller than the accepted uncertainty of the calibration. NOTE: standard deviations obtained from mass calibrations will generally not reflect the process repeatability of this procedure, therefore repeatability must be assessed using this procedure.

2.3.2 Calibrated mass standards, with recent calibration values and which have demonstrated metrological traceability to the international system of units (SI), which may be to the SI through a National Metrology Institute such as NIST.. Ordinarily, standards of ASTM Class 2 or 3 or OIML Class F₁ or F₂ weight specifications are required.

2.3.3 Calibrated thermometers, accurate to ± 0.1 °C, with recent calibration values and which have demonstrated metrological traceability to the international system of units (SI), which may be to the SI through a

National Metrology Institute such as NIST to determine water temperature.

- 2.3.4 Calibrated thermometer accurate to ± 0.50 °C with recent calibration values which have demonstrated metrological traceability to the international system of units (SI), which may be to the SI through a National Metrology Institute such as NIST to determine air temperature.¹ to determine air temperature.¹
- 2.3.5 Calibrated barometer accurate to ± 135 Pa (1 mm Hg) with recent calibration values which have demonstrated metrological traceability to the international system of units (SI), which may be to the SI through a National Metrology Institute such as NIST to determine air pressure.¹
- 2.3.6 Calibrated hygrometer accurate to ± 10 percent with recent calibration values which have demonstrated metrological traceability to the international system of units (SI), which may be to the SI through a National Metrology Institute such as NIST to determine relative humidity.¹
- 2.3.7 Distilled or deionized water (See GLP 10) of sufficient quality and quantity for the calibration. Do not use tap water for this procedure!
- 2.3.8 Stopwatch or other suitable timing device (does not need to be calibrated.)

2.4 General Considerations

2.4.1 Cleanliness checks

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. All glassware must be meticulously cleaned, prior to calibration. When clean, the walls will be uniformly wetted. Instructions for cleaning are given in GMP 6 or 7. An exception is plastic ware, which will not be wetted. Follow manufacturer's instructions for cleaning such vessels. Do not use cleaning agents that will attack, discolor, or swell plastic ware.

- 2.4.2 Use water that is temperature-equilibrated with the laboratory environment. Equilibration can be achieved by storing the water in clean containers in the laboratory.

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.

- 2.4.3 Volumetric calibrations to a marked interval are critically dependent on the setting of a meniscus. See GMP 3 for guidance in reading a meniscus.
- 2.4.4 Use GLP 13 as the procedure to dry any container to be calibrated on a “To Contain” basis.
- 2.4.5 Wet down (not used for any container calibrated “To Contain”)

For glassware and hand-held test measures: 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 (\pm 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.

For provers: Fill the container to capacity with distilled or deionized water, then empty. Time the drain once the main cessation of flow is complete for 30 s and close the valve.

2.5 Calibration Procedure for Burets

- 2.5.1 Weigh an empty transfer vessel or flask.
- 2.5.2 Clamp the buret vertically on a support stand. Also clamp a plain glass test tube, large enough to hold a thermometer, in the vicinity of the buret.
- 2.5.3 Fill buret with water and test for absence of leaks from the tip and stopcock. Drain and fill several times to condition the buret. Fill when ready to test.
- 2.5.4 Drain and record delivery time, defined as the time of unrestricted flow from the zero mark to the lowest graduation mark with the stopcock fully open.
- 2.5.5 Fill the buret slightly above zero mark with temperature-equilibrated water and also fill the test tube that holds the thermometer. Record water temperature.
- 2.5.6 Set the meniscus on the zero mark and touch the tip with the wetted wall of a beaker to remove any excess water. The buret tip must be full.
- 2.5.7 Fully open the stopcock and discharge contents of buret into the previously weighed flask or transfer vessel. The tip should be in contact with the wall of the flask. When the level in the buret is within a few millimeters above the line being calibrated, slow the discharge and make an accurate setting. When the setting is completed, move the flask horizontally to break contact with the tip. Recheck the setting.
- 2.5.8 Stopper (or cover) and weigh the filled transfer vessel or flask.
- 2.5.9 Measure and record the temperature of water in the container.

- 2.5.10 Test the next interval in the same manner - from the zero mark to the next interval of test.
 - 2.5.11 For burets with a specified waiting time, empty as in 2.5.6 to within a few millimeters of the calibration mark. Pause for the specified waiting time (e.g., 10 s), then adjust the meniscus to the graduation line as in 2.5.6.
 - 2.5.12 Make a duplicate determination for each interval (Run 2).
 - 2.5.13 Calculate the volume for each interval as described in Section 3.
- 2.6 Calibration Procedure for Pipets (One-Mark)
- 2.6.1 Weigh an empty transfer vessel or flask.
 - 2.6.2 Fill the pipet to the index mark and measure the delivery time with the tip in contact with the internal surface of a beaker.
 - 2.6.3 Refill the pipet by suction, slightly above the index line. Record the water temperature. Wipe tip with filter paper, then slowly lower level to the index line, using a stopcock or pinch clamp for fine control. The tip must be in contact with the wetted wall of a beaker while this setting is being made. Do not remove any water remaining on tip at this time.
 - 2.6.4 Hold pipet in a vertical position and deliver water into a previously weighed weighing flask, with the tip in contact with the inside wall or neck.
 - 2.6.5 After flow has ceased, wait two seconds then remove the pipet from contact with the flask.
 - 2.6.6 Stopper (or cover) and weigh the filled transfer vessel or flask.
 - 2.6.7 Make a duplicate determination for each interval (Run 2).
 - 2.6.8 Calculate the volume as described in Section 3.
- 2.7 Calibration of Flasks (To Contain) – Transfer vessel may not be used.
- 2.7.1 Clean and dry flask as described in GLP 13, then stopper and weigh the flask. Record the Empty Flask value.
 - 2.7.2 Place an appropriate sized funnel in neck and fill flask to just below the reference graduation while maneuvering the flask to wet the entire neck below the stopper.
 - 2.7.3 Let stand for two minutes then adjust the meniscus to the reference graduation line.
 - 2.7.4 Determine the temperature of the water by putting some in a beaker or test tube containing a thermometer.
 - 2.7.5 Weigh the filled flask and record the Filled Flask mass value.

- 2.7.6 Make a duplicate determination (Run 2) after drying the flask per GLP 13.
- 2.7.7 Perform volume calculations as described in Section 3.
- 2.8 Calibration of Flasks (To Deliver)
 - 2.8.1 Clean but do not dry a transfer vessel or flask.
 - 2.8.2 Weigh the empty transfer vessel or flask and record the mass.
 - 2.8.3 Place an appropriately sized funnel in the neck and fill the flask to just below the reference graduation while maneuvering the flask to wet the entire neck below the stopper.
 - 2.8.4 Let the flask stand for two minutes, then adjust the meniscus to the reference graduation line, then weigh the full vessel, with cap or stopper.
 - 2.8.5 Empty the flask over a 30-second period by gradually inclining it so as to avoid splashing. When the main drainage has ceased, hold the flask in vertical position for 10 seconds unless another drain time is specified, then touch off the drop of water adhering to the top of the flask.
 - 2.8.6 Cover the flask or transfer vessel and reweigh.
 - 2.8.7 Make a duplicate determination (Run 2).
 - 2.8.8 Calculate the volume of the flask as described in Section 3.
- 2.9 Calibration of Other Volumetric Glassware.
 - 2.9.1 Measuring Pipets - Calibrate in a manner similar to that used to calibrate burets.
 - 2.9.2 Graduated Cylinders - Calibrate in a manner similar to that used for flasks.
- 2.10 Calibration of Slicker-Plate Type Standards
 - 2.10.1 Condition the slicker-plate type standards with several wet-down runs to fully ensure wet down and smooth valve operation.
 - 2.10.2 Weigh an empty transfer vessel and record the mass.
 - 2.10.3 Fill the slicker-plate standard to just above the rim of the standard. Record the water temperature. Slide the slicker plate across the level top. Set the transfer vessel below the nozzle to ensure all volume is transferred into the vessel and that no splashing occurs.
 - 2.10.4 Open the slicker-plate standard valve and remove the plate simultaneously and smoothly to deliver the water into the transfer vessel. Time the drain for 30 s after the cessation of the main flow and close the valve. Cover the transfer vessel and move it from beneath the standard to ensure additional drops of water are not transferred.

- 2.10.5 Weigh the filled transfer vessel and record the mass.
- 2.10.6 Make a duplicate determination for each interval (Run 2).
- 2.10.7 Calculate the volume as described in Section 3.
- 2.11 Calibration of Graduated Neck Type Provers
 - 2.11.1 Condition the graduated neck type standards with several wet-down runs to fully ensure wet down and smooth valve operation.
 - 2.11.2 Weigh an empty transfer vessel and record the mass.
 - 2.11.3 Fill the standard to the nominal graduation mark. Record the water temperature. Set the transfer vessel below the nozzle to ensure all volume is transferred into the vessel and that no splashing occurs.
 - 2.11.4 Open the standard valve smoothly to deliver the water into the transfer vessel. Time the drain for 30 s after the cessation of the main flow and close the valve. Cover the transfer vessel and move it from beneath the standard to ensure additional drops of water are not transferred.
 - 2.11.5 Weigh the filled transfer vessel and record the mass.
 - 2.11.6 Make a duplicate determination for each interval (Run 2).
 - 2.11.7 Calculate the volume as described in Section 3.
- 2.12 Weighing Procedures
 - 2.12.1 Weighing (Option A – One point balance calibration)
 - 2.12.1.1 Zero the balance and record reading as O_1 . Place a standard mass, M_5 , on the balance platform (where possible, M_5 should be slightly larger than the mass of the filled vessel.) Record reading as O_2 .
 - 2.12.1.2 Zero the balance. Place dry or “wet-down” container or empty transfer vessel on the balance platform, as appropriate, and record reading as O_3 .² Caution: all containers must be dry on the outside for all weighing.
 - 2.12.1.3 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 or transfer vessel and record the reading as O_4 .
 - 2.12.1.4 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.
 - 2.12.1.5 Record air temperature, barometric pressure, and relative humidity at the time of the above measurements.
 - 2.12.1.6 Make a duplicate determination (Run 2).

² When calibrating “to deliver” vessels, O_4 may be measured before O_3 . If a transfer vessel is used, the drained mass or empty mass is usually measured before the filled mass.

2.12.2 Weighing (Option B – Two point balance calibration.)

- 2.12.2.1 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 vessel, dry vessel, or empty transfer vessel.) Record reading as O_2 .
- 2.12.2.2 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 weighing.
- 2.12.2.3 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 .
- 2.12.2.4 Fill standard 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 or transfer vessel and record reading as O_6 .
- 2.12.2.5 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.
- 2.12.2.6 Record air temperature, barometric pressure, and relative humidity at the time of the above measurements.
- 2.12.2.7 Make a duplicate determination (Run 2).

3 Calculations

- 3.1 Option A – One-point balance calibration. Compute the volume, V_t , for each determination using the equation:

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

- 3.2 Option B – Two point balance calibration. Compute the volume, V_t , for each determination using the equation:

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

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)

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

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

where α is the cubical coefficient of expansion of the container being calibrated, (see NISTIR 6969, Table 9.10), and, t , is the temperature (°C) of the water. Compute the mean V_{20} for the duplicate measurements.

- 3.4 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:

$$V_{\text{ref}} = V_t [1 - \alpha (t - t_{\text{ref}})]$$

3.5. Other Reference temperatures may be used. Common reference temperatures for other liquids follow:

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

4 Measurement Assurance

- 4.1 Duplicate the process with a suitable check standard (See GLP 1, SOP 30, and NISTIR 6969, Sec. 7.4) or conduct replicate measurements per SOP 17 or 20. Average values of the range or standard deviation of similarly sized flasks or volumetric standards may be tracked on a single range chart or standard deviation chart according to SOP 17 or 20. A minimum of 12 replicate measurements are required to establish initial process limits.
- 4.2 Plot the check standard volume and verify it is within established limits. 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 and may be used to identify or signify problems with the volume standard or changes in water quality.
- 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 standards, 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 . Multiple mass standards are often used, so 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 when a check standard is available. It may also be estimated based on replicate measurements over time. Replicate measurements over time may provide a pooled standard deviation that may be used or the average range is used to estimate the standard deviation per SOP 17 or 20. This value incorporates a repeatability factor related to the precision of the weighings and the setting of the meniscus when present, but does not include uncertainties associated with errors in reading the meniscus.

- 5.3 Include uncertainties associated with the reading of the meniscus when present. See GMP 3 for details.
- 5.4 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		Operator		
Material		Date		
Cubical Coefficient of Expansion			Before	After
Balance		Temperature		
Load		Pressure		
Standard deviation of the process, from control chart, s_p		Relative Humidity		
Degrees of Freedom		Water temperature (for reference)		

Mass standard(s) data:

ID (Note ID and for Filled or Empty Load)	Nominal	Mass Correction*	Expanded Unc: From cal. report	Unc: k factor	Density g/cm^3
S					
S					
S					
S					
S					

*Mass Correction = *True Mass* if using buoyancy correction. Density is required for buoyancy corrections.

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			

Example Gravimetric Calibration Data Sheet (Option A)

Laboratory data and conditions:

Vessel ID	321	Operator	10/1/99	
Material	Soda-lime glass	Date	GH	
Cubical Coefficient of Expansion	0.000025 / °C		Before	After
Balance	LC 5100	Temperature	22.4 °C	22.6 °C
Load	2 L	Pressure	747.6 mm Hg	748.0 mm Hg
Standard deviation of the process, from control chart, s_p	0.042 mL	Relative Humidity	43 %	47 %
Degrees of Freedom	216	Water temperature (for reference)	22.8 °C	22.6 °C

Mass standard(s) data:

ID (Note ID and for Filled or Empty Load)	Nominal	Mass Correction*	Expanded Unc: From cal. report	Unc: k factor	Density g/cm ³
S	2 kg	0.000123 g	2 mg	2	7.95
S					
S					
S					
S					

*Mass Correction = *True Mass* if using buoyancy correction. Density is required for buoyancy corrections.

Observations:

Run 1	Weights	Balance Observations, Units <u>g</u>	
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	0.000
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

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 :

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

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

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:

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

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

Run 2:

$$V_t = (2\,661.365 - 667.351) \left(\frac{2\,000.000\,123}{1\,999.998 - 0} \right) \left(1 - \frac{0.001\,169\,625}{7.95} \right) \left(\frac{1}{0.997\,633\,78 - 0.001\,169\,625} \right)$$

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

$$V_t = (1994.014) (1.003\,401\,812) = 2\,000.797\,261 \text{ mL}$$

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

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

$$V_{20} = 2000.797\,261 [1 - 0.000025 (22.6 - 20)] = 2000.667\,209 \text{ mL}$$

Calculate the mean V_{20} :

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

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.

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

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

$$u_o = 0.00018 \text{ mL}$$

$$u_c = \sqrt{(0.001)^2 + (0.042)^2 + (0.00018)^2}$$

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

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

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		Operator		
Material		Date		
Cubical Coefficient of Expansion			Before	After
Balance		Temperature		
Load		Pressure		
Standard deviation of the process, from control chart, s_p		Relative Humidity		
Degrees of Freedom		Water temperature (for reference)		

Mass standard(s) data:

ID (Note ID and for Filled or Empty Load)	Nominal	Mass Correction*	Expanded Unc: From cal. report	Unc: k factor	Density g/cm^3
S					
S					
S					
S					
S					

*Mass Correction = *True Mass* if using buoyancy correction. Density is required for buoyancy corrections.

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		

Appendix

Test Notes for Large Provers

1 Pour and drain times.

It is impractical to completely drain a filled container, because some of the contents will remain as a film. By strict adherence to a specified procedure, the residual contents can be held essentially constant so that, reproducible calibration constants can be obtained. The conditions conventionally selected are as follows:

- a For bottom-drain containers: open drain valve fully and allow contents to discharge at maximum rate. When flow ceases, wait 30 s, close valve, and touch off any drops adhering to spout.
- b For pour-type containers: pour contents by gradually tilting container to an 85 ° angle, so that virtually all is delivered in 30 s. Allow to drain for an additional 10 s, then touch off any drops adhering to the lip.

The instructions described above must be precisely followed during calibration and use of the calibrated vessels.

2 Evaporation losses.

A suitable cap should be placed on the top of open vessels to minimize evaporation losses. If used, the cap must be included in all weighings.

3 Slicker-plate.

When a slicker-plate standard is calibrated, the plate should be used to fix the water level in it. This plate must be weighed with the standard during each such operation (unless a transfer vessel is used).