SOP No. 14

Recommended Standard Operating Procedure
for
Gravimetric Calibration of Volumetric Standards 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" (TD) or "To Contain" (TC) 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 good measurement practices such as those required for precision mass calibrations must be used. The procedure uses an electronic balance and is suitable for all sizes of gravimetric calibrations only limited by the capacity and resolution of the balance and handling capabilities. Detailed measurement ranges, standards, equipment, and uncertainties for this SOP are generally compiled in a separate document in the laboratory. This procedure calculates the average volume based on two runs. Note: NIST calibrations generally make use of the average of five replicates.

1.2 Conformity Assessment

Standards that are calibrated for use in legal weights and measures applications should be evaluated for conformance to the appropriate specifications and tolerances that apply. Where compliance is required by law, conformity evaluations should be conducted prior to performing calibrations. See Section 6.2 for reporting results.

1.3 Prerequisites

1.3.1

Verify that valid calibration certificates with appropriate values and uncertainties are available for all the standards used in the calibration. All standards must 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.

1.3.2

Verify that the mass standards to be used have sufficiently small standard uncertainties for the level of calibration. Reference mass standards should not be used for gravimetric calibration due to the risk of water contamination. Weights of ASTM Class 2 or 3 or OIML Class F_1 or F_2 are recommended for this procedure. Working standards of other classes are generally not designed to maintain adequate stability needed; however, corrections obtained within a few days of the volume calibration may

provide adequate stability and may be used if the uncertainty is sufficiently small and the density is available for performing buoyancy corrections.

1.3.3 Verify that the balance used is in good operating condition with adequate capacity, sufficiently small resolution, and sufficiently small process standard deviation, as verified by a valid control chart or preliminary experiments using this procedure. Note: standard deviations obtained from mass calibrations do not reflect the process repeatability of gravimetric calibrations; therefore, process repeatability must be obtained using this procedure! The accuracy of the balance and weighing procedures should be evaluated to minimize potential bias in the measurement process.

1.3.4 Verify that the operator is experienced in precision weighing techniques and has had specific training in NISTIR 6969 SOP 2, SOP 4, SOP 29, GMP 3, GMP 10, and gravimetric calibrations.

1.3.5 Verify that an adequate quality and supply of distilled or deionized water (see GLP 10) is available. Note: Do not use tap water for this procedure!

1.3.6 Verify that air currents are minimized in the laboratory when weighing is performed. 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	18 °C to 23 °C Stable to ± 1 °C / 1 h, during the calibration	40 % to 60 % Stable to ± 10 % / 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 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 procedure is generally only appropriate for micropipettes when additional evaporation corrections are made. The precision of calibration depends on the care exercised in adjusting the various volumes and strict adherence to the various steps of the procedure. The accuracy attainable depends on the ability of the operator to read and set the meniscus, uncertainties of the standard weights, the air buoyancy corrections, and thermal expansion corrections that are made.

2.2 Summary

The electronic balance used is calibrated by incorporating standard masses into the procedure. 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 the nominal capacity and at various capacities when multiple neck graduations are present. Transfer vessels may be used for all procedures except for flasks and containers marked.

2.3 Standards and Equipment Requirements

2.3.1 An electronic balance having sufficient capacity to weigh the loaded vessel is required. The balance selection affects the potential measurement errors associated with this procedure. Prior to use and where available, it is recommended to use the adjust/calibrate feature on balances. Option A provides a single point calibration factor for the balance. In general, concerns are greater for balances or mass comparators larger than 5 kg due to corner loading errors, non-linearity, and repeatability over the range of use. Option B as described in the calculation section for larger volumes corrects for balance non-linearity in both the filled and empty/drained ranges of use. Option B will also likely be required on mass comparators that have multiple ranges. It also provides corrections for variations in air density that may occur over a longer weighing process on larger volumes. For all procedures in this SOP, the balance should be zeroed prior to each measurement to minimize possible effects due to balance drift. The sensitivity or resolution of the balance may be a limiting factor in the accuracy of the measurement. The resolution and repeatability must be smaller than the accepted uncertainty of the calibration. Linearity errors or additional uncertainties may need to be considered when the mass standards are slightly less than the volume or container being measured.

2.3.2 Sufficient quantity of calibrated mass standards. Mass standards are selected so that they are slightly larger than the combined mass of the volume and container or transfer vessel that will be weighed. When summations of masses are used, the summation mass is used, and the "effective density" must be calculated, taking care not to use "average" density values.

2.3.3 Thermometer with resolution and uncertainty less than 0.1 °C to determine water temperature.

2.3.4 Thermometer with resolution and uncertainty less than 0.50 °C to determine air temperature.[1]

[1] See NISTIR 6969, SOP 2 for calculating air density and requirements for temperature, barometric pressure, and relative humidity.

2.3.5 Barometer with resolution and uncertainty less than 135 Pa (1 mmHg) to determine air pressure.[1]

2.3.6 Hygrometer with resolution and uncertainty less than 10 % to determine relative humidity.[1]

2.3.7 Distilled or deionized water (See GLP 10) of sufficient quality and quantity for the calibration. Note: Do not use tap water for this procedure!

2.3.8 Stopwatch or another 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 and GMP 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 thermally equilibrated with the laboratory environment. Equilibration can be achieved by storing the water in clean containers in the laboratory. It is important to use water that is equilibrated in the laboratory as much as possible to minimize potential calibration errors and convection currents during the calibration. Consider water to be equilibrated when within ± 5 °C of the laboratory temperature.

2.4.3 Volumetric calibrations to a marked volume (graduation line) 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 (± 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 for a transfer vessel that is used to weigh a delivered volume of water.

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

2.5 Calibration Procedure for Burets

2.5.1 Clamp the buret vertically on a support stand. Also clamp a plain glass test tube or beaker, large enough to hold a thermometer, near the buret.

2.5.2 Fill the 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.

2.5.3 Drain and record the delivery time, defined as the time of unrestricted flow from the zero mark to the lowest graduation mark with the stopcock fully open.

2.5.4 Fill the buret slightly above the zero mark with temperature-equilibrated water and fill the test tube that holds the thermometer. Record the water temperature.

2.5.5 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.

2.5.6 Measure and record the air temperature, air pressure, and relative humidity.

2.5.7 Zero the balance and then place a known mass standard on the balance pan that is slightly larger than the filled capacity of the empty transfer vessel or flask when filled with water. Record the reading as O_1.

2.5.8 Zero the balance and then weigh an empty transfer vessel or flask including the stopper or cover to be used. Record as O_2.

2.5.9 Fully open the stopcock and discharge the contents of the buret into the previously weighed flask or transfer vessel. The tip of the buret 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.

2.5.10 Stopper (or cover) the filled transfer vessel or flask. Check to make sure that the outside of the transfer vessel or flask is not wet. Zero the balance and then weigh the filled transfer vessel or flask. Record the balance reading as O_3.

2.5.11 Measure and record the temperature of water in the container.

2.5.12 Test the next interval in the same manner - from the zero mark to the next interval of test.

2.5.13 For burets with a specified waiting time, empty as in 2.5.9 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 2.5.9.

2.5.14 Measure and record the air temperature, air pressure, and relative humidity.

2.5.15 Make a duplicate determination for each interval (Run 2).

2.5.16 Calculate the volume for each interval as described in Section 3, Option A.

2.6 Calibration Procedure for Pipets (One-Mark)

2.6.1 Measure and record the air temperature, air pressure, and relative humidity.

2.6.2 Zero the balance and then place a known mass standard on the balance pan that is slightly larger than the filled capacity of the empty transfer vessel or flask when filled with water. Record the reading as O_1.

2.6.3 Zero the balance and then weigh an empty transfer vessel or flask, including the stopper or cover that will be used. Record the balance reading as O_2.

2.6.4 Fill the pipet to the index mark and measure the delivery time with the tip in contact with the internal surface of a beaker (not the transfer vessel that will be used.)

2.6.5 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 the beaker while this setting is being made. Do not remove any water remaining on tip.

2.6.6 Hold the pipet in a vertical position and deliver water into the previously weighed transfer vessel or flask, with the tip in contact with the inside wall or neck.

2.6.7 After the flow has ceased, wait two seconds then remove the pipet from contact with the flask. Check to make sure that the outside of the transfer vessel or flask is not wet.

2.6.8 Stopper (or cover) the filled transfer vessel or flask. Zero the balance and then weigh the transfer vessel or flask. Record the balance reading as O_3.

2.6.9 Measure and record the temperature of water in the container.

2.6.10 Measure and record the air temperature, air pressure, and relative humidity.

2.6.11 Make a duplicate determination for the pipet (Run 2).

2.6.12 Calculate the volume as described in Section 3, Option A.

2.7 Calibration of Flasks (To Contain) – Transfer vessel must **not** be used.

2.7.1 Clean and dry the flask to be calibrated as described in GLP 13. Then stopper the flask.

2.7.2 Measure and record the air temperature, air pressure, and relative humidity.

2.7.3 Zero the balance and then place a known mass standard on the balance pan that is slightly larger than the filled capacity of the flask when filled with water. Record the reading as O_1.

2.7.4 Zero the balance and then weigh the dry flask including its stopper or cover. Record the balance reading as O_2.

2.7.5 Place an appropriately sized funnel in neck and fill the flask to just below the reference graduation while maneuvering the flask to wet the entire neck below the stopper. Let stand for two minutes then adjust the meniscus to the reference graduation line, taking care to avoid wetting the neck above the capacity graduation.

2.7.6 Check that the outside surface of the flask, and its internal surface above the water level are dry, and that neither bubbles or foam are present in the water. Remove visible water droplets if needed with a laboratory wipe. Stopper or cover the flask.

2.7.7 Zero the balance and then weigh the filled flask and its stopper or cover, and record the balance reading as O_3.

2.7.8 Measure and record the temperature of the water in the flask or another container.

2.7.9 Measure and record the air temperature, air pressure, and relative humidity.

2.7.10 Make a duplicate determination (Run 2) after drying the flask per GLP 13.

2.7.11 Perform volume calculations as described in Section 3, Option A.

2.8 Calibration of Flasks (To Deliver)

2.8.1 Clean but do not dry the flask to be calibrated. Condition the flask by filling and emptying the flask over a 30 s period by gradually inclining it to avoid splashing. When the main flow has ceased, hold the flask in a nearly vertical position for 10 seconds unless another drain time is specified, then touch off the drop of water adhering to the tip of the flask.

2.8.2 Measure and record the air temperature, air pressure, and relative humidity.

2.8.3 Zero the balance and then place a known mass standard on the balance pan that is slightly larger than the filled capacity of the flask when filled with water. Record the reading as O_1.

2.8.4 Zero the balance and then weigh the drained (empty) flask including its stopper or cover. Record the balance reading as O_2.

2.8.5 Fill the flask to just below the reference graduation. Let the flask stand for two minutes, then adjust the meniscus to the reference graduation line. Do not dry the inside of the flask above the graduation line but take care to ensure that the outside of the flask is dry.

2.8.6 Zero the balance and then weigh the filled vessel, with cap or stopper. Record the balance reading as O_3.

2.8.7 Measure and record the temperature of the water in the flask.

2.8.8 Measure and record the air temperature, air pressure, and relative humidity.

2.8.9 Make a duplicate determination (Run 2).

2.8.10 Calculate the volume of the flask as described in Section 3, Option A.

Note: The order of weighing the filled and drained flask in Section 2.8 may be reversed. In that case, the filled vessel is still weighed and recorded as O_3, the flask is drained as in 2.8.1, and the properly drained vessel is weighed and recorded as O_2.

2.9 Calibration of Other Volumetric Glassware

2.9.1 Measuring Pipets (non-single-mark) – Calibrate in a manner like that used to calibrate burets (2.5).

2.9.2 Graduated Cylinders – Calibrate in a manner like that used for flasks (To Deliver cylinders, use section 2.8; To Contain cylinders, use section 2.7).

2.10 Calibration of Slicker-Plate Type Standards

2.10.1 This calibration makes use of Option B where equivalent mass standards are used at both the filled and empty loads on the balance. A transfer vessel is recommended.

2.10.2 Condition the slicker-plate type standards with several wet-down runs to fully ensure wet down and smooth valve operation.

2.10.3 Measure and record the air temperature, air pressure, and relative humidity.

2.10.4 Zero the balance and then place a standard mass, M_{S1}, on the balance platform (M_{S1} should be slightly larger than the mass of the drained vessel, dry vessel, or empty transfer vessel.) Record reading as O_1.

2.10.5 Zero the balance. Place the dry or "wet-down" transfer vessel on the balance platform, as appropriate, and record reading as O_2. Caution: all containers must be dry on the outside for all weighing.

2.10.6 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.

2.10.7 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 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. Note: Never fill the transfer vessel while it is sitting on the balance platform to ensure that the balance is not damaged with water and to avoid errors associated with balance drift and hysteresis.

2.10.8 Zero the balance and then place a standard mass, M_{S2}, on the balance platform. M_{S2} should be slightly larger than the mass of the filled vessel. Record the balance reading as O_3.

2.10.9 Zero the balance and then weigh the filled transfer vessel and record the balance reading as O_4.

2.10.10 Immediately after weighing, check the temperature of the water in the filled container. Ensure that the water has not changed by more than 0.2 °C during the measurement process or repeat the run.

2.10.11 Measure and record the air temperature, barometric pressure, and relative humidity.

2.10.12 Make a duplicate determination (Run 2).

2.10.13 Calculate the volume as described in Section 3, Option B.

2.11 Calibration of Hand-held Graduated Neck Type Provers

2.11.1 A hand-held test measure is weighed empty and filled much like the procedure for To Deliver flasks (section 2.8). However, this calibration makes use of Option B where equivalent mass standards are used at both the filled and empty loads on the balance.

2.11.2 Condition the test measure by filling and draining using a 30 s pour followed by a 10 s drain. Take care to avoid splashing of water on the outside of the

measure. The wet-down will help equilibrate the test measure with the water temperature.

2.11.3 Measure and record the air temperature, air pressure, and relative humidity.

2.11.4 Zero the balance and then place standard masses, M_{S1}, on the balance platform. M_{S1} should be slightly larger than the mass of the drained vessel. Record reading as O_1.

2.11.5 Zero the balance and then place the "wet-down" test measure on the balance platform, and record the balance reading as O_2. Caution: all containers must be dry on the outside for all weighing.

2.11.6 Fill the graduated neck type test measure to just below the nominal volume mark. Record the water temperature. Adjust the meniscus to nominal.

2.11.7 Zero the balance and then place standard masses, M_{S2}, on the balance platform. M_{S2} should be slightly larger than the mass of the filled vessel. Record the balance reading as O_3.

2.11.8 Zero the balance and then weigh the filled transfer vessel and record the balance reading as O_4.

2.11.9 Immediately after weighing, check the temperature of the water in the filled container. Ensure that the water has not changed by more than 0.2 °C since step 2.11.6 or repeat the run.

2.11.10 Measure and record the air temperature, barometric pressure, and relative humidity.

2.11.11 Make a duplicate determination (Run 2).

2.11.12 Calculate the volume as described in Section 3, Option B. You may use the average water temperature in calculations. If a neck scale plate verification is performed, additional weighings may be performed after setting the meniscus at each level.

2.12 Calibration of Large Volume Graduated Neck Type Provers

2.12.1 This calibration makes use of Option B where approximately equivalent mass standards are used at both the filled and empty loads on the balance. A transfer vessel is recommended. The unknown vessel to be calibrated must be elevated to facilitate transfer of water into the transfer vessel.

2.12.2 Condition the prover with a wet-down run to fully ensure smooth valve operation, temperature equilibration, and wet-down of the delivery system.

2.12.3 Measure and record the air temperature, air pressure, and relative humidity.

2.12.4 Zero the balance and then place standard masses, M_{S1}, on the balance platform. M_{S1} should be slightly larger than the mass of the drained vessel, dry vessel, or empty transfer vessel. Record reading as O_1.

2.12.5 Zero the balance. Place dry or "wet-down" transfer vessel including cover on balance platform, as appropriate, and record reading as O_2. Caution: all containers must be dry on the outside for all weighing.

2.12.6 Fill the graduated neck type prover to just below the nominal volume mark. Record the water temperature. Adjust the meniscus to nominal. Set the transfer vessel below the nozzle to ensure all volume is transferred into the vessel and that no splashing occurs. Use hoses and piping of minimum length to avoid errors associated with retention during delivery. Hoses should be translucent so that cessation of the main flow is visible. Care should be taken to ensure that there are no loops or sags in the hose that may hold water. When using hoses or piping, be sure to include them as part of the wet-down process.

2.12.7 Open the unknown prover valve 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 prover to ensure additional drops of water are not transferred.

2.12.8 Zero the balance and then place standard masses, M_{S2}, on the balance platform. M_{S2} should be slightly larger than the mass of the filled vessel. Record the balance reading as O_3.

2.12.9 Zero the balance and then weigh the filled transfer vessel and its cover. Record the balance reading as O_4.

2.12.10 Immediately after weighing, check the temperature of the water in the filled container. The temperature should not change by more than 0.2 °C if the prover and water have been equilibrated in the laboratory environment.

2.12.11 Measure and record the air temperature, barometric pressure, and relative humidity.

2.12.12 Make a duplicate determination (Run 2).

2.12.13 Calculate the volume as described in Section 3, Option B. You may use the average water temperatures for calculations.

3 Calculations

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

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

Note: The O_3 value is the filled volume container or transfer vessel and O_2 is the dry, empty, or drained value. If the order of any weighing operations were changed, the calculated volume may indicate a negative value.

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

$$V_t = \left[\frac{O_4}{O_3} M_{s2}\left(1 - \frac{\rho_a}{\rho_{s2}}\right) - \frac{O_2}{O_1} M_{s1}\left(1 - \frac{\rho_a}{\rho_{s1}}\right)\right]\left(\frac{1}{\rho_w - \rho_a}\right) \quad \text{Eqn. (2)}$$

Table 2. Variables used in 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/cm³)
ρ_w	density of water at the temperature of measurement (g/cm³)
ρ_a	density of air at the conditions of calibration – may be different for filled and empty/drained conditions (g/cm³)
V_t	represents either the "To Contain" or "To Deliver" volume (depending on whether O_2 represents a dry or a "wet down" container at the temperature of the measurement) (cm³ 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:

$$V_{20} = V_t\left[1 - \alpha(t - 20)\right] \quad \text{Eqn. (3)}$$

where α is the cubical coefficient of expansion of the container being calibrated (°C^{-1}), (see NISTIR 6969, Table 9.10), and, t, is the temperature (ºC) of the water. Compute the mean V_{20} for the duplicate measurements.

3.4 Test measures and provers are typically calibrated to 60 °F. Compute V_{60}, the volume at 60 °F, for each run, using the expression (taking care to use the cubical coefficient of expansion in °F^{-1}):

$$V_{60} = V_t\left[1 - \alpha(t - 60)\right] \quad \text{Eqn. (4)}$$

3.5 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:

$$V_{ref} = V_t \left[1 - \alpha \left(t - t_{ref} \right) \right] \quad \text{Eqn. (5)}$$

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

Table 3. Reference temperatures for measured volumes.

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)
Compressed Natural Gas (CNG)	15 ºC (60 ºF)
Wine	20 ºC (68 ºF)
Unrefrigerated liquids (e.g., sold unchilled, like soft drinks)	20 ºC (68 ºF)
Hydrogen (H_2)	21 ºC (70 ºF)
Petroleum (Hawaii)	26.67 ºC (80 ºF)

3.6 Calculate water density for air-saturated water, using the equations provided in GLP 10.

3.7 Calculate the air density per NISTIR 6969, Selected Mass Calibration Procedures, SOP 2, Option B.

3.8 Calculate the within process standard deviation, s_w, for the replicate runs and determine the applicable degrees of freedom (number of replicates minus one).

3.9 Calculate the F statistic to compare the observed within process standard deviation, sw, to the accepted (pooled) within process standard deviation for the measurement process. (See NISTIR 6969, Sections 8.4 and 8.9.2, for more information on pooling standard deviations and F-tests.)

$$F = \frac{s^2_{w\,\text{Observed}}}{s^2_{w\,\text{Accepted}}} \quad \text{Eqn. (6)}$$

3.10 The calculated F statistic must be less than the F value obtained from an F table at 95 % confidence level (Table 9.12, NISTIR 6969) to be acceptable. The F value is obtained from the F table for numerator degrees of freedom and denominator degrees of freedom equal to the number of degrees of freedom in the accepted (pooled) within process standard deviation. If the data fails the F-test and the source of the error cannot be determined conclusively, the measurement must be repeated.

3.11 Calculate and report the mean volume of the volumetric standard at its applicable reference temperature.

If adjustments were made during replicate runs, report the "as found" volume or the mean of "as found" volumes and the "as left" volume or mean of "as left" volumes, as applicable, at the appropriate reference temperature. (I.e., do not calculate a mean value by combining "as found" and "as left" values when adjustments are made.)

4 Measurement Assurance

4.1 Where practical, duplicate the process with a suitable check standard (See GLP 1, SOP 30, in NISTIR 6969, or Sec. 7.4, in NBS Handbook 145).

4.1.1 Plot the calculated 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.

$$t = \frac{\left(S_c - \overline{S_c}\right)}{s_p} \qquad \text{Eqn. (7)}$$

The t-statistic is evaluated using Eqn. 7 with a 95 % confidence level. All values must be entered in the control chart, even if failing this statistic to ensure the variability obtained for the process is truly representative of the process and not unduly reduced over time. The observed value of the check standard is compared to the accepted mean value of the check standard and divided by the standard deviation for the check standard observations over time. The limits for the t-test are based on applicable warning and action limits on the control chart. See SOP 20 for applicable t-test limits.

4.1.2 The mean of the calculated check standard values 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.

4.1.3 Check standard observations may also be used to calculate the standard deviation of the measurement process, s_p.

4.2 This procedure uses replicate measurements to monitor the measurement process following SOP 20 and a standard deviation chart (preferred) or a range chart (optional). For standards that may be and are adjusted, do not combine an "as found" value with an "as left" value for the two runs recorded in the chart; use the

adjusted value from Run 1 and the value from Run 2, both at the applicable reference temperature, when entering values in a standard deviation or range chart. Control chart run values must both be from either before adjustment or after adjustment. A minimum of 12 replicate measurements are required to establish initial process limits and 25 to 30 points are required for reporting valid uncertainty values.

5 Assignment of Uncertainties

The limits of expanded uncertainty, *U*, include estimates of the standard uncertainty of the mass standards used, u_s, plus the measurement process repeatability, s_p, and the additional items noted below and in the uncertainty budget table, Table 4, at approximately a 95 percent level of confidence. See NISTIR 6969, 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 and correlations.

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 using this procedure. It may also be estimated based on replicate measurements over time. Replicate measurements over time provide a pooled standard deviation that may be used (alternatively, the average range is used to estimate the standard deviation) per SOP 17 or 20. This standard deviation value is a repeatability factor related to the precision of the measurement process weighings and the setting of the meniscus when present, but does not include uncertainties associated with systematic errors in reading the meniscus. See GMP 3 for details. Use the larger of the s_p from a check standard or the s_w obtained from within process repeatability.

5.3 Include uncertainties associated with the reading of the meniscus when one is 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 mass standards, 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.

5.5 Example components to be considered for an uncertainty budget table are shown in Table 4. Multiple values may need to be considered in some cases.

Table 4. Example uncertainty budget table.

Uncertainty Component Description	Symbol	Source	Typical Distribution
Uncertainty of the standard mass(es) (5.1)	u_s	Calibration certificate	Expanded divided by coverage factor
Accepted standard deviation of the process (5.2)	s_p	Control chart, standard deviation chart	Normal
Water temperature	u_{tx}	Consider accuracy, resolution, and gradients	Rectangular
Water density	$u_{\rho w}$	GLP 10	Rectangular
Cubical Coefficient of Expansion (CCE)	u_{CCE}	5 % to 10 % of the CCE (EURAMET CG-19)	Rectangular
Meniscus reading (when present) (5.3)	u_m	GMP 3	Triangular
Drain time effects (insignificant if following procedures)	u_d	From experimental data	Rectangular
Air temperature (for air density)	u_t	NISTIR 6969, SOP 2	Rectangular
Air pressure (for air density)	u_p	NISTIR 6969, SOP 2	Rectangular
Air relative humidity (for air density)	u_{RH}	NISTIR 6969, SOP 2	Rectangular
Air density (equation)	$u_{\rho a}$	NISTIR 6969, SOP 2	Rectangular
Mass density	$u_{\rho m}$	Assumed reference densities or OIML R111	Rectangular

5.6 Uncertainty Evaluation

Where applicable, uncertainties for volume calibrations that are assessed for conformity must meet decision rule criteria in the applicable documentary standards.

6 Calibration Certificate

6.1 Report results as described in NISTIR 6969 SOP 1, Preparation of Calibration Certificates, with the addition of the following:

"To Contain" or "To Deliver" volume, reference temperature, uncertainty, material, thermal coefficient of expansion (assumed or measured), construction, any identifying markings, tolerances (if appropriate), laboratory air temperature, water temperature(s) at time of test, barometric pressure, relative humidity, and any out-of-tolerance conditions.

6.2 Conformity Assessment

Evaluate compliance to applicable tolerances as needed or required by the customer or by legal metrology requirements. Compliance assessments must note the applicable documentary standard and which portions of the standard were or were not evaluated. The uncertainty for volume calibrations must be less than the tolerances published in the applicable documentary standards. For volume calibrations where the unknown standard can be adjusted, it is standard practice to

adjust the standard or leave the scale plate in a position close enough to its nominal volume to ensure that the absolute value of the measurement result plus the uncertainty is less than the applicable tolerance. Where the unknown standard cannot be adjusted, and a portion of the uncertainty band from the error exceeds tolerance limits, it is not appropriate to state compliance with the tolerances unless additional decision rules are communicated with and agreed to by the end user. Correction values (measurement results) may need to be used by the end user in such cases.

7 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, (2009).

EURAMET Calibration Guide 19, Guidelines on the Determination of Uncertainty in Gravimetric Volume Calibration, (Version 2.1, 03/2012).

Appendix A (Single-Point Balance Calibration)

Gravimetric Calibration Data Sheet (Option A)

Laboratory data and conditions:

Vessel Identification		Operator		
Material		Date		
Cubical Coefficient of Expansion			Before	After
Balance Identification		Temperature		
Load		Pressure		
Standard deviation of the process, from control chart, s_p		Relative Humidity		
Degrees of Freedom		Reference water temperature		

Mass standard(s) data:

Identification (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* values are required.

Observations:

Run 1	Weights – Zero balance before each weighing.	Balance Observations, Units_____	
	M_S	O_1	
	Empty or Drained	O_2	
	Filled	O_3	
		t_w	
Run 2	Weights – Zero balance before each weighing.	Balance Observations, Units_____	
	M_S	O_1	
	Empty or Drained	O_2	
	Filled	O_3	
		t_w	

Appendix B (Two-Point Balance Calibration)

Gravimetric Calibration Data Sheet (Option B)

Laboratory data and conditions:

Vessel Identification		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		Reference water temperature		

Mass standard(s) data:

Identification (Note ID for Empty (M_{S1}) or Filled (M_{S2}) Loads)	Nominal	Mass Correction*	Expanded Unc: From cal. report	Unc: *k* factor	Density g/cm^3
S					
S					
S					
S					
S					
S					
S					

*Mass Correction = *True Mass* values are required.

Observations:

Run 1	Weights – Zero balance before each weighing.		Balance Observations, Units_____	
		M_{s1}	O_1	
		Empty or Drained	O_2	
		M_{S2}	O_3	
		Filled	O_4	
t_w in standard:		t_w in unknown:		Temperature change is less than 0.2 °C? Y/N
Run 2	Weights – Zero balance before each weighing.		Balance Observations, Units_____	
		M_{s1}	O_1	
		Empty or Drained	O_2	
		M_{S2}	O_3	
		Filled	O_4	
t_w in standard:		t_w in unknown:		Temperature change is less than 0.2 °C? Y/N

Appendix C

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 conventionally selected conditions are as follows:

   1.1. For bottom-drain containers: open the drain valve fully and allow contents to discharge at maximum rate. When main flow ceases (flow decreases so that drain opening no longer runs full), wait 30 s, close the valve, and touch off any drops adhering to spout.

   1.2. For pour-type containers: pour contents by gradually tilting container to an 85º angle, so that virtually all liquid 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. A transfer vessel is recommended for use when calibrating a slicker-plate type standard. But if the standard is weighed, the plate must be weighed with the standard during each such operation.