SOP No. 15

Recommended Standard Operations Procedure for
Calibration of Intermediate and Large Volume Standards
Gravimetric Method[1] Using an Equal-Arm Balance[2]

1 Introduction

1.1 Purpose of Calibration

This procedure is applicable to calibrations where high accuracy is needed, or where the volumetric transfer method is not possible. It is especially useful for the capacity range of 5 gal to 100 gal (or larger) using an equal-arm balance and the double substitution weighing method as described in SOP 4. It may also be used for smaller volumes with an equal-arm balance. If an electronic balance is used, see SOP 14.

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 intended 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, and GMP 1, GMP 3, GMP 10, and gravimetric calibrations.

1.2.5 Verify that the laboratory facilities meet the minimum conditions shown in Table 1 to meet the expected uncertainty achievable with this procedure.

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

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[1]Based on the work of J. Houser "Procedure for the Calibration of Volumetric Test Measures" NISTIR 73-287.

[2] Non-SI units are predominately in common use in State legal metrology laboratories, and/or the petroleum industry for many volumetric measurements, therefore non-SI units have been used to reflect the practical needs of the laboratories performing these measurements as appropriate. The reference temperature for petroleum products is 60 ºF and volume values are typically in gallons.

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   Summary

This procedure may be used to determine three calibration values:

2.1.1   The contained volume, V_C, which is the volume of water required to fill the vessel at a specified temperature (usually 60 °F for petroleum products).

2.1.2   The delivered volume, V_D, which is the volume of water that may be poured or drained from the vessel at a specified temperature (usually 60 °F for petroleum products) under specified conditions (see note 1).

2.1.3   The neck scale calibration value, *NSCV*, which relates the true volume of the neck to the value indicated by the neck scale.

The mass of water required to fill the vessel is measured at an observed temperature. The known density of water and coefficient of expansion of the vessel are used to calculate the volume of the vessel at a reference temperature.

The precision attained will depend on the sensitivity of the balance and on the care exercised in carrying out the various operations of the procedure. Cleanliness of the vessel and strict adherence to the prescribed drainage procedure are critical for high precision. The accuracy of calibration depends on all of the above plus the uncertainties of the various weighings, accuracy in reading a meniscus (where present), the volumetric temperature equilibration and corrections, the proper correction for air buoyancy, and the purity of the water used as the standard. The metrologist must critically consider all of the above factors when assigning uncertainty limits to the calibrated volumes.

With careful observance of good measurement practices, an overall relative uncertainty of ± 0.02 % should be attainable.

2.2   Apparatus

2.3.1   Equal-arm balance of adequate capacity and sensitivity (standard deviation of 500 mg or better for 5 gal level).

2.3.2   Weights (meeting ASTM Class 2 or 3 specifications) as appropriate for the accuracy requirements.

2.3.3   Calibrated thermometer accurate to ± 0.1 °C with recent calibration values that are traceable to NIST to determine water temperature.[3]

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[3] 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

2.3.4   Calibrated thermometer accurate to $\pm$ 0.5 °C with recent calibration values that are traceable to NIST to determine air temperature.

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

2.3.6   Calibrated hygrometer accurate to $\pm$ 10 % with recent calibration values that are traceable to NIST to determine relative humidity.

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.)

2.3.9   Cap to place over neck of the vessel.

2.3   Procedure

2.3.1   Preliminary Operations

2.3.1.1 Clean the interior of the vessel with biodegradable low-sudsing detergent (see GMP 6) with gentle scrubbing as necessary. Rinse several times with clean water to remove all detergent, followed by pure water. Check for leaks and for uniform drainage.

2.3.1.2 Clean and dry outside of container to remove any material which might subsequently dislodge and cause an erroneous weighing.

2.3.1.3 Dry inside by rinsing with small amounts of alcohol or by drawing clean, filtered air through the vessel (several hours required). For large vessels the heat from a low wattage light bulb suspended inside the vessel overnight will aid in drying by slightly heating the vessel and creating convection currents through the interior. Allow the vessel to come to thermal equilibrium with the room before proceeding.

2.3.2   Empty Weight

2.3.2.1 Weigh the empty vessel and cap using the double substitution procedure (SOP 4) with air buoyancy correction.

2.3.2.2 Record air temperature, humidity, and barometric pressure as needed for calculating air density (SOP 2) and performing buoyancy corrections.

2.3.2.3 The empty weight is determined as shown in the calculations (Section 3.1, Eqn 2).

2.3.3   Filled Weight

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recommended for high precision calibration. Less accurate equipment can be used with only a small degradation in the overall accuracy of the measurement.

2.3.3.1 Fill the vessel with pure water to the zero point on the neck scale. Be sure the vessel is level. Bounce the liquid to disturb the meniscus to assure it has reached equilibrium level. Record the water temperature and readjust level if necessary. Be sure that no water remains on the outside of the vessel when it is weighed. (See note 2.) The filled weight is determined as shown in the calculations (Section 3.1, Eqn 2).

2.3.3.2 Weigh filled vessel and cap as in 2.3.2.

2.3.4 Drained Weight

2.3.4.1 Drain vessel using appropriate discharge/pour and drain times (see note 1). Replace cap. The empty weight is determined as shown in the calculations (Section 3.1, Eqn 2).

2.3.4.2 Weigh drained vessel and cap as in 2.3.2.

2.3.5 Make a duplicate determination of steps 2.3.2 through 2.3.4 (Run 2).

2.3.6 Neck scale plate verification

2.3.6.1 Fill vessel with water to a scale division near the bottom of the scale range. Record reading (s_{r1}).

2.3.6.2 Make appropriate successive additions of water from a calibrated buret or other suitable volumetric measuring device. Record scale readings after each addition .

2.3.6.3 A plot of scale readings with respect to volume added should be linear and will be a gross check of the validity of this calibration.

2.3.6.4 Calculate the neck scale calibration value, *NSCV*, using the expression

$$NSCV = \frac{V_W}{(sr_f - sr_i)}$$ Eqn. 1

Table 1.   Variables for neck scale calibration value equation

Variable	Description
NSCV	Neck scale calibration value
V_W	Total volume of water added to neck
sr_i	Scale reading, initial
sr_f	Scale reading, final

3   Calculations

     3.1   To calculate the filled, empty, or drained mass, use the following equation from SOP 4 using Option A.

$$M_{(filled, empty, drained)} = M_S \left(1 - \frac{\rho_a}{\rho_S} \right) + \frac{(O_2 - O_1 + O_3 - O_4)}{2} \left[\frac{M_{sw} \left(1 - \frac{\rho_a}{\rho_{sw}} \right)}{(O_3 - O_2)} \right] \qquad \text{Eqn.2}$$

Table 2.   **Variables for Equation 2**

Symbol	Description
S	standard reference weight
sw	small calibrated weight used to evaluate the sensitivity of the balance
M	the mass (true mass) of a specific weight. Subscripts *s, sw, filled, empty, drained* are used to identify the weight (equals Nominal plus Correction in the case of mass standards)
ρ_a	density of air at time of calibration
ρ	density of masses; subscripts s, x, t_s, t_x, sw are used to identify the weight.
O	Balance observations, designated with subscripts 1, 2, 3…, for the observation number

     3.2   To calculate containment volume, V_C, at temperature of measurement, t,

$$V_{Ct} = (M_{filled} - M_{empty}) \left[\frac{1}{(\rho_w - \rho_a)} \right] \qquad \text{Eqn. 3}$$

$$V_{Dt} = (M_{filled} - M_{drained}) \left[\frac{1}{(\rho_w - \rho_a)} \right]$$

     3.3   To calculate delivered volume, V_D, at temperature of measurement, t,

Eqn. 4

     3.4   To correct volumes to reference temperature, t_{ref}, (be sure to match units for cubical coefficient of expansion, α, with temperature units (e.g., degrees C with °C^{-1}).

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

3.5 To convert the volume measured in mL (cm^3) to gal:

$V_{gal} = (0.000\ 264\ 172)\ V_{mL}$ (There are 3 785.411 784 mL per gal.)

Table 2.   Variables for volume equation

Symbol	Description
ρ_w	density of water at temperature of filling
ρ_a	density of air
t	temperature at time of test
t_{ref}	reference temperature, usually 60 °F (or 20 °C)
α	cubical coefficient of expansion of the vessel (must match temperature units in °C^{-1}or °F^{-1})

3.6 Calculate the average volume at reference temperature ($V_{t\,ref}$)

3.7 Physical Constants

   3.7.1 Density of Air

      Value at environmental conditions at time of weighings calculated from the equation given in the Appendix to SOP 2.

   3.7.2 Density of Water

      Calculate the density of water using the formula given in GLP 10 or look up the value from appropriate tables.

   3.7.3 Cubical Coefficient of Expansion

      Values for the cubical coefficient of expansion of various materials are given in NISTIR 6969, Table 9.10 and are normally printed on the vessel identification plate (for test measures and provers).

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 that it is within established limits OR a *t*-test may be incorporated to check the observed values 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_s, 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 mass 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. See SOP 29 for proper handling of uncertainties when multiple standards are used.

5.2   Standard deviation of the measurement process from control chart performance (See SOP 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 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, the coefficient of expansion, viscosity, reading the meniscus, calculation of air density, standard uncertainties associated with the density of the standards used, improper observance of drainage times, viscosity or the surface effects on the volume of liquid clinging to vessel walls after draining and 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

Test Notes

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 (an empty glass beaker, for example) 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.