SOP 16

Standard Operating Procedure for
Calibration of Measuring Flasks
Volume Transfer Method

1   Introduction

1.1   Purpose of Test

This procedure describes a method for volume transfer calibration of the "to deliver" volume of measuring flasks from calibrated volumetric standards. The test items are then used as volumetric measurement standards, often for packaged commodity verification. If "to contain" calibrations are to be performed, appropriate modifications are needed in the procedure to ensure complete drying of the flask between calibration runs.

1.2   Prerequisites

1.2.1   Verify that valid calibration certificates are available for all of 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.

1.2.2   Verify that the standards to be used have sufficiently small standard uncertainties for the intended level of calibration.

1.2.3   Verify that the standard burets and pipets are clean, free of leaks, and in good operational condition.

1.2.4   Verify the availability of an adequate supply of pure distilled or deionized water (See GLP 10) of sufficient quality and quantity for the calibration. Do not use tap water for this procedure to ensure the reference glassware is maintained with valid reference values!

1.2.5   Verify that the operator has had specific training and is proficient in SOP 16, GMP 3, GMP 7, and is familiar with the operating characteristics and conditioning of pipets and burets.

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

Table 1.   Laboratory environmental conditions.

Procedure	Temperature	Relative Humidity
Volume Transfer	18 °C to 27 °C, Stable to ± 1 °C / 1 h during the calibration	40 % to 60 % Stable to ± 20 % / 4 h

2   Methodology

2.1   Scope, Precision, Accuracy

The method is applicable for the calibration of any size of measuring flask for which standard pipets of comparable volume are available. Typical flasks have volumes in the range of 100 mL to 5 L (1 gill to 1 gallon). 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 will depend on the accuracy of calibration of the volumetric standards used, accuracy in reading the meniscus, together with the precision of the comparison. Clean glassware and strict adherence to the drainage instructions are essential for precise and accurate results.

2.2   Summary

The flask to be calibrated is given an initial wet-down using the correct drain procedure, then nearly filled with water delivered from a calibrated pipet. (This procedure relies on calibrated pipets that deliver slightly less than the full nominal volume.) Additional water is added to the test flask from a calibrated buret until the meniscus in the test item coincides with the calibration graduation mark. The sum of the volumes delivered into the wetted flask is equivalent to its "to deliver" volume. The process described assumes that the flask is marked with a 10-second drain time. If the flask is marked with a drain time other than 10 s, the specified drain time should be used rather than the 10 s drain time described. A 30-second drain time should be used when a flask has no drain time specified.

2.3   Standards and Equipment

2.3.1   Calibrated standard pipet(s) of suitable volumes. These standards are typically made of borosilicate glass.

2.3.2   Calibrated standard buret(s) of 10 mL (or 120 minim[1]) capacity. These standards are typically made of borosilicate glass.

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[1] 1 [US] minim = 0.061615496 milliliter (mL). 120 minim standards were provided to the States as reference standards for use in volume transfer calibrations. These standards have higher resolution than metric standards provided at the same time.

2.3.3 Calibrated thermometers, with resolution and uncertainty to ≤ 0.1 °C to determine water temperature.

2.3.4 Meniscus reading device (See GMP 3).

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

2.4 Procedure

2.4.1 Cleanliness check

Verify that all glassware, including the standards used and the vessels to be calibrated, are internally clean, as evidenced by uniform drainage of water. No water droplets should remain on the internal surfaces as the water drains from the vessels. If this occurs, the glassware must be cleaned with suitable agents and rinsed with pure water until uniform drainage is obtained. (See GMP 7).

2.4.2 Wet-down of pipet and flask

2.4.2.1 Fill the standard pipet to until water flows from the top tip, then completely drain into an empty vessel. Check for uniform drainage. Touch off the pipet outlet tip against the container wall to remove excess droplets and to establish a constant tip retention volume. The pipet and bore of the delivery side of the stopcock should appear to be "empty" and the delivery tip should contain a small volume of water retained in it. This is the "wet-down" condition of the pipet. It must be done at the beginning of each test sequence. Ensure that the outside of the standard pipet is free of water droplets that may fall into the unknown flask.

2.4.2.2 Refill the pipet and use it to fill the flask to be calibrated. Empty the flask using a gentle pour in a 30 s ± 5 s period by gradually inclining the flask so as to avoid splashing of the walls as much as possible. When the main drainage stream has ceased, the flask will be nearly vertical. Allow an additional 10 second drainage after discharge of the flask contents while holding the flask at a 10° to 15° angle from vertical, then touch off the rim of the flask to remove any drops adhering to it. At the same time, check that uniform drainage has been achieved. This establishes the "to deliver" condition of the flask. Note that some small amount of water will remain in the flask. Each flask to be calibrated must be given this "wet-down" treatment immediately before the start of the test.

2.4.3 Conditioning the buret

2.4.3.1 Fill the standard buret to overflow and drain several times to verify uniform drainage. Refill with water. Note that the stopcock bore and delivery tip should be filled with water at all times, in contrast to the condition for the pipet.

2.4.3.2 Touch off the delivery tip against the wall of the receiving vessel, to remove any droplet adhering to the external surface of the tip. This is an operation that must be done every time a measured volume of water is delivered from the buret to ensure consistent volume delivery.

2.4.4 Calibration

2.4.4.1 Run 1. Fill the standard pipet to overflow. The delivery bore and the delivery tip will be empty, except for the small volume retained in the tip. Place the inside of the flask neck in contact with the tip of the pipet or buret, to avoid splashing but in a manner that does not block the flow of water.

2.4.4.2 Deliver the contents of the pipet into the "wet-down" flask. Repeat as necessary to nearly fill the flask to the calibration line. The value recorded for the standard pipet will be the total of the deliveries used.

2.4.4.3 Add water to the flask from the buret until the meniscus coincides with the calibration mark. (See GMP 3 for instructions on how to read a meniscus.) Read the volume of water delivered from the buret and record on a suitable data sheet such as the one in the Appendix. Note: If multiple deliveries of the complete buret contents are required, ensure that at no time the buret water level drops below the lowest graduation mark, or the entire process must be started over. The value recorded for the standard buret will be the sum of the delivered volumes.

2.4.4.4 Empty the measuring flask as described in 2.4.2.2 to re-establish "wet-down."

2.4.4.5 Record all data using the form given in the Appendix or a similar format.

2.4.4.6 Run 2. Replicate Measurement. Repeat the procedure described in 2.4.4. The test measure must be capable of repeating to 0.01 % of the test volume during calibration. Repeatability problems may be due to contamination, poor meniscus readings, lack of cleanliness, or conduct of the calibration in an unstable environment.

Repeatability problems must be corrected before calibration can be completed.

2.4.4.7 Calibration Note: If the test vessel has a graduated neck (in addition to the nominal mark) additional graduations should be inspected for proper marking and calibrated as well.

3 Calculations

3.1 Compute the individual "to deliver" volumes, V_{TD}, for Run 1 and Run 2.

$$V_{TD} = V_P + V_B \qquad \text{Eqn. 1}$$

Table 2.   **Variables for volume equation.**

Variable	Description
V_{TD}	"To deliver" Volume
V_P	"To deliver" calibrated volume of the standard pipet
V_B	Volume of water delivered from the buret, corrected for any calibration values

3.2 Temperature correction

For calibration of glassware that is not made of borosilicate glass, not only should the above temperature conditions be realized but the water temperature must also be known. The water used must be stored in the laboratory until its temperature is equilibrated with its surroundings and the temperature of the discharged water is measured, using the calibrated thermometer. The "To Deliver" volume of the flask, corrected to the reference temperature of 20 °C, V_{TD20}, is computed, using the expression:

$$V_{TD20} = V_{TD}\left[1 + (\alpha - \beta)(t - 20)\right] \qquad \text{Eqn. 2}$$

Table 3.   **Variables for volume temperature correction equation.**

Variable	Description
V_{TD}	observed delivered volume as computed in 3.1
V_{TD20}	"To deliver" volume at the reference temperature of 20 °C
t	Temperature of water at time of calibration
α	Cubical coefficient of expansion of glass of standard (e.g., 0.000010 °C^{-1} for borosilicate glass)
β	Cubical coefficient of expansion of glass of flask (e.g., 0.000025 °C^{-1} for soda-lime glass)

The volumetric standards are typically made of borosilicate glass. If borosilicate flasks are calibrated, no temperature correction is required. This procedure relies on the fact that since deliveries are made over a short period of time, the temperature remains the same in the standard as in the unknown. *When standards and flasks are not of the same material, the water temperature change must be less than 0.5 °C while the water is in the standards and the flask.*

3.3   Report the average volume V_{TD20} as the value for the flask after the temperature correction has been applied to each Run.

4   Measurement Assurance

4.1   Duplicate this process with a suitable check standard (Quality Assurance Reference Flask, QARF) or have a suitable range of check standards for the laboratory with similar size graduations and neck diameters. See SOP 17 and SOP 30.

4.2   Plot the check standard volume and verify that it is within established limits. Alternatively a *t*-test may be incorporated into the process to check the observed value against an accepted reference value. (See NISTIR 6969, Section 8).

4.3   The mean of the check standard value 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.

5   Assignment of Uncertainties

The limits of expanded uncertainty, U, include estimates of the standard uncertainty of the laboratory volumetric standards used, u_s, plus the standard deviation of the process, 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 reports for the pipet and buret used for the calibration. The combined standard uncertainty, u_c, from the calibration report must be used and not the expanded uncertainty, U. Therefore, the reported uncertainty for the standard will usually need to be divided by a coverage factor, k. Multiple standards are used in this procedure; however, they are typically calibrated independently. Multiple standard uncertainties are handled according to SOP 29.

5.2   The standard deviation of the measurement process, s_p, is obtained from control chart performance (See SOP 17 or 20, and SOP 30) for a suitable QARF using the same volume transfer procedures on flasks of comparable size and neck dimensions.

5.3   Other standard uncertainties usually included at this calibration level include uncertainties associated with the ability to read the meniscus, only part of which is included in the process variability (See GMP 3), the cubical coefficient of expansion for the flask under test, use of proper temperature corrections, the accuracy of temperature measurements taking into consideration potential gradients in the glassware during calibration, round robin data showing

reproducibility, environmental variations over time, and bias or drift of the standard.

6   Report

6.1   Report results as described in SOP 1, Preparation of Calibration/Test Results, with the addition of the following items:

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

7   Alternative Reference Temperatures

7.1   Reference temperatures other than 20 ℃ (68 ℉) may occasionally be used. Common reference temperatures for other liquids follow:

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

7.2   When alternative reference temperatures are used, at the request of the user of the field standard, and when the glassware is *not* marked with a reference temperature, the calibrated value of the standard may be reported at a different reference temperature, t_{ref}, by using this equation:

$$V_{TDtref} = V_{TD} \left[1 + \left(\alpha - \beta \right) \left(t - t_{ref} \right) \right]$$ Eqn. 3

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).

Appendix

Calibration of Measuring Flasks
(Volume Transfer Method)

Laboratory data and conditions:

			Before	After
Test Number		Date		
Vessel ID		Operator		
Nominal Volume			Before	After
Coefficient of Expansion		Temperature		
Process standard deviation from control chart, s_p		Pressure		
Degrees of Freedom		Relative Humidity		

Volume standard(s) data:

ID (enter interval if needed)	Nominal	Calibrated Volume	Volume Correction	Coefficient of Expansion	Uncertainty	k factor
Pipet						
Buret						
Buret						
Buret						

Observations:

	Run 1	Run 2
Calibrated Pipet Volume: V_p		
Buret Volume:		
Final Reading		
Initial Reading		
Difference		
Calibration Correction (if required)		
Corrected Buret Volume, V_B		
$V_{TD} = V_P + V_B$		
Water temperature at time of test (t)		
$V_{TD20} = V_{TD}\left[1 + (\alpha - \beta)(t - 20)\right]$		
Average V_{TD20}		