Calibration of Volumetric Glassware

Prepared by Allan Fraser

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APPLICATION Note 1

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1. Purpose

The purpose of this procedure is to provide a method for the calibration of volumetric glassware.

2. Scope

The scope includes volumetric glassware (*i.e.* designed to contain or deliver an accurate volume of solution), including pipettes, volumetric flasks and burettes.

3. Principle

The weight of deionized water contained in the flask or pipette is used to determine the actual volume contained in the glassware. Water weight is corrected for density differences due to temperature. The method involves weighing a specific volume of water either dispensed or to contain. Corrections for buoyancy are very small and are therefore can be neglected. The temperature of the water is measured at time of the calibration after the water has been allowed to equilibrate to a constant temperature. Multiplication of the obtained mass of water at some temperature is converted to the volume it would occupy at 20^{o}C. The difference between the apparent volume (i.e. that at some temperature) and the true volume is the absolute error, which should be less than the glassware tolerance. If so, the glassware is for all practical purposes, acceptable for quantitative work. If the absolute error > the tolerance, a correction factor needs to be introduced to correct to the true volume.

4. Abbreviations and Definitions

g	gram
mg	milligram
m	mass
ml	millilitres
Vol.	Volume

5. Material Types

All volumetric glassware for quantitative work requires calibration.

6. Range

All volumetric glassware used for accurate delivery or to contain specific volumes needs to be calibrated.

7. Apparatus and Equipment

7.1 Analytical balance accurate to 0.1mg (0.001g)

Analytical balance accurate to 0.1g. (For volumes of 100 mL or less, the balance used must be capable of measuring in increments of 0.001 g. For volumes greater than 100 mL, the balance used must be capable of measuring in increments of 0.1 g).

7.1.1 Thermometer (0-100^{o}C)

High Purity Water
Pipette Bulb
Beaker or weighing boat

7.2 Cleaning of Glassware

All glassware to be calibrated must be scrupulously clean before calibration.

1. The test for cleanliness of glass apparatus is that on being filled with deionised water, and the water discarded an unbroken film of water remains.
2. If the vessel is very dirty and greasy, it can be filled with a warm soap solution for 15 minutes, rising several times with deionised water, followed by 50% v/v hydrochloric acid and then rinsed several times with deionised water.

8. Volumetric Flask Calibration

1. Allow a few liters of deionised water in a beaker to equilibrate in terms of temperature by monitoring the temperature of a thermometer placed in the water. The water should be in the same environment in which the calibration of the volumetric apparatus is to be done.
2. Record the equilibrated water temperature (experimental temperature).
3. Record the serial number of the flask. If it does not already exist, add a serial number to the flask in permanent ink or by attaching a label.
4. Wash, dry, weigh, and record the mass of the volumetric flask to be calibrated.
5. Fill the volumetric flask to a few millimeters below the mark with deionized water.
6. Fill to the mark carefully using a medicine dropper or pipette.
7. Wipe dry the outside of the flask and then weigh.
8. Record the weight of the flask with the water in it.
9. Using Table 1, look up and record the density of the water corresponding to the temperature recorded in step 2.
10. Calculate the expected mass of the flask at the experimental temperature (W_{Tx}) as:

$$V_{flask} = \frac{W_{flask+water} - W_{flask}}{\rho_{water}} \qquad [1]$$

Where:

V_{flask} is the nominal volume of the flask (in mL);
$W_{flask + water}$ is the weight of the water recorded in step 8 (in g);
W_{flask} is the weight of the flask recorded in step 4 (in g); and
ρ_{water} is the density of water recorded in step 9 (in gmL^{-1})

11. Repeat steps 4 through 10 for at least six replicates.
12. Calculate and record the mean, standard deviation (s), and twice the standard deviation (2s) of the flask volume based on the replicates. These data are then entered into the MS Excel sheet 'Calibration Example 1'.
13. Identify any aliquots for which the volume is greater than 2s from the average value. If any aliquots are greater than 2s from the average value remove this datum and treat as an outlier.
14. Calculate and record the flask absolute error (i.e. ignore the sign of the computation) based on the following formula:

$$Absolute\ Error = |Nominal\ flask\ volume - Mean\ apparent\ volume| \quad [2]$$

15. Ensure that the absolute error as in [2] is within the limits of a Class A (or B, if that is being calibrated) volumetric glassware as listed in Table 2.
16. If the absolute error, calculated with the aid of Table 2 falls within the tolerance of the class of glassware, the glassware may be taken as accurate for all quantitative purposes. If however, the error is larger than the certified tolerance of the glassware, the simplest procedure is to affix a small label to the flask bearing the true volume and the date of calibration. It should be noted that the true volume should then be used in the calculation of concentrations made up in this flask.
17. Sign and date the data sheet as shown in Appendix 1.

(Skoog & West, 1982)

For pipettes the same procedure as described above is to be followed. With the exception of graduated cylinders, the tolerances for Class B glassware is typically twice that of a Class A glassware. (ASTM E694).

8.1.1 Example Calibration

A 100ml A-class volumetric flask was found to give a mean value (of six replicates) of 99.430g of water at 24^{o}C. Refer to Table 5 for the data in this example. The data in Table 1 is used to calculate the volume occupied at this temperature and is found to be:

$$99.430g\ x\ \frac{1}{0.99732g/ml} = 99.697ml$$

The standard deviation of the six replicates is found to be: 0.82ml. Calculating the $\pm 2s$ for the mean based on 2 x 0.82ml:

$$(98.360 - 101.640)$$

Since one of the values, 98.0336 is outside of the range, it is rejected as an outlier and not included in the mean and standard deviation calculations. A new mean excluding this datum is calculated along with a new standard deviation. The ±2s is now:

$$(99.947 - 100.05)$$

The absolute error is calculated and found to be within the tolerance of 0.08 for the 100ml volumetric flask:

$$Absolute\ error = 100.00 - 100.041 = 0.041$$

Since the criterion of the absolute error < tolerance has been satisfied (i.e. 0.041<0.08), the 100ml volumetric flask is taken as accurate for all quantitative purposes.

Should the absolute error > tolerance of the flask (e.g. 0.10>0.08), then a correction is made for the difference in volume.

Table 1. Density of pure water for various temperatures. Corrections for buoyancy for stainless steel weights and the change in the volume of the container have been applied as per Skoog & West (1982), page 727.

Temperature (°C)	**Density (g mL^{-1})**		**Temperature (°C)**	**Density (g mL^{-1})**
16.0	0.99897		23.5	0.99745
16.5	0.99889		24.0	0.99732
17.0	0.99880		24.5	0.99720
17.5	0.99871		25.0	0.99707
18.0	0.99862		25.5	0.99694
18.5	0.99853		26.0	0.99681
19.0	0.99843		26.5	0.99668
19.5	0.99833		27.0	0.99654
20.0	0.99823		27.5	0.99640
20.5	0.99812		28.0	0.99626
21.0	0.99802		28.5	0.99612
21.5	0.99791		29.0	0.99597
22.0	0.99780		29.5	0.99582
22.5	0.99768		30.0	0.99567
23.0	0.99757			

Table 2. Required tolerances of A- and B class volumetric flasks (source: ASTM E-288-94).

Capacity	**Tolerances (± mL)**	
(mL)	**Class A**	**Class B**
5	0.02	0.04
10	0.02	0.04
25	0.03	0.06
50	0.05	0.10
100	0.08	0.16
200	0.10	0.20
250	0.12	0.24
500	0.20	0.40
1000	0.30	0.60
2500	0.50	1.00

Table 3. Required tolerances of A-class pipettes (source: ASTM E-288-94).

Capacity (ml)	**Tolerance (ml)**
0.5	0.006
1.0	0.006
2.0	0.006
5.0	0.01
10.0	0.02
20.0	0.03
25.0	0.03
50.0	0.05
100.0	0.08

Table 4. Required tolerances of A-class burettes (source: ASTM E-288-94).

Capacity (ml)	**Tolerance (ml)**
5.0	0.01
10.0	0.02
25.0	0.03
50.0	0.05
100.0	0.2

Table 5. Example calculation for the calibration of a 100ml A-class volumetric flask of tolerance 0.08ml. 98.0336 ml is outside of the ±2s tolerance and is therefore excluded in the data evaluation.

Run No.	**Before calibration (mL)**	**W(empty) g**	**T,water ^{o}C**	**Density(g mL^{-1})**	**W, water + flask**	**W(empty+water)-(W,empty) ml**	**V. flask (ml)**	**Range (±2s)**	
1	100	56.534	24	0.99723	156.26	99.723	100.000	99.947	100.053
2	100	56.886	24	0.99723	156.66	99.777	100.054	99.947	100.053
3	100	56.165	24	0.99723	155.94	99.778	100.055	99.947	100.053
4	100	56.321	24	0.99723	156.11	99.789	100.066	99.947	100.053
5	100	56.815	24	0.99723	154.58	97.762	***98.0336***	_	_
6	100	55.557	24	0.99723	155.31	99.753	100.030	99.947	100.053
						Mean Volume=	100.041		
						s=	0.026	Criteria	
				Tolerance (ml) =	**0.08**	**Error (ml)=**	0.041	TRUE	
						Calibration factor=	0.9996		
						Corrected Vol.=	100.00		
						RSD (%)=	0.026		
						ASTM Classification	A		

8.2 Uncertainties in Measurement

Weight of water

Density of water

Error in sighting the level of the water

Error in temperature reading

8.3 How to cite this application note:

To cite this applications note, use the following:

Fraser A.W. (2016). Volumetric Glassware Calibration. Applications note 1. www.allanfraserandassociates.com and the date that the article was accessed.

REFERENCES

ASTM E288-94. Standard speciation for laboratory glass volumetric flasks.

Skoog, D., West, D. (1982). *Fundamentals of analytical chemistry.* 4th Edition. CBS College Publishing. Holt Saunders International Editions:725-728

APPENDIX

Appendix 1. Document for recording of relevant information for volumetric flask calibration. The same format can be used for pipettes.

Volumetric Flask Calibration

Date: ______________ Calibration Due Date: ___________________

Flask Identification

Manufacturer: ______ Nominal Volume: __________mL

Serial Number: ____________Step 3. Tolerance: ±________ mL

Calibration of Flask

Step 4 - Mass of Empty Flask: ___________ g

Run	Step 7 (g)	Step 2 (°C)	Step 9 (g mL^{-1})	Step 12 (mL)
1				
2				
3				
4				
5				
6				

Average Volume: __________ mL

Absolute Error: ___________ mL

Analyst: ____

Signature Date

Chemist: ____

Reviewer Date