Measurement Data Processing

Estimation of uncertainty of volume of a 25 mL A-class volumetric flask

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Abstract

The aim of this work is to select the instruments and the number of measurements required to achieve the desired relative uncertainty of 0.0050 % for the volume of a 25 mL A-class volumetric flask. Volume is estimated by gravimetric method. Three types of balances and thermometers with different metrological characteristics are studied. The solution approach is to evaluate the uncertainty for each set of instruments and determine the number of repetitions for the mass of the filled flask. The most suitable instruments are analytical balance (B1) with 0.01 mg readability and thermometer (T1) with 0.1 °C readability. The minimum number of repetitions is 76. In addition, Monte Carlo simulation is used to estimate the uncertainty. A similar result compared to the GUM uncertainty framework is obtained.

Keywords: volume, flask, uncertainty, Monte Carlo

1 Introduction

Volumetric flasks are flat bottomed glassware with elongated necks with gauge marks. They are calibrated to the gauge mark at a specified temperature. Volumetric flasks together with analytical balances are fundamental tools for the preparation of volumetric standard solutions which are the basis of most chemical analysis [1]. Volumetric flasks are classified according to tolerance limits. Class A and B flask are designated in compliance with applicable construction and tolerance limits requirements [2]. Certain conditions like deterioration, extremes temperatures, cleaning, or hot air drying might change the volumetric flask capacity. Strong chemicals in the laboratory may alter the wetting characteristics of the glass, which may affect draining properties [3]. Before the first use, in-house calibration of glassware allows to verify the calibration certificate of volume. Initial calibration should not normally exceed one year [3]. Periodic calibration can be also necessary. The interval of which should solely depend upon the nature and usage of the laboratory.

Gravimetry is the standard method used both by National Metrology Institutes(NMIs) and accredited laboratories to calibrate volumen instruments. The method consist on weighing empty containers and weighing again the container filled with appropriate liquid, usually distilled water. The glassware should be cleaned and grease free. Gravimetric method for calibrating volumetric flask requires to be accurate and fitted for the intended purpose. Different instruments in the laboratory offer various uncertainties. Instruments with very low uncertainty usually incur in high costs, therefore an uncertainty analysis could establish suitable measuring systems.

In this work, a set of instruments and the number of repetitions are determined to measure the volume with a desired uncertainty and an instrumental tolerance level.

2 Methodology

2.1 Problem

The volume of a 25 mL flask needs to be measured with a desired relative expanded uncertainty of 0.0050 %. Choose which instruments to use and the number of measurement repetitions to get the desired result. The available instruments are described in section 2.4.

2.2 Desired uncertainty

The desired relative expanded uncertainty in this work was set to 0.0050 %.

In addition to the criteria above, instrumental tolerance was used as a referential uncertainty. According to ASTM E288, an A-class 25 mL volumetric glassware requires a tolerance of ±0.03 mL [2], corresponding to 0.14 % expanded uncertainty.

2.3 Solution approach

There are some strategies to solve this problem; for example, mathematical assumptions, linear optimization and trial and error. Mathematical assumptions could lead to biased results. For instance, an equal contribution of uncertainty sources could not be applied in this case as the variability of the filled flask mass is an important contributor among other sources. Whilst linear optimization could be time-consuming and require previous experience in the subject.

In this study, the problem-solving approach is trial and error. It is problem specific and it can be less time-consuming than other methods when a testable number of experiments is low. For this, the number of repetitions for filling the flask is determined and the expanded uncertainty is estimated for each arrangement with the GUM uncertainty framework [4] in a Microsoft Excel® spreadsheet. The solver built-in function is used to determine the most favorable number of repetitions. Repetitions for the mass of the empty flask and temperature are set to 3 and 2, respectively. These last parameters show low variability compared with the mass of the filled flask.

2.4 Equipment and materials

A 25 mL borosilicate flask from BRAND®, A-class DIN EN ISO 1042, and calibrated to with 0.03 mL accuracy is studied. Type I water is form MilliQ Advantage A10 equipment at Chemicum, University of Tartu.

Three (3) balances are considered: **B1** Balance XSR105 from Mettler Toledo with 120 g capacity, 0.01 mg readability; **B2** ME204T Balance from Mettler Toledo with 220 g capacity, 0.1 mg readability; and, **B3** Kitchen balance from Rybakov with 100g-10kg capacity and 0.1 g readability.

Three (3) thermometers are compared: **T1** Hand Held RTD DT-1, 0.01°C readability; **T2** Precision Waterproof Traceable® MA-251, 0.1°C readability; and, **T3** Thermco LS-1810102, 0.1°C readability.

2.5 Measurement procedure

In laboratory, measurements were carried out to specify the practical procedure. For this, the flask was cleaned and dried. Its mass with the stopper was registered as m_1 tree times. The flask was filled with water. Pasteur pipette was used at the end to fill the flask to just below the reference graduation avoiding drops in the neck of the flask. The filled flask was standing for two minutes before adjusting the meniscus to the graduation line. The flask was covered with the stopper. Balance was set to zero and the filled flask was measured. This mass was recorded as m_2 in m_2 repetitions. Measure and record the temperature of the water in the reservoir as T.

2.6 Uncertainty estimation

2.6.1 Identifying uncertainty sources

There is not reference material to evaluate the trueness of the method, so bias depends mainly on the overall control of the parameters affecting the result. Some of them are repeatability for filling the flask, room temperature, calibration and resolution of instruments, dissolved oxygen in water, buoyancy force, humidity, vibration and contamination.

In this report, masses and temperature are considered the most important sources for uncertainty. Repeatability in filling the flask shows to be one of the greatest contributor to variability in volume determination, while temperature defines the water density during the experiment.

2.6.2 Mathematical model

From the definition of density, volume is expressed as,

$$V = \frac{m}{\rho} \tag{1}$$

Herein density is calculated according to a quartic for air-free water in the range 5°C to 40°C [5].

$$\rho = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \tag{2}$$

Considering masses and temperature as the main uncertainty sources for gravimetric volume determination, the mathematical model is described in Eq. 3.

$$V = \frac{m_2 - m_1}{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4} \tag{3}$$

Where, V is volume in mL, m_1 is the mass of clean and dry flask in g, m_2 is the mass of flask filled with water in g, T is temperature of water in °C, a_0 is 9.999×10^{-10}, a_1 is 6.327×10^{-5}, a_2 is -8.524×10^{-6}, a_3 is 6.943×10^{-8} , and a_4 is -3.821×10^{-10}.

2.6.3 Quantifying uncertainty sources

m_1

The mass of a empty 25 mL flask is measured. The flask was cleaned and dried. The stopper was included in the total mass. The main uncertainty sources are repeatability, resolution and instrumental error. The standard uncertainty of m_1 is as follows.

$$u(m_1) = \frac{s_{m_1}}{\sqrt{n_1}} + \frac{resolution}{\sqrt{12}} + \frac{ins.error}{\sqrt{3}} \tag{4}$$

Where, s_{m_1} is the standard deviation of n_1 measurements of the magnitude m_1.

Note that the term *mass* is here used as the measured parameter instead of *weight*. Uncertainty of constants in quadric formula for density are not considered on this estimation.

m_2

A 25 mL flask was filled with type I water and weighed with its stopper. The main uncertainty sources are repeatability, resolution and instrumental error. The standard uncertainty of m_2 is described by Eq. 5.

$$u(m_2) = \frac{s_{m_2}}{\sqrt{n_2}} + \frac{resolution}{\sqrt{12}} + \frac{ins.error}{\sqrt{3}} \tag{5}$$

T

Temperature was read directly from an instrument placed into a type I water reservoir. During the experiment, temperature readings were recorded. The main uncertainty sources are repeatability, resolution and instrumental error. The standard uncertainty of T is:

$$u(T) = \frac{s_T}{\sqrt{n_T}} + \frac{resolution}{\sqrt{12}} + \frac{ins.error}{\sqrt{3}} \tag{6}$$

2.6.4 Calculating the combined standard uncertainty

Uncertainty sources were combined according to propagation of uncertainty assuming independent variables. For $y = f(x_1, x_2, .., x_i)$, combined uncertainty squared, u_c^2, is shown in Eq. (7)

$$u_c^2(y) = \sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i}\right)^2 u^2(x_i) \tag{7}$$

From Eq. 3, partial derivatives are:

$$\frac{\partial V}{\partial m_1} = -\frac{1}{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4} \tag{8}$$

$$\frac{\partial V}{\partial m_2} = \frac{1}{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4} \tag{9}$$

$$\frac{\partial V}{\partial T} = \frac{(m_1 - m_2)(a_1 + 2a_2 T + 3a_3 T^2 + 4a_4 T^3)}{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4} \tag{10}$$

Equation 11 shows the combined uncertainty squared.

$$u_c^2(V) = \left(\frac{\partial V}{\partial m_1}\right)^2 u^2(m_1) + \left(\frac{\partial V}{\partial m_2}\right)^2 u^2(m_2) + \left(\frac{\partial V}{\partial T}\right)^2 u^2(T) \tag{11}$$

2.6.5 Calculating the expanded uncertainty

v_{eff}

The effective degrees of freedom, v_{eff}, is described by the Eq. 12

$$v_{eff}(y) = \frac{u_c^4(y)}{\sum_{i=1}^{n} \frac{c_i^4 u^4(x_i)}{v_i}} \tag{12}$$

The degree of freedom for each variable is defined by Eq. 13. Degrees of freedom for resolution and instrumental error are considered ∞.

$$v_{m_1} = \frac{u^4(m_1)}{\frac{u^4(s_{m1})}{n_1 - 1}} \tag{13}$$

$$v_{m_2} = \frac{u^4(m_2)}{\frac{u^4(s_{m2})}{n_2 - 1}} \tag{14}$$

$$v_T = \frac{u^4(T)}{\frac{u^4(s_T)}{n_T - 1}} \tag{15}$$

The effective degrees of freedom for volume, $v_{eff}(V)$, is

$$v_{eff}(V) = \frac{u_c^4(V)}{\frac{c_1^4 u^4(s_{m1})}{v_{m_1}} + \frac{c_2^4 u^4(s_{m2})}{v_{m_2}} + \frac{c_T^4 u^4(s_T)}{v_T}} \tag{16}$$

Expanded uncertainty

$$U(V) = k_{95\%, v_{eff}} \cdot u_c(V) \tag{17}$$

The coverage factor, k, is calculated according to t-Student distribution with 95% level of confidence and $v_{eff}(V)$ degrees of freedom.

2.7 Monte Carlo simulation

Probability density functions for m_1, m_2 and T were used as inputs to generate a set of V values. The same standard uncertainties of input variables from GUM approach were used as simulation parameters. Mean and standard uncertainty of V were calculated from a sample of 10^5 simulated results. The result was then compared with the GUM method uncertainty.
The R script is shown below.

```
library(ggplot2)
a0<-0.99985308
a1<-6.32693E-05
a2<--8.52383E-06
a3<-6.94325E-08
a4<--3.82121E-10
n <- 100000
for (i in 1:n){
  m1<-rnorm(1, mean=49.8538, sd=0.0001191)
  m2<-rnorm(1, mean=74.7533, sd=0.0005742)
  Temp<-rnorm(1, mean=24, sd=0.03594)
  V<-(m2-m1)/(a0+a1*Temp+a2*Temp^2+a3*Temp^3+a4*Temp^4)
  V_v<-c(V_v,V)
}
n_v<-seq(1,n, by=1)
V<-data.frame(n_v,V_v)
mean(V_v)
sd(V_v)
```

3 Results and discussion

The expanded uncertainty for each set of instrument was calculated. Same balance were used for the measurement of m_1 and m_2. In total, 1 combination of instruments allows to get the desired uncertainty and 8 do not. Some important figures are shown in Table 1. Sets I and IV comply with the desired uncertainty of 0.005 %. However, the numbers of repetitions are not practical; 76 and 336, respectively.

Set	m_1	m_2	T	n_2	$U(V), \%$
I	B1	B1	T1	3	0.0500
				76	0.0050
II	B2	B2	T2	3	0.0438
				999	0.0147
III	B3	B3	T3	999	0.7187
IV	B2	B2	T1	3	0.0508
				336	0.0050
V	B3	B3	T1	999	0.7186

Table 1: Expanded uncertainty with $k_{95\%,v_{eff}}$ for different set of instruments and repetitions, n_2.

Considering instrumental tolerance as a referential uncertainty of 0.14 %, sets I, II and IV comply with it even since 3 repetitions for m_2. In this case, set IV complies using a typical analytical balance, without the need of measuring to 0.01 mg. For set IV, the B1 thermometer increases the uncertainty in low repetitions but reduces it when the number of repetitions is bigger.

When using the B3 balance (sets III and V), any change in the type of thermometer or in the number of measurements does not reach to the desired uncertainty or tolerance level. This could be explain as a large contribution of error when using B3 balance. This error in masses keeps the total uncertainty in a minimum value (e.g. 0.7187 % for set III).

Set I is considered the best option of instruments for measuring the volume with the desired uncertainty. The relative expanded uncertainty for this measurement ($k_{95\%,v_{eff}} = 1.99$) is 0.0050 % and the number of repetitions for m_2 is 76. In regard to the tolerance level of the instrument, sets II and IV enable the measurement with uncertainty 0.14 % from 3 repetitions.

The uncertainty budget for set I (Fig.1) shows that the major contributor is m_2. The repeatability in filling the flask affects significantly to the uncertainty of volume while other factors as temperature and initial mass are not critical. Using a proper technique in the manipulation of volumetric flask during calibration and daily operation could help to reduce uncertainty due to volume. Control of temperature with precise instruments could help also to reduce total uncertainty, as shown by the set IV result.

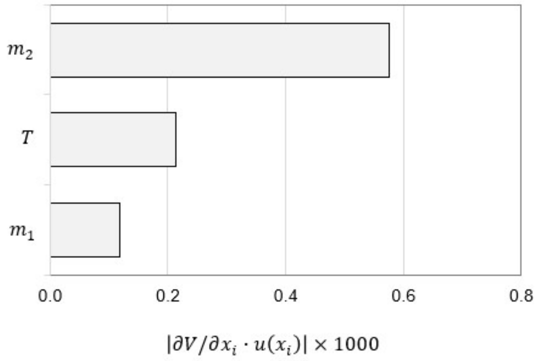

Figure 1: Uncertainties in volume determination

The estimation of standard uncertainty of volume by Monte Carlo method for set I is 0.00063 mL. The relative expanded uncertainty ($k_{95\%,v_{eff}} = 1.99$) is 0.0050 %. The frequency distribution of simulated values for V is shown in Fig. 2. This result coincides with what is obtained by the GUM method, and it also suggests that inputs variables relates mainly linearly with the measurement result.

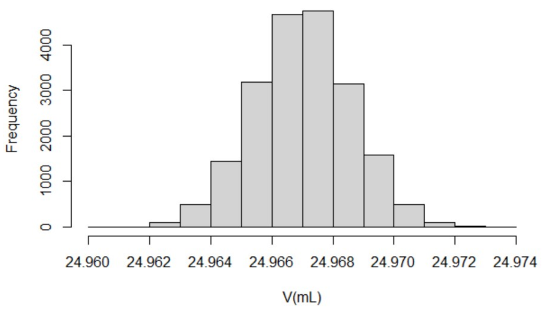

Figure 2: Distribution of simulated volumes

4 Conclusions

Set I, measurement system consisting of B1 balance and T1 thermometer, is the best instrumental option to measure the volume of a 25 mL A-class flask with the desired uncertainty ($k_{95\%,v_{eff}}$) of 0.005 %. For this, the minimum number of repetitions n_2 is 76.

Sets I, II, and IV comply with the referential uncertainty of 0.14 % derived from the flask tolerance. In this case, the minimum number of repetitions n_2 is 3.

Sets III and V are not suitable for volume calibration due to the uncertainty contribution for masses measured with the B3 balance.

In addition, Monte Carlo simulation method shows a similar result for the set I uncertainty, supporting the GUM approach and suggesting a mainly linear relationship of the input variables and the measurement result.

Supplementary material

The spreadsheet with additional information and calculations can be found at `https://bit.ly/3CCQidk`. An extended R script for Monte Carlo simulation can be found at `https://bit.ly/3CNYfMZ`.

References

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