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COMPARISON OF TWO DIFERENT APPROACHES IN THE UNCERTAINTY CALCULATION OF GRAVIMETRIC VOLUME CALIBRATION

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Abstract – The uncertainty calculation in the calibration of volumetric instruments is normally performed with the classical approach of the “mainstream GUM”. In order to validate the obtained results, since there is a degree of non linearity involved in handling the corresponding expression of volume, a Monte Carlo method was used as a second approach for calculation of that measurement uncertainty. The results of this comparison and corresponding conclusions are presented.

Keywords: uncertainty, Monte Carlo Method, volume

1. INTRODUCTION

Volume measurements are frequently performed in industry and at the chemical or analytical laboratories. Depending on the needed accuracy the volumetric instruments can be calibrated using a gravimetric method.

The common method for the uncertainty calculation in gravimetric determination of volume is the “mainstream GUM” approach [1]. In this paper a Monte Carlo method is also used as a validation tool. Two different types of volumetric instruments, a 1 000 ml flask and a 50 ml piston burette, with different characteristics were calibrated and the uncertainty calculated by both methods.

2. EXPERIMENTAL METHOD

The calibration of volumetric instruments is carried out in accordance with a procedure based on ISO 4787 [2] standard and depends on the type of instrument (to deliver or to contain liquid). For the calibration, a mass comparator is needed and during the measurements the temperature must be monitored. The volumetric instruments are calibrated using distilled water. From the mass of the contained or delivered liquid, the volume is calculated using the density of water. The temperature is controlled throughout the calibration to be (20 ± 0,5) °C.

The volumetric instrument or the corresponding weight vessel is weighted empty and dry. The volumetric instrument is then filled with water with a controled temperature. The volumetric instrument or the corresponding weight vessel is weighted again, and the mass obtained by difference is a measure of the volume of the volumetric instrument. This process is repeated ten times.

According to the ISO 4787 standard, the volume of volumetric instrument at 20 °C is given by

$$V_{20} = (I_L - I_E) \times \frac{1}{\rho_W - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) \times [1 - \gamma(t - 20)] + \delta V_{men} \quad (1)$$

where

V_{20} – volume, at a temperature of 20 ºC, in ml
I_L – result of the weighting with the recipient full of water, in g
I_E – result of the weighting with the recipient empty, in g
ρ_W – density of the water, at calibration temperature *t*, in g/ml
ρ_A – density of air, in g/ml (0,0012 g/ml)
ρ_B – density of the mass pieces (8,0 g/ml)
γ – cubic thermal expansion coefficient of the material of the calibrated recipient in /ºC
t – water temperature used in the calibration, in ºC
δV_{men} – effect on volume due to position of meniscus

3. CALCULATION OF THE MEASUREMENT UNCERTAINTY

3.1 “Mainstream GUM”

The calculation of measurement uncertainty comprises the following steps:

1. To express, in mathematical terms, the relationship between the measurand and its input quantities.
2. To determine the expectation value of each input quantity.
3. To determine the standard uncertainty of each input quantity.
4. To determine the degrees of freedom for each input quantity.
5. To determine all covariances between the input quantities.
7. To calculate the sensitivity coefficient of each input quantity.
8. To calculate the combined standard uncertainty of the measurand.
9. To calculate the effective degrees of freedom of the measurand.
10. To determine an appropriate coverage factor, *k*, and finally

11. To calculate the expanded uncertainty.

In our case study the mathematical model is defined by equation (1) and the uncertainty components came by the mass of the instrument, water temperature, water density, air density, mass pieces density, cubic thermal expansion coefficient of the material associated with the instrument under calibration, meniscus reading (if applicable) and the resolution of the calibrated equipment (if applicable). These standard uncertainty components are expressed in the following way:

Mass

$$u(m)=\left[2\left(\frac{u(bal)}{2}\right)^2+\left(\frac{s(\mathrm{m})}{\sqrt{n}}\right)^2+2\left(\frac{R/2}{\sqrt{3}}\right)^2\right]^{1/2}\text{(g)} \quad (2)$$

where

u(bal) - standard uncertainty of the balance calibration

s(m) – standard deviation of the mass measurements

R – balance resolution

n- number of measurements

Water temperature

$$u(t)=\left[\left(\frac{u(ter)}{2}\right)^2+\left(\frac{s(t)}{\sqrt{n}}\right)^2\right]^{1/2}\text{(ºC)} \quad (3)$$

where

u(ter)-standard uncertainty of the used thermometer

s(t) – standard deviation of the temperature measurements

n – number of measurements

Water density

$$u(\rho_W)=\frac{(\rho_w(t+R_{term})-\rho_w(t-R_{term}))/2}{\sqrt{3}}\ \text{(g/ml)} \quad (4)$$

where

ρ_W – density of the water

t – water temperature

R_{term} - resolution of the thermometer

Air density

If the laboratory ambient conditions are within the limits presented in the Spieweck's work [3], the air density uncertainty may be expressed according Equation (5):

$$u(\rho_A)=\frac{0{,}0000005}{\sqrt{3}}\ \text{(g/ml)} \quad (5)$$

Mass pieces density

The value presented in the calibration certificate of the balance can be used or it can be assumed the values described in OIML R 111-1:2004 [4].

Cubic thermal expansion coefficient of the material of the calibrated recipient

$$u(\gamma)=\frac{R\gamma/2}{\sqrt{3}}\quad \text{(/ºC)} \quad (6)$$

where

$R\gamma$–resolution of the expansion coefficient number

Meniscus

$$u(meniscus)=\frac{\pi\times\left(\frac{d}{2}\right)^2\times h}{\sqrt{3}}\ \text{(ml)} \quad (7)$$

where

d – diameter of the calibrated instrument neck

h – operator volume reading error

Resolution of the calibrated instrument

$$u(R)=\frac{R_{inst}/2}{\sqrt{3}}\quad \text{(ml)} \quad (8)$$

The sensitivity coefficients of each input quantity were then calculated.

The expression for the combined standard uncertainty of V_{20} was obtained from the equation (1), using the law of the propagation of uncertainty. The resulting expression reads as:

$$u(V_0)=\left[\left(\frac{\partial V_0}{\partial m}\right)^2u^2(m)+\left(\frac{\partial V_0}{\partial t}\right)^2u^2(t)+\left(\frac{\partial V_0}{\partial \rho_w}\right)^2u^2(\rho_w)+\left(\frac{\partial V_0}{\partial \rho_A}\right)^2u^2(\rho_A)+\left(\frac{\partial V_0}{\partial \rho_B}\right)^2u^2(\rho_B)+\left(\frac{\partial V_0}{\partial \gamma}\right)^2u^2(\gamma)+u^2(\delta V_{men})+u^2(R)\right]^{\frac{1}{2}} \quad (9)$$

From the values obtained for the *k*-factor and of the combined standard uncertainty of the measurand, the expanded uncertainty is deduced by:

$$U=k\times u(V_{20})\ \text{(ml)} \quad (10)$$

For the two types of volumetric instruments, 1 000 ml and 50 ml, values of k = 2,04 and k = 2,20 were determined, corresponding to a number of effective degrees of freedom of ν_{eff} = 31 and ν_{eff} = 11, respectively. Results for the expanded uncertainty and associated coverage intervals are illustrated in Table 1.

3.1 Monte Carlo

In cases where the applicability of the GUM uncertainty framework is questionable, a Monte Carlo method (MCM) is, generally, a valid alternative and can be applied as a validation tool [5].

It implements the propagation of distributions, in which a functional model is used to relate the measurand to model input quantities, by repeated random sampling from the probability density functions (PDFs) assigned to the input quantities to provide a discrete representation of the distribution for the measurand. From this posterior PDF the statistics parameters associated with the measurand, including expectation, variance and a coverage interval, can readily be obtained.

Having access to the PDF associated with the measurand, that does not have to be Gaussian or even symmetric, and from which much richer information can be extracted, together with the fact that MCM can be applied regardless of the nature of the model, represent important advantages of this approach in relation to the GUM. It also means that if the output PDF is not symmetric, say, the GUM will give less reliable results. In most cases, the expectation value of the measurand, obtained by both methods may be similar, but the coverage interval can differ very significantly.

4. RESULTS

A 1 000 ml flask and a 50 ml piston burette were calibrated according to the gravimetric method.

The results of volume and uncertainty evaluation using the GUM and the Monte Carlo are the following:

Table 1. Comparison between GUM and MCM results.

Volumetric instrument	Volume (ml)	GUM		Monte Carlo	
		U (ml)	Coverage Interval	Volume (ml)	Coverage Interval
Flask	999,880	0,030	[999,850-999,911]	999,892	[999,863-999,921]
Burette	49,7951	0,019	[49,776-49,814]	49,7954	[49,7764-49,8145]

The results show that the GUM methodology is valid in this application. In fact, the differences are such that the maximum difference value is 0,0013 % for the lower limit of the coverage interval, in the 1 000 ml experiment. The output PDF as determined by the MCM is illustrated in Figure 1.

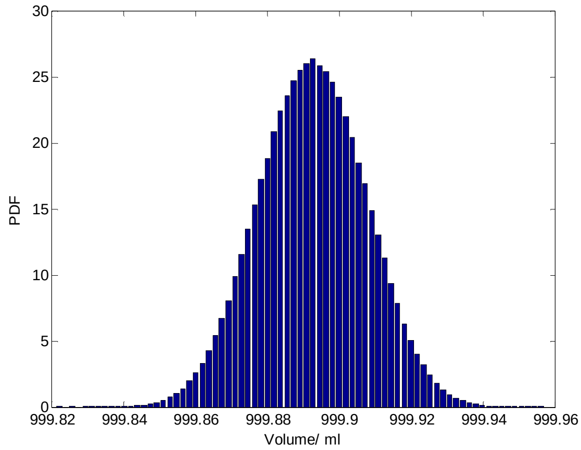

Fig.1. Output PDF for volume 1 000 ml.

Parametric studies will investigate if these conclusions can be extended to a broader variation of the values associated with the input variables, or if they are only valid for this particular set of values.

5. CONCLUSIONS

The GUM uncertainty framework was properly validated in its application to volumetric measurements, for values of the input variables as those used in this study. However, caution is always advisable when applying the GUM to models not strictly complying with its underlying principles, and proper validation, for a different set of values would be required in other applications

REFERENCES

[1] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML, 1995, *Guide to the expression of uncertainty in measurement*, 2nd ed. (Genève: International Organization for Standardization).

[2] ISO 4787, 1984, Laboratory glassware - Volumetric glassware - Methods for use and testing of capacity

[3] Spieweck F., Bettin H.,1992, Review: Solid Liquid density determination, Tm- Technisches Messen, 59 , 237-292

[4] OIML R 111 (2004) - Weights of classes E1, E2, F1, F2, M1, M2, M3

[5] BIPM, Evaluation of measurement data – Supplement 1 to the "Guide to the expression of uncertainty in measurement" – Propagation of distributions using a Monte Carlo method, JCGM 101:2008, 1st ed. 2008