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Evaluation of measurement uncertainty in volumetric operations: the tolerance-based approach and the actual performance-based approach

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Abstract

Although relatively small compared to other sources of uncertainty in an analytical procedure, uncertainty in volumetric operations needs to be properly evaluated. In this paper, the problem of volumetric uncertainty is addressed with the critical examination of the procedure for its evaluation recommended in the EURACHEM Guide *Quantifying Uncertainty in Analytical Measurement*. Some characteristic features of volumetric apparatus as a measuring device are considered in relation to accuracy specification usually expressed in the form of "capacity tolerances". On the basis of the underlying metrology, written standards to which volumetric ware is manufactured, and evidences available from experimental studies, it is shown that the tolerance already includes a random error inherent in the use of volumetric apparatus. Therefore, no additional allowance, except for temperature effects, needs be made if the uncertainty is derived from the tolerance. A detailed analysis of relevant uncertainty sources is presented, with two different procedures for evaluating the uncertainty identified; one of them relies on the prescribed tolerance while the other is based on the experimental estimation of the actual performance in the user's hand. The uncertainty budget for each of these two approaches is evaluated, analysed and illustrated with a numerical example.

Keywords: Volumetric operation; Capacity tolerance; Measurement uncertainty; Uncertainty budget

1. Introduction

Simple volumetric operations such as preparation of a solution in a volumetric flask, transferring a required volume of liquid with a pipette, or delivering a known volume with a burette in titration techniques are the basis of analytical work. Being a part of most analytical procedures, these operations are commonly performed using volumetric glassware. This might be called a basic measuring instrument in an analytical laboratory, after the balance, and with just this all chemistry students begin their laboratory exercises in a course of analytical chemistry. And as with every measuring instrument and operation, the question of the accuracy, which they can ensure, has always been important.

It is a general requirement now to accompany the result of a measurement with a statement of its uncertainty, which is needed to judge the results properly. Therefore, much attention is being given to the methods of evaluation of measurement uncertainty. Following the principles laid down in the *ISO Guide to the Expression of Uncertainty in Measurement* [1], the problem amounts to identifying, evaluating, and budgeting all practically significant uncertainty sources involved in a measurement and thus calculating the combined uncertainty. As applied to analytical measurement—by this term quantitative chemical analysis is meant—the detailed methodology was developed in a specific guidance document, *Quantifying Uncertainty in Analytical Measurement*, issued by EURACHEM in 1995 and in revised form (jointly with CITAC) in 2000 [2]. This guide provides a number of examples, relating to different analytical problems; they illustrate the uncertainty estimation process in detail.

Although relatively small compared to other sources of uncertainty in an analytical procedure, volumetric uncertainty needs to be properly evaluated. A practical way of doing this is to use the capacity tolerances for volumetric apparatus, taken from the specification. Additionally, an uncertainty contribution due to the temperature dependence of volume needs to be accounted for, derived from possible temperature variations. Note that both of the uncertainty components can be evaluated based on available information, *with pen and paper* only.

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Meanwhile, the procedure for the estimation of volumetric uncertainty, presented in the available examples ([2] (Appendix A), [3,4]), is more complicated than that outlined above. This suggests accounting not only for the manufacturer's tolerance but also (and obligatory) for the random variation that should be estimated in a volumetric repeatability experiment. A series of fill-and-weigh or fill-delivery-weigh operations with water is performed in such an exercise to get the experimental standard deviation. Thus, it appears that *experimentation* is necessary to inform the uncertainty estimate.

Two questions arise immediately. The first concerns the random variation inherent in the use of volumetric apparatus. Has it not really been included in the stated tolerance so that no additional allowance would be required? The second question is as follows. If nevertheless the actual performance has been studied, why should it be used in calculating the uncertainty along with the tolerance, not instead of it, so resulting in redundancy in uncertainty estimation?

In subsequent sections, different aspects of specifying performance of volumetric laboratory apparatus are highlighted in the context of the problem of uncertainty estimation. Using a cause-and-effect analysis, a detailed uncertainty budget is evaluated, with two alternative procedures identified for the determination of volumetric uncertainty. One of them relies on the prescribed tolerance while the other is based on the experimental estimation of the performance in the user's hand. Which of these two ways to follow depends on actual circumstances, chiefly, the level of accuracy required in the volume measurement.

In our treatment of the problem, we adhere to the principle, known in quality issues as "fitness for purpose", that measurement should be made with that level of uncertainty that is required for its intended application. Adequate effort is essential in the uncertainty estimation process just as much. From this point of view, the procedure for evaluating volumetric uncertainty, recommended in the guide [2], seems to be excessive. The aim of this note is to make this clear and avoid overcounting.

2. Volumetric apparatus and its specified accuracy

The measurement of volume in analytical procedures falls, in the language of metrology, within a category of so-called direct measurement in which the measurement process is limited to the use of a single, direct-reading measuring instrument only. Such an instrument, being commercially available, shall meet certain metrological requirements, normally in the form of "maximum permissible error", specified by a written standard to which the instrument is made. If the compliance with the specification is originally guaranteed by the manufacturer or demonstrated by an independent authority, it is accepted that the errors produced *while the equipment is in use* do not exceed its specified limit of permissible error. This is a basic tenet of the quality assurance system established for measuring instruments in various measurement fields, including volume measurement. According to this very principle, the limits of volumetric error laid down in standard specifications for volumetric apparatus have long been used for estimation of errors occurring in volumetric operations in chemical analysis [5]. And no extra error contribution, apart from the capacity tolerance, was required.

Some characteristic features of volumetric apparatus as measuring device are worth pointing out here. Only in a broad sense, a volumetric flask, pipette, burette or measuring cylinder can be called a measuring instrument, though they are often referred to as such. Actually, all these are material measures of volume or, more specifically, material measures of capacity. (The capacity of a vessel is equal to the volume of liquid contained by or delivered from the vessel under prescribed conditions.) Material measure, or simply measure, is a "device intended to reproduce or supply, in a permanent manner during its use, one or more known values of a given quantity" [6]. Among other material measures an analyst deals with, a balance weight as a measure of mass and a reference material as a measure of a specific quantity measured in analytical measurement should be mentioned.

Suppose that a measure of capacity, for instance, a 100 ml volumetric flask, is used. The quantity "100 ml" marked on the flask expresses the nominal capacity, that is, the nominal value of the measure. It is this value that is usually recorded as a result of the volume measurement. The true volume contained in the flask will naturally not be exactly equal to the nominal capacity; the difference between the nominal value and the true value is commonly referred to as the volumetric error. Since the true value remains unknown in a volumetric operation, so is the volumetric error that is considered. In practice, it is important, however, only to ensure that the error does not exceed an established limit and the question emerges of how this limit is specified. We will return to this point in Section 3, restricting the consideration to some general remarks here.

The total volumetric error is conveniently divided into two components: (1) intrinsic error apparent when the measure is used under the reference temperature, usually 20 °C; and (2) influence error caused by the departure from that temperature. As the contribution of the influence error is mainly determined by the properties of the liquid to be measured, the intrinsic error alone is specified as a tolerance limit. This is a standard way of expressing the accuracy of volumetric apparatus (and measuring instruments); it is also used for classifying them according to their accuracy. So, the capacity tolerances for volumetric glassware have been established corresponding to two accuracy classes: class A and class B, with the tolerance of class B volumetric glassware being approximately twice those of class A.

The use of volumetric apparatus involves a series of operations such as filling the vessel, setting or reading the meniscus against a reference line or scale, and draining if the device is intended for delivery. In other words, the value

of capacity is reproduced by the measure by following some operating procedure that an analyst has to implement. This leads to the situation where the accuracy inherent in this material measure, as opposed, say, to the accuracy of a weight, cannot be evaluated in isolation, by ignoring the contribution of a procedural error that is inseparable.

If however, all significant error sources in a measurement process are known and kept under control by following an operating procedure, the limits to the procedural error and hence the total measurement error may be inferred from relevant consideration without a great risk of being incorrect. It is therefore conventional for *hand–eye-operated* volumetric apparatus to incorporate the random error contribution, typical for its proper use, into the limit of volumetric error. Normal variations in manipulating and reading volumetric glassware are supposed to be included in the specified tolerance.

By contrast, a different situation arises with the mechanical action, *piston-operated* volumetric apparatus, for instance, piston pipettes that dispense their specified volume. Besides the operator's technique, many other factors such as the instrument's state of repair, environmental conditions, physical properties of the liquid being delivered, affect the performance of those pipettes; and as with any mechanical device it deteriorates over time. Further, the factory-set adjustment of a piston pipette can be altered by the user, directly creating a bias in the instrument. Therefore, for such delivering devices the tolerance limits on both random and systematic errors are separately set in the specification. Since the performance of a mechanically operated volumetric apparatus needs be determined and controlled experimentally on a regular basis, evaluation of the uncertainty in its use is based on the performance tests rather on the specifications. Being a separate issue, this problem is beyond the scope of the paper.

3. Capacity tolerance and random error: requirements for meeting standards, and experimental evidence

Let us turn to written standards that have been internationally established for different aspects of design, specifications and application of laboratory glass volumetric apparatus [7–9]. The standards set out principles of specifications applicable to any article of volumetric glassware. The question of how the limit of volumetric error is specified is of our concern now.

The limit of error is fixed by taking into account of several factors [7,9]. First, this is a design value—a volume that should occupy a readily visible length of tube (e.g. the flask neck) of the maximum diameter allowed. From operational considerations, the basic linear equivalent of the class A tolerance has been set equal to 0.4 mm. And an additional linear allowance for potential parallax error in reading the meniscus is made, which is also based on the diameter of the tube. Accordingly, a formula has been derived ([7], Annex B), made up of the two components, which relates the limit of volumetric error to the maximum internal diameter of the tube at the meniscus.

Table 1
One-mark pipette precision and capacity tolerances

Pipette nominal capacity (ml)	Repeatability standard deviation[a] (ml)	Class A tolerance[b] (ml)	99.7% confidence interval as a fraction of the tolerance
2	0.0018	0.01	0.5
5	0.0029	0.015	0.6
	0.0040		0.8
10	0.0041	0.02	0.6
	0.0045		0.7
25	0.0065	0.03	0.6
	0.0068		0.7
50	0.0092	0.05	0.6
	0.0113		0.7

[a] The numbers in the first (and single) line in each row are taken from [10] (Table XXIV); the numbers in the second line are taken from [11] as a pooled estimate for three different ways of draining a pipette.
[b] Taken from [14] with the symbol "±" omitted.

Concurrently with this, another requirement comes into play for glassware intended for delivery, where an error may be significant due to a variation in the technique of draining the vessel. For this apparatus, the limit of volumetric error is prescribed to be *not less than four times the experimental standard deviation obtained under repeatability conditions*. Hence, it follows that a possible run-to-run variation that can reasonably be expected to be in use has been taken into account in the tolerance value. Expressed as 95% or 99.7% confidence interval, this error contribution may evidently range up to a half or, respectively, three-fourths of the limit of volumetric error.

An example may be taken of One-marked (transfer) pipettes, which were examined over the years. Table 1 summarises the repeatability standard deviations and the calculated 99.7% confidence intervals compared with the corresponding class A tolerances for pipettes of capacity from 2 to 50 ml. The original data have been taken from two extensive studies [10,11] on random errors made in delivering from pipettes of the ordinary type. (Another study [12], in which different contributions to the overall precision were also investigated, resulted in values of the standard deviation that were 5−10 times lower than those found in the first two studies, owing to special means of improving precision. In one more paper [13], precision estimates were presented, which were associated with the use of 10 and 20 ml pipettes by a class of students, with the repeatability standard deviation for a 10 ml pipette near to that indicated in Table 1.) One can see from the data of Table 1 that the contribution of random error falls between 0.5 and 0.8 of the tolerance value, which agrees well with the proportion ($\leq$3/4) expected from the standard specification.

We emphasise that this feature is characteristic of volumetric glassware normally used in a laboratory. Still smaller random variation should be expected when a higher level of accuracy is aimed at, particularly, in calibration cervices. This is quite apparent from the data on long-term precision in calibration of laboratory glassware, which was gathered at the US National Bureau of Standards [15,16]. With that data, presented as a difference three-standard deviation limits, it can be easily shown that the 99.7% confidence intervals do not exceed approximately 0.2 of the class A tolerances for all articles processed.

The above findings are evidences in favour of the fact that the capacity tolerance is the limit to allowable error in the *use* of volumetric ware, not specifically in its *calibration* as the EURACHEM Guide designates in worked examples and in the summary of *Common Sources and Values of Uncertainty* ([2], Appendix G). It stands to reason that the procedures for proper use of the volumetric glassware must be followed by qualified and motivated personnel. They have all been written down in the ISO standards cited [7,8] as well as applicable national standards, not to mention many textbooks on quantitative analysis (e.g. [17,18]) which include chapters describing the subject in detail.

4. Identifying uncertainty sources

Using a cause-and-effect diagram, also known as the "fishbone" or Ishikawa diagram is an effective means of uncertainty analysis, which helps to identify, explore and display relevant uncertainty sources. This is a useful teaching tool as well, since it shows the relationships between the effect and causes responsible for it. Such a diagram for a volumetric operation is drawn in Fig. 1.

In the diagram, four main branches are depicted for which contributory cause factors are added where necessary.

- *Branch 1 (Procedure):* It is representative of the procedural contribution to the total uncertainty, incorporates several factors such as cleanliness of apparatus, setting or reading the meniscus, and drainage effects for the apparatus used to deliver liquids. The last component, as influenced by the time of delivery and delivery technique, is due to the tendency of retaining the liquid on the walls of the tube during delivery. (For instance, an error due to after-drainage in using a burette is negligible if it has a delivery time long enough to allow the liquid to drain and rejoin the main column. The burette shall meet this requirement, and minimum times for tubes of different graduated lengths have been specified in the standards.)
- *Branch 2 (Temperature effects):* Two different effects are taken into consideration when the temperature of measurement differs from the reference temperature of 20 °C. This is the variation of density of liquid with temperature and the change in the capacity of the vessel itself with the change of temperature. The two effects act "in opposition", with the former usually of much greater magnitude than the latter.
- *Branch 3 (Calibration):* It includes its own subsidiary branches: *procedure* and *temperature*, the latter with the two arrows as explained above, and some additional effects, specifically those associated with mass determination by weighing. Among them are balance performance and differential air buoyancy between the weighted object (water) and the balance weights. For a small volume delivered, particularly with a micropipette, it may be also important to consider the evaporation loss (not shown in the diagram).
- *Branch 4 (Physical properties of the liquid):* It is mainly concerned of the delivery processes, takes account of a difference in properties such as the viscosity and surface tension of the liquid being measured and water, which can cause a departure of the measured volume from that stated in calibration. It is usual to assume that for dilute aqueous solutions ordinary employed in volumetric analysis these effects are so small that they can be disregarded. (The truth of this statement was experimentally demonstrated [19] as early as at the end of the 19th century. However, exceptions have long been intimated [20]; and further, the use of non-aqueous solvents may call into question the

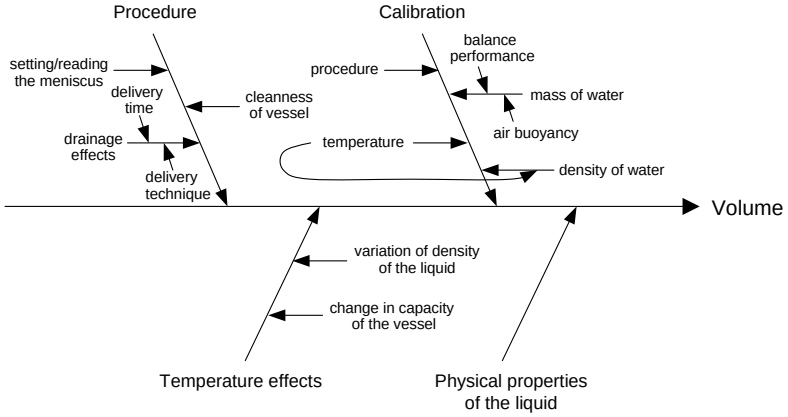

Fig. 1. Cause-and-effect diagram for a volumetric operation.

validity of water-related calibration, although the error was not found to be high in a case study [21].)

Not all of the factors identified in the diagram act as sources of uncertainty as such, that is, a random variable with zero mean value. Some of them, particularly those involved in calibration, result in a systematic deviation of the volume measured subsequently, i.e. a measurement bias. Others, such as drainage effects, bring about uncertainty and bias contribution alike. Still others may appear either as an uncertainty or as a bias, depending on circumstances. This last case is true, for instance, in regard to temperature effects where a possible variation about a mean room temperature (for a totality of measurements) results in an uncertainty, but a certain deviation from the reference temperature (for a particular measurement) results in a bias.

5. Quantifying volumetric uncertainty

Let us consider a typical case where volumetric glassware with some nominal capacity and manufacturer's tolerances is used, and our task is now to evaluate measurement uncertainty in the volumetric operation. The question is to what extent the capacity tolerance carries built-in information about possible error, from which the uncertainty can reasonably be derived. From what has been said in the previous sections it appears that all the influence factors relating to the upper branches, *procedure* and *calibration*, in the cause-and-effect diagram are covered in the stated tolerance. Only the bottom branches, particularly that one which represents the possible temperature variation, must additionally be allowed for. With this supplementary contribution, the use of the capacity tolerance converted to the standard uncertainty following the principles of the ISO Guide [1] is well justified in estimating volumetric uncertainty.

One may say that this is true when volumetric apparatus from a reliable manufacturer is dealt with and operated in the proper way. That is right indeed. If there is a doubt that an item of volumetric glass has been calibrated properly, it is generally recommended to test it for accuracy by making a single calibration. There may be, of course, situations where it is reasonable to assess the actual *single apparatus operator* performance in a precision (repeatability) experiment that is a calibration experiment in a way. This is necessary, for example, when a high level of accuracy, not attainable with the specified tolerances, is required or when manufacturer's specification cannot be confidently relied upon (specifically, with mechanical piston-operated apparatus).

Such a calibration experiment is based on the gravimetric method repeatedly applied to determine the actual volume contained or delivered, with apparatus manipulated in the same manner as in its use and the number of replicates not less than seven to ensure a meaningful uncertainty estimate. In this way, the factory calibrated volumetric apparatus now becomes in-house calibrated. Then, we can use in subsequent work the estimated true capacity instead of the nominal capacity and also the experimental standard deviation of the mean as a more specific estimate of calibration uncertainty than that derived from the tolerance limit. Minor contributions to the uncertainty from remaining effects such as the uncertainty in weighing and the uncertainty of reference values of the density of water (due to small temperature variation in calibration process) should be combined with the standard deviation of the mean to form a combined calibration uncertainty.

An important point is that the uncertainties originating at the measurement procedure and calibration are both estimated here in terms of the experimental standard deviation, so that there is no longer any necessity for utilising the manufacturer's tolerances. Thus, we come to recognise that in quantifying volumetric uncertainty the specified tolerances and the estimated variability shall be used alternatively, not conjointly as the guide [2] recommends. We are dealing with two different procedures that can be referred to as the tolerance-based approach and the actual performance-based approach according to whether the volumetric apparatus has been factory calibrated or in-house calibrated.

An uncertainty budget for these two approaches is drawn up in Tables 2a and 2b respectively, where different uncertainty components are formulated and quantified with a numerical example taken from actual practice. The items included in the budget are just the same as the ones displayed in the cause-and-effect diagram except for the branch *Physical properties of the liquid*, whose contribution is assumed negligible. With such analysis the distinction in methodology becomes clearer for two "modes" of calibration. In one case, a tolerance-based uncertainty is associated with the measurement result equal to the nominal capacity, while in the other case the estimated true capacity (of a particular volumetric apparatus) is taken as the result, which is usually provided with much smaller uncertainty.

6. Uncertainty budget analysis

In general, the accuracy requirements arising from an intended application of a measurement result determine the method, the instrument, and the conditions under which the measurement is performed, and as a consequence, the way the uncertainty is calculated. In Section 5, two different procedures for evaluating volumetric uncertainty were referred to as the tolerance-based approach and the actual performance-based approach. The uncertainty budget for the two approaches (Table 2) provides a means of comparing different contributions to the total uncertainty, which allows us to judge the efficiency and suitability one way or the other. It is apparent that there is little point in "mixing" the two procedures by combining the standard uncertainty derived from the tolerance with the repeatability standard deviation from the experiment.

Table 2
Uncertainty budget for a volumetric operation

Uncertainty source	Standard uncertainty	
	Formula[a,b]	Example[c] (ml)
(a) The tolerance-based approach		
Procedure Calibration	$\frac{\Delta_v}{\sqrt{6}}$	0.082
Temperature[d]	$\frac{V\alpha\,\Delta t}{\sqrt{6}}$	0.034
Combined standard uncertainty		0.089
Expanded uncertainty ($k = 2$)		0.18
Result of a measurement		100.00 ± 0.18
(b) The actual performance-based approach		
Procedure	s	0.014
Calibration[e]		
Procedure	$\frac{s}{\sqrt{n}}$	0.0044
Balance performance[f]	$\frac{1}{\rho_w}\sqrt{s_b^2 + 2\frac{\Delta_{nl}^2}{3}}$	0.00013
Density of water/temperature[g]	$\frac{V}{\rho_w}\left(\frac{d\rho_w}{dt}\right)_t \frac{\Delta_t}{\sqrt{6}}$	0.0017
Temperature[d]	$\frac{V\alpha\,\Delta t}{\sqrt{6}}$	0.034
Combined standard uncertainty		0.037
Expanded uncertainty ($k = 2$)		0.074
Result of a measurement		100.15 ± 0.07

[a] In these formulae: Δ_v is the capacity tolerance specified by manufacturer, V the nominal capacity for a volumetric apparatus factory calibrated or the estimated true capacity for that in-house calibrated, α the coefficient of cubical thermal expansion of the liquid measusred, Δt the limit of possible temperature variation about the mean working temperature, s the standard deviation from the repeatability (calibration) experiment with the number of replicates equal to n, ρ_w the density of water as calibrating fluid, s_b the repeatability of the balance specified as the standard deviation, Δ_{nl} the non-linearity of the balance specified as the maximum allowable deviation from the linear characteristic function, and Δ_t is the limit of possible temperature variation in calibration process.

[b] The value of $\sqrt{6}$ in the denominator in the formulae is used to convert the capacity tolerance, Δ_v, and also the limits of the temperature ranges, Δt and Δ_t, to the respective standard uncertainties based on a symmetric triangular probability distribution of the occurring errors. Yet the value of $\sqrt{3}$ based on a symmetric rectangular distribution was used to calculate the standard uncertainty associated with the balance non-linearity in the same manner as in Ref. [22]. For details in choosing an appropriate model probability distribution when uncertainty estimates are made through professional judgement, so called Type B evaluation, see the ISO Guide [1] (clauses 4.3 and F.2.3.3) and also Ref. [23].

[c] As an example, the uncertainties in use of a 100 ml class B volumetric flask were calculated based on the specification [24] ($\Delta_v = 0.20$ ml) and the repeatability (calibration) experiment. This experiment involved a series of 10 fill-and-weigh operations with distilled water at 20.4 °C ($\Delta_t = 0.2$ °C), which gave the mean value of capacity $V = 100.152$ ml and the repeatability standard deviation $s = 0.009$ ml. The results of testing other pieces of the same glassware were available, so it was reasonable to use the pooled estimate of the standard deviation, $s = 0.014$ ml, based on more than 90 observations. The following values of parameters were put to the calculation: $\alpha = 2.1 \times 10^{-4}\,°C^{-1}$, $\Delta t = 4$ °C, $\rho_w = 1.0\,g\,ml^{-1}$, $s_b = 0.05$ mg, $\Delta_{nl} = 0.15$ mg, the latter two taken from the balance (Sartorius MC210P) specification.

[d] The coefficient of cubical thermal expansion of liquids is at least one order of magnitude higher than that of glass. Therefore, only the first effect of the two relating to the temperature influence was accounted for in the evaluation of uncertainty caused by ambient temperature variation.

[e] The sources of bias in calibration such as temperature influence and air buoyancy are not included in the budget; these effects have normally been built in the calculation of the volume, adjusted to 20 °C, from the observed mass of water by reference to the appropriate table [8,16], with water temperature, air temperature, and air pressure as input parameters. So, in-house calibration is held to have no bias.

[f] In estimating the uncertainty originating from analytical balance, only the two most significant contributions, due to repeatability and non-linearity, were taken into account out of others that are relevant according to Ref. [22].

[g] In estimating the uncertainty caused by the temperature influence on the density of water, we set $\left(\frac{d\rho_w}{dt}\right) = 2.1 \times 10^{-4}\,g\,ml^{-1}\,°C^{-1}$, a good approximation in the room temperature range.

As is clear from the example relating to a 100 ml class B volumetric flask, the estimate of uncertainty can be reduced significantly if it is based on the actual performance rather than the specification. So the combined standard uncertainty decreases from 0.089 to 0.037 ml in the example. This is evidently due to the small uncertainty that the random variation actually introduces in the budget, and still smaller remaining contributions to calibration uncertainty. Furthermore, the significant calibration bias equal to 0.15 ml is revealed here, emphasising the importance of

in-house calibration. Nevertheless, it does not follow from these facts that the analyst must necessarily be engaged in a performance exercise with his volumetric glassware in order to estimate the (lower) uncertainty. An adequate effort is required in evaluating the uncertainty in a measurement.

It can be seen that the combined procedure–calibration contribution to the budget is reduced so that the uncertainty caused by the temperature variation becomes the largest in the total uncertainty (Table 2(b)). The standard uncertainty due to the temperature variation (0.034 ml) was calculated with the normal assumption that fluctuations in temperature are possible within ±4 °C about the mean room temperature. The inference from this graphic example is as follows: in-house calibration is unjustified when the temperature control in use of volumetric apparatus is lacking. It is unreasonable to make calibration with the highest level of accuracy that is not required and not ensured in the measurement.

The situation may however reverse where the temperature is under regulatory control owing to more stringent requirements being placed on accuracy of the measurement. So, in the special case that the actual temperature of volumetric solution is measured, the corresponding uncertainty contribution (0.034 ml) will be reduced to a negligible uncertainty of the temperature measurement, with the combined uncertainty essentially decreased to the level determined by the procedure contribution (0.014 ml). The in-house calibration would be advantageous in such cases. Note that if the actual temperature is measured, the effect caused by its difference from the reference temperature is manifested as bias to be corrected for. Alternatively, thermostatting at 20 °C before setting the meniscus is recommended in the most accurate work; this cancels the bias directly.

7. Conclusions

The capacity tolerance specified for volumetric apparatus can suitably be used in evaluating volumetric uncertainty. This procedure, here named as the tolerance-based approach, requires only the tolerance value to be converted into the standard uncertainty following the established rules. It is essential that normal variations in manipulating and reading volumetric glassware are understood to be included in the stated tolerance, and thus no additional allowance, except the temperature effects, is needed for obtaining the total uncertainty.

Alternatively, the actual performance has to be estimated in a repeatability (calibration) experiment, irrespective of the prescribed tolerance. Much lower uncertainty is attained this way because of the small uncertainty that the random variation actually introduces in the budget, and the still smaller remaining contributions to calibration uncertainty that are relevant. As a consequence, the uncertainty caused by the temperature variation may become the dominating contribution to the total uncertainty where the temperature in use of volumetric apparatus varies within several degree celcius. Thus, the actual performance-based approach is advantageous provided the precise temperature control is exercised.

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