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ABSTRACT

Standard solutions are fundamental tools to guarantee traceability in chemical analysis, however, they might suffer solvent evaporation during long storage periods. In this work a measurement model is presented to consider this behaviour and assure the retention of metrological traceability by taking into account solvent evaporation through subsequent weightings at the start and end of the storage period. The proposed iterative formulation is tailored to suit three different experimental setups depending on the available information. Uncertainty budgets based on the proposed models were produced and filled with simulated data to test the contribution of parameters and increment to the combined variance. The results highlighted strengths and drawbacks for each approach but ultimately asserting their suitability within the testing conditions. General considerations were also drawn with recognition of the limitations of the proposed modelisation and the great importance reserved to the knowledge of matrix interactions.

1. Introduction

Measurements imply a comparison of the investigated measurand with the quantity of its corresponding (SI) unit [1]. This is usually achieved through adoption of measurement standards which assure metrological traceability. To this aim, standards represent embodiments of defined quantities reporting stated values and associated uncertainties [2]. In the chemical analysis field, due to the nature of the measurand (hereafter called analyte) and analytical techniques, solutions with known mass fraction of a substance are vastly adopted as reference measurement standards; however, despite the advantage given by their flexibility and ease of use, the conservation of a solution brings concerns involving effects, such as the evaporation of the solvent, that might possibly alter its certified value in the long term. Manufacturers try to limit the effects due to evaporation by adopting various countermeasures: typically, they indicate a maximum shelf life for the opened (in use) and unopened (new) solution or, less likely, they state a monthly evaporation rate in order to help the user performing a correction that takes into account the loss of solvent during storage. Also, end users can periodically monitor the mass of the opened solution looking for unexpected solvent losses.

In this work a measurement model to follow the evaporation of reference standard solutions is proposed together with a discussion concerning general considerations about metrological aspects, possible applications and drawbacks. The intended aim is to allow end users to keep track of the traceability of their solutions by taking into account the evaporation rather than neglecting it.

In the following sections the base model is presented and discussed and theoretical and practical considerations are drawn based on different experimental setups.

2. Methods and procedures

Commercial standard solutions are provided by the manufacturers with a certificate of analysis which states the mass fraction of the element of interest. However, solvent evaporation during storage might lead to an increase in the reported value.

2.1. Theory

A convenient methodology to keep solvent evaporation under control can be to check the mass of the bottle (container and standard solution), m , by weighing on a balance every time before and after use. Usually, bottles are kept in storage conditions until they are needed for analysis, thus an aliquot is taken and they are returned to storage afterwards. During the i th storage period the (analyte) mass fraction, $w = \frac{m_{\text{ANA}}}{m_{\text{ANA}} + m_{\text{SOL}}}$, might change because of mass loss from the solvent, m_{SOL} , due to evaporation, assuming m_{ANA} stays unaltered.

A relationship between subsequent mass fraction values can be established calculating their ratio:

$$\frac{w_{(1,i)}}{w_{(0,i)}} = \frac{m_{\text{ANA } i} + m_{\text{SOL } (0,i)}}{m_{\text{ANA } i} + m_{\text{SOL } (1,i)}}, \quad (1)$$

with $w_{(0,i)}$ and $w_{(1,i)}$ the mass fraction values at the beginning and end of the i th storage period, respectively, and $m_{\text{SOL } (0,i)}$ and $m_{\text{SOL } (1,i)}$ the corresponding mass of solvent. It is worth to note that the term solvent is here used in a loose way, i.e. it may also include any other molecule dissolved in the solution except the certified analyte.

Measuring the decrease in mass of the bottle during the i th storage time, $\Delta m_i = m_{(1,i)} - m_{(0,i)} = m_{\text{ANA } i} + m_{\text{SOL } (1,i)} + m_{\text{C}} - (m_{\text{ANA } i} + m_{\text{SOL } (0,i)} + m_{\text{C}})$, makes possible to evaluate $w_{(1,i)}$ by rearranging (1):

$$w_{(1,i)} = \frac{w_{(0,i)}}{\left(\frac{m_{(1,i)} - m_{(0,i)}}{m_{(0,i)} - m_C} + 1\right)}, \quad (2)$$

with m_C the mass of the container.

Since the m_C value is never provided by manufacturer, its knowledge depends on the information available to the user: in case the solution is transferred to a custom container (as for example is recommended with some NIST standard solutions) it is straightforward to weight the new container beforehand, while in case the solution is kept in the original container (as for most of commercial standard solutions) the certificate might provide values about volume, V_0 , and density, d_0 , of the solution suitable to evaluate m_C according to:

$$m_C = (m_{(0,0)} - d_0 V_0), \quad (3)$$

with $m_{(0,0)}$ the weighted mass of a new bottle just before taking the first aliquot.

When the standard solution is used for analysis, the bottle is retrieved from storage and weighted to obtain $m_{(1,i)}$, a suitable aliquot is taken, then the bottle is weighted again to obtain $m_{(0,i+1)}$ and returned to storage. During this operation the mass of the solution changes but not its mass fraction, given homogeneity of the solution is not compromised and the time while the bottle is open is short enough that the evaporation is negligible (usually completing this task is a matter of few seconds). If this is the case, $w_{(0,i+1)} = w_{(1,i)}$, and from (2) it follows

$$w_{(0,i+1)} = \frac{w_{(0,i)}}{\left(\frac{m_{(1,i)} - m_{(0,i)}}{m_{(0,i)} - m_C} + 1\right)}, \quad (4)$$

where $i \geq 1$ is the i^{th} storage period.

When a new solution is opened and the 1st aliquot used, the certified mass fraction value w_{cert} is adopted and assigned to $w_{(0,1)}$. In case the mass fraction increment rate due to evaporation, R , is provided by the manufacturer, a correction is applied to calculate $w_{(0,1)}$ according to:

$$w_{(0,1)} = w_{\text{cert}} + Rt, \quad (5)$$

with t the time from certified value date to bottle opening.

In subsequent uses, when the n^{th} aliquot with mass $m_{\text{ALI } n}$ is taken after the i^{th} storage period, the certified mass fraction value corrected for evaporation at the end of storage period i (or, equivalently, at the beginning of storage period $i+1$), $w_{(0,i+1)}$, is given by (4).

The formulation presented in (4) allows to condense information of the whole storage history tracing back to the original mass fraction reported in the certificate of analysis and is achieved by just weighing the mass of the bottle in two occasions every time before storing and before using the standard solution.

2.2. Application

In order to test the use of the model (4), uncertainty budgets were obtained in Microsoft Excel software by application of the spreadsheet method [3] and filled with experimental and/or simulated data in different setups in order to evaluate the mass fraction and its combined uncertainty at the end of storage periods, including information on most important contributors.

Each uncertainty budget accounted for 10 storage periods (i in (4) ranging from 1 to 10) and 10 aliquots taking out to obtain value and combined uncertainty at the end of every storage period up to $w_{(0,11)}$. The correction due to evaporation before opening the bottle according to (5) was not considered; accordingly, $w_{(0,1)} = w_{\text{cert}}$.

The investigated setups applied to the measurement model were: (i) m_C evaluated by (3) through density and volume of the solution, and weighted mass of the bottle, (ii) m_C weighted once and (iii) m_C weighted at every step. In details, (i) describes the situation where the solution is

kept in its original container and the only information available to quantify m_C comes from density and volume, (ii) the situation where the freshly opened solution is immediately transferred into a weighted container and kept there, (iii) the situation where the solution is transferred into a new weighted container at every step. The selection between the first two depends on the container type of the standard solution and what information is available in the certificate while the latter is an ideal experimental setup investigated as a benchmark as it should theoretically produce the lowest uncertainty.

Uncertainty budgets were filled in with data concerning use and storage of a mono-elemental standard solution of about 100 cm^3 and $1 \times 10^{-3} \text{ g g}^{-1}$ certified mass fraction. The mass decrease of the solution due to evaporation from start to end of each storage period lasting 6 weeks and the mass of the aliquot were fixed to 50 mg and 4 g, respectively. The total simulated storage period was 60 weeks. Simulated mass values were based on experience: a decrease of 26 mg was observed on a 100 g Co solution $1 \times 10^{-2} \text{ g g}^{-1}$ certified mass fraction over a storage period of 3 weeks in a dry environment kept at 20°C while the 4 g is due to our practice to transfer an excess aliquot of the solution being used into a 5 mL temporary vial to avoid pipetting directly from the bottle.

A summary of the input parameter values and investigated uncertainty ranges adopted for model (4) is reported in Table 1; uncertainty limits were assigned to evaluate the impact on combined uncertainty.

Uncertainty limits reported in Table 1 represent common values associated to the corresponding parameter: relative uncertainty on certified mass fractions of highest quality commercial standard solutions usually lies between 0.1 % and 0.3 % ($1.0 \times 10^{-6} \text{ g g}^{-1}$ and $3.0 \times 10^{-6} \text{ g g}^{-1}$ for $1.0 \times 10^{-3} \text{ g g}^{-1}$ mass fraction, respectively) while resolutions of laboratory balances go from 0.1 mg to 1 mg, or even lower for analytical ones; uncertainty of the solution density might not be stated on the certificate but usually an informative value is reported with last significant digit having order of magnitude from 0.001 g cm^{-3} to 0.01 g cm^{-3} ; on the contrary, the volume is always reported as a nominal value thus the large uncertainties assigned.

3. Results and discussion

The first consideration concerns the balance required to apply the proposed methodology: in order to measure the decrease in mass of the bottle due to evaporation during storage periods and aliquot taken out, a suitable resolution is required. To this aim, it is useful to define the relative mass fraction variation at the end of the i^{th} storage period, $\Delta w_{(0,i+1)} = \frac{w_{(0,i+1)} - w_{(0,i)}}{w_{(0,i)}}$. By setting $\Delta m_i = 1 \text{ mg}$ in Table 1 and applying (4), the $\Delta w_{(0,2)}$ and $\Delta w_{(0,11)}$ values result 1.25×10^{-5} and 8.55×10^{-6} , i. e. negligible compared to the relative uncertainty of w_{cert} . Thus, since balances with resolution of 1 mg are common in every laboratory, the

Table 1

Values and uncertainty limits of parameters introduced in the test budgets. Superscripts (i), (ii) and (iii), indicate the parameter is only adopted in the corresponding experimental setup.

Parameter / unit	Value	Uncertainty limits
$w_{\text{cert}} / \text{g g}^{-1}$	1.0×10^{-3}	1.0×10^{-6} 3.0×10^{-6}
$\Delta m_i / \text{mg}$	50	—
$m_{\text{ALI } n} / \text{g}$	4	—
$m_{(0,0)} / \text{g}$	117.0000	0.0001
$m_{(0,1)} / \text{g}$	$m_{(0,0)} - m_{\text{ALI } n}$	0.001
$m_{(0,i)} / \text{g}$	$m_{(0,0)} - i(m_{\text{ALI } n} + \Delta m_i)$	—
$m_{(1,i)} / \text{g}$	$m_{(0,i)} - \Delta m_i$	—
$m_C^{(\text{ii}, \text{iii})} / \text{g}$	17.0000	—
$d_0^{(\text{i})} / \text{g cm}^{-3}$	1.000	0.001 0.01
$V_0^{(\text{i})} / \text{cm}^3$	100.0	1.0 2.5

ubiquitous application of this method is not difficult to imagine.

Model (4) was used iteratively to obtain mass fraction values $w_{(0,i+1)}$ in case of experimental setup (i) with lower limit uncertainties reported in Table 1. Resulting values were used to calculate the relative mass fraction variation cumulated at end of the i^{th} storage period, $\Delta W_{(0,i+1)} = \frac{w_{(0,i+1)} - w_{(0,1)}}{w_{(0,1)}}$, plotted in Fig. 1.

In the framework here represented, at the end 4th storage period, i.e. after 24 weeks from the opening of the solution, the effect of evaporation makes the bias of $w_{(0,5)}$ equal to upper limit of the 95 % confidence interval assigned to the certified mass fraction value. At the end 10th storage period, i.e. after 60 weeks, the bias of $w_{(0,11)}$ reaches $5 \times 10^{-6} \text{ g g}^{-1}$, i.e. $\Delta W_{(0,11)} = 0.5 \%$. This makes the correction necessary to maintain the traceability of the mass fraction value in case of similar or longer storage periods.

It is useful to investigate the uncertainty budget of $w_{(0,11)}$ to spot out major contributors to the combined uncertainty for the experimental setups (i), (ii) and (iii); moreover, the relative increment of combined uncertainty $\Delta u(w_{(0,11)}) = \frac{u(w_{(0,11)}) - u(w_{\text{cert}})}{u(w_{\text{cert}})}$ is calculated to quantify the added uncertainty due to correction for evaporation. Adopted values and uncertainties of input parameters are given in Table 1. Results obtained with the lower and upper uncertainty limits are shown in Tables 2 and 3, respectively.

More extensive results are provided for uncertainties between lower and upper limits reported in Table 1 in case of highest quality commercial standard solutions with a 0.1 % relative standard uncertainty of the certified mass fraction ($1.0 \times 10^{-6} \text{ g g}^{-1}$ for $1.0 \times 10^{-3} \text{ g g}^{-1}$ mass fraction). Specifically, $\Delta u(w_{(0,11)})$ is plotted versus $u(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)})$ and $u(V_0)$ in Fig. 2 for experimental setup (i); the $u(d_0)$ value was fixed to 0.001 g cm^{-3} .

In addition, $\Delta u(w_{(0,11)})$ is plotted versus $u(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)})$ and $u(m_c)$ in Fig. 3 for experimental setups (ii) and (iii).

Index contribution to variance show that the w_{cert} reported in the certificate has the greatest impact on the combined uncertainty while $m_{(0,0)}$, $m_{(0,1)}$, $m_{(0,i)}$ and $m_{(1,i)}$ measured with the balance have almost negligible effect. The effect due to knowledge (or lack thereof) of m_c represents the most striking difference between the three experimental setups; in fact, the resulting higher uncertainty associated with m_c in (i) makes its contribution to variance non-zero. Surprisingly, despite the comparatively large uncertainty assigned to d_0 and V_0 (respect to their m_c counterpart in (ii) and (iii)), their effect via m_c on the combined uncertainty is limited, thus making (i) a viable option in case of incomplete knowledge. Uncertainties evaluated for (ii) and (iii) show similar behavior between each other, as noticeable in Fig. 3 where the two surfaces are fully superimposed; since information concerning m_c comes from mass measurements, the parameter is well known; however,

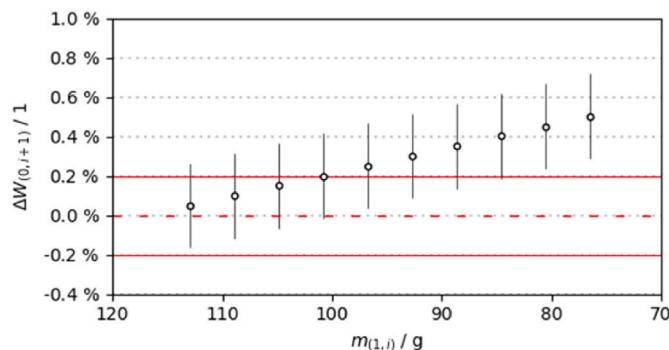


Fig. 1. Relative mass fraction variation cumulated at the end of i^{th} storage period versus corresponding bottle mass for 10 storage periods, 6 weeks each, and 10 aliquots taken out; error bars represent 95 % confidence intervals. The horizontal dashed and solid lines represent the certified mass fraction value w_{cert} and its 95 % confidence interval.

Table 2

Results from uncertainty budgets for experimental setups (i), (ii) and (iii) adopting values and lower uncertainty limits of input parameters reported in Table 1; a) index contribution to variance of most relevant parameters, I , and b) relative increment of combined uncertainty $\Delta u(w_{(0,11)})$.

a) Parameter	(i)	(ii)	(iii)
$I(w_{\text{cert}})$	99.84 %	100.0 %	100.0 %
$I(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)})$	0.00 %	0.00 %	0.00 %
$I(m_c)$	0.16 % ^(a)	0.00 %	0.00 %
b) Result	(i)	(ii)	(iii)
$\Delta u(w_{(0,11)})$	0.393 %	0.314 %	0.314 %

^a m_c is calculated by (3) using V_0 , d_0 and $m_{(0,0)}$.

Table 3

Results from uncertainty budgets for experimental setups (i), (ii) and (iii) adopting values and upper uncertainty limits of input parameters reported in Table 1; a) index contribution to variance of most relevant parameters, I , and b) relative increment of combined uncertainty $\Delta u(w_{(0,11)})$.

a) Parameter	(i)	(ii)	(iii)
$I(w_{\text{cert}})$	99.84 %	99.96 %	99.96 %
$I(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)})$	0.03 %	0.04 %	0.04 %
$I(m_c)$	0.13 % ^(a)	0.00 %	0.00 %
b) Result	(i)	(ii)	(iii)
$\Delta u(w_{(0,11)})$	0.388 %	0.330 %	0.330 %

^a m_c is calculated by (3) using V_0 , d_0 and $m_{(0,0)}$.

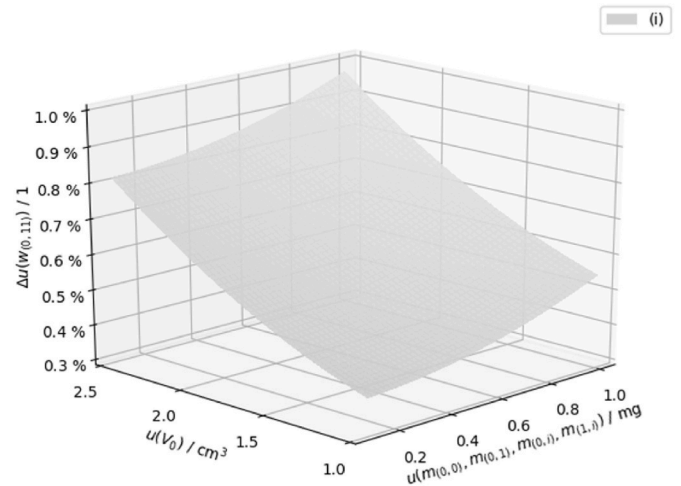


Fig. 2. Surface displaying $\Delta u(w_{(0,11)})$ (z axis) versus $u(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)})$ (x axis) and $u(V_0)$ (y axis) calculated for experimental setup (i).

in (ii) the same value is adopted among all steps under the assumption that the container mass remains stable for all its lifespan while in (iii) a new value is provided at every step and considered fully uncorrelated with respect to the previous ones.

Each of the three experimental setups applies to a particular situation and also highlights specific advantages and drawbacks: (i) displays larger uncertainty compared to the other two but also requires the least amount of experimental work, (ii) heavily relies on the assumption of stability of m_c which cannot be verified unless weighting the container again, and (iii) solves the issues with m_c in exchange for a more cumbersome experimental work and negligible improvement on combined uncertainty.

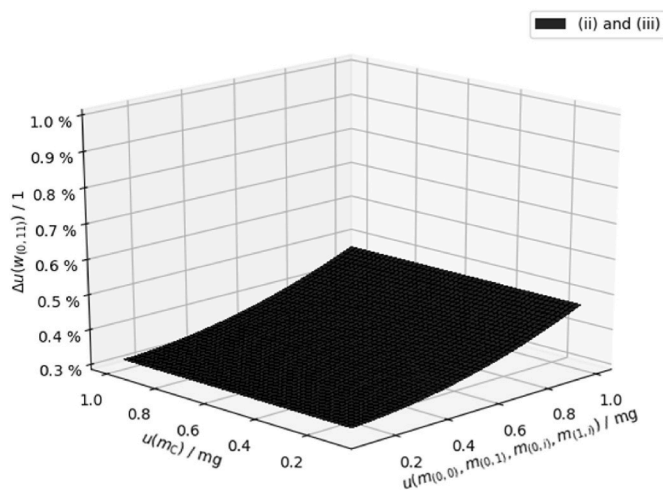


Fig. 3. Surface displaying $\Delta u(w_{0,11})$ (z axis) versus $u(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)})$ (x axis) and $u(m_c)$ (y axis) calculated for experimental setups (ii) and (iii).

Despite differences in the m_c evaluation, all three models require a balance calibrated with SI traceable weights to perform mass measurements; moreover, since for non-routine analysis the subsequent weightings could be a few weeks apart or more, great care should be observed in order to keep all the experimental and environmental conditions as stable as possible. E.g., if the bottle is weighted without its cap (recommended to avoid effects due to different internal air pressure), next weighing must be carried out without cap. Moreover, the temperature of the solution should be kept as constant as possible during consecutive weighing by stabilizing the bottle in a laboratory with controlled environmental conditions.

All those prerequisite are a capital part to assure the correct implementation of the proposed methodology.

4. Conclusions

In this work a methodology to take into account evaporation of a standard solution during storage and assure traceability of the certificate value is proposed and tailored to suit three different setups.

Simulated data based on experimental evidence of evaporation observed on a mono-elemental solution showed that the correction is required to maintain the SI traceability of the mass fraction in case of storage periods longer than 24 weeks after opening the bottle.

The analysis of uncertainty budgets revealed that the methodology applied in all three experimental setups could be serviceable for the task. In detail, upon inspecting the budgets, a couple of considerations were deduced; notably, the mass of the bottle containing the solution does not need to be known with a high level of accuracy as long as it remains stable throughout the whole process; similarly, common analytical

balances with suitable measuring interval and resolution should be appropriate for this task, however, they need to be regularly verified in order to rule out major departures over time due to long term instabilities.

Overall, the stability of all the experimental conditions is a paramount requisite for the application of the methodology. On the other hand, since the proposed approach is specifically tailored for solvent evaporation, if additional effects are in place (e.g. substance precipitation, leaching) their contribution is not accounted for, leading to inappropriate results. As its especially the case for chemical measurements, the knowledge of measurand and matrix interactions represents a primary part of the measure that should not be understated; moreover, the proposed procedure must be applied in conjunction with the meticulous care already reserved for handling and storing standard solutions and is not meant as a substitute.

Ultimately, the methodology here reported was developed with the aim to keep track of the mass fraction for reference solutions undergoing evaporation over time thus help retaining SI traceability in the framework of quality assurance required by accreditation according to ISO/IEC 17025 [4]; it requires minimum experimental work, at least for setups (i) and (ii), and could be straightforwardly implemented into laboratory routines.

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