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Original
Keeping track of evaporating solutions to maintain traceability / Di Luzio, Marco; D'Agostino, Giancarlo. - In: MEASUREMENT. - ISSN 0263-2241. - 264:(2026). [10.1016/j.measurement.2025.120274]

Publisher:
Elsevier B.V.

Published
DOI:10.1016/j.measurement.2025.120274

Measurement 264 (2026) 120274

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Keeping track of evaporating solutions to maintain traceability[☆]

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ARTICLE INFO

Keywords:
Standard solutions
Evaporation
Traceability

ABSTRACT

In chemical analysis the use of standard solutions is instrumental to guarantee traceability of measurements, however, they could be at risk of suffering solvent evaporation during long storage periods consequently affecting the certified mass fraction of the element/compound of interest. In this work, a measurement model is presented with the aim to take into account this behavior and retain metrological traceability. The proposed strategy revolves around the evaluation of solvent evaporation by just subsequent weightings at the start and end of the storage period. This formulation, iteratively applied, is suitably applicable to three different experimental setups depending on the available information. Multiple simulations and measurements were performed in order to test the model and give an estimate of the expected value and combined variance (thus assessing the increased uncertainty exclusively due to the application of the model). Both strengths and drawbacks were finally pointed out for the proposed model by the reported results, although a conclusive validation with Neutron Activation Analysis was not possible due to the magnitude of the investigated process which makes it highly challenging to quantify. General considerations were finally drawn with recognition of the limitations of the proposed modelization and the great importance reserved to the knowledge of matrix interactions.

1. Introduction

Performing a measurement means, at its core, performing a comparison between the quantity to be measured in the sample (the measurand) and its corresponding unit of measurement [1]. The usual strategy to assure this link is achieved through the use of measurement standards. They are well characterized materials for which the quantity of interest is certified, thus providing metrological traceability to the International System of Units (SI).

A plethora of standards are currently available [2] having different certified measurands, features, physical states. In the field of chemical analysis, measurement standards in solution are largely utilized. Solutions are preferable as they allow flexibility and ease of use and most of the chemical analytical techniques are exclusively applicable to solutions.

Despite these advantages, solutions are less stable than materials in solid state as they could be more easily affected by environmental factors such as temperature, light, moisture [3]. In order to preserve the stability of the solution, controlled storage conditions are always recommended by the manufacturers, usually meaning placing the solution bottles sealed or tightly closed in a dry environment away from direct sunlight while keeping constant temperature around 20 °C. However, even when proper storage conditions are in place, transpiration through the walls of the container is still possible with the result of losing solvent through evaporation thus increasing the mass fraction of the compound of interest.

Since these effects could potentially alter the certified mass fraction, they have to be taken into consideration by standard solution manufacturers. The most commonly adopted approach consists of stating in the certificate an expiration date for the opened bottle based on long-term stability studies [4]. Additionally, manufacturers might occasionally provide other information or recommendations. For example, some standard solution from Supelco provides a value for the monthly evaporation rate correction to apply to the certified mass fraction [5]. Although this is a simple and straightforward approach it relies on the assumption of a constant evaporation rate over time and the value is reported without uncertainty thus questioning the traceability of the corrected certified value. On the other hand, SRMs solutions from NIST are issued with just recommendation on how transferring the solution from the original phial to a working container while delegating the user to establish procedures to evaluate the suitable maximum shelf-life [6].

In this work, a measurement model suitable to evaluate the variation in mass fraction of reference standard solutions, by performing

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[☆] This article is part of a Special issue entitled: 'MEASUR_XXIV IMEKO World Congress' published in Measurement.

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https://doi.org/10.1016/j.measurement.2025.120274
Received 23 June 2025; Received in revised form 28 December 2025; Accepted 31 December 2025

sequential mass measurements, is proposed. The aim is to provide users with a simple and straightforward tool to experimentally monitor changes in the certified mass fraction due to evaporation while evaluating the resulting uncertainty in order to maintain traceability even in cases where the values strongly departs from the certified one or the shelf-life has expired.

This paper is an extended version of a contribution presented at the XXIV IMEKO world congress [7].

2. Methods and procedures

2.1. Model for measuring the change in the mass fraction of the analyte from solvent evaporation

In the common practice, solutions are stored in controlled conditions for the most part and only taken out of storage in the times when they are needed for analysis.

An immediate strategy to take into account solvent evaporation while dealing with solution would consist in the weighting of the bottle containing the liquid in order to monitor the mass loss. In the procedure proposed in this manuscript, the mass of the bottle is repeatedly weighted every time before and after use. Here and hereafter, the mass of the bottle is defined as the sum of the masses of the container and all its content.

For simplicity, in the following exposition a mono-elemental standard solution is taken into account, however, the proposed strategy might be applied to any standard solution. At any time it is possible to define the mass fraction of the certified element as the ratio between the mass of the considered element and the total mass of the solution, $w = \frac{m_{\mathrm{ANA}}}{(m_{\mathrm{ANA}}+m_{\mathrm{SOL}})}$ with m_{ANA} the mass of the certified element and m_{SOL} the mass of the solvent. During the storage period this value can change due to evaporation assuming only solvent is affected and the certified element stays unaltered. A relationship between subsequent mass fraction values can be established by calculating their ratio:

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

with $w_{(0,i)}$ and $w_{(1,i)}$ being the mass fraction values at the beginning and end of the i^{th} storage period, respectively, and $m_{\mathrm{SOL}\,(0,i)}$ and $m_{\mathrm{SOL}\,(1,i)}$ the corresponding masses of solvent. It needs to be highlighted that in this context the word solvent has a broader meaning since it also includes any other molecule dissolved in the solution other than the certified analyte of interest.

Measuring the decrease in mass of the bottle during the i^{th} storage time, $\Delta m_i = m_{(1,i)} - m_{(0,i)} = m_{\mathrm{ANA}\,i} + m_{\mathrm{SOL}\,(1,i)} + m_{\mathrm{C}} - \left(m_{\mathrm{ANA}\,i} + m_{\mathrm{SOL}\,(0,i)} + m_{\mathrm{C}}\right)$, allows the evaluation of $w_{(1,i)}$ following rearrangement of (1):

$$w_{(1,i)} = \frac{w_{(0,i)}}{\left(\frac{m_{(1,i)}-m_{(0,i)}}{m_{(0,i)}-m_{\mathrm{C}}} + 1\right)}, \tag{2}$$

with m_{C} the mass of the container.

Despite a quite simple formulation, achieving knowledge of masses present in the denominator of (2) is not as straightforward as it might seem. In fact, the masses obtained through weighing are affected by air buoyancy which decreases the value read by the instrument [8]. A correction for this effect can be devised based on the instrument response and various densities:

$$m = L\,k_{\mathrm{B}} = L\left(1 + \rho_{\mathrm{a}}\left(\frac{1}{\rho} - \frac{1}{\rho_{\mathrm{c}}}\right)\right), \tag{3}$$

with L the mass indication read from the instrument, k_{B} the buoyancy correction, ρ_{a} the air density, ρ the density of the whole object being weighed and ρ_{c} the density of the reference mass used to calibrate the balance. Value for ρ_{c} is fixed and depends on the material of the reference mass. On the other hand, ρ values might be considered constant throughout the measurement campaign in case containers of similar density with respect to that of the solution are used. In fact, the container material is not expected to change and the density variation due to the solution itself is minimal. Variations in air density are usually negligible while performing a series of weighings, however, since in this scenario successive measurements can be performed a long time apart, the corresponding environmental conditions can largely vary thus affecting the ρ_{a} value. A way to evaluate ρ_{a} is achieved by monitoring parameters such as pressure, relative humidity and temperature while performing the weighing [9]:

$$\rho_{\mathrm{a}} = \frac{0.34848p - 0.009RH\,e^{0.061T}}{273.15 + T}. \tag{4}$$

with, p the barometric pressure, RH the relative humidity of air and T the temperature.

Considering the buoyancy correction, Eq. (2) becomes:

$$w_{(1,i)} = \frac{w_{(0,i)}}{\left(\frac{L_{(1,i)}k_{\mathrm{B}(1,i)} - L_{(0,i)}k_{\mathrm{B}(0,i)}}{L_{(0,i)}k_{\mathrm{B}(0,i)} - m_{\mathrm{C}}} + 1\right)}. \tag{5}$$

In addition to the buoyancy effect, the m_{C} value is never provided by the manufacturer, thus its knowledge can only be gained from other 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 would be straightforward to weight the new container beforehand. On the other hand, if the solution is kept in its original container (as it is the case for common commercial standard solutions), the certificate might provide values about volume of solution, V_0, and density of solution, d_0, though they might be stated without uncertainty. In this second scenario, these information could be suitable for the evaluation of m_{C} according to:

$$m_{\mathrm{C}} = \left(m_{(0,0)} - d_0 V_0\right), \tag{6}$$

with $m_{(0,0)}$ being the mass of the newly open bottle containing the solution and weighted before taking the first aliquot.

At the end of a storage period i, the bottle is retrieved and used for analysis. Performing a mass measurement at this point provides the value for $m_{(1,i)}$. After the aliquot of the solution to be used is taken, another mass measurement is performed giving $m_{(0,i+1)}$, the solution mass corresponding to the start of the next storage period, as the solution is stored again afterwards. Between $m_{(1,i)}$ and $m_{(0,i+1)}$ there is just a difference in mass since the solution mass fraction is not modified as long as the solution homogeneity is kept and the evaporation from the open bottle during the aliquot taking is negligible. This is a fair assumption as the transfer operation only takes a few seconds. When these conditions are satisfied $w_{(0,i+1)} = w_{(1,i)}$, thus, from (2) it follows:

$$w_{(0,i+1)} = \frac{w_{(0,i)}}{\left(\frac{m_{(1,i)}-m_{(0,i)}}{m_{(0,i)}-m_{\mathrm{C}}} + 1\right)}, \tag{7}$$

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

Accordingly, the formulation of Eq. (7) considering the buoyancy effect is also reported:

$$w_{(0,i+1)} = \frac{w_{(0,i)}}{\left(\frac{L_{(1,i)}k_{\mathrm{B}(1,i)} - L_{(0,i)}k_{\mathrm{B}(0,i)}}{L_{(0,i)}k_{\mathrm{B}(0,i)} - m_{\mathrm{C}}} + 1\right)}. \tag{8}$$

When the standard solution is first unsealed, the mass fraction value, $w_{(0,1)}$, could be assigned equal to the certified value. However, since a long time might have been passed from the certificate date to when the solution is first used, the mass fraction might have already increased due to evaporation. Luckily, some manufacturer may provide an indication of the expected mass fraction increment rate [5], R, to perform this correction by taking into account the time span between certified date to the first time usage, t:

$$w_{(0,i)} = w_{\mathrm{cert}} + Rt. \tag{9}$$

The formulation highlighted in (8) can be adopted iteratively for any number of storage periods i and it translates into a strategy to tie the mass fraction of the element of interest in the solution at i^{th} step to its original certified value, thus assuring traceability. It is worth to note that this is achieved only relying on mass measurements which are usually dependable and easy to perform.

2.2. Application

The formulation proposed in (8) is applicable, in practice, in different ways depending on available information. Three experimental situations could occur all revolving around how m_{C} is quantified: (i) m_{C} is calculated through (6) from knowledge of density and volume of the solution and a mass measurement of the bottle, (ii) m_{C} is evaluated by transferring the unsealed solution into a new container previously weighted assuming it will remain stable and (iii) m_{C} is evaluated by transferring the solution into a new weighted container before every storage period. The three experimental situations here mentioned are taken into account in this study with a particular focus on (i) and (ii) since they are the most common ones.

In order to test the suitability of the proposed model (8) and draw some consideration, a few experiments were performed. In particular, a simulation to evaluate the expected value and uncertainty of the mass fraction value of a solution after multiple storage periods in defined conditions was performed, together with a further simulation test aimed at evaluating the effect of environmental parameters on the single mass measurement (Section 2.2.1). An experiment involving a real solution monitored over a long period of time was performed and the mass fraction results obtained by application of the proposed method were reported (Section 2.2.2). A measurement test was performed to check up to what extent mass fraction variations were identifiable by means of neutron activation analysis [10] (Section 2.2.3).

2.2.1. Simulation

In order to test the model and evaluate the achievable uncertainty considering plausible input parameters, MonteCarlo simulations using the numerical library of the python programming language (numpy) were performed [11].

The situation being simulated involved the use and storage of a mono-elemental standard solution of about $100\,\mathrm{cm}^3$ with certified mass fraction of the investigated element in the order of $1 \times 10^{-3}\,\mathrm{g\,g^{-1}}$. 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 $50\,\mathrm{mg}$ and $4\,\mathrm{g}$, respectively. These particular values were based off previous measurements on a similar sample: specifically, a decrease in mass of $26\,\mathrm{mg}$ for a $100\,\mathrm{g}$ Co solution $1 \times 10^{-2}\,\mathrm{g\,g^{-1}}$ certified mass fraction was observed over a period of 3 weeks while the solution was kept in typical storage conditions (i.e. dry environment at 20 °C). The $4\,\mathrm{g}$ mass values assigned to the taken aliquot comes from the practice to avoid transferring the solution directly from the bottle and use a temporary buffer solution instead. In fact, we use to take around $4\,\mathrm{g}$ since we adopt a $5\,\mathrm{mL}$ vial to contain the buffer, so it is a purely practical reason. A total number of 10 storage periods were simulated (i in (8) ranging from 1 to 10) corresponding to a timespan of 60 weeks in order to have a picture of the situation after more than a year of usage/storage. It is worth to note this time span is way beyond the usual shelf-life for standard solutions. In this simulation exercise, the correction due to evaporation before opening the bottle according to (9) was not considered, thus, $w_{(0,i)} = w_{\mathrm{cert}}$.

Apart from the general simulation on the overall model, a further simulation test was then performed to specifically evaluate the effect of random environmental parameters variability on the buoyancy correction affecting the weighting procedure.

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

Table 1 reports values and uncertainty limits for all influence parameters in (8) that are plausible in most common experimental situations. In fact, mass fraction and masses are usually well known and/or measurable with very small uncertainties. Density of the bottle and volume of the solution, on the other hand, are never known, however, they can be calculated or assumed from other information present in the certificate, thus, the larger uncertainty they display. Environmental parameters are given without uncertainty but as a possible range of values randomly drawn mimicking their change considering measurements performed over a long period of time. However, since the air density value resulting from them can be known quite well due to the application of (4) the uncertainty of ρ_{a} is reported as $0.01\,\mathrm{kg\,m^{-3}}$ corresponding to a relative uncertainty at the percent level. The densities for the solution to be monitored, ρ, and the reference calibration mass, ρ_{c}, are not expected to change thus their values are fixed with very small uncertainties.

For both simulation exercises, values of the input parameters included in the model were extracted from normal distributions (`random.normal()` function of the *numpy* module) with the exception of p, T, RH for which uniform distributions (`random.uniform()` function of the *numpy* module) were employed, as a first approximation, in order to simulate the variability of environmental conditions within the boundaries declared in Table 1. Ultimately, their values were then adopted to calculate the local value of ρ_{a} for which the normal distribution was adopted. The number of iterations was always set to 1×10^6.

2.2.2. Real case study

In order to test the proposed procedure on a real situation, a Co standard solution was monitored for about 60 weeks, a total period of similar length to that evaluated in the simulation test in the previous paragraph 2.2.1. The Co under investigation consisted in a commercially available solution with $1.0 \times 10^{-2}\,\mathrm{g\,g^{-1}}$ certified mass fraction that was seldom adopted as a standard for neutron activation analysis in our laboratory. The polyethylene bottle was opened the first time the solution was used and kept in storage in a cabinet placed in a room at a controlled temperature of 22 °C until the next use for a total of 4 storage periods. All mass measurements were performed on an analytical balance, with resolution $0.000\,01\,\mathrm{g}$, placed in a room with controlled temperature and humidity via conditioning system. The value and uncertainty of the Co mass fraction were calculated through an uncertainty budget obtained in Microsoft Excel by application of the spreadsheet method [12] including all the parameters present in Eq. (7).

2.2.3. Method validation study with NAA

Additionally, a further test was performed to check up to what extent variations in mass fraction of the investigated solution are measurable with neutron activation analysis. At the end of the last storage period of the experimental test previously performed, an aliquot of about $8\,\mathrm{mL}$ volume was taken and put in a container of known mass. From that solution, 3 further $30\,\mu\mathrm{L}$ aliquots were swiftly pipetted onto absorbent paper discs and regarded as reference samples and assumed to have the same mass fraction. The remaining solution was then placed, open, on an analytical balance to continuously monitor the decrease in mass over time and calculate the corresponding mass fraction increments with (2). At mass decreases corresponding to mass fraction increments of about 0.5 %, 1.5 % and 4.0 % an aliquot was taken and pipetted onto absorbent paper disc and regarded as concentrated sample. Mass of all pipetting depositions were also measured on the balance.

All 6 pipetted samples were evaporated in air and sealed afterwards with two foils of adhesive tape. Each concentrated Co sample was coupled, within a polyethylene container, with one of the reference samples initially taken and the 3 pairs were inserted into an irradiation

Table 1
Values and uncertainty limits of parameters introduced in the simulation tests. Superscripts (i), (ii) and (iii) indicate the parameter is only adopted in the corresponding experimental setup.

Parameter / unit	Value	Uncertainty limits
w_{cert} / $\mathrm{g\,g^{-1}}$	1.0×10^{-3}	1.0×10^{-6} - 3.0×10^{-6}
Δm_i / mg	50	–
m_{ALIn} / g	4	–
$L_{(0,0)}$ / g	117.0000	0.0001 - 0.001
$L_{(0,1)}$ / g	$m_{(0,0)} - m_{\mathrm{ALIn}}$	0.0001 - 0.001
$L_{(0,i)}$ / g	$m_{(0,0)} - i\left(m_{\mathrm{ALIn}} + \Delta m_i\right)$	0.0001 - 0.001
$L_{(1,i)}$ / g	$m_{(0,i)} - \Delta m_i$	0.0001 - 0.001
${m_{\mathrm{C}}}^{(\mathrm{ii,iii})}$ / g	17.0000	0.0001 - 0.001
${d_0}^{(\mathrm{i})}$ / $\mathrm{g\,cm^{-3}}$	1.000	0.001 - 0.01
${V_0}^{(\mathrm{i})}$ / $\mathrm{cm^3}$	100.0	1.0 - 2.5
p / hPa	600.0 - 1100.0	–
T / °C	15.0 - 27.0	–
RH / %	20.0 - 80.0	–
ρ_{a} / $\mathrm{kg\,m^{-3}}$	0.72 - 1.26	0.01
ρ / $\mathrm{kg\,m^{-3}}$	1000	10
ρ_{c} / $\mathrm{kg\,m^{-3}}$	8000	70

Table 2
Values, with standard uncertainties in parenthesis, of the pipetted solution mass related to the reference sample, $m_{\mathrm{pipetted}}\,(\mathrm{ref})$, and the concentrated sample, $m_{\mathrm{pipetted}}\,(\mathrm{conc})$, of the 3 pairs of samples measured; The mass fraction ratio for the concentrated with respect to the reference, R_w, is also stated.

Pair	$m_{\mathrm{pipetted}}\,(\mathrm{ref})$ / g	$m_{\mathrm{pipetted}}\,(\mathrm{conc})$ / g	R_w / 1
1	0.032 62(3)	0.032 73(3)	1.005 524(6)
2	0.032 61(3)	0.032 34(3)	1.016 651(9)
3	0.032 61(3)	0.032 84(3)	1.038 718(11)

container for neutron exposure. Relevant information on the 6 samples is reported in Table 2.

Neutron exposure lasted for 1 h and was performed in the central channel of the TRIGA Mark II reactor of Pavia at 250 kW power. Samples were evaluated by γ-spectrometry: each one of the 6 samples was acquired for 8 h real time at a distance of 20 cm from the detector end-cap of a ORTEC HPGe detection system (50 % relative efficiency, 1.9 keV full-width half maximum at 1332.5 keV) connected to a DSPEC and a personal computer running gamma vision software.

3. Results and discussion

3.1. Simulation

For the first simulation experiment, the measurement model (8) was iteratively applied in order to evaluate $w_{(0,i+1)}$ for each simulated storage step. Values and lower limit uncertainties from Table 1 were adopted to define the gaussian distributions for the parameters with the only exception being the ρ_{a} value which was calculated from random (uniform) picks within p, T and RH ranges.

In order to easily evaluate mass fraction variations during the evaporation periods two parameters are defined: the *relative mass fraction variation during* i^{th} *storage period*, $\Delta w_{(0,i+1)}$, and the *relative mass fraction variation up to the* i^{th} *storage period*, $\Delta W_{(0,i+1)}$. The former being defined as $\Delta w_{(0,i+1)} = \frac{w_{(0,i+1)} - w_{(0,i)}}{w_{(0,i)}}$ quantifying the mass fraction increase after a single storage period while the latter as $\Delta W_{(0,i+1)} = \frac{w_{(0,i+1)} - w_{\mathrm{cert}}}{w_{\mathrm{cert}}}$ quantifying the mass fraction increase with respect to the initial certified value.

The $\Delta W_{(0,i+1)}$ trend for the experimental setup (ii) is reported in Fig. 1.

The simulation here reported depicted the increasing trend of the investigated Co solution mass fraction value which, in the simulated conditions, is expected to exceed the 95 % confidence interval of the reference value after just 4 storage periods (corresponding to 24 weeks) and depart completely in later storage periods. This result supports the importance of not neglecting evaporation effects especially when working with solutions having very low uncertainty on certified mass fraction.

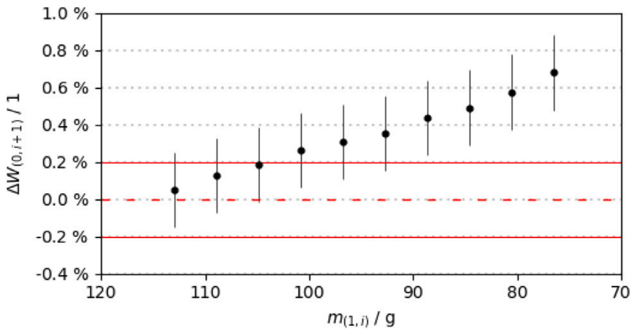

Fig. 1. Simulated relative mass fraction variation cumulated at the end of i^{th} storage period *versus* corresponding bottle mass for 10 storage periods, 6 weeks each, and 10 aliquots taken out; error bars represent 95 % confidence intervals. The horizontal dashed and solid lines represent the certified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

As it is noticeable from the errorbars depicted in Fig. 1, the application of the measurement model does not significantly increase the uncertainty assigned to the original standard solution. In order to quantify this aspect, *relative increment of combined uncertainty after 10 storage steps*, $\Delta u\left(w_{(0,11)}\right) = \frac{u\left(w_{(0,11)}\right) - u\left(w_{\mathrm{cert}}\right)}{u\left(w_{\mathrm{cert}}\right)}$, was calculated for each of the three experimental setups. The $\Delta u\left(w_{(0,11)}\right)$ values were evaluated over the main input parameters' uncertainty ranges stated in Table 1 through GUM uncertainty framework (GUF) [13] applied on (7), taking into account a mono-elemental solution of about 100 g with 0.1 % relative uncertainty on the mass fraction and neglecting buoyancy correction altogether: $L = m$.

Results are reported in Fig. 2 for experimental setup (i) and Fig. 3 for experimental setups (ii) and (iii).

The impact of the buoyancy correction was evaluated by simulating the expected relative variation on the instrument indication recorded by two successive weightings of the same mass in various environmental conditions, $\frac{\Delta L}{m} = \left(\frac{1}{k_{\mathrm{B}(1)}} - \frac{1}{k_{\mathrm{B}(2)}}\right)$. The range investigated for the air

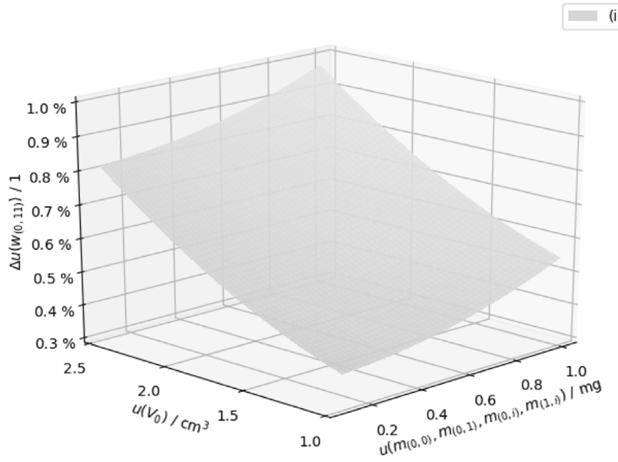

Fig. 2. Surface displaying $\Delta u\left(w_{(0,11)}\right)$ (z axis) *versus* $u\left(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)}\right)$ (x axis) and $u\left(V_0\right)$ (y axis) calculated for experimental setup (i) [7].

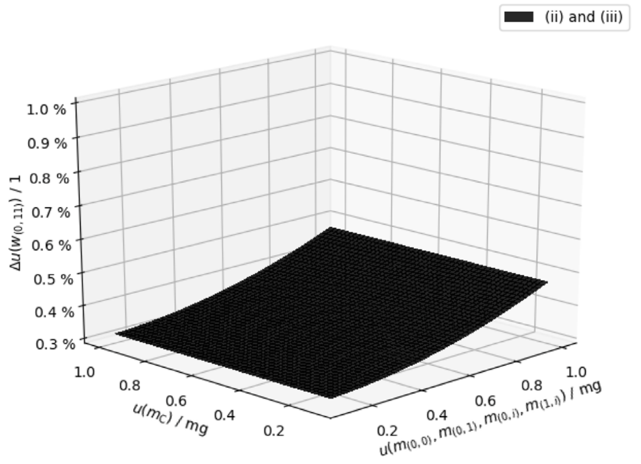

Fig. 3. Surface displaying $\Delta u\left(w_{(0,11)}\right)$ (z axis) *versus* $u\left(m_{(0,0)}, m_{(0,1)}, m_{(0,i)}, m_{(1,i)}\right)$ (x axis) and $u\left(m_{\mathrm{C}}\right)$ (y axis) calculated for experimental setups (ii) and (iii) [7].

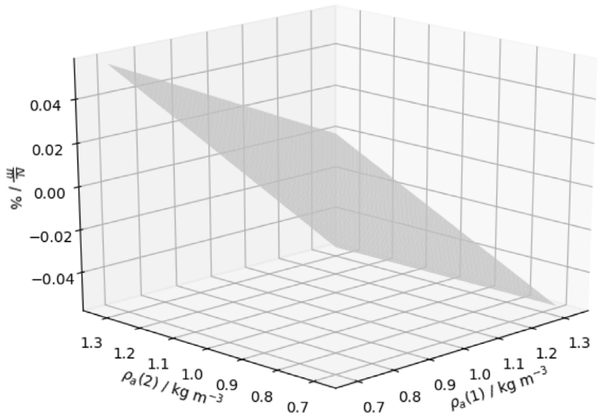

Fig. 4. Surface displaying $\frac{\Delta L}{m}$ (z axis) *versus* $\rho_{\mathrm{a}}(1)$ (x axis) and $\rho_{\mathrm{a}}(2)$ (y axis) for any ρ_{a} ranging from $0.7\,\mathrm{kg\,m^{-3}}$ to $1.3\,\mathrm{kg\,m^{-3}}$.

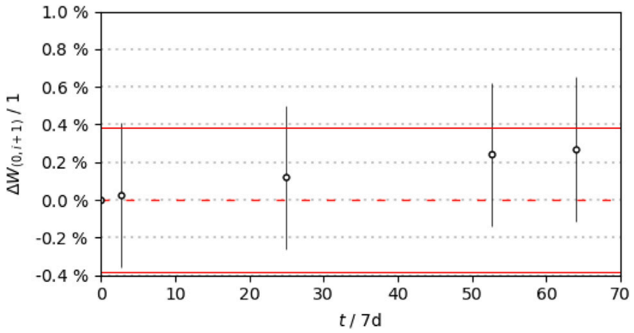

Fig. 5. Relative mass fraction variation evaluated by application of the proposed method to a $1 \times 10^{-2}\,\mathrm{g\,g^{-1}}$ Co standard solution monitored over a 64 weeks span comprising 4 storage periods of irregular length; error bars represent 95 % confidence intervals. The horizontal dashed and solid lines represent the certified mass fraction value w_{cert} and its 95 % confidence interval.

density at the moments of successively weightings 1 and 2, $\rho_{\mathrm{a}}(1)$ and $\rho_{\mathrm{a}}(2)$, respectively, being the main influence parameters to k_{B} values, was taken from Table 1 (see Fig. 4).

The $\frac{\Delta L}{m}$ trends linearly from being negligible when ρ_{a} and ρ_{a} are similar to achieve the maximum $|0.056|\,\%$ for the largest considered variation in air density, $\left|\rho_{\mathrm{a}}(1) - \rho_{\mathrm{a}}(2)\right| = 0.640\,\mathrm{kg\,m^{-3}}$. In contrast to $\frac{\Delta L}{m}$, the absolute variation in instrument indication, ΔL, depends on the considered mass: for a weighted mass in the order of 100 g, for which variability on indication of 1 mg is tolerated, corresponds to an allowed difference in air density of $|0.0057|\,\mathrm{kg\,m^{-3}}$ (0.89 % of the investigated range), instead for a weighted mass in the order of 10 g with same 1 mg tolerated variability on indication the allowed difference in air density corresponds to $|0.057|\,\mathrm{kg\,m^{-3}}$ (8.9 % of the investigated range).

3.2. *Real case study*

The outcome of the application of the proposed method to the real Co solution is reported in Fig. 5.

The overall Co mass fraction increment was estimated as $2.68 \times 10^{-5}\,\mathrm{g\,g^{-1}}$ over the total investigated period of 64 weeks, this meant that after more than a year the Co mass fraction value still within the uncertainty range. Conversely, as the simulation study highlighted, that should have not be the case for a $1.000(1) \times 10^{-3}\,\mathrm{g\,g^{-1}}$ solution. Moreover, slight variability in the slope of the line passing through the data could hint at a non-constant evaporation rate along the whole investigated period. The reason of this suspected tendency is not accounted for due to the low magnitude with respect to the measurement uncertainty; thus it might derive from environmental effects or it might reflect the actual behavior of the solution; or even be completely random.

3.3. *Method validation study with NAA*

The results obtained from the measurement exercise are reported in Table 3. Relevant results for each pair of concentrated and reference samples are the expected mass fraction ratio, R_w, and the measured mass fraction ratio, M_w. The former is calculated using (7) iteratively to calculate $R_w = w_{(1,j)}/w_{(0,1)}$, with $j = 1, 2, 3$, from knowledge of solution masses during their corresponding storage times while on the balance. The latter is calculated from NAA input parameters through rearrangement of the comprehensive relative-standardization model described in (5) in [14], in order to get the ratio $M_w = w_{\mathrm{smp}}/w_{\mathrm{std}}$, with w_{smp} being the mass fraction of Co in the concentrated sample and w_{std} the mass fraction of Co in the reference sample. Table 3 includes also the z-score to evaluate the agreement between M_w and R_w. Since

Table 3

Values of the expected mass fraction ratio, R_w, and measured mass fraction ratio, M_w, for the three pairs, z-score, is also stated.

Pair	R_w / 1	M_w / 1	z-score / 1
1	1.005 524(6)	0.9974(40)	−2.04
2	1.016 651(9)	1.0152(41)	−0.34
3	1.038 718(11)	1.0315(42)	−1.73

Table 4

Uncertainty budget of the measurement M_w for pair 1. For each input parameter, X_i, unit, $[X_i]$, value, x_i, uncertainty, $u(x_i)$ and contribution to combined uncertainty, I are shown.

X_i	$[X_i]$	x_i	$u(x_i)$	I / %
net area ratio	1	1.000	2.3×10^{-3}	33
decay ratio	1	1.000	5.1×10^{-6}	0
k_0 ratio	1	1.000	0	0
neutron flux ratio	1	1.000	2.8×10^{-3}	50
efficiency ratio	1	1.000	1.0×10^{-3}	6
mass ratio	$\mathrm{g\,g^{-1}}$	9.97×10^{-1}	1.3×10^{-3}	11
blank correction	$\mathrm{g\,g^{-1}}$	0.000	0.0	0
U fission correction	$\mathrm{g\,g^{-1}}$	0.000	0.0	0
M_w (1)	1	9.974×10^{-1}	4.0×10^{-3}	100.0

$z\text{-score} = (M_w - R_w)/\sqrt{u^2(M_w) + u^2(R_w)}$, a z-score value ≤ 2 is usually considered acceptable with a level of confidence of 95 %.

Additionally, for the measurement of standards pair with smallest mass fraction difference, an example of uncertainty budget is reported in Table 4 to highlight the contribution to combined uncertainty.

The results reported in Table 3 highlighted agreement between the NAA measurements with the corresponding expectations calculated with the weighings method as testified by the z-score. However, the reported measurement uncertainty in the case of pair 1 resulted of a similar magnitude than the ratio being measured highlighting the limit of what is possibly measurable with the current NAA experimental setup. Since the ratio expected in pair 1 is the closest to mass fraction variations in typical storage periods, validation of the weighing method within working range cannot be claimed from the results of this experiment. From inspection of the uncertainty budget in Table 4, the main contribution to the combined uncertainty is the *neutron flux ratio* parameter which is mainly dependent on neutron self-shielding correction. Possible strategies for reducing this contribution might concern intervening on the measurement samples by changing the support material and/or diluting the Co absorbed in it, however, reaching the ultimate sub-0.1 % uncertainty would still be quite challenging and only possible for a limited number of elements.

3.4. Discussion

The evaluation of uncertainty increase due to the application of the proposed method and reported in Figs. 2 and 3 highlighted a small increment with respect to the certified uncertainty for experimental setups (ii) and (iii) and a larger one for experimental setup (i). However, each of three setups here described might possibly be suitable for the task since, in the worst case, the increment resulted in about less than 1 % of the certified uncertainty of 0.1 %. Ultimately, the choice of one over the others is contingent upon the available solution and knowledge about it.

The strategy here proposed to maintain SI traceability is heavily based on mass measurements of the solution to analyze, thus, balances are the main instrument and need to be suitable for the task. Common laboratory balances with 0.1 mg resolution are, theoretically, already fit for purpose since a variation at resolution level would correspond to an increment in the order of $1 \times 10^{-6}\ \mathrm{g\,g^{-1}}$ for a 100 g solution with $1 \times 10^{-3}\ \mathrm{g\,g^{-1}}$ mass fraction. Although the resolution can be an indication of the suitability of an instrument, it has to be considered that the weighting uncertainty also depends on multiple aspects other than the resolution, such as repeatability, non-linearity, experimental setup, the measurand itself. To this point, it has been demonstrated that, even excluding buoyancy related effects, weighting uncertainty of an analytical electronic balance could be already five- to tenfold larger than the instrument resolution [15]. Considering that buoyancy effects are in many cases the main contributors to weighting uncertainty it becomes clear that environmental conditions should also be monitored with great care. The latter is not as trivial as it might appear since those measurement are supposed to be performed over large time intervals from one another.

Validation of the method performed within this study ended up being not conclusive as the attempt performed with NAA on the real solution resulted in values showing an achieved uncertainty bigger than the magnitude of the investigated mass fraction variations, where major contribution was due to self-shielding effects provoked by the abundant Co mass present in samples. Even in optimized experimental setup [16,17] lower uncertainties than 0.1 % on mass fraction are rarely achieved making NAA validation of the proposed methodology a challenging feat.

Finally, a set of recommendations concerning the applicability of the method described in this study is reported to facilitate users willing to adopt it in their laboratories. Providing adequate balances and environmental monitoring, the method is suited to maintain traceability for standard solutions having well known chemical stability that are seldom used, where seldom here indicates a frequency of use in the order of once every few weeks or months. On the contrary, for solutions that are very frequently used thus having a total storage time below a few months this method, as any other evaporation correction, is not needed as the mass fraction increase due to the evaporation will be negligible and too little to be quantified through mass measurements anyway. The adequate balance and environmental monitoring mentioned before translate into having a scale with weighting range encompassing the whole masses solution can possibly attain, ranging for example in the case of a typical 100 mL solution from a minimum of around 30 g up to around 130 g. The recommended resolution of the instrument would be in the range 0.01 mg - 0.1 mg considering usually a 5 to 10 times higher corresponding weighting uncertainty, that has to be carefully evaluated. Environmental conditions to be controlled during mass measurements are temperature, relative humidity and pressure. A common barometric station should be already suitable to check the variation of these parameters and evaluate their uncertainty. However, it has to be stressed that those recommendations are just guidelines and individual understanding and critical evaluation of each laboratory's needs is always preferable.

4. Conclusions

This study presents a measurement model aimed to manage mass fraction variations of certified entities in standard solutions due to evaporation of solvent. Three ways of applying the model are described covering three experimental setups that are almost equally viable in terms of uncertainty.

As highlighted by the simulation studies reported in this work, the effect of evaporation for certain conditions of storage times could not be negligible and since the proposed model is only based on mass measurements it should be easily applicable in any laboratory, providing a comfortable solution to the problem.

On the other hand, the measurement test performed in this study to assure validation of the method was not conclusive, thus further experiments will be needed in this topic. Moreover, the model is specifically suited for evaporation effects, meaning other interactions like leaching or precipitation could not be correctly managed. Thus, knowledge of chemical interactions should not be underestimated and good practice in handling and storing solutions cannot be substituted.

In summary, the methodology here reported was developed as a starting point to track mass fraction for reference solutions accounting for evaporation effects over time and, in doing so, retaining traceability to SI (according to ISO/IEC 17025 [18]) even past the conventionally adopted expiration times.

CRediT authorship contribution statement

Marco Di Luzio: Writing – original draft, Visualization, Software, Methodology, Investigation. **Giancarlo D'Agostino:** Writing – review & editing, Supervision, Conceptualization.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

A link to the Zenodo repository [19], containing much of the research data, is included in the text.

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