Application of secondary pH measurement method for homogeneity and stability assessment of reference materials

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Abstract
In this work, the development and optimization of a secondary method for pH measurement using a differential potentiometric cell are described. The method was optimized and validated by measurement of three certified primary buffer solutions (CRMs) with nominal pH values of 4.005, 6.865 and 9.180 at 25 °C. The method was applied to assess homogeneity and stability of phosphate buffer solution with nominal pH of 7.000 at 25 °C which will be used as test item in proficiency testing schemes for pH measurement of testing laboratories. The experiments carried out and described in this article proved that this particular design of secondary differential potentiometric cell requires small volume of solutions, is fast, accurate and precise and is suitable for the characterization of secondary buffer solutions and assessment of homogeneity and stability of buffer solutions.

Keywords pH · Differential potentiometric cell · Homogeneity · Stability · Certified reference material (CRM)

Introduction
pH is among the most frequently measured chemical quantities in many fields—from industry to health. pH measurements of real samples are mostly carried out using a glass electrode cell connected to a digital pH meter. However, the use of these devices requires calibration in order to correct for the various systematic effects which introduce errors of unknown magnitude as well as to assure their metrological traceability [1, 2]. The calibration is done using certified standard buffer solutions (certified reference materials, CRMs) traceable to primary pH standards. On the other hand, field laboratories measuring pH, if accredited, are required to demonstrate their measurement capabilities by participation in proficiency tests (PTs) [3]. Therefore, to assure the quality of the measurements, CRMs are used both for glass electrode calibration and as test item in proficiency tests.

At present, there are seven buffer solutions prepared from six buffer materials which fulfil the requirement to have the highest metrological quality according to the definition of a primary standard [4] and thus are accepted by the International Union of Pure and Applied Chemistry (IUPAC) as primary buffer solutions [1]. Although their nominal chemical composition is stated, measurement of their pH is required when a new batch is produced because a variation in the stoichiometry or presence of impurities in the solid material can cause variation in the pH of the produced buffer solution [1]. To be certified as primary buffer solutions, the pH value shall be measured by a primary pH measurement method.

The only method that meets the strict criteria of a primary method for pH is based on the measurement of the potential difference in an electrochemical cell without transference represented as:

\[\text{Pt} \mid \text{H}_2 \mid \text{buffer S, Cl}^- \mid \text{AgCl} \mid \text{Ag}\]

often referred to as a Harned cell (Cell I) [1]. The method involves a platinum hydrogen gas electrode and a silver/silver chloride reference electrode which are immersed into a selected buffer solution in which a known amount of chloride is added. This primary method is applied mainly by National Metrology Institutes because the highest metrological quality of the produced measurement results is a product of a time-consuming complex procedure for which a sophisticated equipment is used [5, 6].

In many applications, such as glass electrode calibration and PT test item provision, the use of traceable secondary
buffer solutions with sufficient accuracy is preferred. In order to assign a reference value to these solutions, a secondary pH measurement method can be used. The secondary method is internationally recognized and provides metrological traceability through comparison of pH of two buffer solutions—primary and secondary ones [1]. The comparison is carried out in a differential potentiometric cell with single junction (secondary cell) which has been proposed for the first time by F. G. K. Baucke [7]. Although different designs of secondary cells are available [7, 8], all of them consist of two half-cells separated by a single junction. The primary buffer solution is placed in one of the half-cells together with a hydrogen electrode (Pt/H₂) and the secondary solution— into the other half-cell with an identical hydrogen electrode (Pt/H₂) with similar hydrogen pressure. The two buffer solutions are in direct contact via a vertical sintered glass disk with a suitable porosity. To keep the liquid junction potential (LJP) between the two solutions as low as possible (on the order of microvolts), the two solutions should (1) have the same composition, (2) have a nominal pH value in the range from 3 to 11, and (3) have a difference in pH value less than 0.02. Under these conditions the LJP will be less than 10% of the measured potential difference. The proper functioning of the cell should be checked by measuring the potential difference when both half-cells contain the same solution [1, 7].

The secondary method is simpler and requires less expensive equipment than the primary method. The procedure is considerably faster and significantly smaller volume of solutions is needed. The quality of the produced secondary buffer solutions is close to the primary ones [1, 7, 8]. These features make the secondary method suitable for characterization of certified reference materials and especially for their homogeneity and stability assessment.

In this study the development and optimization of a secondary pH measurement method at the Bulgarian Institute of Metrology (BIM) with the support of the Laboratoire National de Métrie et d’Éssais (LNE) are described. The results from its validation are presented. The method was applied for the measurements needed for homogeneity and stability assessment of phosphate buffer solution with nominal pH value of 7.000 at 25 ºC which will be used as test item in PT for pH measurement of testing laboratories.

**Experimental**

**Instrumentation**

To realize the secondary method for pH measurement, a secondary measurement system is required in which the most critical component is the potentiometric cell. In this study, a differential potentiometric cell with single junction (Areko, Bratislava, Slovakia) was used. A scheme of the cell is presented in Fig. 1. The cell is made of glass and is composed of two identical half-cells separated by a D4 porosity sintered-glass disk. Each half-cell is divided by a D1 porosity sintered-glass disk into two compartments, both filled with the buffer solutions. The solution volume needed for each half-cell is only 20 ml. One of the two identical Pt/H₂ electrodes is immersed into the buffer solution of the upper compartment. The electrodes are platinized platinum plates with a surface of 1 cm². The hydrogen, in constant flow, enters into each half-cell through a glass tube, passes the lower compartment where is saturated with vapors, reaches the Pt electrode in the upper compartment behind the sintered-glass disk and leaves the cell through a small hole in the cap. During the measurements, the conditions in the two half-cells are kept as equal as possible, i.e.,—same depth of immersion of the electrodes, same temperature and identical hydrogen flow rate.

The secondary pH measurement system is an automated one which along with the differential potentiometric cell described above, consists of a digital multimeter 8505A (Fluke, USA) with accuracy of 1 µV, a thermostatic water bath (PM Tamson Instruments bv, The Netherlands) with two Pt 100 resistance thermometers, a hydrogen generator (Whatman, USA) producing hydrogen with purity 99.999% at constant flow rate, a monitoring system PHMS-01 (Metrix-MC, Bulgaria) to register the thermostatic bath temperature, and a specialized in-house developed software PH-SCell to collect, process and store the data.
Samples

Two batches of three primary buffer solutions were used: 0.05 mol kg⁻¹ potassium hydrogen phthalate (nominal pH value of 4.005 at 25 °C) (called phthalate buffer solution), 0.025 mol kg⁻¹ disodium hydrogen phosphate + 0.025 mol kg⁻¹ potassium dihydrogen phosphate (nominal pH value of 6.865 at 25 °C) (called phosphate buffer solution) and 0.01 mol kg⁻¹ disodium tetraborate (nominal pH value of 9.180 at 25 °C) (called tetraborate buffer solution). The solutions were characterized using the National primary pH measurement standard of BIM. Certificates for certified reference materials were issued for these solutions. The certified values are stated in Table 1. The CRMs were used during the development of the measurement procedure and its validation.

Phosphate buffer solution (0.02 mol kg⁻¹ potassium dihydrogen phosphate + 0.027 mol kg⁻¹ disodium hydrogen phosphate) with nominal pH value of 7.000 is not a registered CRM of BIM. In this article, it will be called hydrogen phosphate buffer solution to be distinguished from the primary phosphate buffer solution with nominal pH value of 6.865. A buffer solution of pH 7.00 is routinely used by field laboratories thus it was intended to be used as test item in proficiency test for pH measurement organized by BIM. As the hydrogen phosphate buffer solution is still not a CRM, a preliminary sample batch was produced and characterized by the National primary pH measurement standard of BIM. Furthermore, its homogeneity and stability for the time period and temperatures relevant for the PT were assessed using the developed secondary pH measurement system. A full uncertainty budget was established.

A preliminary sample batch of 3 l hydrogen phosphate buffer solution was produced and 2.2 l of it were packed in 22 HDPE bottles, 100 ml each. The pH of the solution (0.8 l) was measured and a reference value of 7.000 ± 0.004 was assigned. The rest of this solution was used as a primary buffer solution during the homogeneity and stability measurements.

The bottles used for homogeneity and stability studies were randomly selected. Ten bottles were taken and measured in duplicate to assess the inhomogeneity of the batch. For short-term stability study 6 bottles were chosen—2 bottles were kept at 4 °C, 2—at 25 °C and 2—at 50 °C (in an oven). After 2 days the buffer solution of each bottle was measured in duplicate. The long-term stability study was carried out using 6 bottles kept at 25 °C for 0 days (2 bottles), 7 days (2 bottles) and 14 days (2 bottles).

Measurement procedure

The secondary pH measurement system is used in order to calibrate (compare) secondary to primary buffer solutions. The pH measurement is based on the measurement of potential difference in a differential potentiometric cell with a junction defined by:

\[ \text{Pt} \mid \text{H}_2 \mid \text{buffer } S_2 \mid \text{buffer } S_1 \mid \text{H}_2 \mid \text{Pt}. \]

The first step of the procedure is to check the proper functioning of the pH measurement system and especially the electrodes’ behavior. This is done by measuring the potential difference when both half-cells are filled with the same primary buffer solution (CRM). The measured potential difference \( E_0 \) is used as off-set to correct the potential difference measured in the subsequent analysis.

The second step is the comparison of the pH of unknown (secondary) buffer solution with the pH of CRM. To do this, one half-cell is filled with the unknown solution while the other half-cell contains the CRM with the same nominal composition. The measured potential difference \( E_x \) is used to calculate the pH of the secondary buffer solution following Eq. 1.

\[
\text{pH}_s = \text{pH}_p - \frac{(\Delta E - E_j)F}{RT\ln10}
\]

where: \( \text{pH}_s \)—pH of secondary buffer solution, \( \text{pH}_p \)—pH of primary buffer solution, \( \Delta E=(E_x-E_0) \)—potential difference measured between the two hydrogen electrodes, \( V; E_j \)—liquid junction potential, \( V; F \)—Faraday constant, C mol⁻¹; \( R \)—molar gas constant, J mol⁻¹ K⁻¹; \( T \)—temperature, K.

The liquid junction potential is included in the equation but according to the literature [6] the bias associated with \( E_j \) is less than 10% of \( \Delta E \), and \( E_j \) may be neglected because

| CRM i.d. No          | Chemical composition                  | pH     | Uncertainty U (k = 2) |
|----------------------|---------------------------------------|--------|-----------------------|
| NCM-CRM-5-304p-2018  | phthalate buffer solution No 1         | 4.008  | 0.005                 |
| NCM-CRM-5-304n-2017  | phthalate buffer solution No 2         | 4.005  | 0.005                 |
| NCM-CRM-5-305n-2019  | phosphate buffer solution No 1         | 6.865  | 0.004                 |
| NCM-CRM-5-305l-2018  | phosphate buffer solution No 2         | 6.864  | 0.004                 |
| NCM-CRM-5-307k-2018  | tetraborate buffer solution No 1       | 9.180  | 0.005                 |
| NCM-CRM-5-307l-2018  | tetraborate buffer solution No 2       | 9.181  | 0.005                 |
the two buffer solutions are quasi-identical in composition, \(|pH_p - pH_e| \leq 0.02\), and \(3 < pH < 11\).

**Results and discussion**

**Development and validation of the secondary pH measurement system**

The most critical parameters of the newly set-up secondary pH measurement system, i.e., the hydrogen gas flow and the measurement time, were tested and optimized. The measurements were done using phthalate, phosphate and tetraborate buffer solutions. The influence of the hydrogen gas flow rate on the measured potential difference was studied and a value of 3–4 bubbles per second was chosen as optimal one. To optimize the measurement time, the data collection was automatically done every 5 s starting from the beginning of the measurement and ending after 30 min (without any initial stabilization time). From the collected data, the software automatically choses the 10 consecutive values with the lowest difference between the highest and the lowest value. The measured potential difference \(E_0\) or \(E_x\) was then calculated as the average of the chosen 10 values. Measurements of phthalate, phosphate and tetraborate buffer solutions were performed in order to find the optimal measurement time. The closest 10 values appeared at different time in the different measurements but usually between 13 and 17 min. Thus, the measurement time was fixed at 20 min.

An example of the dependence of the measurement time vs measured potential difference \(E_x\) of phosphate buffer solution is presented in Fig. 2. A closer view of the part showing the dependence after 12.5 min is also presented. In this case the amplitude between the values from measurement number 150 (12.5 min) to 240 (20 min) was less than 20 \(\mu V\).

The developed secondary pH measurement method was validated using certified reference materials produced by BIM—phthalate, phosphate and tetraborate buffer solutions batches No 1 and No 2. Although all the 6 solutions were CRMs, No 1 was arbitrarily chosen as primary and No 2 as secondary buffer solutions. No 1 was used for \(E_0\) determination and No 2 as unknown samples in the second stage of the measurement procedure.

The results were quantitatively compared with the certified values (Buffer solutions No 2) following the procedure described in the Application Note 1 [9]. This approach compares the difference between the certified and measured values (\(\Delta pH\)) with its expanded uncertainty (\(U_\Delta\)). If \(\Delta pH \leq U_\Delta\), then there is no significant difference between the measured and the certified value. Equations 2, 3 and 4 were used to perform the calculations. The results are summarized in Table 2.

![Figure 2](image)

**Table 2** Results from the validation of the secondary pH measurement method

| CRM i.d. No | pH\(_{CRM}\) | \(U_{CRM}\) (\(k = 2\)) | pH\(_{meas}\) | \(U_{meas}\) (\(k = 2\)) | \(\Delta pH\) | \(U_\Delta\) |
|-------------|-------------|-----------------|-------------|-----------------|---------|---------|
| NCM-CRM-5-304n-2017 phthalate buffer solution | 4.005 | 0.005 | 4.003 | 0.005 | 0.002 | < 0.007 |
| NCM-CRM-5-305l-2018 phosphate buffer solution | 6.864 | 0.004 | 6.865 | 0.004 | 0.001 | < 0.006 |
| NCM-CRM-5-307j-2018 tetraborate buffer solution | 9.181 | 0.005 | 9.182 | 0.005 | 0.001 | < 0.007 |

\(\Delta pH = |pH_{meas} - pH_{CRM}|\),

\(u_\Delta = \sqrt{u_{meas}^2 + u_{CRM}^2}\)

\(U_\Delta = 2 \times u_\Delta\),

where: \(\Delta pH\)—absolute difference between the mean measured value and the certified value; \(pH_{meas}\)—mean measured pH value; \(pH_{CRM}\)—certified pH value; \(u_\Delta\)—combined standard uncertainty of measurement result and certified value; \(u_{meas}\)—standard uncertainty of the measurement result; \(u_{CRM}\)—standard uncertainty (expanded uncertainty divided by a coverage factor as stated in the certificate) of the certified value; \(U_\Delta\)—expanded uncertainty of difference between measurement result and certified value, corresponding to a confidence level of approximately 95%.
The fact that $\Delta \text{pH} < U_{\text{pH}}$ for all measured buffer solutions proves that the results achieved by the secondary method do not statistically differ from the values certified by the primary method.

Measurement uncertainty was estimated for the pH value of each secondary buffer solution according to the Guide to the expression of uncertainty in measurement (GUM) [10]. The uncertainty calculation is based on the equation used for the calculation of pH by the secondary pH measurement method (Eq. 1). An example of uncertainty budget is presented in Table 3.

The main source of uncertainty is the primary buffer solution used for the calibration. The experimental standard measurement uncertainty ($k = 1$) obtained for the pH value of the primary buffer solution is 0.0025. This uncertainty does not take into account the contribution coming from the Bates–Guggenheim convention. The mentioned convention involves extra-thermodynamic assumptions needed to define activity coefficients of single ions in ionic strength solutions below 0.1 mol kg$^{-1}$. Such approach is necessary to assign primary pH values, according to the definition given by IUPAC [1]. Considering the standard uncertainty ($k = 1$) of 0.005 assigned to Bates–Guggenheim convention makes primary pH measurements traceable to SI. However, the uncertainty level of the primary pH CRMs will therefore become higher, to 0.0056 and will further lead to an increase in the uncertainty level of the secondary pH buffer solutions, up to 0.01.

Additionally, although all other contributions are negligible, they are included in the budget. The contribution of the liquid junction potential is also taken into account. It accounts for perturbations caused by small additions of strong acid or alkali. According to the literature [1, 7], $E_j$ contribution is about 10% of the total cell potential difference.

### Application of the secondary pH measurement method

The secondary pH measurement method was used to perform the measurements for homogeneity and stability studies of a preliminary sample batch of hydrogen phosphate buffer solution intended to be used as test item in proficiency test organized by BIM.

The measurements of the homogeneity study were performed under repeatability conditions and in randomized manner. Regression analysis was used to evaluate potential drift during the measurement sequence as well as trends in the filling sequence. No trends were observed at a 95% confidence level. The measurement results are presented in Fig. 3.

Quantification of between-bottle inhomogeneity was done by one-way analysis of variance (ANOVA) which separates the between-bottle from the within-bottle variation. The latter is equivalent to the method repeatability as the individual samples were representative of the whole bottle.

The following equations were used to calculate $s_{bb}$ (between-bottle standard deviation) and $s_{wb}$ (method uncertainty):

$$s_{bb} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N - 1}}$$

$$s_{wb} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N}}$$

where $x_i$ is the individual measurement, $\bar{x}$ is the mean of the measurements, and $N$ is the number of measurements.

![Fig. 3 Results of pH measurements against the sequence in which the bottles were filled](image-url)
repeatability) which are estimates of the true standard deviations [11]:

\[
s_{wb} = \sqrt{MS_{\text{within}}},
\]

\[
s_{bb} = \sqrt{\frac{MS_{\text{between}} - MS_{\text{within}}}{n}},
\]

where: \(MS_{\text{within}}\) is the mean of squares within-bottle; \(MS_{\text{between}}\) is the mean of squares between-bottle; \(n\) — number of replicates per bottle.

As all the samples for the homogeneity study were measured in duplicate, the standard deviation between bottles (\(s_{bb}\)) is the uncertainty component due to between bottle inhomogeneity (\(u_{bb}\)). The calculations in this case resulted in \(u_{bb} = 0.00004\).

The stability studies of hydrogen phosphate buffer solution were carried out using an isochronous design [12]. At the end, the samples were measured simultaneously under repeatability conditions and randomized sequence was used to differentiate any measurement drift from a trend over storage time.

Short-term stability study is used to determine the conditions for dispatch of the solution to the participants. It was assumed that the transportation will last not more than two days and during that time temperature up to 50 °C could be reached. Thus, the selected bottles were stored at 4 °C, 25 °C and 50 °C (2 bottles per temperature). After 2 days, the pH of the hydrogen phosphate buffer solution was measured in duplicate per bottle. The data were evaluated against storage temperature and regression line of pH versus temperature was calculated in order to test for potential change in pH due to shipping conditions. The slope of the regression line was \(2 \times 10^{-6} \text{ °C}^{-1}\) and found statistically insignificant (\(t_{\text{value}} < t_{\text{crit}}\), 95% confidence level) (Fig. 4). The result provides the evidence that the hydrogen phosphate buffer solution can be transported at ambient conditions without special precautions.

The long-term stability study is necessary to establish conditions for storage. In this case, the participants in the PT were asked to do their measurements within 2 weeks after sample receiving. Thus, the long-term stability study duration using the preliminary sample batch was set to 14 days and no extrapolation for longer shelf-life was needed. The selected bottles were kept at 25 °C for 0 days (2 bottles), 7 days (2 bottles) and 14 days (2 bottles). The reference temperature was set to 4 °C as suggested in [13].

Regression analysis was performed to evaluate potential trend in the measurement sequence. No significant trend was detected at 95 % confidence level. Furthermore, the data were plotted against storage time and a linear regression line of pH versus time was calculated. The results are shown in Fig. 5. The slope of the regression line \((4 \times 10^{-5} \text{ day}^{-1}\) was tested and found not significantly different from zero \((t_{\text{value}} < t_{\text{crit}}, \text{at 95}\% \text{ confidence level})\).

Even in the absence of statistically significant trends, it is necessary to quantify the potential degradation that could be hidden by the method repeatability i.e., to evaluate the uncertainty of stability. The uncertainty of stability during storage was estimated as described in [14]. First, the uncertainty of the linear regression line with a slope of zero was calculated and then multiplied by the chosen shelf life using Eq. 7. The value of \(u_{\text{fit}}\) for 14 days shelf life was found to be 0.0004.

\[
u_{\text{fit}} = \frac{s}{\sqrt{\sum (x_i - \bar{x})^2}} \times x_{\text{shl}},
\]

where: \(s\) — standard deviation of all results of the stability study; \(x_i\) — time of the measurement points; \(\bar{x}\) — average of all x; \(x_{\text{shl}}\) — chosen shelf life.

Fig. 4 Influence of temperature over pH of hydrogen phosphate buffer solution

Fig. 5 Results of long-term stability study of hydrogen phosphate buffer solution
The combined uncertainty of a certified reference material (in this case a test item for proficiency test) contains contributions from its characterization, homogeneity, short-term and long-term stability. In the presented case of hydrogen phosphate buffer solution, the main contribution is caused by the characterization (0.004). The short-term stability study introduced no uncertainty as it was used just to select the transportation conditions. The contribution from the homogeneity and long-term stability determined under the conditions selected for production of the PT test item is negligible.

**Conclusion**

A secondary method for pH measurement was successfully developed and optimized. The differential potentiometric cell used was incorporated into an automated measurement system. The volume of buffer solution needed for one replicate measurement was only 20 ml (per half-cell) and stabilization in the potential difference was reached in less than 20 min. The method was validated using 3 buffer solutions (CRMs) at different pH nominal values at 25 °C—phthalate (4.005), phosphate (6.865) and tetraborate (9.180). The results did not statistically differ from the certified reference values and the measurement uncertainty was the same than the one of the primary buffer solutions used for comparison. The secondary method was applied for performance of homogeneity and stability studies of phosphate buffer solution with nominal pH of 7.000. The results show that the repeatability of the method over long series of consecutive measurements is sufficient for homogeneity and stability studies.

The experiments carried out and described in this article proved that the secondary method using this particular design of differential potentiometric cell requires small volume of solutions, is fast, accurate and precise and is suitable for characterization of secondary buffer solutions and assessment of homogeneity and stability of buffer solutions.

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**Availability of data and material** Not applicable.

**Code availability** Not applicable.

**Author contributions** All authors contributed to the study conception and design. Measurements and data collection were performed by Lyudmila Dimitrova. Data analysis was done by Lyudmila Dimitrova, Boryana Koleva and Daniela Stoica. The first draft of the manuscript was written by Boryana Koleva and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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**References**

1. Buck RP et al (2002) Measurement of pH. Definition, standards, and procedures (IUPAC Recommendations 2002). Pure Appl Chem 74:2169–2200

2. Naumann R, Alexander-Weber Ch, Eberhardt R, Giera J, Spitzer P (2002) Traceability of pH measurements by glass electrode cells: performance characteristic of pH electrodes by multi-point calibration. Anal Bioanal Chem 374:778–786

3. ISO/IEC 17025 (2017) General requirements for the competence of testing and calibration laboratories, 3rd edn. International Organization for Standardization, Geneva

4. JCGM 200 (2012) International vocabulary of metrology – Basic and general concepts and associated terms (VIM), 3rd edn. JCGM (BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML)

5. Spitzer P, Seitz S (2010) Metrological traceability chain for pH measurement results. Mapan J Metrol Soc India 25:191–196

6. Spitzer P, Pratt KW (2011) The history and development of a rigorous metrological basis for pH measurements. J Solid State Electrochem 15:69–76

7. Baucke FGK (1994) Differential-potentiometric cell for the redetermination of pH reference materials. J Electroanal Chem 368:67–75

8. Gonzaga FB, Dias JC, Jehnert D, Werner B, Schrapler K, Vyskocil L (2013) Evaluation of a compact differential cell for secondary pH measurements by a bilateral interlaboratory comparison. Electroanalysis 25:1955–1959

9. Linsinger T (2010) Application Note 1. Comparison of a measurement result with the certified value. European Commission, Joint Research Centre https://ec.europa.eu/jrc/sites/jrcsh/files/crm_application_note_1_en.pdf. Accessed 28 Apr 2020

10. JCGM 100 (2008) Evaluation of measurement data – Guide to the expression of uncertainty in measurement (GUM:1995 with minor corrections). 1st edn. JCGM (BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML)

11. Van der Veen AMH, Linsinger T, Pauwels J (2001) Uncertainty calculations in the certification of reference materials. 2. Homogeneity study. Accred Qual Assur 6:26–30
12. Lamberty A, Schimmel H, Pauwels J (1998) The study of the stability of reference materials by isochronous measurements. Fresenius J Anal Chem 360:359–361
13. ISO Guide35 (2017) Reference materials – guidance for characterization and assessment of homogeneity and stability, 4th edn. International Organization for Standardization, Geneva
14. Linsinger TPJ, Pauwels J, Lamberty A, Schimmel HG, Van der Veen AMH, Sickmann L (2001) Estimating the uncertainty of stability for matrix CRMs. Fresenius J Anal Chem 370:183–188

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