Evaluation and validation of detailed and simplified models of the uncertainty of unified $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ measurements in aqueous solutions

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Abstract

The use of the unified pH concept, $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$, applicable to aqueous and non-aqueous solutions, which allows interpreting and comparison of the acidity of different types of solutions, requires reliable and objective determination. The $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ can be determined by a single differential potentiometry measurement referenced to an aqueous reference buffer or by a ladder of differential potentiometric measurements that allows minimisation of inconsistencies of various determinations. This work describes and assesses bottom-up evaluations of the uncertainty of these measurements, where uncertainty components are combined by the Monte Carlo Method (MCM) or Taylor Series Approximation (TSM). The MCM allows a detailed simulation of the measurements, including an iterative process involving in minimising ladder deviations. On the other hand, the TSM requires the approximate determination of minimisation uncertainty. The uncertainty evaluation was successfully applied to measuring aqueous buffers with pH of 2.00, 4.00, 7.00, and 10.00, with a standard uncertainty of 0.01. The reference and estimated values from both approaches are metrologically compatible for a 95 % confidence level even when a negligible contribution of liquid junction potential uncertainty is assumed. The MCM estimated pH values with an expanded uncertainty, for the 95% confidence level, between 0.26 and 0.51, depending on the pH value and ladder inconsistencies. The minimisation uncertainty is negligible or responsible for up to 87% of the measurement uncertainty. The TSM quantified measurement uncertainties on average only 0.05 units larger than the MCM estimated ones. Additional experimental tests should be performed to test these uncertainty models for analysis performed in other laboratories and on non-aqueous solutions.

Keywords: Unified pH scale, differential potentiometry, validation, uncertainty, Monte Carlo Method.

1. Introduction

Hydrogen ions (protons), H^+, play an important role in virtually all material related processes and the pH of solutions. Referring to the activity of the solvated proton [1], pH is probably the most prominent, widely used chemical concept [2,3], thus building interdisciplinary bridges. Accurate measurement of pH values is a highly important task in a wide variety of media in which processes occur, *i.e.,* water or solvents other than water, solvent mixtures, and dispersions, playing a crucial role in understanding and control of important processes in fundamental chemistry, industry and living organisms, including catalysis [4,5], extraction [6], chromatography [7,8], etc.

However, the conventional pH scale is rigorously defined and well established only in dilute aqueous solutions at medium pH values [2]. It has serious limitations – often being unusable – in other solvents or more complex media where most real-life chemistry takes place. Most importantly, comparing the conventional pH values between different media (solvents) is impossible because they have their own pH scales [9].

In view of these problems, a decade ago, the concept of a unified pH scale was put forward [9], defining unified pH ($\mathrm{pH_{abs}}$) via the absolute chemical potential of the solvated proton and using a universal standard state – proton gas at 1 bar with $\mathrm{pH_{abs}} = 0$ by definition. For easier comparability, the $\mathrm{pH_{abs}}$ scale has been "aligned" with the aqueous pH scale, creating the so-called $\mathrm{pH_{abs}^{H_2O}}$ scale [8]. Any medium or solution with $\mathrm{pH_{abs}^{H_2O}}$ 7.00 has the same thermodynamic activity of the solvated proton as an aqueous solution with conventional pH 7.00. Thus, in a dilute aqueous solution the pH and $\mathrm{pH_{abs}^{H_2O}}$ are equal by definition. This conveniently preserves the common way of expressing, and interpreting, pH values while still being related to the universal standard state. The key merit of $\mathrm{pH_{abs}}$ is its strict thermodynamic foundation enabling direct comparability of $\mathrm{pH_{abs}}$ values from different solvents.

Following the theoretical conception of $\mathrm{pH_{abs}}$, the first measurement method of $\mathrm{pH_{abs}^{H_2O}}$ in different solvents and their mixtures was established [8]. Since then, a network of European laboratories has invested in developing fundamental and practical aspects, aiming to improve data quality [10]. The method is based on differential potentiometry [11], and its essence is measuring $\Delta\mathrm{pH_{abs}^{H_2O}}$ values within a set of solutions, which can be prepared in different solvents. When there are reference solutions (e.g. standard aqueous pH buffers) included in the set of solutions tested, the $\mathrm{pH_{abs}^{H_2O}}$ values can be found for all the solutions in the set [10].

The differential potentiometric measurement method is affected by numerous factors and the correct estimation of the uncertainty of the obtained $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values is required for its use. Until now, the reliability of $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values have mostly been estimated using simplistic approaches [10].

This work aims at an in-depth and “bottom-up” [12,13] uncertainty analysis of differential potentiometric method measurement results.

After describing the measurement equation, the uncertainty components are quantified and combined using a first-order Taylor series approximation method, TSM, and the numerical Monte Carlo method, MCM [14,15]. The application of the TSM involves additional simplification of the measurement model but has the advantage of not requiring computational resources for measurement uncertainty simulation [16].

2. Experimental

2.1. Materials

Triethylpentylammonium bis(trifluoromethanesulfonyl)imide $[N_{2225}][NTf_2]$ (Iolitec GmbH, Heilbronn, Germany) was used as salt bridge electrolyte. Standard aqueous pH buffers with pH 2.00, 4.00, 7.00, and 10.00, traceable to the SI (Hydrion, Micro Essential Laboratory) and with expanded uncertainty of 0.02 ($k = 2$ for 95% confidence level) were used as pH reference solutions. Metal solid contact glass electrodes EST-0601 (Izmeritelnaya tekhnika, Moscow, Russia) were used as pH sensing probes. Measurements were done with a Metrohm 713 pH Meter and were thermostated at (25.0 ± 1.0) °C ($k = 2$ for 95% confidence level) (thermostat type U2c, MLW, Germany). The glass cell was produced by Gebr. Rettberg GmbH (Göttingen, Germany). Glass electrodes were calibrated against a saturated calomel reference electrode

(Radiometer K401). Glass cell and electrodes were placed in a Gamry VistaShield™ Faraday cage.

2.2. Analytical method

The difference in potential (ΔE_m) between two glass electrodes is measured in the following differential potentiometry cell [17]:

Glass electrode 2 | Solution 2 | $[N_{2225}][NTf_2]$ | Solution 1 | Glass electrode 1

A schematic representation of the method is given in Figure 1. The cell has two compartments connected by a capillary tube filled with an ionic liquid, $[N_{2225}][NTf_2]$ in this case, thus establishing a salt bridge between the two solutions, 1 and 2. Although the measured potential difference incorporates liquid junction potentials at both junctions, the use of this ionic liquid is assumed to cancel out the residual liquid junction potential contribution [17,18], [19]. This is the reason why no correction is made to the measured potential.

The potential of a glass electrode is linked to pH via the Nernst equation. Thus, the potential difference between two glass electrodes gives the pH difference between the two solutions. The slope of the Nernst equation is used to convert the measured potential into pH in order to obtain ΔpH, which is by definition equal to $\Delta\mathrm{pH}_\mathrm{abs}^{\mathrm{H_2O}}$. Intercept and slope are measured separately for each glass electrode. For the regression parameters' determination, each glass electrode's potential is measured in several standard aqueous pH buffers of known pH against a reference electrode [20].

The $\mathrm{pH}_\mathrm{abs}^{\mathrm{H_2O}}$ values are calculated by applying a least-squares minimization technique to the entire set of measured $\Delta\mathrm{pH}_\mathrm{abs}^{\mathrm{H_2O}}$ values. This is called the "ladder" approach. Adding a new sample pair, made from the same or different solvents depending on the samples, to the set is more useful than repeating a measurement since it results in an overdetermined system, which improves the results of the least-squares minimization. A detailed example of this type of calculation has been published previously [10].

2.3. Measurement uncertainty evaluation

2.3.1. Definition of the measurand

The measurand [21], the quantity intended to be measured in the studied solution, is the value of $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$, referenced to the pH of aqueous solutions determined by the primary reference method (Harned cell) [2].

2.3.2. Measurement model

$\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ can be determined from a single differential potentiometric measurement or a ladder, as mentioned above. A ladder of differential potentiometric measurements allows the determination of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of a single solution by using various reference pH buffers or the determination of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of different solutions referenced to one, or several, reference pH buffers.

2.3.2.1. Single differential potentiometry

If the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of a solution S, $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S})$, is determined by a single differential potentiometric measurement of the studied solution vs. a reference pH solution, $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S_{Ref}})$, the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S})$ is calculated by Eq. (1).

$$\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}) = \frac{\Delta E_m - \Delta E_{\mathrm{LJ}} - E_{K\mathrm{R}} - k_{\mathrm{R}}{}'T\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S_{Ref}}) + E_{K\mathrm{S}}}{-k_{\mathrm{S}}{}'T} \quad (1)$$

where ΔE_m is the measured potential difference (mV), ΔE_{LJ} the residual liquid junction potential (mV), $E_{k\mathrm{R}}$ and $E_{k\mathrm{S}}$ are the practical Nernst intercepts of indicator electrodes used for the reference and unknown solutions, respectively (temperature-independent) (mV), $k_R{}'$ and $k_{\mathrm{S}}{}'$ are the practical Nernst slopes of electrodes per absolute temperature unit (mV K^{-1}), and T is the absolute temperature (K).

The $k_{\mathrm{R}}{}'$ and $k_{\mathrm{S}}{}'$ (mV K^{-1}) are determined by dividing the practical Nernst slopes, k_{R} and k_{S} (mV), by *T*.

The $E_{k\mathrm{R}}$, $E_{k\mathrm{S}}$, k_{R}, and k_{S} values are estimated by calibrating the indicator electrode vs. a reference saturated calomel electrode, in aqueous pH buffers with pH values traceable to the SI.

Assuming the same measurement temperature, with negligible uncertainty, is achieved during the estimation of k_{R} and k_{S} and in the differential potentiometry measurement, and that k_{R} and k_{S} are equivalent (this is achieved by choosing electrodes with slope values which are as close as possible), Eq. (1) can be simplified in Eq. (2):

$$\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(S) = -2\frac{\Delta E_m - \Delta E_{\mathrm{LJ}} - E_{K\mathrm{S}} + E_{K\mathrm{R}}}{k_{\mathrm{S}} + k_{\mathrm{R}}} + \mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S_{Ref}}) \quad (2)$$

This equation is obtained by cancelling the ratio ($k_{\mathrm{R}}'T/k_{\mathrm{S}}{}'T \cong 1$) and changing the denominator ($k_{\mathrm{S}} = k_{\mathrm{S}}{}'T$) of Eq.(1) by the mean slope of both electrodes ($(k_{\mathrm{S}} + k_{\mathrm{R}})/2$). Equation 1 is used, instead of Eq.(2), in this work.

2.3.2.2. Ladder of differential potentiometry measurements

The determination of $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of a solution from a ladder of differential potentiometry measurements involves selecting the analysed unknown solutions and reference pH buffers and determining the potentials, ΔE_m, from cells built from several possible combinations of these solutions. It is essential to take care that the pH difference between any two solutions in the ladder is obtainable by at least two independent pathways of measurements – two ‘steps’ on the measurement “ladder”.

Each ΔE_m allows the calculation of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ difference, $\Delta\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i,\mathrm{S}_j)$, of the studied solutions (S_i and S_j) normalised for electrode sensitivity and test temperature, *T*. Equation 3, derived from Eq. (1), presents the relevant formula for this calculation.

$$\Delta\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i,\mathrm{S}_j)=\frac{\Delta E_m-\Delta E_{\mathrm{LJ}}-E_{Ki}+E_{Kj}}{Tk'}=\frac{k_i{}'}{k'}\mathrm{pH}_{\mathrm{abs}}(\mathrm{S}_i)-\frac{k_j{}'}{k'}\mathrm{pH}_{\mathrm{abs}}(\mathrm{S}_j)\tag{3}$$

where indices *i* and *j* identify the solutions and the parameters that quantify used electrodes’ performance (E_{Ki}, E_{Kj}, $k_i{}'$, and $k_j{}'$). k' is the conventional Nernst slope for a given *T*, used as a constant without uncertainty. The k' is only used to make $\Delta\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i,\mathrm{S}_j)$ similar to ($\Delta\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i,\mathrm{S}_j)=\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)-\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_j)$).

After determining the $\Delta\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i,\mathrm{S}_j)$ of all differential potentiometric measurements, initial estimates of $\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)$ of each unknown solution $\left(\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)=(k_i{}'/k')\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)\right)$ are obtained by treating the respective differential potentiometric measurement against a reference pH buffer (Eq.(4)).

$$\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)=\frac{k_i{}'}{k'}\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)=\frac{\Delta E_m-\Delta E_{\mathrm{LJ}}-E_{Ki}+E_{Kj}+k_j{}'T\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_{\mathrm{Ref}})}{Tk'}\tag{4}$$

The initially estimated $\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)$ values of unknown solutions are randomly changed by adding a positive or negative increment and the sum of the square of the differences, *SSD*, ($\Delta\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i,\mathrm{S}_j)-(\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)_{\#h}-\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_j)_{\#h}$)) is used to quantify the success of the first iteration of $\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values calculated (Eq. (5), where the *h*th iteration, #*h* , is equal to #1).

$$SSD = \sum_{i=1}^{n} \sum_{j \neq i=1}^{n} \left[\Delta \check{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i, \mathrm{S}_j) - (\check{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)_{\#h} - \check{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_j)_{\#h}) \right]^2 \tag{5}$$

If the *SSD* from the first iteration is lower or higher than the *SSD* from the original data ($\#h$ = #0 in Eq. (5)), the following iteration will be based on the new (#1) or previous (#0) set of $\check{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)_{\#h}$. This process is performed 109 times in the developed computational tool, where the first increments are randomly generated values with a normal distribution, with zero mean and a standard deviation of 5×10^{-3}. For each new iteration, the standard deviation of the increment model reduces by 2×10^{-5} units. Ideally, the final *SSD* should be below 0.01. However, minimisation efficiency depends on input data consistency.

After the minimisation process, the adjusted $\check{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)$ values are extracted and converted into $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)$ by multiplying by (k'/k_i'). This numerical process should allow minimisation of the impact of some systematic and random effects on $\check{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_j)$ values.

If the same assumptions as the simplified Eq. (2) are valid, Eq.(6) can be used to estimate $\Delta\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i, \mathrm{S}_j)$:

$$\Delta\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i, \mathrm{S}_j) = \mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i) - \mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_j) = 2\,\frac{\Delta E_m - \Delta E_{\mathrm{LJ}} - E_{K\mathrm{S}} + E_{K\mathrm{R}}}{k_{\mathrm{S}} + k_{\mathrm{R}}} \tag{6}$$

In this work, the determination of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of three unknown solutions, referenced to the same reference pH buffer, is investigated. The same pair of electrodes is used in all differential potentiometric measurements. This ladder design, represented in Figure 2, involves performing six differential potentiometric measurements.

The iterative minimisation can be performed in an MS-Excel spreadsheet using the “Solver” Add-in, or by implementing the same process independently from that software tool.

It is worth noting that it is not possible to define a closed mathematical expression for the determination of the estimated $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of unknown solutions from a ladder of differential potentiometry measurements.

2.3.3. Identification of the uncertainty components

2.3.3.1. Single differential potentiometry

Figure 3 presents the graphical representation of the sources of uncertainty involved in the determination of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of a solution from a single differential potentiometry against a reference solution (Eq.(1)).

In this case, all uncertainty sources are represented by an input quantity in Eq.(1).

2.3.3.2. Ladder of differential potentiometry measurements

Figure 4 presents the cause-and-effect diagram of uncertainty sources for the determination of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of three unknown solutions through a ladder of six differential potentiometry measurements (A to F), anchored to one pH reference, and built from the same pair of indicator electrodes (electrodes 1 and 2). The uncertainty components are associated with all input variables arising from the application of Eq.(3) to the various differential potentiometry measurements, plus a component for the minimisation process (M). Since the same pair of electrodes is used, some correlation between estimated ΔE_m values is expected. If the E_{K1}, E_{K2}, $k_1{}'$, and $k_2{}'$ are estimated from electrode calibration using the same buffer solutions, some correlation between these regression parameters will also occur.

If more indicator electrodes are used, more practical Nernst intercepts and slopes should be considered. If another reference solution substitutes some unknown solutions, then the model inputs need to be changed.

2.3.4. Quantification of the uncertainty components

The uncertainty associated with the characterisation of indicator electrodes' response, represented by variables E_{Ki} and k_i, and due to inconsistency of measurements, represented by the variable M, were quantified differently depending on the approach used for uncertainty evaluation.

For uncertainty components quantified by the Monte Carlo Method (MCM), the uncertainties of E_{Ki} and k_i were determined by simulating the impact of the reference values' uncertainty and signal precision on the estimation of these regression parameters [22,23]. In cases where, during characterisation of a specific indicator electrode, statistically relevant deviations from linear behaviour of measured potential versus reference pH are observed, the signal precision is decreased by simulation until the signal model is adequately described by a linear function. This strategy allows the description of electrode performance with highly precise signals of only three reference buffer solutions.

The uncertainty introduced by the interactive minimisation process was evaluated by the Monte Carlo simulation of 10^4 iteration processes, based on 10^4 sets of all simulated input quantities, to determine the various $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values.

The NIST Uncertainty Machine [24] was not used in MCM simulations because no closed mathematical expression can determine $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values based on a ladder of various differential potentiometric measurements.

When uncertainty components are combined by the TSM, the E_{Ki} and k_i are quantified by the regression model and M from the maximum difference between experimentally observed and estimated $\widetilde{\Delta\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i,\mathrm{S}_j)$ values after the minimisation: the maximum minimisation discrepancy, *MMD*. Equations 7 and 8 present the estimated standard deviations of E_{Ki}, $s(E_{Ki})$, and k_i, $s(k_i)$, determined by the ordinary linear least-squares method (OLS). The OLS assumes the linear variation of potential with the reference pH, potential homoscedasticity, and negligible uncertainty of the reference pH values given signal precision [25]. These assumptions should be tested by using adequate tools [26,27].

$$s(E_{Ki}) = s_{\mathrm{RS}}\sqrt{\frac{\sum_{g=1}^{N}\mathrm{pH}(\mathrm{Ref}_g)^2}{n\sum_{g=1}^{N}\left(\mathrm{pH}(\mathrm{Ref}_g)-\overline{\mathrm{pH}}(\mathrm{Ref})\right)^2}} \tag{7}$$

$$s(k_i) = \frac{s_{\mathrm{RS}}}{\sqrt{\sum_{i=1}^{N}\left(\mathrm{pH}(\mathrm{Ref}_g)-\overline{\mathrm{pH}}(\mathrm{Ref})\right)^2}} \tag{8}$$

where s_{RS} is the residual standard deviation of the regression, $\mathrm{pH}(\mathrm{Ref}_g)$ is the value of the g^{th} reference buffer used to calibrate the electrode (g = 1 to n), and $\overline{\mathrm{pH}}(\mathrm{Ref}) = \sum \mathrm{pH}(\mathrm{Ref}_g)/n$. The s_{RS} is estimated by Eq. (9).

$$s_{\mathrm{RS}} = \sqrt{\frac{\sum_{g=1}^{n}\sum_{h=1}^{m}\left(\Delta E_{gh}-\widehat{\Delta E}_g\right)^2}{nm-2}} \tag{9}$$

where ΔE_{gh} is the h^{th} replicate potential collected for the g^{th} reference buffer (m replicates are collected for each reference buffer), and $\widehat{\Delta E}_g = E_{Ki} + k_i\mathrm{pH}(\mathrm{Ref}_g)$.

The E_{Ki} and k_i are correlated with a covariance, $\mathrm{cov}(E_{Ki}, k_i)$, estimated by Eq. (10) [28].

$$\mathrm{cov}(E_{Ki}, k_i) = \frac{-\overline{\mathrm{pH}}(\mathrm{Ref})\cdot s_{\mathrm{RS}}^2}{\sum_{g=1}^{n}\left(\mathrm{pH}(\mathrm{Ref}_g)-\overline{\mathrm{pH}}(\mathrm{Ref})\right)^2} \tag{10}$$

Differences between MCM and TSM uncertainty evaluations can be observed if the linearity assumption of the TSM is not valid and if pragmatic models are used to overvalue the uncertainties from E_i, k_i, and M.

According to Radtke et al. [19], in the case of the [N_{2225}][NTf_2] ionic liquid, the ΔE_{LJ} is 0 mV with a standard uncertainty, $u(\Delta E_{\mathrm{LJ}})$, of 6.3 mV for juntions between different solvents with very different properties (e.g. water, acetonitrile and N,N-dimethylformamide). This allows for cells built from solutions with different solvents to be measured by differential potentiometry. If cells contain low ionic strength solutions of the same solvent, then in case of using [N_{2225}][NTf_2], a much a lower $u(\Delta E_{\mathrm{LJ}})$, ideally close to zero, is expected. In this work, measurement uncertainty is evaluated with two scenarios: assuming that ΔE_{LJ} has an expanded uncertainty, $U(\Delta E_{\mathrm{LJ}})$, of 0 mV or 6.3 mV (standard uncertainties of 0 mV or 3.6 mV $= 6.3/\sqrt{3}$ for a rectangular distribution). This is done in order to better understand if this uncertainty component is negligible, or to what extent it is compensated through the minimisation of $\widetilde{\mathrm{pH}}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)$ deviation in the ladder.

Table 1 summarises how the uncertainty components were quantified, the range of these variables, and their respective standard uncertainties. These values were collected from various differential potentiometric measurements performed in one laboratory. Therefore, other values and standard uncertainties may be observed under other operational conditions and analysis of other solutions.

2.3.5. Combination and expansion of the uncertainty

The MCM combination of the uncertainty components produces simulated $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S})$ values whose distribution can be described by a kernel density plot. Alternatively, these can be described by a pair of percentiles that define the limits of confidence intervals for the measurand at a defined confidence level. For instance, the 2.5th and 97.5th percentiles represent the limits for a 95% confidence interval. Figure 5 presents the simulated $\mathrm{pH}_{\mathrm{abs}}(S)$ values of a solution determined from a ladder of differential potentiometry measurements. The simulated distribution of the measurement results has a weak asymmetry quantified by a Person's second skewness coefficient of 0.094 [29].

The spreadsheets used for the MCM simulation of $\mathrm{pH_{abs}}(S)$ are made available as Electronic Supplementary material (EMS1). Simulations are performed using macros that run a group of three spreadsheets. The File "A_Input_DATA.xlsm" includes a sheet with the instructions.

The TSM was applied to the simplified determination of $\mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)$ from a single differential potentiometry measurement, referenced to $\mathrm{pH_{abs}^{H_2O}}(\mathrm{S_{Ref}})$ using Eq.(2), where $\mathrm{pH_{abs}^{H_2O}}(\mathrm{S})$ is changed for $\mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)$. The standard uncertainty of $\mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)$, $u\left(\mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)\right)$, is estimated by Eq.(11).

$$u\left(\mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)\right) = \sqrt{\begin{array}{c} \left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial \Delta E_m}\right)^2 u(\Delta E_m)^2 + \left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial \Delta E_{\mathrm{LJ}}}\right)^2 u\left(\Delta E_{\mathrm{LJ}}\right)^2 \\ + \left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial E_{K\mathrm{S}}}\right)^2 u(E_{K\mathrm{S}})^2 + \left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial E_{K\mathrm{R}}}\right)^2 u(E_{K\mathrm{R}})^2 + \\ \left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial k_{\mathrm{S}}}\right)^2 u(k_{\mathrm{S}})^2 + \left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial k_{\mathrm{R}}}\right)^2 u(k_{\mathrm{R}})^2 + \\ \left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S_{Ref}})}\right)^2 u\left(\mathrm{pH_{abs}^{H_2O}}(\mathrm{S_{Ref}})\right)^2 + \\ 2\left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial E_{K\mathrm{S}}}\right)\left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial k_{\mathrm{S}}}\right)\mathrm{cov}(E_{K\mathrm{S}}, k_{\mathrm{S}}) + \\ 2\left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial E_{K\mathrm{R}}}\right)\left(\frac{\partial \mathrm{pH_{abs}^{H_2O}}(\mathrm{S}_i)}{\partial k_{\mathrm{R}}}\right)\mathrm{cov}(E_{K\mathrm{R}}, k_{\mathrm{R}}) \end{array}} \quad (11)$$

where $(\partial y/\partial x)$ is the partial derivative of y with respect to x. Equation 12 presents Eq.(11) after solving the partial derivatives.

$$u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)\right) = \sqrt{\begin{gathered}\left(\frac{2}{k_\mathrm{S}+k_\mathrm{R}}\right)^2\left(u(\Delta E_m)^2+u\left(\Delta E_\mathrm{LJ}\right)^2+u(E_{K\mathrm{S}})^2+u(E_{K\mathrm{R}})^2\right)+\\ u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_\mathrm{Ref})\right)^2+\\ \left(\frac{\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_\mathrm{Ref})-\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)}{k_\mathrm{S}+k_\mathrm{R}}\right)^2\left(u(k_\mathrm{S})^2+u(k_\mathrm{R})^2\right)+\\ 4\left(\frac{\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_\mathrm{Ref})-\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)}{(k_\mathrm{S}+k_\mathrm{R})^2}\right)\left(\mathrm{cov}(E_{K\mathrm{R}},k_\mathrm{R})-\mathrm{cov}(E_{K\mathrm{S}},k_\mathrm{S})\right)\end{gathered}} \tag{12}$$

If the input variables are associated with a high number of degrees of freedom, $u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)\right)$ can be expanded to approximately 95% or 99% confidence level by using a coverage factor, k, equal to 2 or 3, respectively ($U\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)\right) = k\cdot u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)\right)$).

For the determination of a $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)$ value from a ladder of differential potentiometry measurements, $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)^{\boxed{\mathrm{L}}}$, the $u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)^{\boxed{\mathrm{L}}}\right)$ is estimated by considering each single differential potentiometry measurement referenced to the farthest reference pH, $u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)^{\leftrightarrow}\right)$ (greatest difference between values), and an additional uncertainty component due to the minimisation process, $MMD/\sqrt{3}$.

$$u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)^{\boxed{\mathrm{L}}}\right) = \sqrt{u\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)^{\leftrightarrow}\right)^2+\left(\frac{MMD}{\sqrt{3}}\right)^2} \tag{13}$$

The expanded uncertainty, $U\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)^{\boxed{\mathrm{L}}}\right)$, is estimated equivalently to $U\left(\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}(\mathrm{S}_i)\right)$.

The spreadsheet used for TSM evaluations is made available as Electronic Supplementary Material (ESM2) and includes a sheet with instructions.

3. Results

3.1. Validation of uncertainty evaluation

The evaluated uncertainty was assessed experimentally by composing differential potentiometry ladders of four reference pH buffers, where one of the buffers was defined as the reference for the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ determination of the remaining three solutions. The uncertainty evaluation is successful if the three estimated and reference pH values are metrologically compatible (i.e., in agreement) with a success rate consistent with the test confidence level. For 95% and 99% confidence level tests, one in 20 or 100 compatibility tests are expected to fail in each case. These compatibility tests were performed using data collected from one laboratory.

table and 3 present estimated $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values of various reference aqueous pH buffers analysed as unknown solutions in a ladder referenced to another aqueous pH buffer, where uncertainty was determined for the 95% confidence level by the MCM and TSM, respectively. These tables additionally report the difference between estimated and reference values of the solutions for the same confidence level. When zero is included in the difference interval, this indicates the metrological compatibility between estimated and reference values for the defined confidence level. Each table presents results assuming a $U(\Delta E_{\mathrm{LJ}})$ equal to either 0 mV or 6.3 mV.

For MCM or TSM, on average, the uncertainty increases by 0.0076 or 0.0052 pH when $U(\Delta E_{\mathrm{LJ}})$ increases. Interestingly, for MCM uncertainty evaluations of a ladder referenced to pH 2.00, the measurement uncertainty is reduced by increasing $U(\Delta E_{\mathrm{LJ}})$. This difference is explained by the low contribution of this uncertainty component, as well as the variability of the uncertainty determined by the MCM from 100,000 simulations.

The MCM estimates expanded uncertainties between 0.26 and 0.51, and the TSM between 0.32 and 0.58. The uncertainty increases as the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of the analysed solution increases.

On average, the TSM quantifies uncertainties 0.05 pH greater than the MCM ones. However, in 5 of the 24 performed measurements, the TSM quantifies lower uncertainties. The difference between the uncertainty values quantified by the two approaches is not relevant given the variability of the uncertainty evaluation process and MCM simulation. Paragraph E.4.3 of the "Guide to the expression of uncertainty in measurement" discusses the "uncertainty of the uncertainty" that should be considered in this type of comparison [14]. For instance, two estimates of the same expanded uncertainty associated with 50 degrees of freedom can differ up to 1.45 times for a 99 % confidence level.

Therefore, according to the collected information, it is possible to distinguish relative differences between the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of two solutions of about 0.55 ($3\sqrt{2}(0.26/2)$) at the 99% confidence level [30].

More importantly, regardless of the approach used and the uncertainty of liquid junction potential considered, all estimated and reference values are metrologically compatible at a 95% confidence level. Since 24 compatibility tests were performed by each uncertainty evaluation approach, one failure of the compatibility test was expected due to the 5% probability of results mismatch. Therefore, the experimental data proves ΔE_{LJ} is a minor uncertainty source, at least for the analysis of aqueous solutions with low ionic strength.

The simplified TSM evaluations do not significantly overvalue the uncertainty due to the pragmatism in the quantification of the minimization process uncertainty.

Nevertheless, it should be noted that the number of performed tests does not allow a definitive assessment of both models, although results are so far very promising.

It is possible to learn more about how uncertainty is evaluated by calculating the percentage contributions of the uncertainty components.

However, the non-linearity of some $\mathrm{pH}_{\mathrm{abs}}$ determinations with input values uncertainty makes the assessment of the contribution of some uncertainty components by the MCM inaccurate. If the contributions of the uncertainty of components combined by the MCM are estimated by the numerical determination of sensitivity coefficients by the slope between simulated output

(pH_{abs}) and input variables, it can be concluded that the contribution of the minimisation to the uncertainty ranges from 87% to less than 0.5% [23]. The variable relevance of the contribution of uncertainty components is a complex function of the closeness of reference and estimated $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values, and ladder inconsistencies, challenging to predict.

The other more relevant uncertainty contributions come from the intercept and slope of the calibration of the used electrodes that can have a negligible contribution or a contribution up to 50%. For cases where the $U(\Delta E_{\mathrm{LJ}})$ is 6.3 mV, this uncertainty contributes between 0.1 % to 20 % depending on the magnitude of the other uncertainty components. When the ladder is not affected by relevant inconsistencies, the remaining uncertainty components prevail.

The TSM reports uncertainties with less than 1.1 % arising from the minimisation process. Generally, the correlation between the intercept and slope from electrodes calibration could be a relevant contribution that either increases or decreases the uncertainty of measured $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values. Nevertheless, the simplified evaluation method calculates uncertainty values similar to those obtained by the complex MCM.

While the performance of the developed uncertainty evaluation methods observed so far is promising, further application to a variety of aqueous and non-aqueous solutions is expected to bring in more results in support of their applicability.

4. Conclusions

The detailed assessment of the determination of $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ from a ladder of differential potentiometry allowed the bottom-up evaluation of the uncertainty of these measurements. Uncertainty components were combined by the Monte Carlo Method (MCM), allowing taking relevant correlations between input variables into account. The iterative reduction of ladder deviations was also simulated. The MCM ability to assess non-linear functions also guarantees the quality of uncertainty evaluations. The minimisation of ladder deviation is responsible for negligible or up to 87 % of the uncertainty of performed measurements, depending on ladder inconsistencies. The uncertainty associated with Liquid Junction Potential is negligible for ladders of aqueous solutions.

The bottom-up uncertainty evaluation was successfully applied to the determination of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of aqueous buffers with a pH of 2.00, 4.00, 7.00 and 10.00, with a standard uncertainty of 0.01, referenced to a pH buffer with a value different from the unknown solutions of the ladder. The 24 estimated and reference values are metrologically compatible at 95 % confidence level. This approach determined expanded uncertainties, for a 95 % confidence level, between 0.26 and 0.51.

The simplified evaluation of the measurement uncertainty, based on the combination of uncertainty components by the Taylor Series Approximation and the observed maximum deviation on the ladder, also produced results compatible with the reference values. The expanded uncertainties calculated with the simplified approach are between 0.32 and 0.58, on average, 0.051 higher than MCM determinations.

The use of the developed uncertainty evaluation methods will enable further critical assessment.

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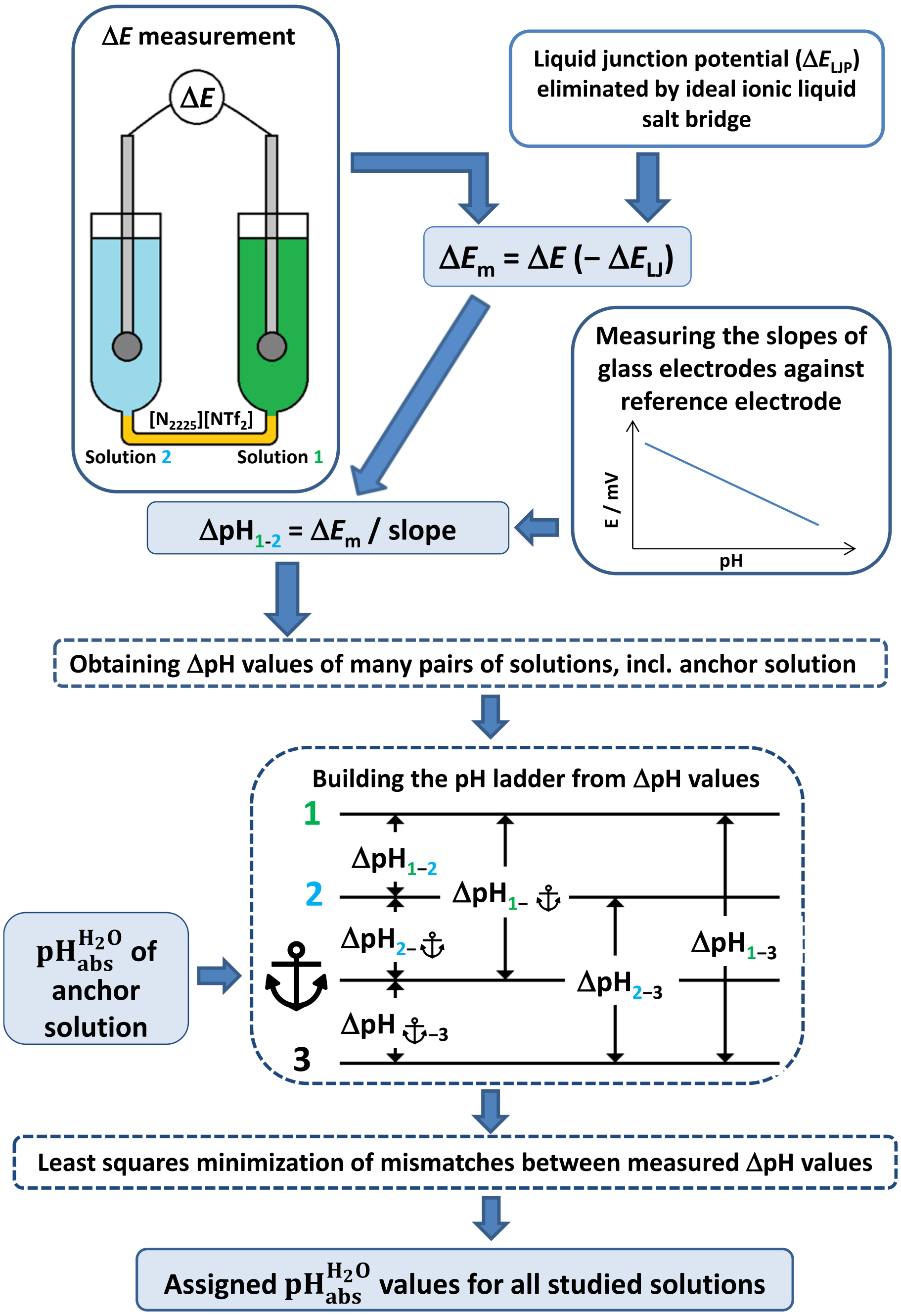

Figure 1. The scheme of the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ measurement procedure.

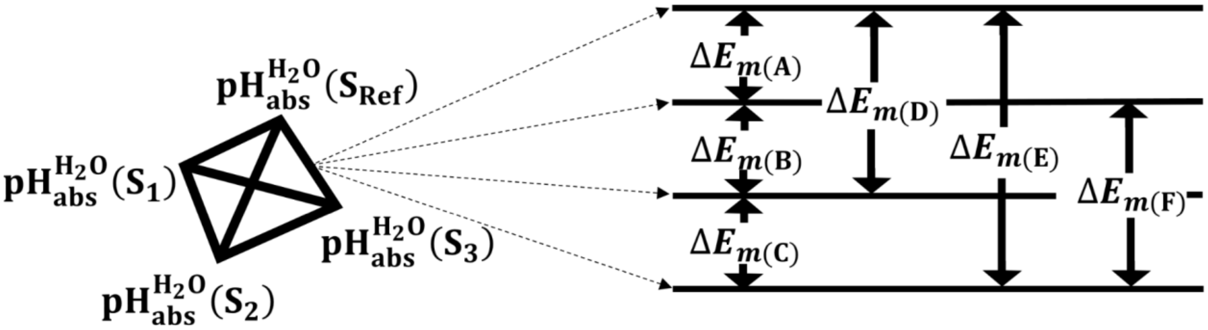

Figure 2. Ladder of differential potentiometry for determining the $pH_{abs}^{H_2O}$ of three unknown solutions (S1, S2 and S3) referenced to one reference solution (S_{Ref}). The $\Delta E_{m(x)}$ represent the potential of cells built from all solutions combination (S_i vs S_j; where $i \neq j$ =1, 2, 3 or Ref).

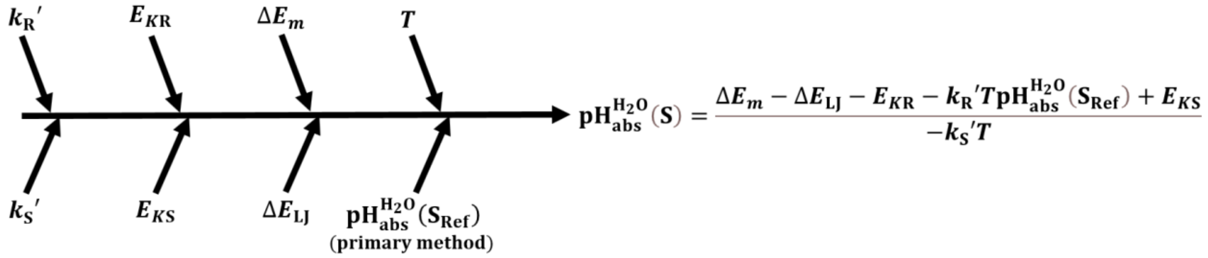

Figure 3. Cause and effect diagram of uncertainty sources involved in the determination of the pH_{abs} of a solution from a single differential potentiometric measurement (Eq.(1)).

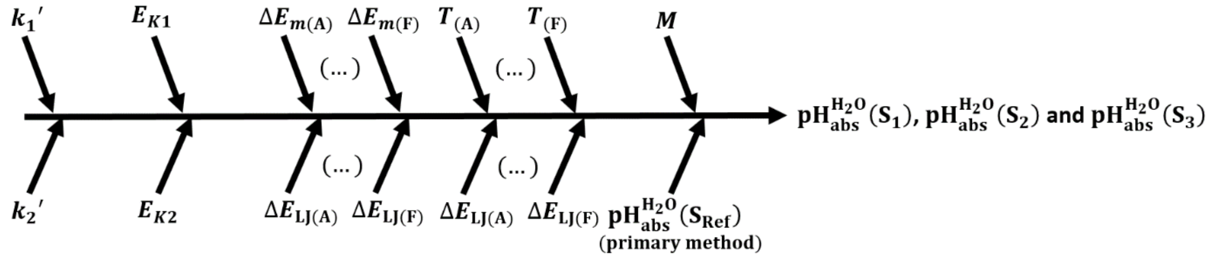

Figure 4. Cause and effect diagram of uncertainty sources for the determination of the $pH_{abs}^{H_2O}$ of three unknown solutions, $pH_{abs}(S1)$, $pH_{abs}(S2)$ and $pH_{abs}(S3)$, through a ladder of six differential potentiometric measurements anchored to one pH reference, $pH_{abs}(S_{Ref})$, and built from the same pair of indicator electrodes (electrodes 1 and 2). *M* represents the minimisation process component.

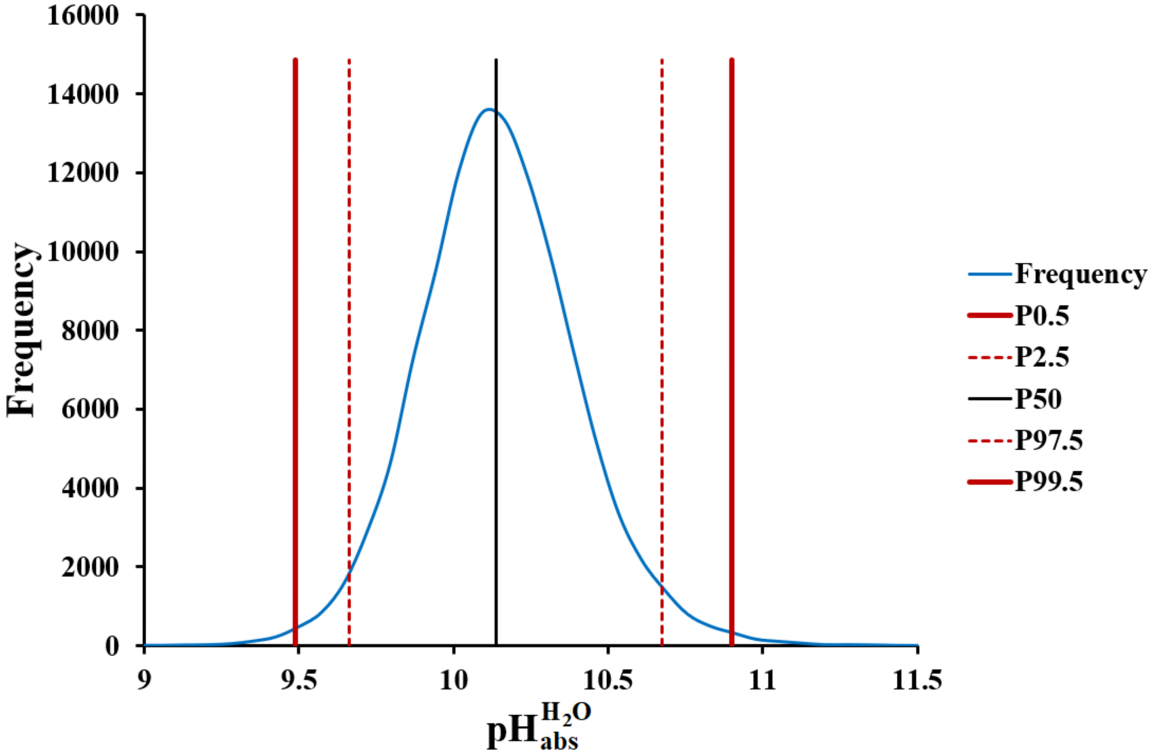

Figure 5. Example of a kernel density plot of simulated $pH_{abs}^{H_2O}$ by the developed MCM using 10^5 simulations (ten times more than the default output of ESM1). Px represents the *X*th percentile of simulated values. Simulated measurement of a pH 10.00 ± 0.02 (*k* =2; c.l. of 95%) reference buffer determined from a ladder with a reference value of pH 2.00 ± 0.02 (*k* =2; c.l. of 95 %). Simulated measurement results with a Person's second skewness coefficient of 0.094, indicating a week skewness, and P2.5 and P97.5 of 9.66 and 10.67, respectively. Assuming distribution asymmetry, the result would be (10.15 ± 0.51) for a 95 % confidence level.

Table 1. List of input variables or other contributions to the measurement uncertainty, uncertainty evaluation methods, and range of variable values and respective standard uncertainty, u.

Input variable	Uncertainty evaluation method	Unit	Distribution type	Range of values	Range of u or U
ΔE_m	Standard deviation of single or mean potential differences	mV	Scaled and shifted t-distribution	121.34 to 480.92	0.13 to 0.42 (u)
ΔE_{LJ}	Type B evaluation	mV	Rectangular	0	0 and 6.3 § (U)
E_{Ki}	MCM: simulation of electrode calibration TSM: Ordinary linear least-squares regression	mV	Simulated or modelled	MCM: 1154 and 1156.8 TSM: 1152.9 and 1154	MCM: 3.9 and 12 (u) TSM: 4.6 and 11 (u)
k_i	MCM: simulation of electrode calibration TSM: Ordinary linear least-squares regression	mV^{-1}	Simulated or modelled	MCM: -58.9 and -59.27 TSM: -58.36 and -58.9	MSM: 0.62 and 3.4 (u) TSM: 0.60 and 1.4 (u)
$\mathrm{pH}(S_{\mathrm{Ref}})$	Certified value	-	Normal	2 to 10	0.01 (u)
T	Combination of Type A and B components by TSM	K	Normal	298.15	0.5 (u)
M	MCM: average *MMD* estimated from the *SSD* TSM: *MMD*	-	Simulated or modelled	MCM: 0 TSM: 0	MCM: 0.033 to 0.41 TSM: 0.029 (U)

MCM – Monte Carlo Method
TSM – first-order Taylor series approximation
u or U – Standard or expanded uncertainty
MMD – Maximum minimisation discrepancy
SSD – Sum of the square of the differences
§ – Tested values

Table 2. Measurement results of $pH_{abs}^{H_2O}$ of four reference aqueous buffers determined from ladders of differential potentiometry referenced to another pH buffer. It is reported the difference between measured and reference values with uncertainty required to assess the compatibility between both estimates. The measurement uncertainty was evaluated by combining relevant uncertainty components by the Monte Carlo Method, assuming liquid junction potential has an expanded uncertainty, $U(\Delta E_{LJ})$, of 0 mV or 6.3 mV.

$U(\Delta E_{LJ})$/mV	0	
Ladder reference §	Measurement result §	Difference between measurement and reference result §
2.00 ± 0.02	4.07 ± 0.36	0.07 ± 0.36
	7.12 ± 0.43	0.12 ± 0.43
	10.15 ± 0.51	0.15 ± 0.51
4.00 ± 0.02	1.98 ± 0.27	-0.02 ± 0.27
	7.06 ± 0.38	0.06 ± 0.38
	10.08 ± 0.32	0.08 ± 0.32
7.00 ± 0.02	1.97 ± 0.26	-0.03 ± 0.26
	4.04 ± 0.32	0.04 ± 0.32
	10.08 ± 0.44	0.08 ± 0.44
10.00 ± 0.02	1.96 ± 0.29	-0.04 ± 0.29
	4.04 ± 0.40	0.04 ± 0.40
	7.08 ± 0.43	0.08 ± 0.43
$U(\Delta E_{LJ})$/mV	6.3	
2.00 ± 0.02	4.06 ± 0.33	0.06 ± 0.33
	7.11 ± 0.39	0.11 ± 0.39
	10.14 ± 0.45	0.14 ± 0.46
4.00 ± 0.02	1.98 ± 0.30	-0.02 ± 0.30
	7.06 ± 0.40	0.06 ± 0.40
	10.08 ± 0.33	0.08 ± 0.33
7.00 ± 0.02	1.93 ± 0.31	-0.07 ± 0.31
	4.01 ± 0.37	0.01 ± 0.37
	10.08 ± 0.50	0.08 ± 0.50
10.00 ± 0.02	1.96 ± 0.34	-0.04 ± 0.34
	4.05 ± 0.45	0.05 ± 0.45
	7.09 ± 0.47	0.09 ± 0.47

§ Expanded uncertainty reported for 95% confidence level.

Table 3. Measurement results of $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of four reference aqueous buffers determined from ladders of differential potentiometry referenced to another pH buffer. It is reported the difference between measured and reference values with uncertainty required to assess the compatibility between both estimates. The measurement uncertainty was evaluated by combining relevant uncertainty components by the Taylor Series Approximation, assuming liquid junction potential has an expanded uncertainty, $U(\Delta E_{\mathrm{LJ}})$, of 0 mV or 6.3 mV.

$U(\Delta E_{\mathrm{LJ}})$/mV	0	
Ladder reference §	Measurement result §	Difference between measurement and reference result §
2.00 ± 0.02	4.08 ± 0.44	0.08 ± 0.44
	7.12 ± 0.50	0.12 ± 0.50
	10.16 ± 0.56	0.16 ± 0.56
4.00 ± 0.02	1.92 ± 0.37	-0.08 ± 0.37
	7.05 ± 0.46	0.05 ± 0.46
	10.08 ± 0.52	0.08 ± 0.52
7.00 ± 0.02	1.88 ± 0.34	-0.12 ± 0.34
	3.95 ± 0.36	-0.05 ± 0.36
	10.03 ± 0.46	0.03 ± 0.46
10.00 ± 0.02	1.84 ± 0.32	-0.16 ± 0.32
	3.92 ± 0.33	-0.08 ± 0.33
	6.97 ± 0.36	-0.03 ± 0.36
$U(\Delta E_{\mathrm{LJ}})$/mV	6.3	
2.00 ± 0.02	4.08 ± 0.46	0.08 ± 0.46
	7.12 ± 0.51	0.12 ± 0.51
	10.16 ± 0.58	0.16 ± 0.58
4.00 ± 0.02	1.92 ± 0.39	-0.08 ± 0.39
	7.05 ± 0.47	0.05 ± 0.48
	10.08 ± 0.53	0.08 ± 0.53
7.00 ± 0.02	1.88 ± 0.36	-0.12 ± 0.36
	3.95 ± 0.38	-0.05 ± 0.38
	10.03 ± 0.47	0.03 ± 0.48
10.00 ± 0.02	1.84 ± 0.35	-0.16 ± 0.35
	3.92 ± 0.35	-0.08 ± 0.36
	6.97 ± 0.38	-0.03 ± 0.38

§ Expanded uncertainty reported for 95% confidence level ($k = 2$)