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PRACTITIONER'S REPORT

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Estimation of uncertainty in routine pH measurement

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Abstract A procedure for estimation of measurement uncertainty of routine pH measurement (pH meter with two-point calibration, with or without automatic temperature compensation, combination glass electrode) based on the ISO method is presented. It is based on a mathematical model of pH measurement that involves nine input parameters. Altogether 14 components of uncertainty are identified and quantified. No single uncertainty estimate can be ascribed to a pH measurement procedure: the uncertainty of pH strongly depends on changes in experimental details and on the pH value itself. The uncertainty is the lowest near the isopotential point and in the center of the calibration line and can increase by a factor of 2 (depending on the details of the measurement procedure) when moving from around pH 7 to around pH 2 or 11. Therefore it is necessary to estimate the uncertainty separately for each measurement. For routine pH measurement the uncertainty cannot be significantly reduced by using more accurate standard solutions than ±0.02 pH units – the uncertainty improvement is small. A major problem in estimating the uncertainty of pH is the residual junction potential, which is almost impossible to take rigorously into account in the framework of a routine pH measurement.

Keywords Measurement uncertainty · Sources of uncertainty · ISO · EURACHEM · pH

Introduction

Quality control and metrology in analytical chemistry are receiving increasing attention [1–3]. Uncertainty estimation for results of measurements is of key importance in quality control and metrology. Many papers have been published on uncertainty estimation of various analytical procedures [1, 4]. The ISO/IEC standard 17025, which is very often the basis of accreditation of analytical laboratories, explicitly prescribes that "Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement"[5].

One of the most widespread measurements carried out by analytical laboratories is determination of pH. A huge amount of work has been published on pH measurement [6–10] including the assessment of uncertainty [11, 12] and traceability [13] of pH measurements. The methods for uncertainty estimation that have been published, however, are applicable mostly to high-level pH measurements [9, 12], not to the routine laboratory measurement.

To the best of our knowledge no procedure for estimation of uncertainty of pH for a routine measurement with identification and quantification of individual uncertainty sources has been published to date. This procedure would be of interest to a myriad of analysis laboratories. Also, estimation of uncertainty of pH is very important when estimating uncertainties of many other physicochemical quantities (pK_a values, complexation constants, etc.) that depend on pH.

In this article we present a procedure for estimation of uncertainty of routine pH measurement using two-point calibration, based on identification and quantification of individual uncertainty sources according to the ISO approach [14], that was subsequently adapted by EURACHEM and CITAC for chemical measurements [15].

It is clear that multi-point calibration is more satisfactory than a two-point one [9, 10, 12], but routine analysis pH-meters usually do not offer the possibility of multi-point calibration.

pH is a very special measurand. It is related to the activity of the H^+ ion – a quantity that cannot be rigorously determined. That is – uncertainty is already introduced by the definition of pH [6, 10, 16]. However, in routine pH determination this fundamental uncertainty (which in the case of the NBS scale amounts to $\Delta pH=\pm 0.005$) [6, 17] will be negligible [12].

Derivation of the uncertainty estimation procedure

The uncertainty estimation procedure derived below is intended for the mainstream routine pH measurement equipment: an electrode system consisting of a glass electrode and reference electrode (or a combined electrode) with liquid junction, connected to a digital pH-meter with two-point calibration (bracketing calibration). The system may or may not have temperature sensor for automatic temperature compensation. This procedure is valid for measurements in solutions that are neither too acidic nor too basic ($2<pH<12$) and do not have too high ionic strength.

Specification of the measurand (defining the mathematical model)

The dependence of the potential of the electrode system on the pH of the measured solution is described by the Nernst equation. In practice various more specialized equations, based on the Nernst equation, are used. For our purpose the most convenient is the one that includes the coordinates of the isopotential point and the slope [6, 7]:

$$E_x = E_{is} - s \cdot (1 + \alpha \cdot \Delta t)(pH_x - pH_{is}) \qquad (1)$$

where E_x is the electromotive force (EMF) of the electrode system, pH_x is the pH of the measured solution, E_{is} and pH_{is} are the coordinates of the isopotential point (the intersection point of calibration lines at different temperatures), s is the slope of the calibration line, α is the temperature coefficient of the slope [7], and Δt is the difference between the measurement temperature and the calibration temperature. When two-point calibration is used then the isopotential pH and the slope can be expressed as follows:

$$pH_{is} = pH_1 + \frac{E_1 - E_{is}}{s} \qquad (2)$$

$$s = \frac{E_2 - E_1}{pH_1 - pH_2} \qquad (3)$$

where pH_1 and pH_2 are the pH values of the standard solutions used for calibrating the pH meter and E_1 and E_2 are the EMF of the standard solutions.

Based on Eq. (1), the pH of an unknown solution pH_x is expressed as follows:

$$pH_x = \frac{E_{is} - E_x}{s \cdot (1 + \alpha \cdot \Delta t)} + pH_{is} \qquad (4)$$

After uniting Eqs. (2)–(4) and simplifying, we get

$$pH_x = \frac{(E_{is} - E_x) \cdot (pH_1 - pH_2)}{(E_2 - E_1) \cdot (1 + \alpha \cdot \Delta t)} + \frac{E_1 - E_{is}}{E_2 - E_1}(pH_1 - pH_2) + pH_1 \qquad (5)$$

Equation (5) will be our initial specification of the measurand (initial mathematical model).

Identifying uncertainty sources

There are two types of sources of uncertainty: the uncertainty contributions of the input parameters from the initial model, i.e., the explicit sources of uncertainty and the uncertainty contributions of other effects not explicitly taken into account by the initial model, i.e., the implicit sources of uncertainty. Below the sources of uncertainty of pH measurement of both types will be examined.

The explicit uncertainty sources

Difference of pH values of standards pH1 and pH2 from their stated values. This source includes the following components:

1. Uncertainty arising from the limited accuracy of the pH values of the standards. We express these as standard uncertainties $u(pH_1, acc)$ and $u(pH_2, acc)$.
2. Uncertainty caused by the temperature effect. This effect is caused by the dependence of the pH values of the standards on temperature. We express these uncertainty components as standard uncertainties $u(pH_1, temp)$ and $u(pH_2, temp)$.

The combined standard uncertainties of pH_1 and pH_2 are expressed as follows:

$$u(pH_1) = \sqrt{u(pH_1, acc)^2 + u(pH_1, temp)^2} \qquad (6)$$

$$u(pH_2) = \sqrt{u(pH_2, acc)^2 + u(pH_2, temp)^2} \qquad (7)$$

Electromotive forces E_x, E_1, and E_2. This source of uncertainty includes the following components:

1. Repeatability of EMF measurements: $u(E_x, rep)$, $u(E_1, rep)$, and $u(E_2, rep)$.

2. Uncertainty caused by the residual junction potential: this contribution is caused by the fact that the diffusion potential in the liquid junction of the reference electrode is not exactly the same in all solutions. Because we are dealing with residual junction potential (i.e., the difference between the junction potentials in calibration standards and the measured solution), it is sufficient to take it into account only with E_1 and E_2. This is one of the most important sources of uncertainty in pH measurements [18, 19]. According to the philosophy of BIPM and the ISO measurement uncertainty guide, residual junction potential as a systematic effect should be corrected for and the uncertainty of the correction should be included in the overall uncertainty calculation [14, 20]. However, the residual junction potential is very difficult (or nearly impossible) to correct for [7, 12] as this correction would require thorough knowledge of the composition of the sample and the geometry of the liquid junction [18]. These problems make it very uncommon in analysis laboratories to estimate the residual junction potential or to correct the results of pH measurements for it. Given these problems we treat the residual junction potential as a random effect and express it via standard uncertainties $u(E_1, \mathrm{JP})$ and $u(E_2, \mathrm{JP})$.
3. Systematic deviations (bias) of the measured EMF value from the actual value: the systematic effects are eliminated by the calibration. However, there is certain drift in all measurement instruments between calibrations. It is sufficient to take the drift into account only for E_x as $u(E_x, \mathrm{drift})$.
4. Stirring effect [7]: the stirring effect has its roots in the differences in junction potential in stirred and unstirred solutions [7] and is for the most part just another way of action of junction potential. If the solution is stirred just enough to mix it and then the stirring is stopped to take the reading or do the calibration (see Experimental) then it can be assumed that the stirring effect is absent. Otherwise its uncertainty contribution can be included in the contribution of the residual junction potential.
5. Sodium error [7]: because the present procedure is not intended for extreme pH values and modern glass electrodes have low sodium errors we do not take it into account.

Thus we have

$$u(E_1) = \sqrt{u(E_1, rep)^2 + u(E_1, JP)^2} \tag{8}$$

$$u(E_2) = \sqrt{u(E_2, rep)^2 + u(E_2, JP)^2} \tag{9}$$

$$u(E_x) = \sqrt{u(E_x, rep)^2 + u(E_x, drift)^2} \tag{10}$$

Uncertainties of E_{is}, α, and Δt. The standard uncertainties of these parameters $u(E_{\mathrm{is}})$, $u(\alpha)$, and $u(\Delta t)$ do not have further components.

The implicit uncertainty sources

The implicit sources of uncertainty will be identified in this section. The expressions for their calculation will be given in the model modification section.

Uncertainty of pH measurement of the unknown solution. This uncertainty source is the uncertainty originating directly from the operation of measurement of the unknown solution. It includes the following components:

1. Repeatability of pH measurement.
2. Uncertainty originating from the finite readability of the pH-meter scale.
3. Uncertainty originating from the drift of the measurement system.
4. Temperature effect: temperature influences the slope of the electrode system. This has not been taken into account by the uncertainties of the pH standards.

The components 1 and 3 have already been taken into account in the uncertainty of E_x but it is more convenient to take them into account in terms of pH by means of an additional term in the model. Component 4 will be taken into account in the uncertainty of Δt.

Modification of the model

The existence of implicit sources of uncertainty indicates that the model should be modified to allow to take these into account. We introduce an additional term $\delta\mathrm{pH}_{\mathrm{xm}}$ into the model (Eq. 5). We define it such a way, that $\delta\mathrm{pH}_{\mathrm{xm}}=0$. Therefore its introduction does not influence the pH_x. However, its uncertainty $u(\delta\mathrm{pH}_{\mathrm{xm}})$ does influence the standard uncertainty $u_c(\mathrm{pH}_x)$. $u(\delta\mathrm{pH}_{\mathrm{xm}})$ is the standard uncertainty originating directly from the operation of pH measurement of the unknown solution. We define the standard uncertainty of $\delta\mathrm{pH}_{\mathrm{xm}}$ as follows:

$$u(\delta\,\mathrm{pH}_{\mathrm{xm}}) = \sqrt{u(\delta\,\mathrm{pH}_{\mathrm{xm}}, rep)^2 + u(\delta\,\mathrm{pH}_{\mathrm{xm}}, read)^2 + u(\delta\,\mathrm{pH}_{\mathrm{xm}}, drift)^2} \tag{11}$$

where $u(\delta\mathrm{pH}_{\mathrm{xm}}, \mathrm{rep})$ is the repeatability component, $u(\delta\mathrm{pH}_{\mathrm{xm}}, \mathrm{read})$ is the readability component, and $u(\delta\mathrm{pH}_{\mathrm{xm}}, \mathrm{drift})$ is the drift component of $u(\delta\mathrm{pH}_{\mathrm{xm}})$. The final model is

$$\mathrm{pH}_x = \frac{(E_{\mathrm{is}} - E_x)\cdot(\mathrm{pH}_1 - \mathrm{pH}_2)}{(E_2 - E_1)\cdot(1 + \alpha\cdot\Delta t)} + \frac{E_1 - E_{\mathrm{is}}}{E_2 - E_1}(\mathrm{pH}_1 - \mathrm{pH}_2) + \mathrm{pH}_1 + \delta\,\mathrm{pH}_{\mathrm{xm}} \tag{12}$$

The repeatability and drift of the measurement of the unknown solution are taken into account via $u(\delta\mathrm{pH}_{\mathrm{xm}})$ and it is not necessary to take them into account by $u(E_x)$ (see Eq. 10). Therefore $u(E_x)$=0 mV and the $u(E_x)$ component can be left out of the combined uncertainty expression. Based on e Eq. (12) the combined standard uncertainty of $\mathrm{pH_x}$ can be presented as [14, 15]

$$u_c(\mathrm{pH_x}) = \sqrt{\begin{aligned} &+\left[\frac{\partial \mathrm{pH_x}}{\partial E_1}u(E_1)\right]^2 + \left[\frac{\partial \mathrm{pH_x}}{\partial E_2}u(E_2)\right]^2 + \left[\frac{\partial \mathrm{pH_x}}{\partial E_{\mathrm{is}}}u(E_{\mathrm{is}})\right]^2 + \\ &+\left[\frac{\partial \mathrm{pH_x}}{\partial(\delta\,\mathrm{pH_{xm}})}u(\delta \mathrm{pH_{xm}})\right]^2 + \left[\frac{\partial \mathrm{pH_x}}{\partial \mathrm{pH_1}}u(\mathrm{pH_1})\right]^2 + \\ &+\left[\frac{\partial \mathrm{pH_x}}{\partial \mathrm{pH_2}}u(\mathrm{pH_2})\right]^2 + \left[\frac{\partial \mathrm{pH_x}}{\partial(\alpha)}u(\alpha)\right]^2 + \left[\frac{\partial \mathrm{pH_x}}{\partial(\Delta t)}u(\Delta t)\right]^2 \end{aligned}} \qquad (13)$$

In this equation the standard uncertainties are those from Eqs. (8), (9), (11), (6), and (7); ($u(E_{\mathrm{is}})$, $u(\alpha)$, and $u(\Delta t)$ do not have further components and therefore no definition equation).

The mathematical model (Eq. 12) is quite complex and manual calculation of analytical partial derivatives, although accomplishable, is very tedious. In dedicated uncertainty calculating software (e.g., GUM Workbench, Metrodata GmbH) or software that automatically calculates analytical derivatives (e.g., MathCAD, Mathsoft Inc.), Eq (12) can be used directly.

With spreadsheet software the spreadsheet method for uncertainty calculation described in the EURACHEM/CITAC guide [15] can be used. According to this approach all the partial derivatives are approximated as follows:

$$\frac{\partial y}{\partial x_i} \approx \frac{y(x_i + \Delta x_i) - y(x_i)}{\Delta x_i} \qquad (14)$$

where $y(x_1, x_2,.. x_n)$ is the output quantity ($\mathrm{pH_x}$ in our case), x_i is the i-th input quantity, and Δx_i is a small increment of x_i. In the EURACHEM/CITAC guide it is proposed to take $\Delta x_i = u(x_i)$, but we have used $\Delta x_i = u(x_i)/10$. This is safer with respect to the possible nonlinearities of the function $y(x_1, x_2,.. x_n)$. For further details on this method see [15].

Experimental

pH meter. Metrohm 744 pH meter was used in this study. The meter has digital display with resolution of 0.01 units in the pH measurement mode. The meter can be calibrated using two-point calibration with one out of five buffer series stored in the memory of the meter. The pH values of the buffer series are stored at various temperatures. If the temperature sensor is connected then the meter automatically uses the correct pH corresponding to the temperature of calibration. If no temperature sensor is connected then the user can input the temperature (default is 25 °C). If the temperature sensor is connected and the measurement temperature is different from the calibration temperature then correction is automatically applied to the slope. The theoretical value 0.00335 $\mathrm{K^{-1}}$ (at 25 °C) for the temperature coefficient α is used [7]. For the E_{is} the pH meter uses value of 0 mV. This value cannot be adjusted with this type of pH meter. However, this is a reasonable average value for Metrohm combined pH electrodes (see below the description of the electrode system). The error limits of the meter are ±1 mV in the mV mode and ±0.01 pH units in the pH mode. The error limits in temperature measurement are ±1 °C. No data on the drift is given in the manual.

Electrode system. Combined glass electrode Metrohm 6.0228.000 was used. The inner reference electrode is Ag/AgCl electrode in 3 mol/l KCl solution with porous liquid junction. The electrode has a built-in Pt1000 temperature sensor. This electrode has sodium error starting from pH values around 12. The E_{is} for this electrode is 0±15 mV.

Calibration. Fisher buffer solutions with pH 4.00±0.02, 7.00±0.02, and 10.00±0.02 were used (pH values are given at 25 °C) as calibration standards. The values are claimed by the manufacturer to be "NIST traceable". In our interpretation this means that the pH values of the solutions are traceable to pH values of the NIST primary pH standards with the stated uncertainties (we assume rectangular distribution [15]). At 25 °C the pH of these standard solutions have a temperature dependence of 0.001, 0.002, and 0.01 pH units per degree centigrade, respectively. The calibration of the system is carried out daily.

Application example

We apply the derived uncertainty estimation procedure to a routine pH measurement example. Both calibration and measurement were carried out on the same day at 25±3 °C. In this example the temperature sensor was not connected and the temperature of the meter was set to 25 °C. The system was calibrated using the 4.00 and 10.00 standard solutions. The EMF values were 180 and –168 mV, respectively. pH value was measured in a solution (a 0.05 mol/l phosphate buffer solution), for which the EMF of the electrode system was –24 mV and the pH value was 7.52. The reading was considered stable if for 30 s (for measurement) or 60 s (for calibration) there was no change. Both measurement and calibration were done without stirring (the solution was stirred just enough to mix it and then the stirring was stopped).

Detailed description of quantifying the uncertainty components (file quant.doc MS Word 97 format) and the calculation worksheet (the first worksheet in the file 4_and_10.xls, in MS Excel 97 format) are available in the Electronic Supplementary Material. The uncertainty budget is presented in the first column of Table 1. From

Table 1 The uncertainty budgets of pH measurement under various conditions. Standard solutions with pH 4.00 and 10.00 were used for calibration

	Conditions[a]										
pH_x	7.52	7.52	10.55	10.55	3.48	3.48	7.52	10.55	7.52	10.55	3.48
Δt	0	0	0	0	0	0	3	3	35	35	35
TS	No	Yes	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes
x_i[b]	Uncertainty budgets (contributions of various input parameters x_i: $(\partial pH_x/\partial x_i)\cdot u(x_i)$[b])										
pH_1	0.005	0.005	–0.001	–0.001	0.013	0.013	0.005	–0.001	0.005	–0.001	0.013
pH_2	0.012	0.007	0.023	0.013	–0.002	–0.001	0.007	0.013	0.007	0.013	–0.001
E_1	0.011	0.011	–0.003	–0.003	0.030	0.030	0.011	–0.003	0.011	–0.003	0.030
E_2	0.016	0.016	0.030	0.030	–0.002	–0.002	0.016	0.030	0.016	0.030	–0.002
δpH_{xm}	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012
E_{is}	0.000	0.000	0.000	0.000	0.000	0.000	–0.001	–0.001	–0.016	–0.016	–0.016
α	0.000	0.000	0.000	0.000	0.000	0.000	–0.001	–0.005	–0.007	–0.057	0.060
Δt	–0.003	0.000	–0.028	–0.001	0.030	0.001	0.000	–0.001	0.000	–0.001	0.001
	Expanded uncertainties (k=2) of pH_x										
$U(pH_x)$	0.054	0.049	0.098	0.070	0.092	0.070	0.049	0.071	0.060	0.138	0.142

[a] The calibration temperature is 25 °C, Δt is the temperature difference between the measurement and calibration temperatures. TS=yes means that temperature sensor is connected and automatic temperature compensation used, TS=no means that automatic temperature compensation is not used and the pH meter assumes 25 °C for both calibration and measurement

[b] x_i is the i-th input quantity; see Eqs. (12) and (13)

the data we find the combined standard uncertainty: $u_c(pH_x)=0.027$. The expanded uncertainty at the 95% confidence level (here and below all expanded uncertainties are given with confidence level 95%, that is coverage factor k=2): $U(pH_x)=0.054$.

Results and discussion

The overall expanded uncertainty $U(pH_x)=0.054$ (we deliberately use uncertainties with three decimal places in order to detect small differences in uncertainty introduced by modifications of the experimental procedure) in the application example above is primarily determined by the uncertainty contributions of δpH_{xm} (mainly the drift component), the residual junction potential, and the large temperature effect of the 10.00 standard solution (see Table 1, second row). Indeed, when taking into account only these contributions we would have $U(pH_x)=0.047$.

We explore now the influence of modifying various parameters of the measurement procedure on the uncertainty with the aid of the model (Eq. 12). The uncertainty budgets are presented in Table 1 (calibration with pH 4.00 and pH 10.00) and Table 2 (calibration with 4.00 and 7.00). We first focus on the more reasonable calibration standards set – pH 4.00 and 10.00. The less satisfactory 4.00 and 7.00 set will be considered afterwards. Calculation worksheets of all the uncertainty budgets discussed here are available in the Electronic Supplementary Material (files 4_and_10.xls and 4_and_7.xls, in MS Excel 97 format).

The effect of the temperature compensation

The pH meter used has the possibility to connect temperature sensor and to make automatic temperature compensation. This temperature compensation works in a twofold manner:

1. It ensures that during the calibration the pH values of the buffer solutions are used that exactly correspond to the actual temperature of the solution.
2. During the measurement of the unknown solution the slope of the electrode system is corrected to correspond to the temperature of the solution.

Taking into account the uncertainty of the temperature measurement ±0.1 °C we get with temperature compensation $U(pH_x)=0.049$ (Table 1, column 3). This improvement is small but the pH 7.52 is well in the middle of the calibration line and near the isopotential point (according to the data, $pH_{is}=7.10$). It is reasonable to expect that the uncertainties due to the temperature will be the higher the more removed is the pH_x from the isopotential point. This is indeed so. The trend is visualized in Fig. 1. It is clearly seen that the further away the pH is from pH_{is} the more advantageous it is to use temperature compensation.

With automatic temperature compensation the uncertainties at pH 10.55 and pH 3.48 are practically equal (Table 1, columns 5 and 7), because these pH values are about equally removed from the isopotential point. Without temperature compensation the uncertainty at 3.48 is slightly lower due to the ten times higher temperature dependence of the pH value of the pH 10.00 standard compared to the pH 4.00 standard. The main contributors to the uncertainty in the case of pH 10.55 and pH 3.48

Table 2 The uncertainty budgets of pH measurement under various conditions. Standard solutions with pH 4.00 and 7.00 were used for calibration

	Conditions[a]										
pH_x	7.52	7.52	10.55	10.55	3.48	3.48	7.52	10.55	7.52	10.55	3.48
Δt	0	0	0	0	0	0	3	3	35	35	35
TS	no	yes	no	yes	no	yes	yes	yes	yes	yes	yes
x_i[b]	Uncertainty budgets (contributions of various input parameters x_i: $(\partial pH_x/\partial x_i)\cdot u(x_i)$[b])										
pH_1	–0.002	–0.002	–0.014	–0.014	0.014	0.014	–0.002	–0.014	–0.002	–0.014	0.0136
pH_2	0.014	0.014	0.026	0.025	–0.002	–0.002	0.014	0.025	0.014	0.025	–0.0020
E_1	–0.005	–0.005	–0.033	–0.033	0.032	0.032	–0.005	–0.033	–0.005	–0.033	0.0325
E_2	0.033	0.033	0.061	0.061	–0.005	–0.005	0.033	0.061	0.033	0.061	–0.0048
δpH_{xm}	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.0119
E_{is}	0.000	0.000	0.000	0.000	0.000	0.000	–0.001	–0.001	–0.016	–0.016	–0.0157
α	0.000	0.000	0.000	0.000	0.000	0.000	–0.001	–0.005	–0.007	–0.057	0.0601
Δt	–0.003	0.000	–0.028	–0.001	0.030	0.001	0.000	–0.001	0.000	–0.001	0.0009
	Expanded uncertainties (k=2) of pH_x										
$U(pH_x)$	0.076	0.075	0.162	0.151	0.096	0.075	0.075	0.152	0.083	0.192	0.145

[a] The calibration temperature is 25 °C, Δt is the temperature difference between the measurement and calibration temperatures. TS=yes means that temperature sensor is connected and automatic temperature compensation used, TS=no means that automatic temperature compensation is not used and the pH meter assumes 25 °C for both calibration and measurement

[b] x_i is the i-th input quantity; see Eqs. (12) and (13)

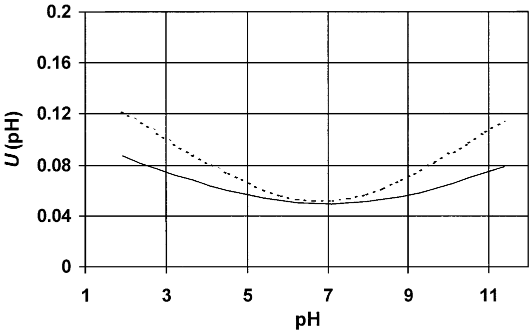

Fig. 1 Dependence of the U(pH) on pH with (*solid line*) and without (*dotted line*) automatic temperature compensation. Standard solutions pH 4.00 and pH 10.00 were used for calibration

are the $u(E_2)$ and $u(E_1)$ respectively, and $u(\Delta t)$ if no temperature compensation is used. It is also interesting to note, that although the uncertainties of α and E_{is} are large, their contribution to the overall uncertainty is negligible at Δt=0.

As can be seen from Table 1, small differences in measurement and calibration temperature almost do not introduce any additional uncertainty if the temperature compensation is used; if calibration is carried out at 25 °C and measurement at 28 °C (that is, Δt=3 °C) then the increase in expanded uncertainty is not more than 0.001 (Table 1, columns 8 and 9). Things are completely different, however, if Δt is higher, and especially if at the same time pH_x is far from pH_{is} (Table 1, last columns). Thus if calibration is carried out at 25 °C and measurement at 60 °C (Δt=35 °C) then at pH 10.55 and pH 3.48 the expanded uncertainty is 0.138 and 0.142, respectively. In this case the combined uncertainty is heavily dominated by the uncertainty of α. If we neglected all other uncertainty components, then we would have $U(pH_x)$=0.114 and 0.120 respectively. The slightly higher uncertainty at pH 3.48 is because this pH value is slightly more distant from the pH_{is}.

The effect of the standard solution set

Other combinations of standard solutions than pH 4.00 and pH 10.00 can be used for pH meter calibration. We will explore the changes that take place when switching to the set of pH 4.00 and pH 7.00 (Table 2, Fig. 2).

It can be seen from Table 2 and Fig. 2 that practically in all the cases (except a narrow region between pH=5–6) this leads to higher uncertainties. The effect is particularly disastrous at high pH values. Thus, at pH 10.55 if using temperature compensation the $U(pH_x)$ is more than twice as high as with the 4.00 and 10.00 standard set (Tables 1 and 2, column 5).

This effect is not unexpected. The calibration line is now fixed by two points that are closer to each other and therefore the line becomes less determined. In addition, at high pH values the determination of pH involves significant extrapolation. The lines for the temperature-compensated and non-compensated measurements on Fig. 2 are closer in this case. This is because the temperature effect on the slope has remained the same, while the overall uncertainty is higher. Therefore the relative contribution of $u(\Delta t)$ is smaller now. This effect is especially dramatic at higher pH values where the overall uncertainty is high. The fact that the pH of the standard

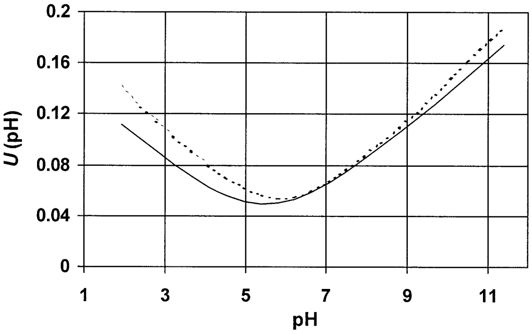

Fig. 2 Dependence of the U(pH) on pH with (*solid line*) and without (*dotted line*) automatic temperature compensation. Standard solutions pH 4.00 and pH 7.00 were used for calibration

7.00 is five times less sensitive to temperature is also a contributor.

Accuracy of the standard solutions

From Tables 1 and 2 it is apparent that with this experimental setup the uncertainty of pH cannot be significantly reduced if using standard solutions that are more accurate than ±0.02 pH units. Even if the uncertainties of the pH values of the standards were 0, the improvement in the overall uncertainty would be small. For example at pH=10.55 the expanded uncertainties would be 0.065 instead of 0.070 and 0.094 instead of 0.098 with and without temperature compensation, respectively (Table 1, columns 5 and 4, respectively).

Limitations of the procedure

There are several additional sources of uncertainty, mostly related to the correctness of measurement, that have not been taken into account:

1. Use of aged calibration buffers. The storage life of standard buffer solutions is often only a few days [7].
2. Too infrequent calibration of the system.
3. Sample carryover
4. The reading is not allowed to stabilize either during the calibration or the measurement.
5. Improper handling or storage of the electrodes.

Several of these (e.g., the sample carryover, which depends on the previous sample) are practically impossible to quantify with any rigor. It is therefore necessary to assure that due care is taken when measuring pH so that the above described procedure would give an adequate estimate of uncertainty of pH.

It is well known and widely recognized that the properties of the sample are very important in measurement of pH [6]. The procedure presented here is intended for measurements with samples that are aqueous solutions with ionic strength not greater than around 0.2. Only for such solutions can a quantitative meaning in terms of activity of the hydrogen ion be ascribed to pH [6].

Application of the procedure to routine work

The presented procedure of uncertainty estimation may seem too complex for routine use. However, this is not the case. Although the procedure involves 9 input parameters and 14 components of uncertainty, it is not necessary to quantify these each time a pH measurement is carried out, because most of them (e.g., those referring to the particular pH meter, particular electrode, etc.) will remain the same from one measurement to another.

We propose to use spreadsheets, like the ones in the Electronic Supplementary Material, or the GUM Workbench package for routine implementation of the procedure. This way the equipment-specific and procedure-specific components need to be quantified only once – during the method validation. Calibration data need to be input only when a new calibration is carried out. Only the E_x needs to be input separately for each measurement and when this is done the pH and its uncertainty will be automatically calculated by the software.

Conclusions

No single uncertainty estimate can be ascribed to a pH measurement procedure. The uncertainty of pH strongly depends on changes in experimental details (standard solution set, temperature compensation, etc.) and on the pH value itself. The uncertainty is the lowest near the isopotential point (usually around pH 7) and in the center of the calibration line and can increase by a factor of 2 (depending on the details of the measurement procedure) when moving from around pH 7 to around pH 2 or 11. Therefore it is necessary to estimate the uncertainty separately for each measurement.

At room temperature the expanded uncertainties (at k=2 level) of pH values at pH 7.52 are around U(pH)=0.05 either with or without automatic temperature compensation (calibrated with standards pH 4.00 and pH 10.00). At a pH value more distant from the isopotential pH the automatic temperature compensation becomes clearly advantageous: U(pH)=0.07 and 0.1 with and without temperature compensation, respectively, at pH 10.55.

For routine pH measurement with an experimental setup similar to that described here the uncertainty cannot be significantly reduced by using more accurate standard solutions than ±0.02 pH units – the uncertainty improvement is small.

A major problem in estimating the uncertainty of pH is the residual junction potential, which is almost impossible to take rigorously into account in the framework of a routine pH measurement.

Electronic supplementary material available

Detailed description of quantifying the uncertainty components is available in the file quant.doc in MS Word 97 format. Calculation worksheets of all the uncertainty budgets discussed in this article are available in the files 4_and_10.xls and 4_and_7.xls in MS Excel 97 format. This material is available via the Internet at http://link.springer.de.

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