Evaluation of the residual liquid junction potential contribution to the uncertainty in pH measurement: A case study on low ionic strength natural waters

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1. Introduction

The potentiometric pH determination that is performed perhaps every day in every chemical (biochemical, clinical, environmental) laboratory is influenced by several effects reducing the accuracy of the result. The problem of uncertainty evaluation in routine pH measurement is given much attention in recent years and relevant components of the uncertainty have been identified and quantified using different approaches \cite{1–6}. Among these uncertainty components are those arising from calibration procedure, quality of calibration standards, temperature effects, drift of the measurement system, and others (see also Ref. \cite{7}, Section 11.1, for the list of relevant effects).

A peculiar source of error in pH measurement, which is generally difficult to evaluate and control, is the residual liquid junction potential (RLJP), i.e., the difference in junction potentials between measurements with the test and standard solutions.

The electromotive force $E$ measured in pH measurement with a glass/reference electrode pair is expressed in terms of the potentials of the glass electrode, $E_{\text{glass}}$, the reference electrode, $E_{\text{ref}}$, and the residual liquid junction potential, $E_j$, developed between the reference half cell and the test/standard solution:

$$E = E_{\text{glass}} - E_{\text{ref}} + E_j \quad (1)$$

If $X$ represents an unknown (test) solution and $S$ a standard solution of assigned pH value, $\text{pH}(S)$, then the pH of the unknown solution, $\text{pH}(X)$, is determined from the difference in the respectively measured e.m.f. values, $E(X)$ and $E(S)$, as follows:

$$\text{pH}(X) = \text{pH}(S) - \frac{E(X) - E(S)}{\kappa} \quad (2)$$

where $\kappa$ is the slope factor. It is theoretically expressed as $RTF^{-1}$ in 10 and equal to 59.16 mV pH$^{-1}$ at 25 °C. In practical measurements $\kappa$ is usually found experimentally from the two-point or multi-point calibration.

Eq. (2) that provides the “operational definition” \cite{8–10} of pH and forms the basis for practical pH measurement assumes an ideal condition of the measurement—the liquid junction potentials $E_j$ in

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Eq. (1) are the same when the standard solution (or solutions) used for calibration is replaced by the test solution, so that their difference, i.e., the RLJP, equals zero. Such an assumption is based on the fact that liquid junction potentials are considered small and reproducible because they are determined by the high KCl concentration in the salt bridge, and quasi-independent of the composition of the test solution. As a matter of fact, this is only true provided that (see, e.g., [9]):

1. carefully designed liquid junctions are used;
2. the ionic strengths of the standard and test solutions are not too different;
3. the intermediate pH range \(3 \leq \text{pH} \leq 11\) is considered, since the hydrogen and hydroxyl ions have distinctly high mobility compared with all other ions.

These prerequisites cannot be fulfilled rigorously and errors, often significant, may be introduced in practical pH measurement. Hence the uncertainty contribution due to the RLJP should be accounted for if the metrological approach to pH recommended by IUPAC [7] is implemented.

In the paper [1] devoted to the uncertainty in pH determination, the emphasis is laid on a multi-point calibration procedure that provides some advantages [2,11] over the common two-point (bracketing) calibration procedure. Several regression techniques, such as ordinary least squares regression, orthogonal regression, inverse regression, and Monte Carlo simulation were discussed and compared [1] with regard to their performance in prediction of confidence regions for the multi-point calibrations.

In a more practical aspect the multi-point calibration was used in the work [2] where the ordinary least squares regression was applied to calculate the uncertainty of the final measurement result from calibration data. The employment of commercial reference electrodes with different junction devices such as capillary, Pt, glass sleeve, and ceramic plug allowed a device-dependent liquid junction potential contribution to the pH measurement uncertainty to be assessed. Owing to this contribution the uncertainty of measurement in a buffer solution of pH 7.0, expressed as expanded uncertainty with the coverage factor \(k=2\), was found to increase from 0.02 (for electrodes having capillary junctions) to 0.09 (for those with ceramic junctions).

However, any calibration procedure, either conventional bracketing or multi-point calibration, gives no way of revealing in full extent the residual junction potential error inherent in pH measurement. The point is that the standard buffer solutions commonly used in calibration were formulated with the aim of minimizing junction error. Although with different pH and composition, they have closely related ionic strengths (0.02–0.1 mol kg\(^{-1}\)) and give no indication that there would be problems with other solutions, which appear when a test solution markedly differs in ionic strength from calibration buffers. It follows that the pH measurement uncertainty derived from (multi-point) calibration data may only account for deviations in liquid junction potentials among the calibration buffers, not covering the difference between the buffers and the sample.

This situation is quite similar to the use of matrix-mismatched reference materials for calibration in chemical analysis. Can the uncertainty in a future routine measurement be derived from the spread of responses about the fitted line established with those calibration standards? The evident answer is “no”. Two independent measurement events, calibration and measurement itself, are generally involved in analytical measurement, with a specific uncertainty due to the mismatch in composition and relevant properties of calibration standards and measurement objects introduced at the second one.

Another paper [3] draws inferences about the uncertainty of a pH measurement result in a test sample from the statistical analysis of simulated calibrations. The uncertainty of the result is considered there as a combination of two components: the uncertainty in pH values of calibration buffers and the instrumental uncertainty. Sophisticated statistical techniques such as Monte Carlo method and bivariate regression are used to simulate a calibration function, and the residual standard deviation of a calibration line is numerically derived as a function of the two factors above. However, even if the predicted standard deviations of the calibration lines correlate, as demonstrated, with those from the experiment, the conclusions made in this way are of little help in the effort “to optimize the choice of pH-meter and buffers” because the uncertainty in calibration is only part of the measurement uncertainty.

The authors [4] (including one of the present authors, i.L.) have attempted to make up the full uncertainty budget in routine pH measurement. No single uncertainty value was obtained for the pH measurement result, since the resulting uncertainty depends on experimental details and on the pH value itself. For measurement in a phosphate buffer solution, pH 7.5, using an ordinary bracketing procedure with two calibration buffers, pH 4.00 and 10.00, the expanded \((k=2)\) uncertainty was found to be around 0.05 at room temperature. This estimate lies approximately in the middle of the range of uncertainties (from 0.02 to 0.09) obtained in Ref. [2] for a similar test sample by using the five-point calibration on pH electrodes with different junction devices.

The difficulties in estimating the uncertainty connected to the RLJP were conspicuous in Ref. [4] where, although the RLJP uncertainty seems to have been allowed for, this has not been done properly yet. What has actually been taken into account is the uncertainties – designated as \(u(E_i, JP)\) and \(u(E_J, JP)\) – associated with the liquid junction potentials of the calibration buffers, not the uncertainty originating in the difference between that of the test solution and calibration solution(s), which is meant by the RLJP. This was improved in the next paper from the same group [5] where the uncertainties relating to pH measurement were estimated as components of the uncertainty in pK\(_a\) values determined by potentiometric titration. Separate uncertainties caused by junction potentials have been assigned there to both five calibration buffers, designation \(u(E_i, JP)\), and a test solution, designation \(u(E_J, JP)\), all of them included into the extended mathematical model. The magnitudes of these uncertainty components, however, are difficult to estimate rigorously, particularly, having regard to the performance of commercial reference electrodes.

In a similar manner – by assigning separate uncertainties due to liquid junction potentials to the calibration buffers and the test solution – the uncertainty budget was addressed just recently as applied to industrial pH measurement [6]. By using a flowing measurement system, the junction potentials for a number of test samples, mainly foodstuff, were experimentally determined to be within ±3 mV in the average pH range. Other estimates, however, would be obtained at other conditions and with other electrodes. (Note that this uncertainty contribution ranges from 2 to 9 mV in a series of calculation examples presented in Ref. [6].) It is evident that a justified assignment of this uncertainty is problematic, especially where no specific data on the liquid junction potentials are available.

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1. The instrumental standard uncertainties as they are evaluated in Ref. [3] invite some questions. These uncertainties, expressed in mV, are numerically equal to the maximum permissible errors given in the instrument specifications [12] for either voltage measurement (Metrohm 744 pH Meter) or pH measurement (Radio meter PHM 240 pH/Ion Meter). Furthermore, no account is taken in these “standard uncertainties” of the performance of the electrode system involved, since the accuracy of a pH meter is specified without measuring probes.
Thus, the problem of the RLJP that “is almost impossible to take rigorously into account in the framework of a routine pH measurement” [4] still needs to be solved in some way or another. An empirical approach to this challenging problem is developed in this paper.

2. Evaluation of liquid junction potentials: simple models, high-level pH measurements, and a dose of reality

The liquid junction potential arises primarily from unequal diffusion of ions having differing ionic mobilities in the two directions across the junction, resulting in a separation of charge. In principle, this diffusion potential can be calculated using one of the known approximations, specifically, the Henderson equation for a junction of the continuous-mixture type [13] that is regarded as a simple model for liquid junctions realized in practice. This model assumes a linear concentration gradient across the junction and neglects the activity coefficients; also the transference numbers of ions are expressed in terms of limiting equivalent conductivities. In spite of the simplified assumptions, the Henderson approximation and expressed in terms of limiting equivalent conductivities. In spite of the simplified assumptions, the Henderson approximation and also another one, the Plank approximation derived from the constrained diffusion model [13], are generally considered as yielding useful semiquantitative estimates of liquid junction potentials. For junctions formed between standard pH buffers and saturated potassium chloride, the diffusion potentials predicted by the Henderson equation are such in magnitude (see Table 5 in Ref. [9]) that the maximum difference for a pair of buffer solutions, which is the case for 0.01 mol dm$^{-3}$ (1:1) acetate–0.025 mol kg$^{-1}$ (1:1) phosphate, does not exceed 1.5 mV which is equivalent to 0.025 pH units at 25°C. For junctions between unbuffered solutions and saturated KCl, the potentials are reasonable to estimate using a dilute solution of a strong mineral acid as a model. So, application of the Henderson equation to the 0.5 mol dm$^{-3}$ sulphuric acid with respect to the standard phthalate buffer gives a potential difference of 1.9 mV [14] which is equivalent to 0.032 pH units. Similar results are obtained from the calculations for hydrochloric acid solutions and these RLJPs progressively increase up to 4 mV (0.07 pH units) with decreasing the solution concentration from $10^{-2}$ to $10^{-6}$ mol dm$^{-3}$ (Fig. 2 in Ref. [15]). The positive sign of the predicted RLJP error means that the measured pH will be higher than the true pH value.

It is pertinent to note that more recent computer calculations [16] using diffusion concentration profiles and including the dependence of activity coefficients and transference numbers on the composition of solutions resulted in junction potentials which are in poor agreement with the previous values calculated by the Henderson equation. For many junctions, for instance, between the 0.1 mol dm$^{-3}$ HCl and saturated KCl and also between standard pH buffers and saturated KCl, the junction potentials appeared opposite in sign to the Henderson values, with the discrepancy between the two sets of data running up to 6 mV. These findings cast doubt on the validity of calculations of individual junction potentials at all, particularly, simple calculations such as those based on the Henderson equation.

The available experimental data on junction potentials in electrolyte solutions cannot provide the basis for evaluation of the RLJP uncertainty either. The problem of junction potential is closely linked to that of “absolute” hydrogen ion activity $a_H^+$, since the values of $E$ and $p_{H^+}$ are interdependent [9,17]. Conventional (because based on the Bates–Guggenheim convention for the activity of the chloride ion) ionic activities have been accepted in assigning $p_{H^+}$ values for standard buffer solutions, and most of the data on junction potentials have been obtained with those buffer solutions.

As was suggested by Bates [18], the RLJP errors for standard pH buffers can be evaluated by comparing the pH value measured “operationally”, using the cell containing two liquid junctions (of the free-diffusion type) separated with a salt bridge, with the corresponding $p_{H^+}$ value derived from the measurements of the cell without liquid junction. The results of such measurements, typically plotted against pH values of the buffers (see Fig. 2 in Ref. [7]), demonstrate that the errors in pH due to the RLJP are within ±0.01 at 25°C except for the calcium hydroxide buffer.

It is surprising that similar measurements in dilute buffer solutions with the ionic strength 0.004–0.025 mol kg$^{-1}$ showed the RLJPs to be within ±0.5 mV [20], that is, roughly at the same level of ±0.01 in pH as with the standard pH buffers. Following the basic pattern, the RLJP shall increase with increasing the difference in ionic strength of the solutions compared. This was clearly demonstrated by Picknett’s calculations, confirmed by experiment, of liquid junction potentials between dilute electrolytes and saturated potassium chloride [21].

The results above that can be referred to high-level pH measurement have been obtained using a free-diffusion liquid junction which is known to have the best performance providing the small junction potentials. However, in practical work commercial reference electrodes and combination pH electrodes are used in which the junction is formed in a constraining element, usually a ceramic frit or some other constrained type junction device. One should expect that the transition from the optimized methodology developed at the higher level into the much broader and less defined domain of practical pH measurements brings about additional measurement errors.

There is indeed evidence (e.g., [22–24]) that commercial reference electrodes are the source of considerable residual junction potential error. Specifically, a large negative transient error and other kinetic complications may occur [23], particularly, for no-flow reference electrodes or those where the flux is restrained by clogging. (The junctions of conventional Ag/AgCl electrodes become clogged with precipitated silver chloride because of the drop in solubility of silver chloride across the junction when internal KCl solution effuses into the dilute sample solution [25].) Negative errors associated with poor junction performance, up to the tenths [26] or even the whole pH units [24], were observed in dilute aqueous solutions.

With these findings it is recognized that a further source of error, besides that attributed to unequal ionic interdiffusion, is deficiencies in the performance of a particular junction device. Two contributions to the observed deviation from the correct pH value can be referred [27] to as “classical” RLJP error and “non-classical” one resulting from charge anomalies in the liquid junction. The latter which may be both positive and negative in sign and much more in magnitude than the (positive) “classical” RLJP error depends on the type of liquid junction involved, the condition of the junction, and the history of the electrode.

From the above discussion it appears that reliance cannot be placed on either theoretical or experimental data on liquid junction potentials, obtained under idealized measurement conditions. The actual RLJP error estimated with reference to an appropriate measurement standard, for a specific class of analytical objects, on a variety of measurement conditions may provide a more solid basis for pH measurement uncertainty evaluation.

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1 One cannot but notice the different location of some points on the plots published earlier [10,19] and presented now [7], specifically, for the tetraoxalate and tartrate buffers, which raises questions about the reliability of the data.
3. Treatment of junction bias from experimental studies on pH measurements at low ionic strength

As noted above, the residual junction potential error, i.e., the "junction bias", is revealed when a glass/reference electrode pair normally calibrated with standard buffer solutions is used to measure pH in solutions of appreciably high or low ionic strength. Fresh natural waters that differ in ionic strength (I < 10^{-2} mol kg^{-1}) from calibration buffers by more than two orders of magnitude can serve as a practically important example of such analytical objects. The ability of commercial electrodes to measure pH of low ionic strength waters was the subject of numerous studies in the eighties [14,15,24,28-31] when the problem of surface water acidification became pointed. In those studies, the junction bias (often along with other performance characteristics such as the stirring shift and noise) was assessed for a selection of electrodes from different manufacturers. Interlaboratory comparisons of pH measurements in natural waters were also conducted [32-34]. All these are sources of valuable information to be used in our consideration.

The measurement bias is commonly estimated against a reference value carried by a suitable reference material. A reference method can alternatively be applied which is known to be free from bias. Accordingly, three main methodologies have been developed in the accuracy assessment of pH measurements at low ionic strength:

(1) comparison of the pH measured in a dilute (at the level of 10^{-4} mol dm^{-3}) reference solution of a strong acid such as hydrochloric, nitric, or sulphuric acid with a "theoretical" pH value, pOH = -log([H_3]H), calculated from the hydrogen ion concentration and the activity coefficient derived from one of the variations of the Debye–Hückel equation or known from the experimental data, assuming that the individual ionic activity coefficient equals to the mean ionic activity coefficient in the dilute solution;

(2) as a modification of (1)—comparison of two "pH 4 standards", the standard phthalate buffer (pH 4.005 at 25°C [7]) and the dilute strong acid solution (pH 4.005 for 1.00 × 10^{-4} mol dm^{-3} HCl or HNO_3 and 4.006 for 5.00 × 10^{-5} mol dm^{-3} H_2SO_4 [35]); the measured e.m.f. difference is converted into the difference in pH;

(3) comparison of the pH of a water sample or dilute acid, measured with a working reference electrode, with that obtained with a standard reference electrode that incorporates a free-diffusion junction.

In cases (1) and (3) it is assumed that the electrode system is previously calibrated with standard pH buffers but with methodology (2), this is generally not required.

The results from five independent studies of the accuracy of pH measurements in low ionic strength solutions are collected and analyzed in Table 1 where all three methodologies mentioned above are presented. A wide spectrum of measurements, from routine determination of pH in environmental laboratories (data set II) to an extensive electrode performance study in which a special technique was applied to reduce the measurement error (data set IV) is covered. Furthermore, studies of the two types are included in the consideration, those where the relevant influence factors such as different electrodes, different instruments, different operators, and so forth, varied deliberately within a single laboratory and those where they were changed "passively", in a collaborative trial.

Some of the sets of raw data appeared to be "contaminated" with anomalous results attributable to electrodes or laboratories that showed unsatisfactory performance. These results showed large negative deviation from the reference value were rejected without reservation if a reason for the anomaly was discovered in the
original study, for instance, if specific electrodes were suspected of malfunctioning as in Ref. [14]. Otherwise, a decision based on a statistical outlier test was made (see footnotes e–g to Table 1 for details). By doing this the “classical” RLJP bias can largely be isolated. Nevertheless, a spread of the estimates due to quite different experimental conditions should be expected. Indeed, the bias values obtained range from 0.021 to 0.078 pH units as shown in Table 1.

The “quality” of the bias estimates from different studies can be evaluated using the measurement uncertainty methodology. For this purpose uncertainty budgets have been made up presented in Table 2 where relevant uncertainty sources are listed and corresponding contributions to the combined uncertainty are quantified based on all the available information.

By the definition of measurement bias estimated as the difference between the mean measured value and the reference value, the uncertainty in bias, \( u(b) \), is given as a combination of two groups of components associated with the mean value (m.v.) and the reference value (r.v.), respectively, according to

\[
    u(b) = \sqrt{\sum u^2_{(m.v.)} + \sum u^2_{(r.v.)}} \quad (3)
\]

The first group of uncertainties is primarily represented in Table 2 by the experimental standard deviation of the mean, that ranges from as low as one thousandth (due to the very large number of measurements to be averaged, data set IV) to several hundredths (which occurred in routine pH measurements in the collaborative study, data set II). It is significant that the relevant influence factors that are involved in the second term in Eq. (3) are randomised in a particular study and so have been accounted for by the estimated standard deviation. Only those effects should additionally be taken into account that were not varied during the study. The uncertainty of values carried by calibration standards (see the list of uncertainty sources in Table 2) is an example of those “systematic” effects.

The second group of uncertainties above is originating at the dilute acid standard that is established either from measurement or preparation/calculation. For the latter case, the uncertainties in the hydrogen ion concentration and the hydrogen ion activity coefficient are taken into consideration as well as a potential bias due to atmospheric carbon dioxide; the last two contributions appeared negligible in the budgets.

The combined uncertainties derived from the budgets are presented graphically in Fig. 1 as expanded uncertainty intervals \( U_i = 2u_i \) around each bias value \( b_i \) (i denotes the data set) as is usually done with the results of interlaboratory comparisons.

A meaningful estimation of the overall bias is possible on the assumption that the values \( b_i \) although having different uncertainties \( u_i \) are all the estimates of one and the same unknown quantity.

### Table 2

<table>
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<tr>
<th>Source of uncertainty</th>
<th>Standard uncertainty from the specific data set</th>
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<tr>
<td></td>
<td>I</td>
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<tr>
<td>Measured value</td>
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<tr>
<td>Experimental standard deviation of the mean</td>
<td>0.005</td>
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<tr>
<td>B. 0.059</td>
<td></td>
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<tr>
<td>Values carried by calibration standards</td>
<td>0.002(^a)</td>
</tr>
<tr>
<td>Reference value</td>
<td></td>
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<tr>
<td>Dilute acid standard established from measurement</td>
<td>0.002(^d)</td>
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<tr>
<td>in a cell without liquid junction</td>
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<tr>
<td>or</td>
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<tr>
<td>in a cell with a free-diffusion junction</td>
<td>–</td>
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<tr>
<td>or</td>
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<tr>
<td>Dilute acid standard established by preparation/calculation:</td>
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<tr>
<td>hydrogen ion concentration</td>
<td>–</td>
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<tr>
<td>hydrogen ion activity coefficient</td>
<td>–</td>
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<tr>
<td>atmospheric carbon dioxide</td>
<td>–</td>
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<tr>
<td>Combined standard uncertainty</td>
<td>0.006</td>
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<td>B. 0.059</td>
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</table>

\(^a\) This is the uncertainty of the NBS SRM 185 and SRM 186a/186b used for preparing calibration buffers in the original study, specified as not exceeding ±0.005 pH unit in the NBS certificates [37] and expressed as standard uncertainty, assuming a triangular probability distribution. (This so-called Type B evaluation of standard uncertainty is detailed in Ref. [38], item 4.3.9, and Ref. [39].)

\(^b\) In this case, AnalaR grade chemicals (BDH) were used for preparing calibration buffers, so that a direct evaluation of the uncertainty in pH is a problem. It was demonstrated however that these chemicals if used as pH standards are almost identical with the corresponding NBS SRMs: the potential difference measured on a cell consisted of the AnalaR and SRM potassium hydrogen phthalate solutions was found to be less than 0.1 mV [10], which is equivalent to the pH difference within 0.002. The uncertainty calculated combines contributions from the SRM uncertainty (0.002), the SRM batch-to-batch variation (0.003 as a range, Ref. [7], item 6.2), and the pH difference revealed (0.002 as an uncorrected bias).

\(^c\) The estimate is derived from the specification limits (±0.01) for certified pH buffer solutions used in the original study, assuming a triangular probability distribution.

\(^d\) This is a typical standard uncertainty for pH measurement in a cell without liquid junction [7].

\(^e\) There is no information (NI). This uncertainty is assumed negligible, particularly, in view of the low precision of the measurement in that study.

\(^f\) This is the between batch standard deviation in preparation of the dilute acid standard, estimated to be 0.5 mV at 25 °C in Ref. [14].

\(^g\) This uncertainty estimate is derived from the concentration limits of \( m_{1\pm0.0005} \) mol dm\(^{-3} \) sulphuric acid, assigned to the dilute acid standard in the original study [31] due to the reagent concentration errors and volumetric ware errors. Assuming a triangular probability distribution within the limits, the standard uncertainty \( u(m_{1\pm0.0005}) \) is estimated to be 0.002 × 10\(^{-5} \) mol dm\(^{-3} \), which results in the corresponding uncertainty in pH \( u(pH_{m1\pm0.0005}) = 0.4344u(m_{1\pm0.0005})/m_{1\pm0.0005} = 0.002 \).

The hydrogen ion activity coefficient \( \gamma_{H^+} \) in a very dilute aqueous solution of a strong electrolyte such as hydrochloric acid is conventionally equal to the mean ionic activity coefficient \( \gamma_m \), that is experimentally determined from observed electromotive forces. According to Harned and Qwen (Ref. [40], Appendix A, Table (II-4-1A)) the activity coefficient \( \gamma_m \) in 0.0001 mol dm\(^{-3} \) HCl solution is 0.9891 at 25 °C. The accuracy of this value cannot be, however, better than ±0.001 considering that the error in the e.m.f. measurement was of the order of ±0.05 mV and, furthermore, an extrapolation procedure was used in this low concentration range (see Ref. [40], pp. 466–467). Note also that in the official compilation [41], the values of the mean activity coefficients are given to the third decimals only. From this information, with the assumption of a triangular probability distribution for the variable within the limits ±0.001, the standard uncertainty \( u(\gamma_{H^+}) \) is found as 0.0004, resulting in the uncertainty in pH \( u(pH_{\gamma_{H^+}}) = 0.4344u(\gamma_{H^+})/\gamma_{H^+} = 0.0002 \). (This intrinsic uncertainty of the convention that the individual ionic activity coefficient equals the mean ionic activity coefficient is disregarded here.)

\(^h\) This is a bias in pH of a 10\(^{-4} \) mol dm\(^{-3} \) strong monoprotic acid solution, caused by the influence of atmospheric carbon dioxide \( (p_{CO2} = 10^{-1.5} \text{ atm}) \). The dissolution, hydration, and ionization equilibria of CO\(_2\) in acid solution are described by the equation \( [H^+] [\text{HCO}_3^-] = K_{al}K_{PCO2}, \) where \( [\text{HCO}_3^-] = [H^+] \gamma_{CO2} \) is the additional hydrogen ion concentration due to the carbon dioxide present. Numerical values of \( pK_{al} = 1.47 \) and \( pK_{1} = 6.35 \) at 25 °C [42] were used in the calculation.
a true bias $B$, i.e., the results from different studies are mutually consistent. Then, the best estimate of $B$ is given by the weighted mean $b_w$ according to

$$b_w = \frac{\sum_i w_i b_i}{\sum_i w_i} \tag{4}$$

where the weights are equal to the reciprocals of the squares of the corresponding standard uncertainties, $w_i = u_i^{-2}$; and the standard uncertainty of the mean, $u_w = u(b_w)$, is defined by the equation:

$$u_w^2 = \frac{1}{\sum_i w_i} \tag{5}$$

Recently, the matter of consistency of measurement data has received much attention with regard to the evaluation of Key Comparisons performed under the aegis of the Consultative committees of the Comité International des Poids et Mesures (CIPM). Several consistency tests were studied (see [43] and references therein), from which the $\chi^2$ test is recommended [44] in a general way.

Thus, in testing the consistency of the pH bias data we used the statistic $T$:

$$T = \sum_i (b_i - b_w)^2 / u_i^2 \tag{6}$$

that has a $\chi^2$ distribution with $n - 1$ degrees of freedom for $i = 1, \ldots, n$. For the data under consideration the calculation gives: $T = 9.45$. This is lower than the critical $\chi^2$ value equal to 11.07 at 5 degrees of freedom (the significance level $P = 0.05$). This means that all of the six results (from data sets I–V) are accepted, including those having both an extremely low and extremely high uncertainty.

The resulting mean bias calculated from Eq. (4) is $b_w = 0.043$ with its expanded $(k = 2)$ uncertainty derived from Eq. (5) $u_w = 0.007$. Obtained on the variety of measurements with reference to the $10^{-4}$ mol dm$^{-3}$ strong acid solution, this figure represents an overall estimate of the RLJP error in pH measurement at low ionic strength.

4. Accounting for the RLJP bias in pH uncertainty calculation

The question now arises of how to handle the estimated bias in the pH uncertainty calculation. The bias is statistically significant ($b_w > U_w$) and clearly attributable to a specific cause, the nonzero RLJP in pH measurement. This gives grounds, in accordance with the basic measurement uncertainty methodology [38:3.2.4], for a correction, equal in magnitude to $b_w$, to be applied to each result of the measurement of pH in low ionic strength solutions. An alternative way is increasing the uncertainty interval by one of the approaches [45,46] suggested to take uncorrected bias into account, since making correction is often considered impractical in routine chemical measurement. We used the methods for handling uncorrected bias, as a more common case, to assess the RLJP uncertainty contribution in pH measurement.

Table 3 compiles the results of calculations by applying two of such methods, that result in symmetrical uncertainty intervals $±U$. One of the methods (abbreviated SUMU$_{\text{Max}}$) enlarges the uncertainty by adding the absolute value of bias, while the other one (RSSu) does it by root-sum-squaring all the components. (The latter method has recently been standardized in gas analysis [47].) Both approaches ensure high coverage probabilities, as it follows from simulation studies (see [45] and references therein).

As a basic uncertainty $u_c$ to which the bias-related components are added, the combined standard uncertainty $u_c(\text{pH})$ found in Ref. [4] was taken. Two typical values of $u_c$, 0.027 and 0.048, were selected from those reported there for a number of experimental conditions, corresponding to pH$_x$ 7.5 and 3.5 obtained (at 25 °C; without automatic temperature compensation) on calibration with the respective pair of buffer solutions having pH 4.00/10.00 and 4.00/7.00. (The second set of conditions is close to that of pH determination in water, specifically, in interlaboratory studies [33,34].)

As is seen from Table 3, the expanded uncertainties obtained by SUMU$_{\text{Max}}$ and RSSu are not signiﬁcantly different for a particular value of $u_c$. The inclusion of the RLJP contributions results in the expanded uncertainty $U$ of about 0.10 at pH$_x = 7.5$, near the isopotential point and in the center of the calibration range, where the basic uncertainty $u_c$ is known to be minimal (see, e.g., Fig. 1 in Ref. [4]). A higher uncertainty is observed at pH$_x = 3.5$ that is beyond the calibration range limited in this case by the phthalate and phosphate standard buffers. The uncertainties at other pH$_x$ values (within the expected measurement range) or other conditions of the measurement can directly be obtained from the corresponding standard uncertainties $u_c(\text{pH})$ calculated by following the procedure described in Ref. [4].

In this way, quite realistic uncertainty values for routine pH measurement in water are produced. The level of uncertainty obtained agrees well with the available practical estimates, namely, ±0.1 pH unit as accepted in Standard Methods [48,49] to represent the “limit of accuracy” under normal conditions for measurement in water and poorly buffered solutions. (The pertinent ISO standard [50] gives only indirect evidence on the uncertainty of the measurement, stating that the result should in general be expressed to one decimal place.)

Finally, it should be pointed out that the estimates of $b_w$ and $u_w$ used in the uncertainty calculation have been derived from the results of experimental studies, with a few anomalous results caused by malfunctioning electrodes rejected. Accordingly, in following this strategy it is assumed that a quality control procedure that consists in checking the electrode system against a dilute acid standard should be in operation in analytical laboratory to ensure

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<thead>
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<th>Abbreviation</th>
<th>Formula</th>
<th>$\text{pH}_x$</th>
<th>$U(k=2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUMU$_{\text{Max}}$</td>
<td>$U = k \sqrt{u_c^2 + u_w^2 +</td>
<td>b_w</td>
<td>}$</td>
</tr>
<tr>
<td>RSSu</td>
<td>$U = k \sqrt{u_c^2 + u_w^2 + b_w^2}$</td>
<td>7.5</td>
<td>0.102</td>
</tr>
</tbody>
</table>

* Abbreviations and formulae for the methods are given according to Ref. [45].
the validity of the uncertainty statement in pH measurements produced in the laboratory.

5. Conclusions

Being a peculiar source of error in pH measurement, the residual liquid junction potential needs to be accounted for in pH uncertainty estimation. This problem, although often mentioned as being of principal importance, has not been properly solved so far as is evident from current literature. Particularly, the role of the multipoint calibration as a means of accounting the variation in liquid junction potentials should not be overemphasized, since this variation does not allow for the differences in ionic strengths and relevant properties between the test samples and calibration solutions.

Neither the results of theoretical calculations nor the available experimental data on liquid junction potentials, obtained under idealized measurement conditions, can be used to advantage in pH uncertainty calculation performed following the model (uncertainty propagation) approach. A more efficient way is to account for the actual RJP error estimated for a specific class of analytical objects under a variety of measurement conditions.

Evaluation of the data from five independent studies on pH measurement in low ionic strength waters resulted in the weighted mean bias of 0.043 ± 0.007 (k = 2) as observed in the 10⁻³ mol dm⁻³ strong acid solution. With this estimate of the RJP, the measurement uncertainties reported in Ref. [4] can be enlarged by one of the methods suggested in literature for taking the uncorrected bias into account. The resulting expanded uncertainty that gives a symmetrical uncertainty interval ±U (k = 2) about the measured pH value was found to be around 0.10 at room temperature, near the isopotential point and in the center of the calibration range. Higher uncertainty is observed at less favorable conditions.

The uncertainty obtained is typical for the results of pH measurement in dilute and poorly buffered aqueous solutions, and this uncertainty estimate will be valid for future measurements, provided that a quality control procedure checking the electrode performance is in operation in the laboratory.

Acknowledgment

I.L. is grateful for support provided by the targeted financing project SF0180061s08 from the Ministry of Education and Science of Estonia.

References

[34] D. Midgley, Determination of pH in poorly buffered waters: results of a programme of collaborative analytical quality control, Central Electricity Generating Board, Leatherhead, 1985;