# Combined Measurement Uncertainty for *pH*-Values Using Certified Reference Materials in Potentiometric Measurements with Glass Electrodes

**Samuel Wunderli**

**Abstract** The practical realisation of *pH*-measurements with Harned-cell type equipment used for the measurement of primary standards as recommended by IUPAC is shortly outlined. In contrast to the Harned-cell without transference, the glass electrode with a junction is preferred and more practical for field laboratories. The combined measurement uncertainty is evaluated step by step in a systematic way according to ISO-GUM for a sample *pH*-value measured using a glass type electrode system, that was calibrated with two certified *pH*-reference material solutions.

**Keywords** *pH*-measurement · Hydrogen electrode · *pH*-glass electrode · Harned-cell · Certified *pH*-reference materials · CRM · Uncertainty · Calibration · ISO-GUM

## 1 Measurement of *pH*, IUPAC 2002 Recommendation in Short

The measurement of *pH*-values is among the most widespread and frequent analytical-chemical measurement tasks. The knowledge of the hydrogen ion activity $a(H^+)$ in a water type medium expressed as a *pH*-value is important in numerous fields of activities with almost uncountable applications. To name just a few of the application fields: analytical chemistry, clinical chemistry, biochemistry, biology, water chemistry, nutrition production, environmental chemistry, geochemistry, etc. Often the *pH*-value is even of dominant importance such as e.g. in groundwater or in biological fluids. The logarithmic scale of *pH* in water ranges from 0 to 14. Values for the *pH* of a solution are mostly measured by instruments since its first definition by Søren Peter Lauritz Sørensen in 1909 [1] as the logarithm of a concentration value.

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Later on it was recognised that not the concentration $c(\mathrm{H}^+)$ but the chemical activity $a(\mathrm{H}^+)$ is the quantity involved in Sørenson's measurements. For a long time two *pH* scales where in use and it was also recognised, that without an extra-thermodynamic assumption *pH*-values could not be accessed purely by measurement. Single-ion activities can only be evaluated if the value of the activity of a counter ion is known or defined by a suitable convention. Single ion activities are not accessible directly by measurement without such an assumption and knowledge of the activity of a counter ion. This dilemma was ultimately approached by a IUPAC working group of scientists and published as the todays valid IUPAC-definition of *pH* [2, 3], based mainly of the fundamental work of R. G. Bates, R. A. Robinson, R. H. Stokes, R. A. Durst, A. K. Covington, F. G. K. Baucke, R. Naumann and many other researchers.

Using the convention of Bates-Guggenheim [4] the activity of the chloride ion was defined. It holds for ionic strength values less than or equal 0.1 mol kg$^{-1}$ solvent ($\leq$0.1 m).

$$\log\left\{\gamma\left(\mathrm{Cl}^-\right)\right\} = -\frac{A \cdot \sqrt{I}}{1 + 1.5 \cdot \sqrt{I}} \quad A \text{ Debye−Hückel constant, } I \text{ ionic strength}$$

For all temperatures and all type of solutions the ion size parameter $a$ multiplied by the Debye-Hückel-$B$-constant in the above equation is set to be 1.5 (mol kg$^{-1}$)$^{-0.5}$.

Bates-Guggenheim-Convention for the activity coefficient of chloride:

$$\log\left\{\gamma(\mathrm{Cl}^-)\right\} = -\frac{A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} = -\frac{A \cdot \sqrt{I}}{1 + 1.5 \cdot \sqrt{\frac{I}{m^0}}}$$

$A$ Debye-Hückel constant or Debye-Hückel slope:

$$A = \left(\frac{1}{4 \cdot \varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T}\right)^{3/2} \cdot e^3 \cdot (2 \cdot N_A \cdot \rho_w)^{1/2} \cdot \frac{1}{\pi \cdot \ln 10}$$

| | |
|---|---|
| $A$ | 0.5062 (mol kg$^{-1}$)$^{-0.5}$ at 20 °C |
| $B.a$ | $B \cdot a = 1.5$ (mol kg$^{-1}$)$^{-0.5}$ $a$ is the ion size parameter, set fix for 5 °C–50 °C, Debye-Hückel $B$-constant |
| $I = \frac{1}{2} \cdot \sum_i m_i \cdot z_i^2$ | ionic strength on the molal scale ($m_\mathrm{i}$: mol per kg solvent) |
| $e$ | elementary charge of the electron: 1.602176634 × 10$^{-19}$ C (exact) |
| $\varepsilon_0$ | electric field constant (vacuum electric permittivity): 8.8541878128(13) × 10$^{-12}$ F m$^{-1}$ |
| $\varepsilon_r$ | dielectricity constant of water: 80.2 at 20 °C [5] |
| $k$ | Boltzmann constant: 1.380649 × 10$^{-23}$ J K$^{-1}$ (exact) |
| $N_A$ | Avogadro constant: 6.02214076 × 10$^{23}$ mol$^{-1}$ (exact) |
| $\rho_w$ | density of water: 998.2067(8) kg m$^{-3}$ at 20 °C [6] |
| $T$ | absolute temperature K |

Standard uncertainties are given in parentheses ( ) and represent the last digits of the value.

Data are from CODATA: https://pml.nist.gov/cuu/Constants/.

These temperature dependent Debye-Hückel constants *A* are numerically calculated as the following values: 0 °C: 0.4922, 5 °C: 0.4953: 10 °C: 0.4987, 15 °C: 0.5024, 20 °C: 0.5062, 25 °C: 0.5103, 30 °C: 0.5146, 35 °C: 0.5191, 40 °C: 0.5239.

In practice the IUPAC definition is useful in the *pH* range of 3–10. For seawater with higher ionic strength values up to about 0.93 mol $\text{kg}^{-1}$ an approach based on the semi-empirical theory, the ion-interaction theory of Pitzer [7], which uses a virial-expansion-equation for the Gibbs-free energy, is more appropriate but not yet standardised on an international level. These Pitzer-type semi-empirical activity coefficients can be calculated for complex electrolyte mixtures up to high ion strengths values [8, 9].

The *pH*-value is defined as follows:

$$pH = -\log\{a_\mathrm{H}\} = -\log\left\{\frac{\gamma_\mathrm{H} \cdot m_\mathrm{H}}{m^0}\right\}$$

$a_\mathrm{H}$ activity of the hydrogen ion $H^+$
$\gamma_\mathrm{H}$ molal activity coefficient of the hydrogen ion $H^+$
$m_\mathrm{H}$ molality of the hydrogen ion $H^+$
$m^0$ standard-molality: 1 mol $\text{kg}^{-1}$ solvent (water)

This definition requires the knowledge of a single ion activity. A measurement of a single ion activity is impossible and a sound estimation or a convention for the activity of the counter ion (chloride in this case) is necessary in order to tackle the problem.

The present day method of measurement for *pH* is broadly accepted and recommended by IUPAC. It was published in the year 2002 by a working group of experts [2].

Before this time two different *pH*-scales were in use. It was clear that such a condition was untenable from a metrological point of view, although the inconsistencies were not great [10].

The recommended electrochemical cell by IUPAC used for primary standards measurements is without transference and is named Harned-cell:

$$\text{Pt} \,|\, \text{H}_2 \,|\, \text{buffer S, Cl}^- \,|\, \text{AgCl} \,|\text{Ag}$$

In this redox-cell hydrogen is oxidised on the surface of a platinum electrode producing hydrated protons. A pictorial description may be as such: Molecular hydrogen $H_2$ as a gas is energetically favorably adsorbed on the solid surface of the platinum electrode, the single bond H–H is weakened through adsorption, possibly broken up, resulting in two adsorbed hydrogen atoms per molecule, subsequently these adsorbed hydrogen atoms are oxidised and immediately hydrated by water molecules in a concerted way producing the hydrated protons.

The two conducting electrons from the hydrogen molecules in the platinum electrode are moving through the metallic conductor from the cathode towards the anode where silver chloride is reduced to silver atoms that frees chloride ions from the solid AgCl. The chloride ion diffuses into the water based electrolyte solution.

The cell reaction is therefore shortly described as:

$$\tfrac{1}{2}\mathrm{H_2} + \mathrm{AgCl} \rightarrow \mathrm{Ag(s)} + \mathrm{H^+_{aq}} + \mathrm{Cl^-_{aq}}$$

The measured potential difference, referenced to a partial pressure of the hydrogen gas of the standard atmosphere 1 atm (101325 Pa) is expressed by the following approach in a Nernst equation:

$$E_I = E^0 - \left(\frac{R \cdot T}{F} \cdot \ln 10\right) \cdot \log\left\{\left(\frac{m_{\mathrm{H}} \cdot \gamma_m}{m^0}\right) \cdot \left(\frac{m_{\mathrm{Cl}} \cdot \gamma_{\mathrm{Cl}}}{m^0}\right)\right\}$$

| | |
|---|---|
| $E^0$ | standard potential of the Ag/AgCl reference electrode |
| $R$ | molar gas constant $R = N_A \cdot k$: 8.314462618 ... J $\mathrm{mol}^{-1}$ $\mathrm{K}^{-1}$ (exact) |
| $T$ | absolute temperature K |
| $F$ | Faraday constant $F = N_A \cdot e$: 96485.33212 ... C $\mathrm{mol}^{-1}$ (exact) |
| $\gamma$ | activity coefficient of hydrated proton rep. chloride |
| $m_{\mathrm{H}}$, $m_{\mathrm{Cl}}$ | molality of hydrated proton and of the chloride |
| $m^0$ | the standard molality (1 mol $\mathrm{kg}^{-1}$ solvent) |

Data are from CODATA: https://pml.nist.gov/cuu/Constants/.

For the equation to be valid the lead attached to the hydrogen electrode has to be connected with the minus pole of the high–impedance voltmeter.

The measured potential is linearly proportional to the absolute temperature $T$. $E^0$ is the standard potential for the silver/silver chloride electrode with respect the standard hydrogen electrode, which is the zero point for all temperatures.

The so called acidity function $p(a_{\mathrm{H}} \cdot \gamma_{\mathrm{H}})$ results from this equation [11]. The operator $p$ denominate the negative decadic logarithm:

$$a_{\mathrm{H}} = \frac{m_{\mathrm{H}} \cdot \gamma_{\mathrm{H}}}{m^0}$$

$$p(a_{\mathrm{H}} \cdot \gamma_{\mathrm{Cl}}) = -\log\{a_{\mathrm{H}} \cdot \gamma_{\mathrm{Cl}}\} = \left(\frac{E_I - E^0}{(R \cdot T/F) \cdot \ln 10}\right) + \log\left\{\frac{m_{\mathrm{Cl}}}{m^0}\right\}$$

By measuring the potential of a Harned cell with the solution in question and e.g. three different solutions with and added sodium or potassium chloride ($m_{\mathrm{Cl}}$ range: 0.005 mol kg$^{-1}$ to 0.02 mol kg$^{-1}$) with known ion strength and linear extrapolation of the acidity function to zero molality for chloride. This procedure gives the *pH*-value of the primary standard (PS):

$$pH(\mathrm{PS}) = \lim_{m_{\mathrm{Cl}} \to 0}\left\{\frac{\left(E_I - E^0\right)}{[RT/F]}\ln 10\right\} + \log\left\{\frac{m_{\mathrm{Cl}}}{m^0}\right\} - \frac{A\sqrt{I}}{\left[1 + 1.5 \cdot \sqrt{\frac{I}{m^0}}\right]}$$

The molal activity coefficients of the chloride ions in the three solutions mentioned above are calculated using the Bates-Guggenheim Convention (cf. above).

For the practical realisation of a hydrogen electrode guidance can be found in Chap. 5 of the handbook of reference electrodes [12].

In practice the operation of a hydrogen electrode is fundamental and used to measure values für primary and secondary *pH*-standards. But its operation is not suitable for applications in field laboratories. Therefore in most field laboratories the combined *pH*-glass electrodes with either fine pored diaphragm or a glass sleeve or membrane or a capillary type systems are in use.

By this it becomes unavoidable that the diffusion potential or junction potential between the sample solution and the electrolyte solution of the outer reference electrode system is effective and has to be considered for a correct *pH*-measurement.

On the following pages the uncertainty evaluation of *pH*-values measured by a combined *pH*-glass electrode system is outlined in detail step by step as suggested by the EURACHEM-CITAC Guide 3rd.ed. 2012 (Quantifying uncertainty in analytical measurement) or the JCGM-100:2008 guide (Guide to the Expression of Uncertainty in Measurement, which is the so called ISO-GUM with minor corrections). Both documents are available free of charge as .pdf-documents on the BIPM (JCGM-100) and the EURACHEM homepage. Additional suitable informations on potentiometric *pH*-measurement with glass electrodes are given by a number of authors in the literature references [11, 13–30]. Part of their approaches are used in the following elaboration.

## 2 Uncertainty Evaluation for a *pH*-Value Measured Using a Combined *pH*-Glass Electrode

### Step 1: Specification of the measurand

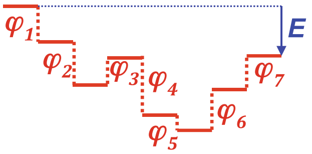
The combined *pH*-glass electrodes contain an inner as well as an outer reference electrode system as well as a proton selective glass membrane and a diaphragm or other connections to the outer reference electrode. Special glasses have the ability to reversibly take up hydrated protons in their network. The selectivity is never perfect and leads to the so called alkali error which is minimised by using suitable glass compositions. The selective surface uptake of hydrated protons results in local charge separation, which manifests itself as a change in Galvani-potential at the boundary.

The silver/silver chloride electrodes [12, Chap. 5.2.1 by K. Maksymiuk, A. Michalska, A. Kisiel, Z. Galus] serve as connecting links between the electron-conducting part of the measuring system and the ion-conducting part. At each phase boundary the potential changes (work per charge). The potentiometric measurement device shows the sum of all potential differences (galvanic voltages, diffusion voltages, ohmic resistances) over the entire cell. Ideally, the potential difference at the interface between the proton selective glass membrane and the sample solution changes in proportion to the logarithm of the activity of the hydrated proton according to Nernst. In practice, however, the measured cell potential is also dependent on the size of the diffusion potential resulting from the different mobilities $u_\mathrm{i}$ of the ions between the electrolyte of the outer reference and the sample solution. Strongly acidic and strongly basic solutions generally lead to a large diffusion potential, since both the hydrated proton $H^+$ and the hydroxyl ion $OH^-$ are much more mobile than other ions due to their special mechanism of charge conduction.

The schematic structure of a pH glass electrode assembly as a cell diagram shows seven phase boundaries:

Ag | AgCl | KCl 3M, buffer | glass membrane | sample solution $a_\mathrm{H}$ || KCl 3M | AgCl | Ag.
Ag $\boldsymbol{\varphi_1}$ AgCl $\boldsymbol{\varphi_2}$ KCl 3M, buffer $\boldsymbol{\varphi_3}$ glass membrane $\boldsymbol{\varphi_4}$ sample solution $a_\mathrm{H}$ $\boldsymbol{\varphi_5}$ KCl 3M $\boldsymbol{\varphi_6}$ AgCl $\boldsymbol{\varphi_7}$ Ag.

Since only the Galvani-potential difference $\boldsymbol{\varphi_4}$ is actually of interest, all other voltage differences must be kept constant for calibration and sample measurements. In addition to the potential changes at the interfaces, the ohmic resistances of the conducting phases are added. Virtually no current flows, as the internal resistance of the pH-voltmeter used is very high (usually approx. $10^{12}\ \Omega$–$10^{15}\ \Omega$). At the phase boundaries of the various materials, a charge separation takes place, which leads to galvanic voltages. These cannot be determined individually since there are always at least two such phase boundaries involved in a cell. The sum of all these Galvani voltages $\boldsymbol{\varphi_i}$ or potential differences [12, Chap. 1, György Inzelt] occurring at each interface are measured with the potentiometer.



| | |
|---|---|
| $\boldsymbol{\varphi_1}$ | potential difference between metallic silver and solid silver chloride |
| $\boldsymbol{\varphi_2}$ | potential difference between solid silver chloride and 3M KCl dependent on the activity $a_{\mathrm{Cl}}$ of the internal buffer |
| $\boldsymbol{\varphi_3}$ | potential difference between glass membrane inside and inner buffer, dependent on the pH-value of the internal buffer |
| $\boldsymbol{\varphi_4}$ | potential difference between glass membrane outside and measuring solution, dependent on the pH-value of the measuring solution |
| $\boldsymbol{\varphi_5}$ | diffusion potential (junction potential, $E_J$) [12, Chap. 3, Galina Tsirlina] between measuring solution and the electrolyte of the outer reference electrode, dependent on the ion mobilities $u_i = \lambda_i \big/ F$ ($\lambda_i$: equivalence conductivity, $F$: Faraday constant), the concentrations $c_{\mathrm{i}}$ and the electrical charges $z_{\mathrm{i}}$ of all ions in these two phases $_{1,\,2}$: cf. Henderson-equation: |

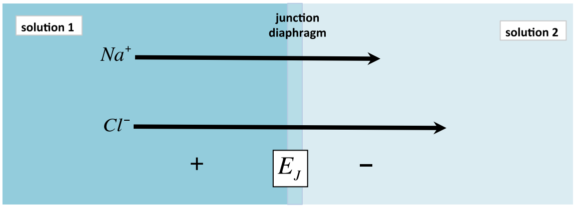
$$E_J = \frac{R\cdot T}{F}\cdot\frac{\left(\sum u^{+}_{i,1}\cdot c_{i,1} - \sum u^{-}_{i,1}\cdot c_{i,1}\right) - \left(\sum u^{+}_{i,2}\cdot c_{i,2} - \sum u^{-}_{i,2}\cdot c_{i,2}\right)}{\left(\sum u^{+}_{i,1}\cdot c_{i,1}\cdot z_i - \sum u^{-}_{i,1}\cdot c_{i,1}\cdot z_i\right) - \left(\sum u^{+}_{i,2}\cdot c_{i,2}\cdot z_i - \sum u^{-}_{i,2}\cdot c_{i,2}\cdot z_i\right)}$$
$$\cdot \log\left\{\frac{\left(\sum u^{+}_{i,1}\cdot c_{i,1}\cdot z_i + \sum u^{-}_{i,1}\cdot c_{i,1}\cdot z_i\right)}{\left(\sum u^{+}_{i,2}\cdot c_{i,2}\cdot z_i + \sum u^{-}_{i,2}\cdot c_{i,2}\cdot z_i\right)}\right\}$$

Henderson-equation for $E_J$ is an approximation with approximately linear ion concentration distributions along the normal to the boundary:

Residual liquid junction potential:

$$\Delta E_{J,r} = E_{J,cal} - E_{J,sample}$$

It is the difference of the two diffusion potentials between the sample solution and the calibration solution (cf. Table for 3M KCl outer reference). The diffusion potential for the sample solution is generally unknown and can only be guessed.



KCl 3M, outer reference

| solution | $E_\mathrm{l}$ ; mV |
|---|---|
| NaCl, 0.001 M | - 3.96 |
| NaCl, 0.01 M | - 2.77 |
| NaCl, 0.1 M | - 1.23 |
| NaCl, 1 M | 1.79 |
| NaCl, 3M | 4.36 |

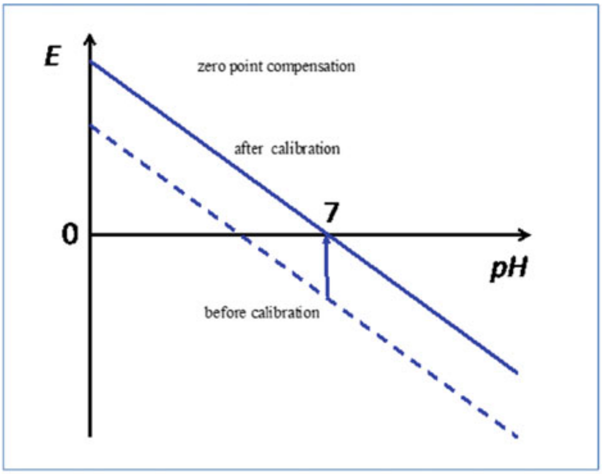
| solution | $E_\mathrm{l}$ ; mV |
|---|---|
| $MgCl_2$, 0.001 M | - 3.58 |
| $MgCl_2$, 0.01 M | - 2.22 |
| $MgCl_2$, 0.1 M | -0.26 |
| $MgCl_2$, 1 M | 6.78 |
| $MgCl_2$, 3 M | 12.48 |

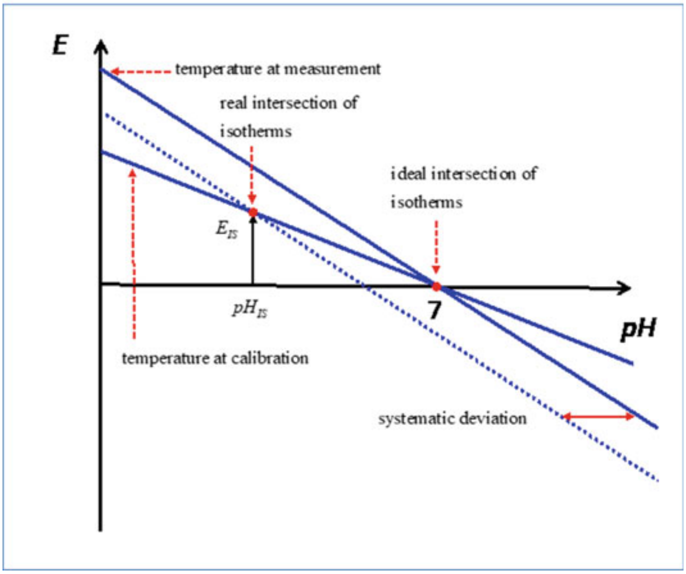
The diffusion potential is small when the electrolyte of the outer reference electrode solution contains ions of equal or similar mobility {e.g. electrolyte KCl: $u(K^+) \approx u(Cl^-)$} and when this electrolyte is highly concentrated (4.8 mol $kg^{-1}$ KCl, counter ion logarithm large and possibly the same or similar value as the denominator, e.g. CsCl 11.3 mol $kg^{-1}$ or RbCl 7 mol $kg^{-1}$, $LiSO_4$ 3M). If the diffusion potential is large, the chain voltage is often depending on the stirring speed of the sample solution. Such an influence is to be avoided.

In practice, however, the residual diffusion potential (RLJP, residual liquid junction potential) is of most importance. That's the difference between the diffusion potentials produced between the calibration and the sample solution due to mainly differences in ionic strength and ion composition. The ionic strength and the composition of calibration and sample solutions should be as similar as possible. Diffusion potentials or junction potentials can be estimated using the Henderson equation.

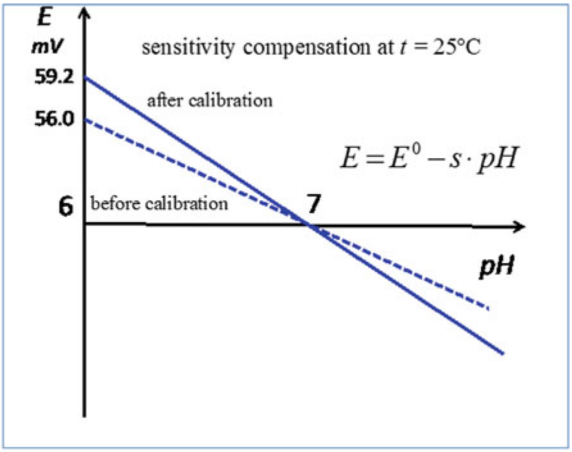
$\boldsymbol{\varphi_6}$ Potential difference between 3M KCl and solid silver chloride (=$\boldsymbol{\varphi_2}$)
$\boldsymbol{\varphi_7}$ Potential difference between solid silver chloride and metallic silver (=$\boldsymbol{\varphi_1}$)

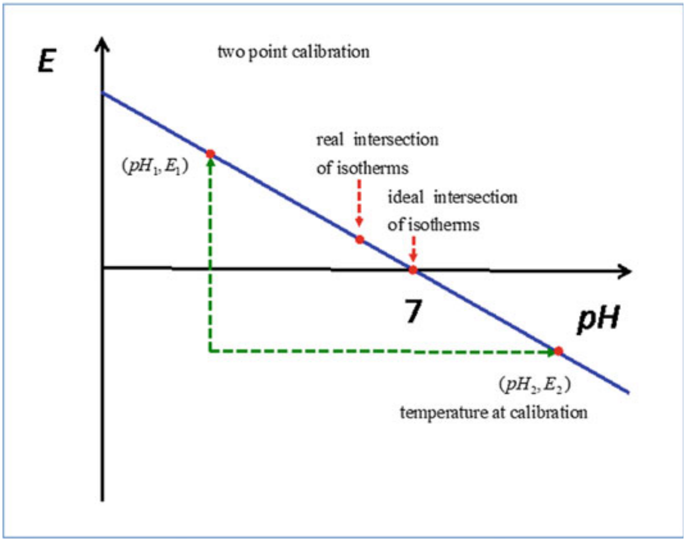
For the calibration of the measuring device, there are various methodical approaches (one-point, two-point, bracketing calibration, multiple-points, etc.). The most commonly used method is the two-point calibration method with two solutions whose pH values ($pH_1$, $pH_2$) are known, i.e. certified reference materials documents. From this calibration, the practical slope ($\Delta E/\Delta pH$) value, ideally according to Nernst, would be 59.2 mV/$pH$ at 25 °C, in general ($R \cdot T/F \cdot \ln 10$) and the zero point are obtained. The zero point of a cell voltage corresponds to the $pH$ value at which the measured cell voltage is zero. It is usually close to $pH = 7$. The zero point is dependent on all individual voltage differences at each phase boundary of a $pH$ electrode assembly and can change therefore.





Isotherm intersection at $\{pH_{\mathrm{IS}}, E_{\mathrm{IS}}\}$ not at $\{pH = 7, E = 0\}$





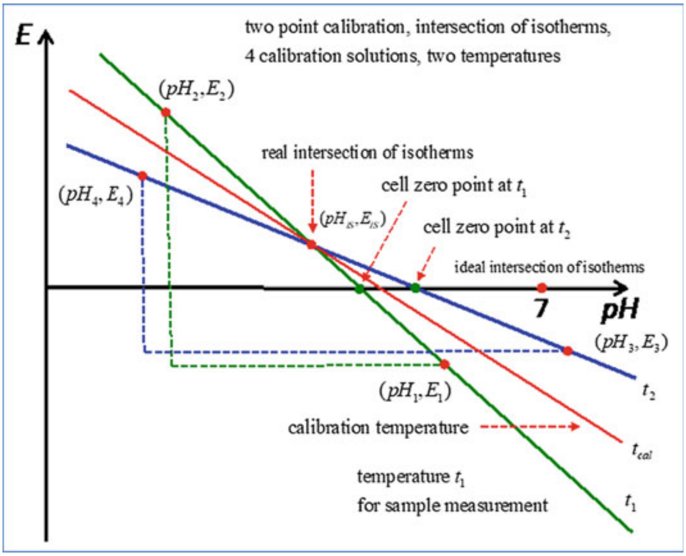
Two point calibration using CRMs at a defined temperature

The practical zero point of the cell is the intersection of the calibration line with the $pH$ axis at $E = 0$. The calculation requires the values for the cell voltage at two different $pH$ values:

$$pH_{0,t_1} = \frac{pH_2 \cdot E_1 - pH_1 \cdot E_2}{E_1 - E_2} \quad pH_{0,t_2} = \frac{pH_4 \cdot E_3 - pH_3 \cdot E_4}{E_3 - E_4}$$

An equilibrium voltage is read if the potential change has reached less than 0.1 mV per 10 s measurement time.

The sensitivity (slope) of the calibration line ($E$ vs. $pH$) changes with temperature because the Nernst voltage is temperature dependent. The change is linear. Calibration lines recorded at different temperatures intersect at the isothermal intersection point ($pH_{\mathrm{IS}}, E_{\mathrm{IS}}$). With symmetrical cells (identical or equal inner and outer reference systems) the straight lines intersect at one point. If one uses an automatic temperature compensation with an asymmetrical cell, a systematic deviation results. The isotherm intersection point is determined using four standards at two temperatures.



Four point calibration with CRMs at two temperatures defines the isotherm intersection point $\{pH_{\mathrm{IS}}, E_{\mathrm{IS}}\}$

The behaviour of the $pH$ glass electrode can be described in the range from approx. $pH = 2$ to $pH = 12$ using a linear equation which is characteristic for a straight line bundle that passes through the fixed point ($pH_{\mathrm{IS}}$, $E_{\mathrm{IS}}$). The straight line ($E_{\mathrm{x}}$ vs. $pH_{\mathrm{x}}$) is defined by the two calibration points ($pH_1$, $E_1$), ($pH_2$, $E_2$).

$$E_x = -s(t) \cdot pH_x + C \quad E_{IS} = -s(t) \cdot pH_{IS} + C \Rightarrow C = E_{IS} + s(t) \cdot pH_{IS}$$

For the experimental slope (sensitivity) at the temperature used for the calibration the following holds:

$$s = \frac{E_2 - E_1}{pH_1 - pH_2}$$

This slope can also be determined from the isotherm intercept ($pH_{\mathrm{IS}}$, $E_{\mathrm{IS}}$) and a calibration point (e.g., ($pH_1$, $E_1$):

$$s = \frac{(E_1 - E_{IS})}{(pH_{IS} - pH_1)} \quad \Rightarrow \quad pH_{IS} = pH_1 + \frac{(E_1 - E_{IS})}{s}$$
$$= pH_1 + \frac{(E_1 - E_{IS})}{(E_1 - E_1)} \cdot (pH_2 - pH_1)$$

The effective experimental slope $s(t)$ is temperature dependent:

$$s(t) = \left( \frac{(E_2 - E_1)}{(pH_2 - pH_1)} \right) \cdot (1 + \alpha \cdot (t - t_{cal})) = s \cdot (1 + \alpha \cdot \Delta t)$$

For the intercept $C$, the following applies:

$$C = E_{IS} + s(t) \cdot pH_{IS}$$

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

| | |
|---|---|
| $\alpha$ | temperature coefficient of the effective slope $s(t)$ |
| $t_{cal}$ | temperature of the solutions at the calibration with the $pH$-values $pH_1, pH_2$ |
| $t$ | temperature of the sample when measured |
| $\Delta t$ | difference of the temperatures between calibration and measurement $(t - t_{cal})$ |

The $pH$ of the unknown solution $pH_x$ turns out to be:

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

Insertion of the experimentally determined slope $s$:

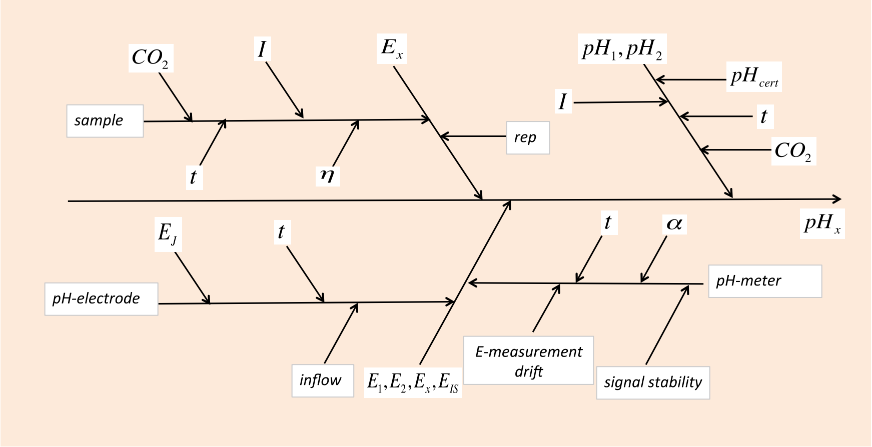
$$pH_x = \frac{(E_{IS} - E_x) \cdot (pH_1 - pH_2)}{(E_2 - E_1) \cdot (1 + \alpha \cdot \Delta t)} + pH_{IS}$$

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

This is the equation for the measurand $pH_x$, which is the $pH$-value attributed to the sample.

Certain influences, such as the inflow, the ionic strength $I$, the carbon dioxide $CO_2$ content of the air, chemical effects at large and small $pH$ values on the integrity of the glass membrane are not taken into account here.

**Step 2: Identification of the sources of uncertainty**



The fish-bone diagram for the pH-measurement helps to identify influence parameters, but it gives no information about the functional relationship of the variables that are part of the model equation for the measurand.

List of main influences:

| | |
|---|---|
| $pH_x$ | measurand, *pH* value of the sample solution (measurement solution) |
| $pH_1$, $pH_2$ | *pH*-values of the calibration solutions (certified values for $pH_1$, $pH_2$) |
| $E_1$, $E_2$ | measured voltages of the cell for the calibration solutions |
| $E_x$ | measured voltage of the cell for the sample solution |
| $E_J$ | diffusion potential (junction potential $E_5$ at diaphragm) |
| $I$ | ionic strength ($I = \frac{1}{2} \cdot \sum_i c_i \cdot z_i^2$, ion $i$, concentration $c_i$, ion charge $z_i$) |
| $\eta$ | viscosity of the sample solution |
| *Rep* | repeatability |
| $CO_2$ | influence of the carbon dioxide $CO_2$ contained in air (may be relevant for basic sample and calibration solutions if no precautions are taken) |
| *Effect from inflow* | sensitivity from stirring |
| $t$ | temperature influences slope, intersection point of isotherms, etc. |
| $\alpha$ | temperature coefficient of effective Nernst slope $s(t)$ |

Uncertainties arising from the *pH* values of the standards used $pH_1$, $pH_2$ and uncertainties of the measured voltage values $E_1$, $E_2$, $E_x$, $E_{IS}$ are to be distinguished.

For the *pH* standards used, both the value from the certificate and the effect of temperature on these values must be taken into account. The respective contributions should be additive. The standard uncertainty of the *pH* values for the standards can therefore be stated as follows:

$$u(pH_1) = \sqrt{u^2(pH_1, cert) + u^2(pH_1, t)}$$

$$u(pH_2) = \sqrt{u^2(pH_2, cert) + u^2(pH_2, t)}$$

The potentiometric measurement of the cell voltages $E_1, E_2, E_\mathrm{x}$ are subject to the following significant influences:

Repeatability of the measured values $u(E_1, rep)$, $u(E_2, rep)$, $u(E_x, rep)$, residual diffusion potential (difference of the diffusion potentials for the measurement of the calibration standards and the measurement of the sample). The diffusion potential is different for each solution if the ionic strength are not exactly the same or at least very similar. This is a well-known systematic influence that needs to be corrected and whose uncertainty plays a very important role in determining the combined measurement uncertainty. Estimates are possible but mostly inaccurate. Henderson's approach is itself an approximation and the equation for a theoretical value of $E_\mathrm{J}$ can only be used if the composition as well as the geometry of both liquid phases are known. For field laboratories such considerations usually go too far. Although wrong, this systematic effect is only calculated with an uncertainty for the measured values of the calibration standards $E_1$ and $E_2$ and not additionally as bias $\Delta pH_{EJ}$: $u\left(E_1, \Delta E_{J,1}\right)$, $u\left(E_2, \Delta E_{J,2}\right)$:

For the sample solution, this systematic influence is approximately taken into account. There remains an instrumental drift: $u(E_x, drift)$.

A possible stirring effect is already included in the consideration of the diffusion potential. The above effects are all additive.

The uncertainty of the measured potentials leads to the following approach:

$$u(E_1) = \sqrt{u^2(E_1, rep) + u^2\left(E_1, \Delta E_{J,1}\right)}$$

$$u(E_2) = \sqrt{u^2(E_2, rep) + u^2\left(E_2, \Delta E_{J,2}\right)}$$

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

The parameters $E_{IS}$, $\alpha$, $\Delta t$ have no influence factors of second order. The corresponding uncertainties are therefore simple: $u(E_{IS})$, $u(\alpha)$, $\alpha$, $u(\Delta t)$.

When measuring the unknown sample, at least the following four influencing parameters can be effective, some of which have already been taken into account.

1. Repeatability of the measurement (*rep*), 2. Uncertainty from the limited display of the *pH* meter (*read*), 3. Uncertainty due to drift of the measuring system (*drift*), 4. Temperature effect which affects the sensitivity (*slope*). This last influence has not yet been taken into account in the standards for calibration. The influences 1 and 3 are already taken into account (see $u(E_\mathrm{x})$ above). The influence of the deviating

temperature is taken into account in $u(\Delta t)$. Therefore it would be useful to extend the model equation for the measurand by adding an influence term of the *pH* measurement of the sample $\delta pH_{xm}$. The expectation value of which is zero, but not its uncertainty stemming from repeatability, readability and drift:

A more advanced model for the measurand $pH_x$ is:

$$\boxed{pH_x = \frac{(E_{IS}-E_x)\cdot(pH_1-pH_2)}{(E_2-E_1)\cdot(1+\alpha\cdot\Delta t)} + pH_1 + \frac{(E_1-E_{IS})}{(E_2-E_1)}\cdot(pH_1-pH_2) + \delta pH_{xm}}$$

$$u(\delta pH_{xm}) = \sqrt{u^2(\delta pH_{xm}, rep) + u^2(\delta pH_{xm}, read) + u^2(\delta pH_{xm}, drift)}$$

As repeatability and drift are now included in $u(\delta pH_{xm})$, the standard uncertainty becomes $u(E_x) = 0$.

## Step 3: Quantification of the uncertainties and conversion into standard uncertainties

*Information about the pH-meter used*:

*pH*-meter 780 from Metrohm. The pH meter needs the value $E_{IS} = 0$ mV for the isothermal intersection. The resolution is 0.1 mV in the mode for the potential measurement and 0.001 for the *pH* display resolution. The uncertainty of the temperature measurement is 0.1 °C. There are no data available for drift.

*Information about the pH-electrode sensor system used*:

*pH*-glass electrode filled with Ag/AgCl with 3M KCl inner and outer reference systems, ceramic diaphragm, integrated Pt1000 thermocouple, electrode zero point at 0 ± 15 mV ($pH = 7$), isotherm intersection $E_{IS}$ at 0 ± 15 mV. Electrode slope larger than 0.97 (relative to Nernst). Temperature range for application 0–80 °C.

In the literature, values for the residual diffusion potential for dilute buffer solutions of about 0.1–1.6 mV can be found. This corresponds to 0.002–0.027 *pH* units at 25 °C, or $([1 - \exp\{-\Delta E\cdot F/(R\cdot T\cdot \ln(10)\}]$.

*Theoretically*:

$$\alpha_{(25)} = \frac{1}{\Delta t}\left(\frac{R\cdot 298.15/F\cdot \ln\{10\}}{R\cdot T/F\cdot \ln\{10\}} - 1\right) = \frac{1}{(t-25)}\cdot\left(\frac{298.15}{273.15+t} - 1\right)$$
$$= 3.354\times 10^{-3}\,\mathrm{K}^{-1}$$

*Experimentally*:

$$\alpha_{(25)} = \frac{1}{(t_2-t_1)}\left(\frac{s(t_1)}{s(t_2)} - 1\right) = \frac{1}{(t_2-t_1)}\cdot\left(\frac{(E_3-E_4)\cdot(pH_2-pH_1)}{(pH_4-pH_3)\cdot(E_1-E_2)} - 1\right)$$

*Information about the certified pH-calibration solutions*:

Three certified *pH* standard reference solutions with traceable *pH* values at 25 °C:

$$pH = 4.00 \pm 0.02, pH = 7.00 \pm 0.02, pH = 10.00 \pm 0.02.$$

The temperature dependencies of the three references are in order 0.001, 0.002, 0.01 *pH* units per °C (indication of the manufacturer, certificate).

It is somewhat unfortunate, that most commercial suppliers of calibration solutions do not offer any information about the ionic strength of the certified *pH*-reference material solutions. In order to minimise the residual junction potential such information would be very usefull.

**Uncertainty components (measured: Type A, estimated: Type B)**:

| | | |
|---|---|---|
| $u(E_{IS})$ | 1 mV | B |
| $u(\alpha)$ | $0.002 \times 10^{-3}\ \mathrm{K}^{-1}$ | B |
| $u(\Delta t)$ | 1 °C | A |
| $u(E_x)$ | 0 mV | in $u(\delta pH_x)$ |
| $u(E_x) = \sqrt{u^2(E_x, rep) + u^2(E_x, drift)}$ | | |
| $u(E_x, rep)$ | 0 mV | in $u(\delta pH_x)$ |
| $u(E_x, drift)$ | 0 mV | in $u(\delta pH_x)$ |
| $u(E_1)$ | 1.56 mV | A |
| $u(E_1) = \sqrt{u^2(E_1, rep) + u^2\left(E_1, \Delta E_{J,1}\right)}$ | | |
| $u(E_1, rep)$ | 0.5 mV | A |
| $u\left(E_1, \Delta E_{J,1}\right)$ | 1.48 mV | B |
| $u(E_2)$ | 1.56 mV | A |
| $u(E_2) = \sqrt{u^2(E_2, rep) + u^2\left(E_2, \Delta E_{J,2}\right)}$ | | |
| $u(E_2, rep)$ | 0.5 mV | A |
| $u\left(E_2, \Delta E_{J,2}\right)$ | 1.48 mV | B |
| $u(pH_1)$ | 0.02 | B |
| $u(pH_1) = \sqrt{u^2(pH_1, cert) + u^2(pH_1, t)}$ | | |
| $u(pH_1, cert)$ | 0.02 | B |
| $u(pH_1, t)$ | 0.001 | B |
| $u(pH_2)$ | 0.0201 | B |
| $u(pH_2) = \sqrt{u^2(pH_2, cert) + u^2(pH_2, t)}$ | | |
| $u(pH_2, cert)$ | 0.02 | B |
| $u(pH_2, t)$ | 0.002 | B |
| $u(\delta pH_{xm})$ | 0.0201 | B |

(continued)

(continued)

| $u(\delta pH_{xm}) = \sqrt{u^2(\delta pH_{xm}, rep) + u^2(\delta pH_{xm}, read) + u^2(\delta pH_{xm}, drift)}$ | | |
|---|---|---|
| $u(\delta pH_{xm}, rep)$ | 0.002 | A |
| $u(\delta pH_{xm}, read)$ | 0.001 | B |
| $u(\delta pH_{xm}, drift)$ | 0.02 | B |

### Step 4: Propagation of the standard uncertainties for the calculation of the combined measurement uncertainty

The combined measurement uncertainty is obtained by differentiation of the measurand according to all known variables (second order contributions are not considered):

$$u_c(pH_x) = \sqrt{\begin{array}{l} \left(\frac{\partial pH_x}{\partial E_1}\right)^2 \cdot u^2(E_1) + \left(\frac{\partial pH_x}{\partial E_2}\right)^2 \cdot u^2(E_2) + \left(\frac{\partial pH_x}{\partial E_{IS}}\right)^2 \cdot u^2(E_{IS}) \\ +\left(\frac{\partial pH_x}{\partial E_x}\right)^2 \cdot u^2(E_x) + \left(\frac{\partial pH_x}{\partial \delta pH_{xm}}\right)^2 \cdot u^2(\delta pH_{xm}) + \left(\frac{\partial pH_x}{\partial pH_1}\right)^2 \cdot u^2(pH_1) \\ +\left(\frac{\partial pH_x}{\partial pH_2}\right)^2 \cdot u^2(pH_2) + \left(\frac{\partial pH_x}{\partial \alpha}\right)^2 \cdot u^2(\alpha) + \left(\frac{\partial pH_x}{\partial \Delta t}\right)^2 \cdot u^2(\Delta t) \end{array}}$$

The calculations of the partial derivatives are carried out according to known rules of differentiation or can be calculated approximately by means of difference quotients.

$$\left(\frac{\partial pH_x}{\partial E_1}\right) = \frac{(pH_1 - pH_2) \cdot (E_{IS} - E_x)}{(E_2 - E_1)^2 \cdot (1 + \alpha \cdot \Delta t)} + \frac{(-E_{IS} + E_1) \cdot (pH_1 - pH_2)}{(E_2 - E_1)^2} + \frac{(pH_1 - pH_2)}{(E_2 - E_1)}$$

$$\left(\frac{\partial pH_x}{\partial E_2}\right) = -\frac{(E_{IS} - E_x) \cdot (pH_1 - pH_2)}{(E_2 - E_1)^2 \cdot (1 + \alpha \cdot \Delta t)} - \frac{(-E_{IS} + E_1) \cdot (pH_1 - pH_2)}{(E_2 - E_1)^2}$$

$$\left(\frac{\partial pH_x}{\partial E_{IS}}\right) = \frac{(pH_1 - pH_2)}{(E_2 - E_1) \cdot (1 + \alpha \cdot \Delta t)} - \frac{(pH_1 - pH_2)}{(E_2 - E_1)}$$

$$\left(\frac{\partial pH_x}{\partial E_x}\right) = -\frac{(pH_1 - pH_2)}{(E_2 - E_1) \cdot (1 + \alpha \cdot \Delta t)}$$

$$\left(\frac{\partial pH_x}{\partial pH_1}\right) = \frac{(E_{IS} - E_x)}{(E_2 - E_1)\cdot(1+\alpha\cdot\Delta t)} + \frac{(-E_{IS} + E_1)}{(E_2 - E_1)} + 1$$

$$\left(\frac{\partial pH_x}{\partial pH_2}\right) = \frac{(E_{IS} - E_x)}{(E_2 - E_1)\cdot(1+\alpha\cdot\Delta t)} - \frac{(-E_{IS} + E_1)}{(E_2 - E_1)}$$

$$\left(\frac{\partial pH_x}{\partial \delta pH_{xm}}\right) = 1$$

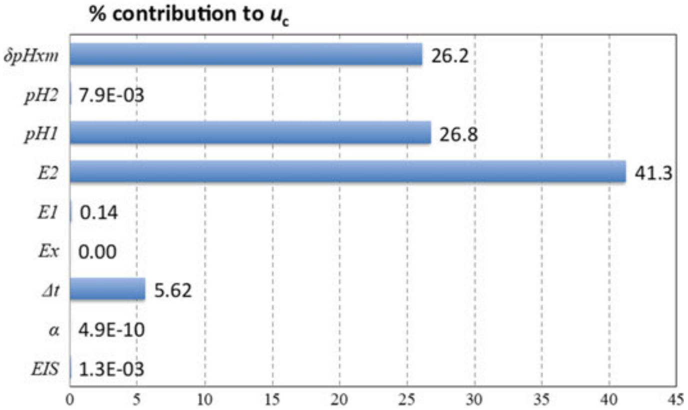
$$\left(\frac{\partial pH_x}{\partial \alpha}\right) = -\frac{(pH_1 - pH_2)\cdot(E_{IS} - E_x)\cdot\Delta t}{(E_2 - E_1)\cdot(1+\alpha\cdot\Delta t)^2}$$

$$\left(\frac{\partial pH_x}{\partial \Delta t}\right) = -\frac{(pH_1 - pH_2)\cdot(E_{IS} - E_x)\cdot\alpha}{(E_2 - E_1)\cdot(1+\alpha\cdot\Delta t)^2}$$

**Expectation values for the variables**:

| Influence parameter | Value | Standard uncertainty | Sensitivity factor |
|---|---|---|---|
| $E_{IS}$ | 1 mV | $u(E_{\mathrm{IS}}) = 1$ mV | $\left(\frac{\partial pH_x}{\partial E_{IS}}\right) = 1.44 \times 10^{-4}$ |
| $\alpha$ | $3.334 \times 10^{-3}\ \mathrm{K}^{-1}$ | $u(\alpha) = 2 \times 10^{-6}\ \mathrm{K}^{-1}$ | $\left(\frac{\partial pH_x}{\partial \alpha}\right) = 4.36 \times 10^{-2}$ |
| $\Delta t$ | −2.5 °C | $u(\Delta t) = 1$ °C | $\left(\frac{\partial pH_x}{\partial \Delta t}\right) = 9.31 \times 10^{-3}$ |
| $E_x$ | 161.4 mV | $u(E_{\mathrm{x}}) = 0$ mV | $\left(\frac{\partial pH_x}{\partial E_x}\right) = -1.73 \times 10^{-2}$ |
| $E_1$ | −2.6 mV | $u(E_1) = 1.56$ mV | $\left(\frac{\partial pH_x}{\partial E_1}\right) = 9.54 \times 10^{-4}$ |
| $E_2$ | 172.5 mV | $u(E_2) = 1.56$ mV | $\left(\frac{\partial pH_x}{\partial E_2}\right) = 1.62 \times 10^{-2}$ |
| $pH_1$ | 7.00 | $u(pH_1) = 0.02$ | $\left(\frac{\partial pH_x}{\partial pH_1}\right) = 1.02$ |
| $pH_2$ | 4.00 | $u(pH_2) = 0.0201$ | $\left(\frac{\partial pH_x}{\partial pH_2}\right) = 1.74 \times 10^{-2}$ |
| $\delta pH_{xm}$ | 0 | $u(\delta pH_{xm}) = 0.0201$ | $\left(\frac{\partial pH_x}{\partial pH_{xm}}\right) = 1$ |

**Budget of the influences on the combined measurement uncertainty $u_c$ graphically**:



### Step 5: Calculation of the expanded measurement uncertainty and reporting of the result

| | Values *pH*, mV, $°C^{-1}$, °C | Standard-uncertainty *u* | Sensitivity factors | (Sensitivity factors)$^2$ $*u^2$ | Contributions % |
|---|---|---|---|---|---|
| $pH_1$ | 7.00 | 0.02 | 1.02 | 4.14E−4 | **26.8** |
| $pH_2$ | 4.00 | 0.0201 | 0.0174 | 1.22E−7 | **7.9E−3** |
| $\delta pH_{xm}$ | 0 | 0.0201 | 1 | 4.04E−4 | **26.2** |
| $E_x$ | 161.4 | 0 | −1.75E−02 | 0 | **0** |
| $E_1$ | −2.6 | 1.56 | 9.54E−04 | 2.22E−6 | **0.14** |
| $E_2$ | 172.5 | 1.56 | 1.618E−2 | 6.37E−4 | **41.3** |
| $E_{IS}$ | 1 | 1 | 1.46E−01 | 2.07E−08 | **1.3E−3** |
| *a* | 3.334E−03 | 2.00E−06 | −7.07 | 7.6E−15 | **4.9E−10** |
| *Δt* | −2.5 | 1 | 9.43E−03 | 8.68E−05 | **5.62** |

Combined measurement uncertainty $u_c$:

$$u_c(pH_x) = 0.0393$$

Expanded uncertainty $U = k{\cdot}u_c$:

$$U(pH_x) = 2 \cdot u_c(pH_x) = 0.078 (k = 2)$$

Result:

$$\boldsymbol{pH_x = 4.167,\ U(pH_x) = 2 \cdot u_c(pH_x) = 0.078(k = 2)}$$

The largest contribution to uncertainty comes from $E_2$. Therein, the contribution of the residual diffusion potential is decisive.

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