Supplementary material

Appendix

Uncertainty budgets

The estimation of the measurement uncertainty in the examples follows the "Guide to the Expression of Uncertainty in Measurement" (GUM) [9] and the EURACHEM/CITAC Guide "Quantifying Uncertainty in Analytical Measurement" [10]. In the first example the sample pH is measured following a two-point calibration (bracketing procedure) of the pH measuring chain, referred to as pH electrode. In the second example the potential difference of the pH electrode in five reference buffer solutions (CRMs) is measured to establish the calibration line. The temperature, the stirring conditions and the parameters of the pH meter are the same for measuring the potential difference (emf, mV reading), referred to as potential, in the sample and in the CRMs. The CRMs (standards) are secondary reference buffer solutions of the same chemical composition as primary pH standards [2].

The following equipment was used: pH meter (resolution : 0.1 mV)

- combined pH electrode (single rod electrode)
- temperature sensor
- thermostated bath
- stirring system

To ensure traceability also the pH meter and the temperature sensor are calibrated followed by an adjustment. The calibration results are taken into account automatically by many modern pH meters. The user should make sure that the pH meter manage the CRMs pH variations as a function of temperature. The meter mostly does the following calculations to get the electrode parameters. Usually the output of the standard uncertainty associated with the parameters is not a feature of the meter.

Example 1

Sample pH (X) is measured following a two-point calibration (bracketing procedure) of the pH electrode

Input quantities (parameters)

pH(S1)	certified pH value of CRM 1
pH(S2)	certified pH value of CRM 2
$E(X)$	potential, measured in the sample
$E(1)$	potential, measured in CRM 1
$E(2)$	potential, measured in CRM 2

Output quantities (results)

pH(X)	pH of the sample
k´	practical slope of the pH electrode
pH_0	zero point

Calibration procedure

The calibration result yields the two electrode parameters practical slope, k´, and intercept at a potential of the pH electrode equal to zero volt,the zero point, pH_0. The calibration cycle typically consists of the following two steps:

1. The pH electrode is rinsed with deionised water.
2. The pH electrode is dipped into the first CRM, the potential of the pH electrode is measured as soon as the stability criterion has been reached. The temperature of the CRM also is recorded.

This cycle is repeated for the second CRM.

Calculations

The equation to calculate the sample pH (X) is given by. A1.

$$pH(X) = pH(S1) + \frac{(E(X) - E(S1))}{k´} \quad (A1)$$

The practical slope $k´$ and the zero point, pH_0 are computed according to Eq. (A2) and (A3).

$$k` = \frac{E(S2) - E(S1)}{pH(S1) - pH(S2)} \quad (A2)$$

$$pH_0 = pH(S1) + \frac{E(S1)}{k'} \qquad (A3)$$

Description of the individual standard uncertainties

The uncertainties **$u(pH(S1))$ and $u(pH(S2))$** are associated with the CRMs pH(S1) and pH(S2), resp., commonly available from the calibration certificates shipped with the CRMs. In the case the expanded uncertainty U is given in the certificate, U must be divided by the coverage factor stated in the certificate (usually $k = 2$)

- The standard uncertainties **$u(E(S1))$ and $u(E(S2))$** include contributions from the:
- response time of the electrode
- temperature of the sample,
- liquid junction potential (ljp): ljp may vary if S1 is replaced by S2 and depends on the geometry of theliquid junction device (ceramic, sleeve, etc)
- resolution of the meter
- kind of the buffer used (possible CO_2 influence)

These uncertainties must be estimated by the user.

Provided that the measurement parameters, e.g. response time and the temperature are the same during calibration and measurement, the main contribution to $u(E(S1))$ and $u(E(S2))$ is the residual liquid junction potential. It is desirable that an estimation for the liquid junction potential for the CRMs recommended for calibration should be stated for every type of commercial pH electrodes by the producer. The liquid junction potential increases if the electrode is not in proper conditions, e.g., if the liquid junction device (diaphragm) is clogged.

If the calibration cycle is repeated N times the uncertainty due to the repeatability, $u(rep)$, can be estimated according to Eq. A4.

$$u(rep) = \sqrt{\frac{\sum_{i=1}^{N}(E(1)_i - \overline{E}(1))^2 + \sum_{i=1}^{N}(E(2)_i - \overline{E}(2))^2}{2(N-1)}} \quad , i = 1...,N \qquad (A4)$$

Thereby $\bar{E}$ is the mean value of the measured potential in CRM (S1) or (S2).

The combined standard uncertainty for the potential measured in CRM (1) and CRM (2) is calculated according Eq.A5 from the individual contributions associated with the residual liquid junction potential E_{lj}, due to the resolution E_{res} of the meter and due to the repeatability of the potential measurement

$$u(E(S)) = \sqrt{u(E_{lj})^2 + u(E_{res})^2 + u(rep)^2} \qquad (A5)$$

For the standard uncertainty of the potential in the sample, **u(E(X))** a reasonable estimate is required. In most cases the liquid junction potential between the reference electrode electrolyte and the sample solution is unknownThis potential can be minimised by using calibration and sample solutions of similar ionic strength.

If the sample is repeatedly measured K times, the uncertainty due to the repeatability is given by Eq. A6:

$$u(rep, X) = \sqrt{\frac{\sum_{k=1}^{K}(E(X)_k - \overline{E}(X))^2}{(K-1)}} \qquad (A6)$$

$k = 1,...,K$

Hence, the combined standard uncertainty for the potential measured in the sample is given in Eq. A7:

$$u(E(X)) = \sqrt{u(E_{lj})^2 + u(E_{res})^2 + u(rep, X)^2} \qquad \textbf{(A7 The combined standard}$$

uncertainty of pH(X)

The combined standard uncertainty u_c (pH(X)) is equal to the positive square root of the combined variance computed from the standard uncertainties of the input quantities $u(x_i)$ as described above, multiplied by the sensitivity coefficient c_i associate with.

For example the sensitive coefficient (partial derivative) $\partial(pH(X))/\partial(pH(S1))$ describes how the output quantity pH(X) varies with changes in the input quantity pH(S1).

Equations (A1) and (A2) can be rearranged to give Eq. A8:

$$pH(X) = pH(S1) + (pH(S2) - pH(S1)) \cdot \frac{(E(X) - E(S1))}{(E(S2) - E(S1))} \qquad (A8)$$

The combined standard uncertainty for the sample pH(X) is therefore computed according to Eq. A9:

$$u_c^2(pH(X)) = \left[\left(\frac{\partial pH(X)}{\partial pH(S1)} \right)^2 \cdot (u(pH(S1)))^2 \right] + \left[\left(\frac{\partial pH(X)}{\partial pH(S2)} \right)^2 \cdot (u(pH(S2)))^2 \right]$$

$$+ \left[\left(\frac{\partial pH(X)}{\partial E(1)} \right)^2 \cdot (u(E(1)))^2 \right] + \left[\left(\frac{\partial pH(X)}{\partial E(2)} \right)^2 \cdot (u(E(S2)))^2 \right] + \left[\left(\frac{\partial pH(X)}{\partial E(X)} \right)^2 \cdot (u(E(X)))^2 \right] \qquad (A9)$$

Uncertainty of the electrode parameters

Uncertainty of the slope, k´

Using Eq. A2 the combined standard uncertainty of the slope of the electrode $u_c(k')$ can be computed according to Eq. A10.

$$
u_c^2(\mathrm{k}') = \left[\left(\frac{\partial k'}{\partial \mathrm{pH(S1)}}\right)^2 \cdot (u(\mathrm{pH(S1)}))^2\right] + \left[\left(\frac{\partial k'}{\partial p\mathrm{H(S2)}}\right)^2 \cdot (u(\mathrm{pH(S2)}))^2\right]
$$
$$
+ \left[\left(\frac{\partial k'}{\partial E(1)}\right)^2 \cdot (u(E(1)))^2\right] + \left[\left(\frac{\partial k'}{\partial E(2)}\right)^2 \cdot (u(E(2)))^2\right]
$$

(A10)

Uncertainty of the zero point, pH$_0$

The combined standard uncertainty of the zero point , pH$_0$, of the electrode is given by Eq. A11. The sensitivity coefficients are derived from Eq.A3.

$$
u_c^2(\mathrm{pH}^0) = \left[\left(\frac{\partial \mathrm{pH}^0}{\partial \mathrm{pH(S1)}}\right)^2 \cdot (u(\mathrm{pH(S1)}))^2\right] + \left[\left(\frac{\partial \mathrm{pH}^0}{\partial E(S1)}\right)^2 \cdot (u(E(S1)))^2\right] + \left[\left(\frac{\partial \mathrm{pH}^0}{\partial k'}\right)^2 \cdot (u(k'))^2\right] \textbf{(A11)}
$$

Example 1

Two-point calibration

pH(X) ≈ 7, 77 (HEPES)

Each potential is measured only one time, there is no contribution $u(\mathrm{rep})$.

Input quantities

pH(S1) = 4.005
pH(S2) = 9.184
$E(1)$ = 174.64 mV
$E(2)$ = -130.57 mV
$E(X)$ = -47.090 mV

Output quantities

The slope and zero point of the electrode as well as pH(X) has been computed according to Eqs. A1, A2 and A3.

k`= 58.93 mV

$pH_0 = 6.97$

$pH(X) = 7.77$

Standard uncertainties of the input quantities:

$U(pH(S1)) = U(pH(S2)) = 0.003$; Stated in the certificate with a coverage factor of $k = 2$, therefore:

$u(pH(S1)) = u(pH(S2)) = 0.002$

$u(E(S1)) = u(E(S2))$

The pH meter has a resolution of 0.1 mV from which the correction for resolution is estimated to be within ±0.05mV. Assuming a rectangular distribution the uncertainty $u(E_{res})$ due to the resolution of the meter can be calculated according to Eq. A12

$$u(E_{res}) = \frac{0.05}{\sqrt{3}} = 0.029 \text{ mV} \tag{A12}$$

In the example the uncertainty due to the liquid junction potential $u(E_{ljp})$ is estimated from literature [1,4] to 2 mV for commercial electrodes in CRMs of the same nominal composition as primary pH standard buffer solutions.

$u(E_{ljp}) = 2 \text{ mV}$

$u(E_{res}) = 0.029 \text{ mV}$

The uncertainty due to the resolution of the meter is ten times smaller as $u(E_{lj})$ and is therefore not taken into account.

According to eq.(A5) the standard uncertainties associated with the potential measured in the CRMs are:

$u(E(S1)) = u(E(S2)) = 2 \text{ mV}$;

For the given example, $u(E(X))$ is estimated also to 2 mV.

Sensitivity coefficients

Sensitivity coefficients calculated using Eq. A9:

$$\frac{\partial pH(X)}{\partial pH(S1)} = 1 - \frac{(E(X) - E(S1))}{(E(S2) - E(S1))} = 0.274$$

$$\frac{\partial pH(X)}{\partial pH(S2)} = \frac{(E(X) - E(S1))}{(E(S2) - E(S1))} = 0.726$$

$$\frac{\partial pH(X)}{\partial (E1)} = \frac{-(pH(S2) - pH(S1))}{(E(S2) - E(S1))} + (pH(S2) - pH(S1))\frac{(E(X) - E(S1))}{(E(S2) - E(S1))^2} = 0.0046$$

$$\frac{\partial pH(X)}{\partial(E2)} = -\big(pH(S2) - pH(S1)\big)\frac{\big(E(X) - E(S1)\big)}{\big(E(S2) - E(S1)\big)^2} = 0.012$$

$$\frac{\partial pH(X)}{\partial(EX)} = \frac{\big(pH(S2) - pH(S1)\big)}{\big(E(S2) - E(S1)\big)} = -0.017$$

The combined standard uncertainty $u_c(pH(X))$ results from Eq. A9:

$u_c(pH(X)) = 0.043$

The expanded uncertainty[9],[10], defining an interval about the result of the measurement is given by Eq. A12 for a coverage factor of two.

$$U(pH(X) = 2\,u_c(pH(X)) = 0.086 \tag{A12}$$

The results of the uncertainty calculations are summarised in Tables A1 to A4 and in Fig. A2 and A3.

For the examples given in Tables A1 to A4 the contributions of the individual standard uncertainties of the input quantities have been varied to demonstrate their influence on the combined standard uncertainty of pH(X). It is evident that the main contribution to the combined standard uncertainty is the uncertainty of the potentials measured in the CRMs and in the sample. Only if the uncertainty of the certified reference buffer solutions exceeded $U = 0.01$, this contribution has a strong influence on the overall uncertainty of pH(X).

Uncertainties of the electrode parameters

Practical slope, k'

$$k' = \frac{E(S2) - E(S1)}{pH(S2) - pH(S1)} \text{ with } k' = 58.93$$

Sensitivity coefficients: $\dfrac{\partial k'}{\partial pH(S1)} = \dfrac{-\big(E(2) - E(1)\big)}{\big(pH(S1) - pH(S2)\big)^2} = 11.38$

$$\frac{\partial k'}{\partial pH(S2)} = \frac{\big(E(2) - E(1)\big)}{\big(pH(S1) - pH(S2)\big)^2} = -11.38$$

$$\frac{\partial k'}{\partial E(1)} = \frac{-1}{\big(pH(S1) - pH(S2)\big)} = 0.19 \qquad \frac{\partial k'}{\partial E(2)} = \frac{1}{\big(pH(S1) - pH(S2)\big)} = -0.19$$

The combined standard uncertainty u_c is given by Eq. A10.

$$u_c(k') = 0.55 \text{ mV(cf. Table A4)}$$

Table A4 summarizes the results of the uncertainty calculation of the slope.

Zero point, pH$_0$

$$pH^0 = pH(S1) + \frac{E(S1)}{k'} = 6.97$$

Sensitivity coefficients:

$$\frac{\partial pH_0}{\partial pH(S1)} = 1$$

$$\frac{\partial pH_0}{\partial E(S1))} = \frac{1}{k'} = 0.017$$

$$\frac{\partial pH_0}{\partial k'} = \frac{-E(S1)}{k'^2} = -0.05$$

The combined standard uncertainty u_c is given by Eq. A11.

$$u_c(pH_0) = 0.044 \text{ (cf. Table A5)}$$

Table A5 summarises the results of the uncertainty calculation of the zero point of the electrode, pH$_0$

Example 2

Sample pH(X) measurement by multi-point calibration

Input quantities (parameters)

pH(S1),..,pH(S5)   certified pH value of CRM 1 to CRM 5

$E(X)$ potential difference (emf) measured on the sample

$E(1)... E(5)$ potential difference (emf), measured in CRM 1...CRM5

Output quantities (results)

pH(X)   pH of the sample

k'   practical slope of the pH electrode

pH_0 zero pH

$E^{0'}$ standard potential of the electrode

Calibration procedure

The calibration function is given by Eq. A13. A linear least squares method is performed. The uncertainties of the CRMs in the order of $U = 0.003$ (coverage factor, $k = 2$) are neglected.

$$E(S) = E^{0'} - k'pH(S) \qquad (A13)$$

The calibration function is used to calculate pH(X) according to Eq. A14.

$$pH(X) = \frac{E^{0'} - E(X)}{k'} \qquad (A14)$$

The calibration results consist in three electrode parameters: 1. practical slope k', 2. standard potential of the electrode $E^{0'}$ and 3. the zero pH, pH_0, corresponding to zero potential of the calibration line

The calibration cycle typically consists of the following steps:

1. The pH electrode is rinsed with deionised water
2. The pH electrode is dipped into the first CRM, the potential difference of the pH electrode is recorded than the stability criterion has been reached. The temperature of the CRM is recorded.

This cycle is repeated for the other CRMs.

Linear least squares method

The regression model for ordinary least squares regression procedure (OLS) for N data pairs is given in Eq. A15

$$y_i = b_0 + b_1 \cdot x_i + e_i \qquad (A15)$$

with i = 1,...,N.

The residual e_i is the difference between the observed value of the dependent variable ($x_i =$ $E(pH(S))$) and the value predicted by the model ($x_i, \hat{y}_i$). The output quantities and their estimated variances are obtained by minimizing the residual sum of squares S in Eq. A16. In using a linear model as given in Eq. A15, it is assumed that the requirements for the application of the linear least-squares regression are fulfilled [15,16].

$$S = \sum_{i=1}^{N} e_i^2 = \sum_{i=1}^{N} (y_i - b_0 - b_1 \cdot x_i)^2 \rightarrow \min \qquad (A16)$$

In order to simlipfy the calculation the following quantities are calculated by the well-known numerical procedures to be found in almost all fundamental text books of statistics or data evaluation given in Eqs. A17 to A22. The calculated quantities are obtained from the example data set in Table A6.

$$Sxx = \sum_{i=1}^{N}(x_i - \bar{x}))^2 \text{ with Sxx = 33.7682} \tag{A17}$$

$$Syy = \sum_{i=1}^{N}(y_i - \bar{y}))^2 \text{ with Syy = } 1.1726 \cdot 10^5 \tag{A18}$$

$$Sxy = \sum_{i=1}^{N}(x_i - \bar{x})(y_i - \bar{y}) \text{ with Sxy = -1.990} \tag{A19}$$

$$\text{and } \bar{x} = \sum_{i=1}^{N}\frac{x_i}{N} ; \ \bar{y} = \sum_{i=1}^{N}\frac{y_i}{N} \tag{A20}$$

The intercept and the slope of the calibration line are given by equation (A21) and (A22).

$$b_1 = \frac{Sxy}{Sxx} \text{ with } b_1 = -58.93 \tag{A21}$$

$$b_0 = \bar{y} - b_1 \cdot \bar{x} \text{ with } b_0 = 410.883 \tag{A22}$$

Variance and covariance of the regression parameters $u^2(b_0)$, $u^2(b_1)$, $u(b_0, b_1)$

The variance $S_R{}^2$ in Eq. A23 is a measure of the overall uncertainty of the fit. The method standard deviation [17] S_{x0} is computed according to Eq. A24. This quantity allows an assessment of the calibration in comparison to previous measurements. The standard uncertainties of the regression parameters results from Eqs. A25 to A27 there A27 gives the covariance between slope b_1 and intercept b_0.

$$S_R{}^2 = \frac{\sum_{i=1}^{N}e_i^2}{N-2} = \frac{\sum_{i=1}^{N}[y_i - (b_0 + b_1 \cdot x)_i)]^2}{N-2} \text{ ; with } S_R{}^2 = 0.0447 \tag{A23}$$

$$S_{x0} = \frac{S_R}{b_1} \tag{A24}$$

$$u(b_1) = S_R \cdot \sqrt{\frac{1}{Sxx}} \text{ with } u(b_1) = 0.036 \tag{A25}$$

$$u(b_0) = S_R \cdot \sqrt{\frac{1}{N} + \frac{\bar{x}^2}{Sxx}} \text{ with } u(b_0) = 0.26 \quad (A26)$$

$$u(b_1, b_0) = \frac{-S_R^2 \cdot \bar{x}}{Sxx} \text{ with } u(b_1, b_0) = -0.0089 \quad (A27)$$

The parameters of the pH electrode and the associated uncertainties

The equation A15 of the calibration line follows from Eqs A1 and A2.

$$E(S) = E^{0'} - k' \cdot pH(S) \quad (A28)$$

The parameters of the electrode and the associated uncertainties are calculated by Eqs.A29 to A34. The x_i values are $pH(S)_i$ values assigned to the CRMs while the y_i values are the experimentally obtained potentials measured in the CRMs.

practical slope k':

$$k' = -b_1 \quad (A29)$$

$$u(k') = u(b_1) \quad (A30)$$

standard potential $E^{0'}$:

$$E^{0'} = b_0 \quad (A31)$$

$$u(E^{0'}) = u(b_0) \quad (A32)$$

zero point, pH_0:

$$pH_0 = -\frac{b_o}{b_1} \quad (A33)$$

electromotive efficiency β :

$$\beta = \frac{k'}{k} \quad (A34)$$

there k = 59.16 mV is the theoretical or Nernst slope at 25 °C.

The uncertainty $u(E(S)_i)$ (Eq. A35) is the combined uncertainty computed from $u(k')$ and $u(E^0)$ and from the covariance $u(k', E^0)$.

$$u(E(S)_i) = S_R \cdot \sqrt{\frac{1}{N} + \frac{(pH(S)_i - pH(\bar{S}))^2}{Sxx}} \quad (A35)$$

If $E(X)$ is measured only one time u(E(X) can be estimated by Eq. A36 [16]

$$u(E(X)) = S_R \qquad \text{(A36)}$$

Calculation of the sample pH(X) from the calibration line

The sample pH, pH(X), the predicted value from the calibration line can be calculated by Eq. A37. The expression for the standard uncertainty of the sample pH(X) can be obtained by applying the law of propagation of uncertainty.

$$\text{pH}(X) = \frac{E^0 - E(X)}{k'} \qquad \text{(A37)}$$

$$\text{pH(X)} = 6.68$$

$$u(\text{pH}(X)) = \frac{S_R{}^2 + (u(E^{0'}))^2 + (\text{pH(X)})^2 \cdot (u(k'))^2 + 2 \cdot \text{pH(X)} \cdot u(E^{0'}) \cdot u(k')}{(k')^2} \qquad \text{(A38)}$$

Eq. A38 can be simplified to Eq. A39

$$u(\text{pH}(X)) = \frac{S_R}{k'} \cdot \sqrt{1 + \frac{1}{N} + \frac{(pH(X) - pH(\overline{S}))^2}{Sxx}} \; ; \; u(\text{pH(X)}) = 0.039 \qquad \text{(A39)}$$

It should be noted that the uncertainty u(pH(X)) = 0.039 is in the same order of magnitude as the average uncertainty of a pH measurement stated previously [12] for a usual 5 point calibration following the MPC protocol. This agreement is fortuitous. In the above discussion, all uncertainties have been stated explicitly. Thus, the complete uncertainty budget is obtained. Thus, the uncertainty in ref. 12 does not consider some uncertainty contributions. On the other hand, in ref. 12, a correction for small sample size by Student t has been made [15]. The procedures in refs. [9,10] do not include a correction for small data sets, e.g., by Student t factor. Using the common .68 percentile confidence level for three degrees of freedom, an increase in the uncertainty by about 25 %, for .95 percentile confidence level an increase of about 30% would result on basis of the assumption that all uncertainties are normally distributed. Since the complete procedure calls for a reasonable estimate of the uncertainty, a larger amount of assumptions and approximations are included and statistical effects like serial correlation etc. cannot be taken into account due to the small data set handled in each calibration. It is acceptable to drop Student's t correction.

Table A1 Uncertainty of pH(X) determination following a two-point calibration (bracketing procedure)

SYMBOL	DESCRIPTION	UNIT	VALUE x_i	STANDARD UNCERTAINTY $u(x_i)$	RELATIVE STANDARD UNCERTAINTY $u(x_i)/x_i$	SENSITIVITY COEFFICIENT c_i	CONTRIBUTION $u_i(y)^2 = u(x_i)^2 \cdot c_i^2$	RELATIVE CONTRIBUTION $u_i(y)$ in %
pH(S1)	CRM1		4.005	0.002	0.00050	0.27	$2.99 \cdot 10^{-7}$	0.016
pH(S2)	CRM 2		9.184	0.002	0.00022	0.73	$2.11 \cdot 10^{-6}$	0.11
E(1)	emf in CRM 1	mV	174.64	2	0.011	0.005	$8.62 \cdot 10^{-5}$	4.66
E(2)	emf in CRM 2	mV	-130.57	2	-0.015	0.012	$6.08 \cdot 10^{-4}$	32.89
E(X)	emf in sample	mV	-47.090	2	-0.043	-0,017	$1.15 \cdot 10^{-3}$	62.32
						$\sum[\, u_i(y)^2]$	$1.85 \cdot 10^{-3}$	100
combined standard uncertainty $u_c(y) = \sum[\, u_i(y)^2]^{1/2}$						$u_c(y)$	0,043	
expanded uncertainty (k =2)						$U(\text{pH}(X))$	0,086	

Table A2 Uncertainty of pH(X) determination following a two-point calibration (bracketing procedure). The standard uncertainty of the emf measured in the sample is estimated to 5 mV and the standard uncertainty of the CRMs is estimated to 0.02

SYMBOL	DESCRIPTION	UNIT	VALUE	STANDARD UNCERTAINTY	RELATIVE STANDARD UNCERTAINTY	SENSITIVITY COEFFICIENT	CONTRIBUTION	RELATIVE CONTRIBUTION
			x_i	$u(x_i)$	$u(x_i)/x_i$	c_i	$u_i(y)^2 = u(x_i)^2 \cdot c_i^2$	$u_i(y)$ in %
pH(S1)	CRM1		4.005	0.02	0.0050	0.27	$2.99 \cdot 10^{-5}$	0.37
pH(S2)	CRM 2		9.180	0.02	0.002	0.73	$2.11 \cdot 10^{-4}$	2.60
E(1)	emf in CRM 1	mV	174.64	2	0.011	0.005	$8.62 \cdot 10^{-5}$	1.06
E(2)	emf in CRM 2	mV	-130.57	2	-0.015	0.012	$6.08 \cdot 10^{-4}$	7.47
E(X)	emf in sample	mV	-47.090	5	-0.11	-0,017	$7.20 \cdot 10^{-3}$	88.50
						$\sum [\, u_i(y)^2]$	$8.13 \cdot 10^{-3}$	100
combined standard uncertainty $u_c(y) = \sum [\, u_i(y)^2]^{1/2}$						$u_c(y)$	0,090	
expanded unceratinty (k =2)						$U(\text{pH(X)})$	0,18	

Table A3 Uncertainty of pH(X) determination following a two point calibration (bracketing procedure). The standard uncertainty of the CRMs is assumed to be 0.002, the residual liquid junction potential for CRM 1 and CRM 2 is estimated to 0.6 mV

SYMBOL	DESCRIPTION	UNIT	VALUE	STANDARD UNCERTAINTY	RELATIVE STANDARD UNCERTAINTY	SENSITIVITY COEFFICIENT	CONTRIBUTION	RELATIVE CONTRIBUTION
			x_i	$u(x_i)$	$u(x_i)/x_i$	c_i	$u_i(y)^2 = u(x_i)^2 \cdot c_i^2$	$u_i(y)$ in %
pH(S1)	CRM1		4.005	0.002	0.00050	0.27	$2.99 \cdot 10^{-7}$	0.025
pH(S2)	CRM 2		9.184	0.002	0.00022	0.73	$2.11 \cdot 10^{-6}$	0.17
E(1)	emf in CRM 1	mV	174.64	0.6	0.034	0.005	$7.76 \cdot 10^{-6}$	0.64
E(2)	emf in CRM 2	mV	-130.57	0.6	-0.046	0.012	$5.47 \cdot 10^{-5}$	4.50
E(X)	emf in sample	mV	-47.090	2	-0.043	-0,017	$1.15 \cdot 10^{-3}$	94.67
						$\sum [\, u_i(y)^2]$	$1.22 \cdot 10^{-3}$	100
	combined standard uncertainty $u_c(y) = \sum [\, u_i(y)^2]^{1/2}$					$u_c(y)$	0,035	
	expanded unceratinty (k =2)					$U(\text{pH(X)})$	0,070	

Table A4 Combined standard uncertainty of the practical slope of the pH electrode following a two point calibration procedure (bracketing)

SYMBOL	DESCRIPTION	UNIT	VALUE x_i	STANDARD UNCERTAINTY $u(x_i)$	RELATIVE STANDARD UNCERTAINTY $u(x_i)/x_i$	SENSITIVITY COEFFICIENT c_i	CONTRIBUTION $u_i(y)^2 = u(x_i)^2 \cdot c_i^2$	RELATIVE CONTRIBUTION $u_i(y)$ in %
pH(S1)	CRM 1		4.005	0.02	0.0050	11.38	$5.18 \cdot 10^{-4}$	0.17
pH(S2)	CRM2		9.184	0.02	0.0022	-11.38	$5.18 \cdot 10^{-4}$	0.17
E(1)	emf in CRM1	mV	174.64	2	0.011	0.19	0.15	49.83
E(2)	emf in CRM 2	mV	-130..57	2	-0.015	-0.19	0.15	49.83
						$\sum[\, u_i(y)^2]$	0.30	100
combined standard uncertainty $u_c(y) = \sum[\, u_i(y)^2]^{1/2}$						$u_c(k')$	0.55	

Table A5 Uncertainty of the zero point, pH$_0$, of the pH electrode following a two point calibration procedure (bracketing)

SYMBOL	DESCRIPTION	UNIT	VALUE x_i	STANDARD UNCERTAINTY $u(x_i)$	RELATIVE STANDARD UNCERTAINTY $u(x_i)/x_i$	SENSITIVITY COEFFICIENT c_i	CONTRIBUTION $u_i(y)^2 = u(x_i)^2 \cdot c_i^2$	RELATIVE CONTRIBUTION $u_i(y)$ in %
pH(S1)	CRM 1		4.005	0002	0,00050	1	$4.0 \cdot 10^{-6}$	0.21
E(1)	emf in buffer 1	mV	174.64	2	0,011	0,017	0.0012	60.22
k´	practical slope	mV	58.93	0.55	0.0093	-0,051	$7.57 \cdot 10^{-4}$	39.57
						$\sum [\, u_i(y)^2]$	$1{,}91 \cdot 10^{-3}$	100
combined standard uncertainty $u_c(y) = \sum [\, u_i(y)^2]^{1/2}$						$u_c(\text{pH}_0)$	0,044	

Table A6. Experimental data used in Example 2. The potential $E(X)$ measured in the sample X is $E(X)= 17.17$ mV

pH(S)	E(S) in mV
x_i	y_i
3.639	196.42
4.005	174.64
6.865	6.56
9.184	-130.57
10.011	-178.94

Table A7. Results obtained by OLS (ordinary least squares analysis) on the experimental data from Table A6 (without considering a Student t correction for small sample size)

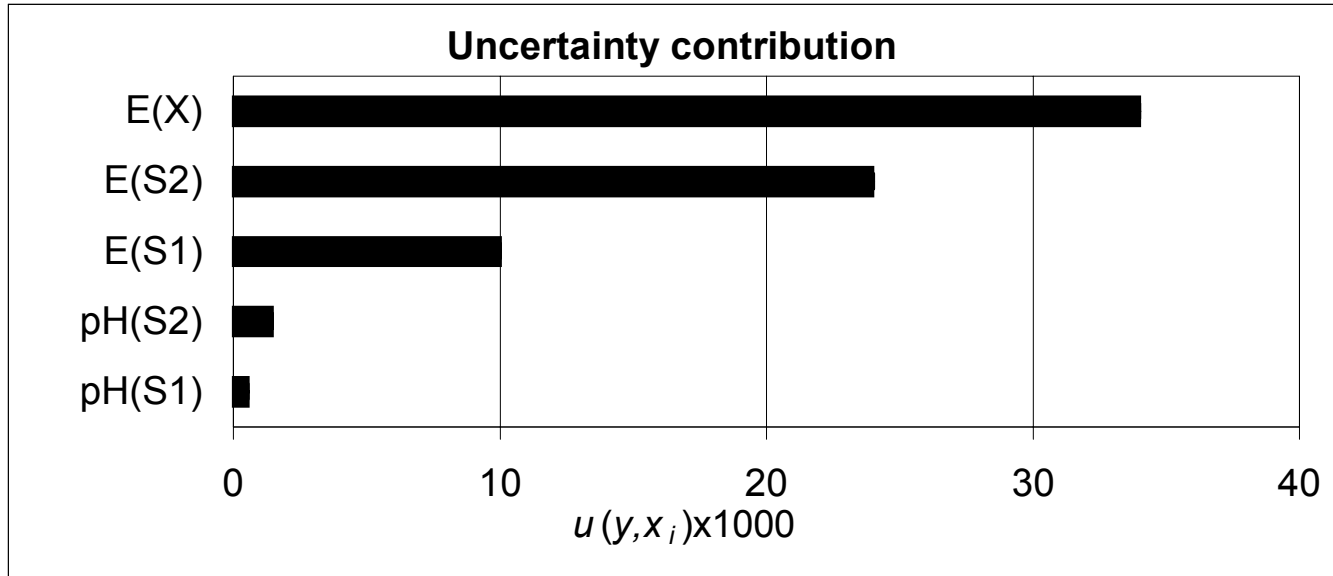|	
$E^{0'} = 410,883$ mV	$u(E^{0'}) = 0,263$ mV
$k' = 58,93$ mV	$u(k') = 0,036$ mV
$pH_0 = 6,973$	
$\beta = 99,61\%$	

Fig. A1. Contribution of the single components to the overall uncertainty of pH(X). The values of the uncertainty contribution $u(y, x_i) = c_i \cdot u(x_i)$ are taken from Table A1
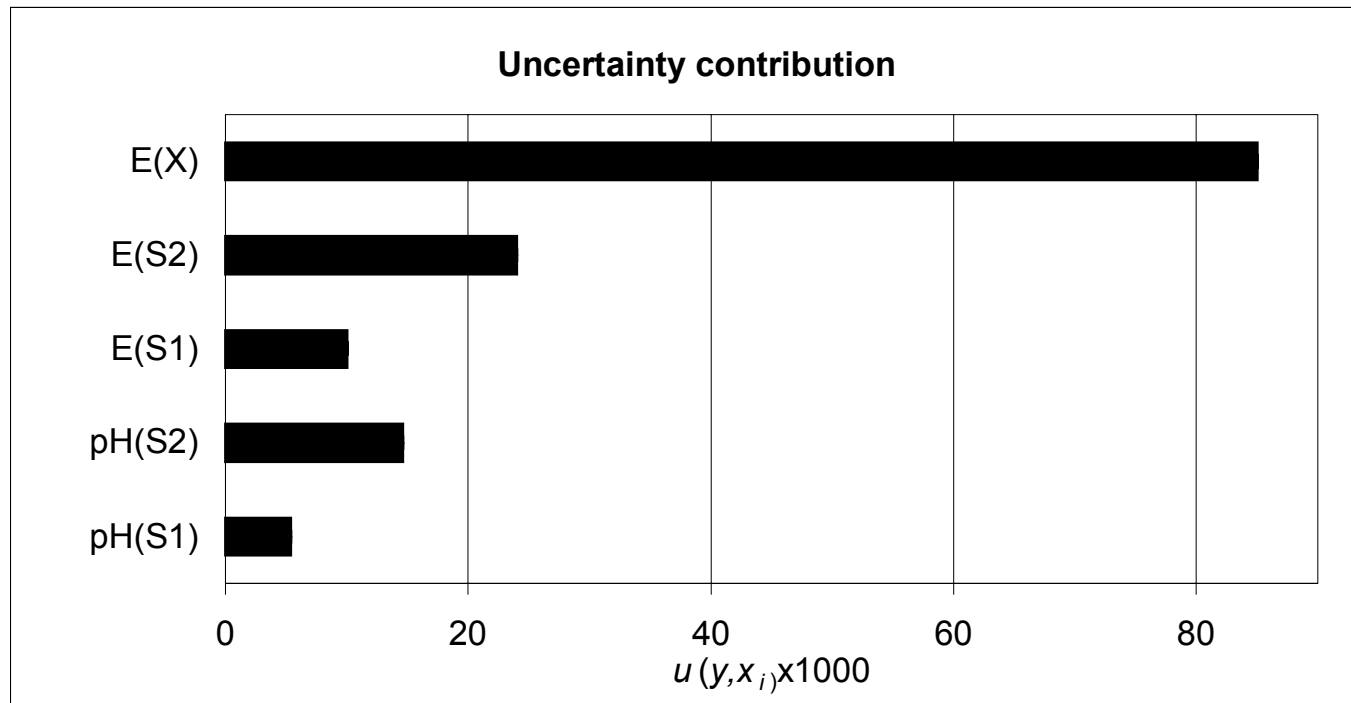
Fig. A2. Contribution of the single components to the overall uncertainty of pH(X). The values of the uncertainty contribution $u(y, x_i) = c_i \cdot u(x_i)$ are taken from Table A2