

Using electronic spreadsheets for different approaches of estimating uncertainty in electrometric pH measurements

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Abstract – This paper explores uncertainty quantification in electrometric pH measurements using a Microsoft® Excel spreadsheet. The aim of this study is to simplify the process for analysts by providing a computational tool that calculates uncertainty based on pH calibration and measurement models. The provided layout allows immediate uncertainty calculation using the GUM, Kragten and Monte Carlo approaches. The GUM approach via partial derivatives confirms with relative uncertainty, while the Kragten approach evaluates the change in the result compared to the standard uncertainty, which reduces the risk of miscalculation. The Monte Carlo approach examines the distribution pattern of the input quantities to calculate the distribution of the result. The combination of these three approaches helps in developing effective strategies and understanding different aspects of the problem. The uncertainty calculator improves statistical management, improves the quality of laboratory results, saves computation time and reduces errors. It also has benefits for testing laboratories' quality systems, improves PT activities and supports the development of reference laboratories.

I. INTRODUCTION

Assessing uncertainty in instrumental calibrations is essential for ensuring the reliability and precision of measurements. This evaluation offers several benefits, including enhanced accuracy, quality assurance, informed decision-making, compliance with industry standards, and risk mitigation. Excel formulae play a vital role in data automation, calculation efficiency, and error reduction. They eliminate manual computation, expedite data processing, and enable dynamic spreadsheet adaptability. By linking cells and executing complex tasks, Excel significantly improves workflow efficiency. Measurement uncertainty is crucial to laboratories, clients, and all stakeholders interpreting results. It is particularly relevant

in repeat measurements, laboratory comparisons, and compliance assessments. Various metrology institutes have developed uncertainty machines and workbenches that support professionals in this field, though some can be costly.

Electrometric pH measurement, a straightforward electrochemical cell-based technique, follows guidelines set by the International Union of Pure and Applied Chemistry (IUPAC). The current pH measurement equation serves as a reference for determining measurement uncertainty. Modern pH meters incorporate user-friendly features while maintaining fundamental measurement principles. The measurement model [2] derived from instrumental readings is utilized to calculate additional uncertainty. Excel worksheets, designed to reflect the measurement model comprehensively, facilitate uncertainty analysis in pH calibration and measurement. These worksheets support both estimation and documentation, ensuring thorough record-keeping and analysis.

II. MATERIALS AND METHODS

In most practical applications, pH glass electrode cells are calibrated using two-point calibration or by bracketing the pH value of the sample (pH_x). The measurement equation for two-point calibration in pH measurement is derived from Eq. (1) [4].

$$pH_x = pH_1 + \frac{(E_x - E_1 - RLJP_x)}{k'_x} \quad (1)$$

where the practical slope factor (k'_x) at the specified temperature is expressed as

$$k'_x = \frac{R \ln 10 (T_c - T_x)}{F} + \frac{\Delta E - RLJP}{\Delta pH}$$

A. Worksheet for input data

The calibration and measurement worksheet is designed to collect data, as shown in Fig. 1. The input quantities and

standard uncertainties are represented by symbols and names. The Name box is used to designate individual cell names rather than cell positions as shown in Table 1. These names are used to associate the values in the input data worksheet with the worksheets for each uncertainty calculation approaches.

Table 1. Definitions of symbols and names used in the worksheet for calibration and measurement input data

Symbol	Name	Description
E_1	E_1	The potential difference when measuring the pH_1
E_2	E_2	The potential difference when measuring the pH_2
pH_1	PH_1	The pH value of the first buffer solution
pH_2	PH_2	The pH values of the second buffer solution.
T_c	TEMPC	The temperature in calibration
T_x	TEMPX	The temperature in measurement the sample
$RLJP, RLJP_x$	RLJP	The residual liquid junction potential in calibration and measurement
$E_{x1}, E_{x2}, E_{x3}, E_{x4}$	EX_1, EX_2, EX_3, EX_4	The potential difference of a sample at three measurements, respectively
R	-	Gas constant
F	-	Faraday's constant
$u(E_1), u(E_2)$	STDU_M	Standard uncertainty of pH meter
$u(pH_1)$	STDU_PH1	Standard uncertainty of the first buffer solution
$u(pH_2)$	STDU_PH2	Standard uncertainty of the second buffer solution
$u(T_c), u(T_x)$	STDU_T	Standard uncertainty of temperature device
$u(RLJP), u(RLJP_x)$	STDU_RLJP	Standard uncertainty of the residual liquid junction potential in calibration and measurement

B. Main steps in the GUM approach [1]

The input quantities in the measurement equation are classified to identify type A and B estimator.

B1. Standard uncertainty Type A

Standard uncertainty of potential difference in repeated sample measurements n times, $u(E_x)$ is obtained from statistical analysis in Eq. (2).

$$u(E_x) = \frac{\sigma_{n-1}}{\sqrt{n}} \quad (2)$$

Fig. 1. The worksheet of calibration and measurement input data

B2. Standard uncertainty Type B

They are derived from input quantities that are not generated from statistical analysis and thus have a distribution pattern determined based on the obtained information as described,

B2.1. Standard uncertainty of practical slope

Its sources of uncertainty originate from the difference potentials, temperature, residual liquid junction potential, and buffer solutions, as outlined below,

The standard uncertainty of the potential difference, $u(\Delta E)$ is defined as Eq. (3), where ΔE is the difference of E_1 and E_2 .

$$u(\Delta E) = \sqrt{u(E_1)^2 + u(E_2)^2} \quad (3)$$

The standard uncertainties of temperature in calibration, $u(T_c)$ and measurement, $u(T_x)$ are determined from temperature measuring instrument information.

The standard uncertainty of residual liquid junction potential in calibration, $u(RLJP)$ is supported by data obtained from published literature or electrode's manufacturer.

The standard uncertainty of the buffer solutions, $u(\Delta pH)$, is obtained from the manufacturer's certifications. The uncertainty can be calculated using Eq. (4), where ΔpH is the difference between pH_1 and pH_2 .

$$u(\Delta pH) = \sqrt{u(pH_1)^2 + u(pH_2)^2} \quad (4)$$

Hence, the combined standard uncertainty of practical slope, $u(k'_x)$ is showed in Eq. (5).

$$u(k'_x) = \sqrt{c_{\Delta E}^2 u(\Delta E)^2 + c_{T_c}^2 u^2(T_c) + c_{\Delta pH}^2 u^2(\Delta pH) + c_{RLJP}^2 u^2(RLJP) + c_{T_x}^2 u^2(T_x)} \quad (5)$$

where

$$c_{\Delta E} = \frac{1}{\Delta pH}$$

$$c_{\Delta pH} = \frac{-\Delta E + RLJP}{\Delta pH^2}$$

$$c_{RLJP} = \frac{1}{\Delta pH}$$

$$c_{T_c} = c_{T_x} = \frac{R \ln 10}{F}$$

B2.2. Uncertainty calculation of pH measurement

Standard uncertainty of residual liquid junction potential in sample measurement, $u(RLJP_x)$, are supported by data obtained from published literature or electrode's manufacturer. Hence, the combined standard uncertainty of pH measurement, $u(pH_x)$, is defined as Eq. (6).

$$u_c(pH_x) = \sqrt{c_{E_x}^2 u(E_x)^2 + c_{E_1}^2 u(E_1)^2 + c_{pH_1}^2 u(pH_1)^2 + c_{RLJP_x}^2 u(RLJP_x)^2 + c_{k'_x}^2 u(k'_x)^2} \quad (6)$$

where the sensitivity coefficient (c_i or $\partial y / \partial x_i$) of each input quantity is

$$\frac{\partial pH_x}{\partial E_x} = \frac{1}{k'_x}$$

$$\frac{\partial pH_x}{\partial E_1} = -\frac{1}{k'_x}$$

$$\frac{\partial pH_x}{\partial pH_1} = 1$$

$$\frac{\partial pH_x}{\partial rlj_p} = -\frac{1}{k'_x}$$

$$\frac{\partial pH_x}{\partial k'_x} = \frac{E_1 - E_x - rlj_{p_x}}{k_x'^2}$$

The effective degree of freedom (v_{eff}) is calculated as Eq. (7).

$$v_{eff} = \frac{u_c(pH_x)^4}{\frac{u(E_x)^4}{n-1} + \frac{u(pH_1)^4}{\infty} + \frac{u(RLJP_x)^4}{\infty} + \frac{u(k'_x)^4}{\infty}} \quad (7)$$

The coverage factor (k) at approximately 95% of confident level is determined in t-distribution table. Consequently, the expanded uncertainty of pH measurement, $U(pH_x)$ is calculated as follows.

$$U(pH_x) = k \cdot u_c(pH_x) \quad (8)$$

In order to avoid the partial derivatives in determining the sensitivity coefficient, the relative standard uncertainty can be calculated [5] as Eq. (9).

$$u(pH_x) = \sqrt{u(pH_1)^2 + \left\{ \left(\frac{\Delta E_x}{k'_x} \right)^2 * \left[\left(\frac{u(\Delta E_x)}{\Delta E_x} \right)^2 + \left(\frac{u(k'_x)}{k'_x} \right)^2 \right] \right\}} \quad (9)$$

where

$$u(k'_x) = \sqrt{k_x'^2 \left[\left(\frac{u(\Delta E - RLJP)}{\Delta E - RLJP} \right)^2 + \left(\frac{u(T_c)}{T_c} \right)^2 + \left(\frac{u(\Delta pH)}{\Delta pH} \right)^2 + \left(\frac{u(T_k)}{T_k} \right)^2 \right]}$$

C. Main steps in the Kragten approach

Using the approach proposed by J. Kragten [3], the uncertainty in the output quantity arising from the uncertainty in each input quantity, $u(y, x_i)$ is represented in Eq. (12). The standard uncertainty of the output quantity, $u(y)$, is then determined by Equation (13).

$$u(y, x_i) \approx (x_i + u(x_i)) - y(x_i) \quad (12)$$

$$u(y) = \sqrt{\sum_{i=1}^n [u(y, x_i)]^2} \quad (13)$$

The structure of the worksheets is as follows: Input quantities and their associated uncertainties are specified in cells B3 to B7 and C2 to G2, facilitating the calculation of k'_x in cell B8 and $k'_{x,xi}$ in cells C8 to G8. Likewise, input quantities and uncertainties are designated in cells B16 to B20 and C15 to G15 for computing pH_x in cell B21 and $pH_{x,xi}$ in cells C21 to G21. The Kragten worksheet is manipulated as illustrated in Fig. 2.

1	A	B	C	D	E	F	G
1	Symbol		$u(\Delta E)$	$u(T_c)$	$u(RLJP)$	$u(\Delta pH)$	$u(T_k)$
2		Value	=SQRT(SUMSQ (2*STDU M)	=STDU TC	=STDU RLJP	=SQRT(SUMSQ (STDU PH1, STDU PH2))	=STDU TX
3	ΔE	=E 2-E 1	=B3-C3	=B3	=B3	=B3	=B3
4	T_c	=TEMPC	=B4	=B4-D3	=B4	=B4	=B4
5	$RLJP$	=RLJP	=B5	=B5	=B5-E2	=B5	=B5
6	ΔpH	=PH 2-PH 1	=B6	=B6	=B6	=B6-F2	=B6
7	T_k	=TEMPX	=B7	=B7	=B7	=B7	=B7-G2
8	k'_x	=R*ln10*(B4-B7)/F-(B3/B6)	=R*ln10*(C4-C7)/F-(C3/C6)	=R*ln10*(D4-D7)/F-(D3/D6)	=R*ln10*(E4-E7)/F-(E3/E6)	=R*ln10*(F4-F7)/F-(F3/F6)	=R*ln10*(G4-G7)/F-(G3/G6)
9	$u(k'_x)$		=C8-B8	=D8-B8	=E8-B8	=F8-B8	=G8-B8
10	$u(k'_x)$		=C9	=D9	=E9	=F9	=G9
11	$u(k'_x)$		=SQRT(SUM(C8:G8))				

15	A	B	C	D	E	F	G
15	Symbol		$u(E_x)$	$u(E_1)$	$u(pH_1)$	$u(RLJP_x)$	$u(k'_x)$
15		Value	=STDV(EX 1 EX 3)/SQRT(4)	=STDU M	=STDU PH1	=STDU RLJP	=B11
16	E_x	=AVG(EX 1 EX 4)	=B11-C12	=B16	=B16	=B16	=B16
17	E_1	=E 1	=B17	=B17-D15	=B17	=B17	=B17
18	pH_1	=PH 1	=B18	=B18	=B18-E15	=B18	=B18
19	$RLJP_x$	=RLJP	=B19	=B19	=B19	=B19-F15	=B19
20	k'_x	=B8	=B20	=B20	=B20	=B20	=B20-G15
21	pH_x	=B18-B16-B17-B19/E20	=C18-(C16-C17-C19)/C20	=D18-(D16-D17-D19)/D20	=E18-(E16-E17-E19)/E20	=F18-(F16-F17-F19)/F20	=G18-(G16-G17-G19)/G20
22	$u(pH_{x,xi})$		=C21-B21	=D21-B21	=E21-B21	=F21-B21	=G21-B21
23	$u(pH_{x,xi})$		=C22	=D22	=E22	=F22	=G22
24	$u(pH_x)$		=SQRT(SUM(C23:G23))				

Fig. 2 Uncertainty worksheets of k'_x and pH_x by Kragten approach

D. Main steps in the Monte Carlo approach [5]

Each input quantity in the measurement model serves as a factor influencing the output quantity. The probability density function (PDF) of each input quantity is taken into account, and the computational simulation is performed repeatedly. In the worksheet, input quantities following the GUM approach are modeled using a normal distribution, such as ΔE , ΔpH , k'_x , and E_x . The formula for normal distribution is given by NORMINV(RAND(),x,u), where x represents the quantity and u denotes its standard

uncertainty. Additionally, some input quantities, such as RLJP and RLJP_x, follow a rectangular distribution, with the formula $x + 2a(\text{RAND}() - 0.5)$, where a represents the given half-width. The uncertainty worksheets for k'_x and pH_x are presented in Fig. 3. The input quantity data is simulated for 10⁵ times and then the minimum and maximum output values by running worksheet 10 times are determined.

1	A	B	C	D	E	F	G
2	Symbol	ΔE	T	RLJP	ΔpH	T _c	k'
3	Value	=E_2-E_1	=TEMPC	=RLJP	=PH_2-PH_1	=	=R*10 ¹⁰ *(C2-F2)/F*(B2-D2)/E2
4	Std.uncer or half-width	=SQRT(SUMSQ(2*(STDU M)))	=STDU TC	STDU RLJP	=SQRT(SUMSQ(STDU PH)))	STDU T	=STDEV(G5:G100005)
5	Distribution	Normal	Normal	Rectangular	Normal	Normal	Normal
6	Simulation	=NORMINV(RAND(), B\$2, B\$3)	=NORMINV(RAND(), C\$2, C\$3)	=D\$2+2*D\$3*(RAND()-0.5)	=NORMINV(RAND(), E\$2, E\$3)	=NORMINV(RAND(), F\$2, F\$3)	=R*10 ¹⁰ *(C5-F5)/F*(B5-D5)/E5
7	100005	=NORMINV(RAND(), B\$2, B\$3)	=NORMINV(RAND(), C\$2, C\$3)	=D\$2+2*D\$3*(RAND()-0.5)	=NORMINV(RAND(), E\$2, E\$3)	=NORMINV(RAND(), F\$2, F\$3)	=R*10 ¹⁰ *(C6-F6)/F*(B6-D6)/E6

1	J	K	L	M	N	O	P
2	Symbol	E	E ₁	C7	RLJP	pH	pH
3	Value	=AVG(EX_1-EX_4)	=E 1	=C7	=RLJP	=PH 1	=O2+(K2-L2-N2)/M2
4	Std.uncer or half-width	=STDV(EX_1-EX_4)/SQRT(4)	=STDU M	=F7	=STDU RLJP	=STDU PH	=STDEV(P5:P100005)
5	Distribution	Normal	Normal	Normal	Rectangular	Normal	Normal
6	Simulation	=NORMINV(RAND(), K2, K3)	=NORMINV(RAND(), L2, L3)	=NORMINV(RAND(), M2, M3)	=N2+2*N3*(RAND()-0.5)	=NORMINV(RAND(), O2, O3)	=O5+(K5-L5-N5)/M5
7	100005	=NORMINV(RAND(), K2, K3)	=NORMINV(RAND(), L2, L3)	=NORMINV(RAND(), M2, M3)	=N2+2*N3*(RAND()-0.5)	=NORMINV(RAND(), O2, O3)	=O6+(K6-L6-N6)/M6

Fig. 3 Uncertainty worksheets of k'_x and pH_x by the Monte Carlo approach

E. Excel Spreadsheets validation.

For simple mathematical calculations, such as Kragten's method, use a calculator to verify that spreadsheet results align with the expected values. For more complex computations, compare them against reliable reference sources to ensure accuracy. The NIST Uncertainty Machine [6] is a web-based application designed to evaluate measurement uncertainty using the GUM framework and Monte Carlo method. It has been used to verify the accuracy of spreadsheet calculations. To compute k'_x and pH_x, follow these steps:

- Select "5" from the dropdown list for the number of input quantities.
- Enter the quantity names, input values, and their respective distributions.
- Keep the correlation random number and symmetrical coverage intervals unchanged.
- Set the number of realizations to 100,000.
- Define the output quantities k'_x and pH_x in a valid R expression according to equation (1).
- Execute the computation.

III. RESULTS AND DISCUSSION

The calibration and measurement data are entered into the worksheet, as shown in Fig. 4. The uncertainty budgets for

k'_x and pH_x, evaluated using the GUM approach and the relative standard uncertainty method, are displayed in Figs 5 and 6. The relative standard uncertainty serves as a valuable tool for confirming the validity of GUM approach, which employs partial derivatives to determine sensitivity coefficients.

1	A	B	C	D	E	F	G	H	I	J	K
2	Symbol	Unit	Value	u(x _i)	c _i	u(x _i)	V _i of V _{eff}	Calibration Condition			
3	Equipment	pH meter	mV	-	0.077			Symbol	unit	value	
4		Temp. device	°C	-	0.1			T _c	°C	28.0	
5		pH electrode	mV	0.6	0.26			k(T)	mV		
6								k'	%	95	
7	Buffer solution	pH	-	6.865	0.005			Acceptance Criteria			
8		pH	-	6.865	0.005			E ₁	mV	30	
9								Calibration Table			
10		pH value	EMF	k'	E ₁						
11			(mV)	(mV/mV)	(%)	(mV)					
12		6.865	22.2	-88.58	99.0	14.3					
13		6.868	189.2								
14								Measurement Condition			
15								Symbol	unit	value	
16								T _x	°C	28.0	
17								Measurement Table			
18		sample no.	pH	EMF(mV)							
19		1	6.867	22.2							
20		2	6.869	22.3							
21		3	6.861	22.2							
22		4	6.861	22.2							

Fig. 4. Calibration and measurement data

1	A	B	C	D	E	F
2	Symbol	Unit	Value	u(x _i)	c _i	u(x _i)
3	ΔE	mV	167.3	0.082	0.350	0.029
4	T _c	K	298.15	0.100	0.198	0.020
5	RLJP	mV	0.6	0.346	0.35	0.121
6	ΔpH	-	-2.86	0.007	20.423	0.144
7	T _x	K	298.15	0.100	0.198	0.020
8	k' _x	mV	-58.348			0.193

10	A	B	C	D	E	F	G
11	Symbol	Unit	Value	u(x _i)	c _i	u(x _i)	V _i of V _{eff}
12	E ₁	mV	22.425	0.025	0.0171	0.000428	3
13	E ₂	mV	22.2	0.0577	0.0171	0.00099	∞
14	pH ₁	-	6.865	0.0050	1.0	0.0050	∞
15	RLJP _x	mV	0.6	0.3464	0.0171	0.0059	∞
16	k' _x	mV	-58.35	0.1928	0.00011	0.000021	∞
17	u _c (pH _x)		6.871			0.00784	335701
18	U _c (pH _x)			k = 2.0		0.0157	

Fig. 5. Uncertainty budgets of k'_x and pH_x by the GUM approach.

1	I	J	K	L	M
2	Symbol	unit	Value	u(x _i)	u(x _i)/x _i
3	ΔE-RLJP	mV	166.7	0.3559	0.0021
4	T _c	K	298.15	0.10	0.0003
5	ΔpH	-	-2.86	0.0071	-0.0025
6	T _x	K	298.15	0.1	0.0003
7	k' _x	mV	-58.348	0.193	

9	I	J	K	L	M
10	Symbol	unit	Value	u(x _i)	u(x _i)/x _i
11	ΔE _x -RLJP _x	mV	-0.4	0.3521	0.939
12	pH ₁	-	6.865	0.0050	
13	k' _x	mV	-58.35	0.1927	-0.0033
14	u _c (pH _x)			0.00784	

Fig. 6. Uncertainty between budgets of k'_x and pH_x by relative standard uncertainty

	A	B	C	D	E	F	G
1	Symbol		u(ΔE)	u(T _x)	u(RLJP)	u(ΔpH)	u(T _x)
2		Value	0.08165	0.1	0.35	0.0071	0.1
3	ΔE	167.3	167.4	167.3	167.3	167.3	167.3
4	T _x	298.15	298.15	298.25	298.15	298.15	298.15
5	RLJP	0.6	0.6	0.6	0.95	0.6	0.6
6	ΔpH	-2.86	-2.86	-2.86	-2.86	-2.85	-2.86
7	T _x	298.15	298.15	298.15	298.15	298.15	298.25
8	k' x, k' x	-58.348	-58.376	-58.328	-58.227	-58.493	-58.368
9			-0.03	0.02	0.12	-0.14	-0.02
10			0.0008	0.0004	0.0147	0.0210	0.0004
11	u(k' x)		0.193				

	A	B	C	D	E	F	G
14	Symbol		u(E _x)	u(E ₁)	u(pH ₁)	u(RLJP _x)	u(k' x)
15		Value	0.025	0.0577	0.005	0.35	0.193
16	E _x	22.4	22.5	22.4	22.4	22.4	22.4
17	E ₁	22.2	22.2	22.258	22.2	22.2	22.2
18	pH ₁	6.865	6.865	6.865	6.870	6.865	6.865
19	RLJP _x	0.6	0.6	0.6	0.6	0.9	0.6
20	k' x	-58.35	-58.35	-58.35	-58.35	-58.35	-58.15
21	pH _x , pH _x	6.871	6.871	6.872	6.876	6.877	6.871
22	u(pH _x)		0.0004	0.001	0.005	0.006	0.00002
23	u(pH _x) ²		2E-07	1E-06	2E-05	4E-05	5E-10
24	u(pH _x)		0.00784				

Fig. 7. Uncertainty budgets of k' x and pH_x by Kragten approach

For Kragten approach, the standard uncertainty of practical slope factor, u(k' x) in cell C11 of Fig. 7 can be described by Eq. (14).

$$u(k' x) = \sqrt{(k' x, \Delta E - k' x)^2 + (k' x, T_c - k' x)^2 + (k' x, RLJP - k' x)^2 + (k' x, \Delta pH - k' x)^2 + (k' x, T_x - k' x)^2} \quad (14)$$

where the practical slope factor for each input quantity (k' x, x_i) is defined in Eq. 15 to 19 as follows:

$$k' x, \Delta E = \frac{R \ln 10}{F} (T_c - T_x) + \frac{\Delta E + u(\Delta E) - RLJP}{\Delta pH} \quad (15)$$

$$k' x, T_c = \frac{R \ln 10}{F} [T_c + u(T_c) - T_x] + \frac{\Delta E - RLJP}{\Delta pH} \quad (16)$$

$$k' x, RLJP = \frac{R \ln 10}{F} (T_c - T_x) + \frac{\Delta E - RLJP + u(RLJP)}{\Delta pH} \quad (17)$$

$$k' x, \Delta pH = \frac{R \ln 10}{F} (T_c - T_x) + \frac{\Delta E - RLJP}{\Delta pH + u(\Delta pH)} \quad (18)$$

$$k' x, T_x = \frac{R \ln 10}{F} [T_c - (T_x + u(T_x))] + \frac{\Delta E - RLJP}{\Delta pH} \quad (19)$$

The uncertainty of pH measurement, as shown in cell C24 of Fig. 7, is determined using Eq. 20.

$$u(pH_x) = \sqrt{(pH_{x, E_x} - pH_x)^2 + (pH_{x, E_1} - pH_x)^2 + (pH_{x, pH_1} - pH_x)^2 + (pH_{x, RLJP_x} - pH_x)^2 + (pH_{x, k' x} - pH_x)^2} \quad (20)$$

where the pH value of each input quantity (pH_{x, x_i}) are

determined according to Eq. 21 to 25.

$$pH_{x, E_x} = pH_1 + \frac{E_x + u(E_x) - E_1 - RLJP_x}{k' x} \quad (21)$$

$$pH_{x, E_1} = pH_1 + \frac{E_x - (E_1 + u(E_1)) - RLJP_x}{k' x} \quad (22)$$

$$pH_{x, pH_1} = pH_1 + u(pH_1) + \frac{E_x - E_1 - RLJP_x}{k' x} \quad (23)$$

$$pH_{x, RLJP_x} = pH_1 + \frac{E_x - E_1 - (RLJP_x + u(RLJP_x))}{k' x} \quad (24)$$

$$pH_{x, k' x} = pH_1 + \frac{E_x - E_1 - RLJP_x}{k' x + u(k' x)} \quad (25)$$

	A	B	C	D	E	F	G
1	Symbol	ΔE	T _x	RLJP	ΔpH	T _x	k' x
2		Value	167.3	298.15	0.6	-2.86	298.15
3	Std.uncer. or half-width		0.082	0.10	0.35	0.0071	0.10
4	Distribution	Normal	Normal	Rectangular	Normal	Normal	
5	Simulation	167.47	298.20	0.41	-2.85	298.33	-58.59
6		167.32	298.00	0.02	-2.86	298.04	-58.48
100005		167.17	298.27	0.61	-2.86	298.19	-58.21

	J	K	L	M	N	O	P
1	Symbol	E _x	E ₁	pH ₁	RLJP _x	k' x	pH _x
2	value	22.4	22.2	6.865	0.6	-58.35	6.871
3	Std.uncer. or half-width	0.025	0.0577	0.005	0.35	0.193	0.00618
4	Distribution	Normal	Normal	Normal	Rectangular	Normal	
5	Simulation	22.404	22.150	6.869	0.572	-58.355	6.875
6		22.445	22.189	6.864	0.355	-58.622	6.865
100005		22.428	22.185	6.863	0.447	-58.147	6.867

Fig. 8. Uncertainty budgets of k' x and pH_x by the Monte Carlo approach

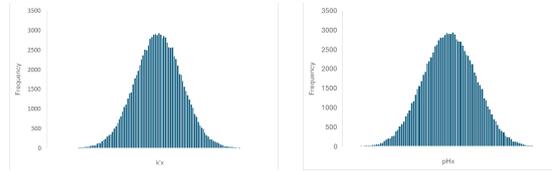


Fig. 9. Simulation results of k' x (left) and pH_x (right) by spreadsheet

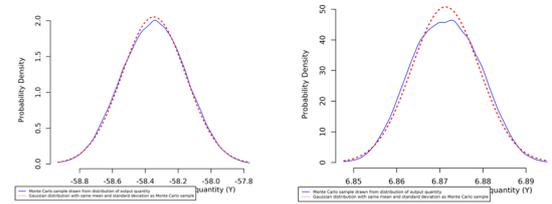


Fig. 10. Simulation results of k' x (left) and pH_x (right) by the NIST Uncertainty Machine

The standard uncertainties of k' x and pH_x, as determined using both the GUM and Kragten approaches, are 0.193 mV and 0.00784, respectively. These values provide a precise quantification of uncertainty, which is essential for ensuring measurement reliability. Alternatively, when the

Monte Carlo approach is applied, the standard uncertainties exhibit slight variations, ranging from 0.1907 to 0.1940 mV for k'_x and 0.00613 to 0.00620 for pH_x . These results demonstrate that the Monte Carlo method accounts for a broader range of variability, allowing for a more dynamic representation of uncertainty.

Despite the predominance of the standard uncertainties associated with residual liquid junction potential in both calibration and measurement using the GUM approach, the Monte Carlo simulation provides additional confirmation. Specifically, the Monte Carlo results indicate that the standard uncertainties of k'_x and pH_x follow a normal distribution, as evidenced by the histogram plot in Fig. 9. This observation reinforces the suitability of the Monte Carlo approach for modeling uncertainty distributions, offering insights into the probabilistic nature of measurement uncertainty.

The NIST Uncertainty Machine is used to validate the reliability of both the GUM approach and the Monte Carlo method in spreadsheet calculations, with the simulation results displayed in Fig. 10. The NIST Uncertainty Machine employs the GUM linear approximation method to estimate output quantities and their corresponding standard uncertainties, yielding values of (-58.35, 0.19) for k'_x and (6.871, 0.0079) for pH_x , based on a coverage interval of approximately 68%. In contrast, a spreadsheet-based implementation of the same method produces slightly different results: (-58.348, 0.193) for k'_x and (6.871, 0.00784) for pH_x , under the same coverage conditions. Although both methods are grounded in the same GUM linear approximation, minor numerical discrepancies can arise due to several factors:

- Rounding precision: Differences in retained significant figures during intermediate calculations can subtly affect the final results.
- Computational algorithms: The NIST tool may employ more refined numerical techniques or higher computational precision than those available in standard spreadsheet environments.
- Input handling and formatting: Small variations in how input values, units, or probability distributions are defined may contribute to slight differences in output.

Despite these small deviations, the close agreement between the two methods reinforces the consistency and reliability of the GUM approach, whether executed via the NIST tool or a spreadsheet-based model.

The NIST Uncertainty Machine utilizes the Monte Carlo method to generate coverage intervals for k'_x and pH_x , yielding (-58.55, -58.15) and (6.863, 6.88) at approximately 68% coverage. Meanwhile, a spreadsheet-based Monte Carlo calculation produces slightly different intervals: (-58.54, -58.15) for k'_x and (6.864, 6.879) for pH_x . Although both approaches use Monte Carlo simulations, the slight variations in results can be

attributed to:

- Sampling Differences: The NIST Uncertainty Machine may use a larger or more refined sample size compared to a spreadsheet-based implementation.
- Randomization Methods: Different random number generators or distribution assumptions can lead to minor variations.
- Computational Precision: The NIST tool may employ higher precision in numerical calculations, affecting the final intervals.

These differences are relatively small, suggesting that both methods provide consistent uncertainty estimates. However, the NIST Uncertainty Machine is specifically designed for rigorous uncertainty analysis, making it a preferred choice for high-accuracy applications.

Overall, the comparative analysis of GUM and Kragten provides robust numerical estimates, and Monte Carlo simulations help to examine these uncertainties by providing a familiar spreadsheet-based view that confirms validity and can support confidence in the reliability of the reported uncertainties of the measurement results.

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