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Original Research/Review

Problems of estimating the uncertainty of water pH measurement

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Abstract

The article analyses the main problems associated with evaluation the combined standard uncertainty of the water pH measurement by the type A and B methods. It is shown that, for a small number n of the tested water samples, the type A standard uncertainty determined by the conventional method is underestimated. Therefore, the correct expression to calculate this component of uncertainty is presented. The authors also highlighted that since in the practical measurement the influencing quantities and sensitivity coefficients are not known absolutely precisely, therefore their uncertainties often have to be taken into account when estimating the combined uncertainty. For this purpose the authors have propose their approach to correctly determine the type B components of combined standard uncertainty caused by not only the values of influencing quantities and sensitivity coefficients, but also their uncertainties. The proposed approaches are illustrated by estimating the uncertainty in the measurement of drinking water pH, presenting the corresponding components of measurement uncertainty budget.

Keywords: estimation, uncertainty, measurement, *pH*, water

1. Introduction

Drinking water, along with air, is the most important environmental factors that are a condition for life, and it has the most significant impact on human health [1], [2]. In general, life on Earth cannot exist without water. Water pollution harms human health, animals that consume water and plants that feed on water, as well as the flora and fauna of rivers, lakes, seas, and oceans, i.e., the entire biological world. Water is one of the main constituent elements in the production of agricultural products, seafood, food, medical devices, in a large number of chemical industry processes, and has an impact on the lifespan of various man-made structures, machinery, equipment, etc [1–6]. Therefore, water quality and its constant monitoring are of great social importance and are a prerequisite to ensuring an appropriate level of quality of life.

It is worth noting that the pH value of water from different sources is different. Bottled drinking water that uses reverse osmosis and ultraviolet (UV) and/or ozonation to kill organisms has a pH between 6.9 and 7.5, non-carbonated bottled mineral water has a pH between 7.1 and 7.5, while carbonated water has a pH between 5.3 and 6. Water from common household filters has a pH close to 7.5, the same as tap water, while boiled tap water has a slightly higher alkaline pH [7]
The paper shows that uncertainty in pH measurement depends on a number of factors, and discusses the key components of uncertainty that affect pH measurement.

One of the most important parameters that characterise the quality of water and other liquids and solutions is the so-called hydrogen pH [3–6]. The measurement of pH is based on the dependence of electrode potentials on the activity and concentration of hydrogen ions and is carried out by measuring the electromotive force of an electrometric cell, which is a set of corresponding galvanic transducers or electrodes, measuring and reference, immersed in the solution under study (here, water). Thus, to measure pH, measuring transducers are used - electrodes and a measuring device that measures the corresponding output electromotive force at the output of the electrodes [3–6].

As with other measurements, the quality of a pH measurement is determined by uncertainty [8–10]. The measurement of pH is one of the measurements that is characterised by a large number of uncertainty components of different nature. The most important uncertainty components in technical pH measurements are [8–10]:

1) uncertainty due to the heterogeneity of the measured solution, which can manifest itself in the instability of the pH measurement results of different samples of the same medium under study - this is a component of uncertainty associated with the object of measurement;
2) uncertainty due to calibration (often referred to as adjustment in the manufacturer's instructions of electrodes with buffer solutions;
3) the uncertainty component of the instrument readings and the conversion function of the measuring transducer (measuring and auxiliary electrodes) under reference measurement conditions;
4) uncertainty components caused by deviations from reference measurement conditions.

During precision pH measurements, other uncertainty components may also be taken into account, such as the component due to incomplete cleaning (rinsing) of the electrodes after the previous measurement, uncertainty due to the mismatch of the calibration conditions and the calibration procedure with reference conditions, discrete readings, a dynamic component (the result is recorded when the instrument has not yet fully settled), etc [6, 8–10] . These uncertainty components will not be discussed further, as they can be neglected in technical pH measurements.

An evaluation of the uncertainty of the pH measurement can be performed using a classical approach [11], [12], or Monte Carlo (MC) simulations [13] can be used. Commercial programmes dedicated to this purpose are also available. The paper [8] presents the advantages and disadvantages of the methods of calculating the uncertainty, i.e., the typical method, the MC method implemented in the software and the spreadsheet, and the commercial programmes; the paper considers the case of pH measurement after two-point calibration.

2. Problems in estimating pH measurement uncertainty

The main problems with determining the uncertainty of the pH measurement uncertainty are that there is no fully correct methodology for estimating the uncertainty, which would correctly calculate the uncertainty components of the Type A and Type B methods [12].

In particular, when calculating the uncertainty of the Type A method according to the accepted methodology [12] with a small number of observations, the resulting standard uncertainty is significantly underestimated, i.e., it is largely approximate. Note that although this problem is mentioned in another part of the [12], no methodology is proposed to correct the value of the standard uncertainty.

The main quantitative indicator of the heterogeneity of the pH of different samples of the same water is the unbiased estimate of the standard deviation, which is calculated using the known expression:

$$s_{pH} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(pH_i - \overline{pH}\right)^2} \tag{1}$$

where:

$$\overline{pH} = \frac{1}{n}\sum_{i=1}^{n} pH_i \tag{2}$$

is the average value of the results of n (typically n = 6... 12) of measurements (observations) of water samples: pH_1, pH_2, ..., pH_n. Based on the standard deviation estimate (1), the standard uncertainty of type A is traditionally estimated using the well-known expression [12]:

$$u_A(pH) = \frac{s_{pH}}{\sqrt{n}} = \sqrt{\frac{1}{n \cdot (n-1)} \sum_{i=1}^{n} \left(pH_i - \overline{pH}\right)^2} \tag{3}$$

However, formally, expression (3) reflects an estimate of the standard deviation of the mean, which is the measurement result. As has been shown [14], [15], according to the definition of uncertainty [12], the uncertainty is not related to the measurement result - the result (here the mean value of (2)) is known - but to the measured quantity - here pH (measurand). Therefore, the pH uncertainty should be determined according to the density of the distribution of possible pH values given the known result (mean) and an estimate of the possible spread, the standard deviation (1).

Since pH measurements are accompanied by a large number of influencing quantities, the calculation of uncertainty using the Type B method also encounters problems due to uncertainties in the values of the influencing quantities and influence factors. It is obvious that in practical measurements the value of the influencing quantity is not known exactly but with a corresponding uncertainty. The same applies to influence factors, which are also known only approximately. Therefore, these uncertainties for some variables should be taken into account when assessing measurement confidence. A detailed analysis of the problems associated with these aspects is provided in Chapter 5.

The standard DSTU 4077:2001 [9] formulates some of the main components of what it calls the measurement "error". This mainly refers to the influence on the measurement result of water sampling, electrode preparation, temperature influence, and correction of this influence.

It is obvious that the pH of drinking water depends on the source from which the water is taken, i.e., on the physicochemical and geological properties of the rocks and soils in which the source is located, as well as other factors, including the time of year, the amount and intensity of precipitation and the time that has passed since the end of precipitation, etc. This causes variability in the pH of drinking water, i.e. its different values at different times. In addition, as a result of these phenomena, various chemical and biological components and mechanical impurities may appear in the water, which change not only the pH of the water but also its composition. Therefore, when measuring the pH of water, it is also advisable to measure its composition. Such results would provide a more objective characterisation of water quality. In view of this, the method of water sampling and preparation according to DSTU 4077:2001 [9] is of great importance during measurements. This standard sets out the relevant requirements for the time intervals between sampling, sample preparation, and measurements, and recommends that water samples be treated, for example, by settling or filtering, in the event of significant contamination.

Failure to comply with these requirements can result in a significant deviation of the measurement results from the true pH value. Most importantly, subsequent estimates of the measurement uncertainty may not take into account factors related to the water itself, which is sampled from a specific source, under specific conditions, at a specific time.

The purpose of the research is to correctly assess the components of the standard uncertainty,, to find the total uncertainty and to present the uncertainty budget of water pH measurement and the measurement result in accordance with the requirements of the standard.

The physicochemical and other aspects of pH measurement are not considered here, and the studies themselves are performed on the basis of known metrological characteristics of the instruments used and known measurement conditions. Specific results relate to the determination of the pH measurement uncertainty of the manufacturer's drinking water: Lvivvodokanal in the Zolochiv direction in the village of Pluhiv. The measurements were made in accordance with: DSTU 4077:2001 [9], ISO 10523:1994 [10] and ISO 10523:2008 [11], and were carried out in the testing laboratory of VEMAKO LLC using a pH metre pH-150M [16], [17] and electrodes ESCL-08M (EKS-10610/7) [18].

3. Uncertainty from heterogeneity of water samples. Estimation of uncertainty using the Type A method

It should be noted once again that, according to the definition [12], measurement uncertainty is a parameter that characterises the dispersion of possible values of a measured quantity around the measurement result. Since all the information about the dispersion of possible values of the measured quantity is contained in the corresponding density of the distribution, the correct calculation of the standard (as well as other) uncertainty must be based on this distribution. If we assume a normal distribution model for the observations (pH_1, pH_2, ..., pH_n) in [14], [15] was was shown that correct value of the Type A standard uncertainty of measurement is:

$$u_A(pH) = \frac{s_{pH}}{\sqrt{n}}\sqrt{\frac{n-1}{n-3}} = \sqrt{\frac{1}{n\cdot(n-3)}\sum_{i=1}^{n}\left(pH_i-\overline{pH}\right)^2} \tag{4}$$

This value directly relates to the t-Student distribution. When the number of observations is small, which is mainly the case for pH measurements, the values of (3) with [12] and (4) differ significantly. In particular, when the number of samples is $n = 6$, the value of (3) is underestimated by 29%, and when $n = 10$, it is underestimated by more than 13%. Only with a large number of observations of several dozen, which is practically impossible to obtain during pH measurements, are values (3) and (4) sufficiently close.

It should be noted that in other models of population density distributions, from which the observation is selected and which is described by two parameters, location and scale, when the standard uncertainty of the measured value is correctly calculated, the factor $\sqrt{(n-3)}$ appears in the denominator. This means that the minimum number of observations for which the standard uncertainty can be calculated correctly is $n = 4$. Therefore, methods for estimating pH measurement uncertainty should explicitly mention this minimum value, i.e., the number of samples should not be less than 4. For $n = 4$, the correct value of the standard uncertainty (4) is:

$$u_A(pH) = \sqrt{\frac{1}{4}\sum_{i=1}^{4}\left(pH_i-\overline{pH}\right)^2} \tag{5}$$

Water samples $n = 4$ were measured and the results obtained: $pH_1 = 7.06$, $pH_2 = 7.02$, $pH_3 = 7.01$, $pH_4 = 7.05$.

We take their average value as the result of the pH measurement (2):

$$pH_x = \frac{pH_1 + pH_2 + pH_3 + pH_4}{2} = 7.035\,\mathrm{pH} \tag{6}$$

According to (4), a measure of the dispersion (heterogeneity) of pH values is their estimated standard deviation (1):

$$s_{pH} = \sqrt{\frac{1}{4-1}\sum_{i=1}^{n}\left(pH_i-\overline{pH}\right)^2} = 0.0238\ \mathrm{pH}. \tag{7}$$

4. Estimating uncertainty using the Type B method under reference conditions

The second category of factors includes all those related to the digital meter and measuring electrodes, as well as the conditions of their use.

For the digital meter and electrodes, as well as for other measuring instruments, the manufacturer has established the maximum permissible errors of their readings $\pm\Delta_{\mathrm{MPE}}$ under reference conditions and the coefficient of influence of temperature deviations from the reference range. Table 1 shows the maximum permissible errors of the device $\pm\Delta_{\mathrm{MPE},dm}$ and measuring electrodes $\pm\Delta_{\mathrm{MPE,el}}$ under reference conditions, as well as $\pm\Delta_{\mathrm{MPE,cal}}$ for electrode calibration.

Table 1: Maximum permissible errors of the digital evice and measuring electrodes [16], [17], [18]

MPE of digital meter: $\pm\Delta_{\mathrm{MPE,dm.}}$	MPE of measuring electrodes	
	calibration $\Delta_{\mathrm{MPE,cal.}}$	reference conditions, $\Delta_{\mathrm{MPE,el}}$
±0.05 pH	± 0.01 pH	±0.02 pH

In general, the estimation of uncertainty using the Type B method for the use of measuring instruments under reference conditions does not cause problems, except for one. Since the estimation of uncertainty requires knowledge of the density of the distribution, this is the main problem for calculating the relevant uncertainty component. The manufacturer usually does not provide information on the distribution of possible deviations of the device readings within $\pm\Delta_{\text{MPE},dm}$. Therefore, according to the recommendation of the [12], focusing on the worst case, we assume a uniform distribution of these deviations. Then the component of the standard uncertainty of the instrument readings under reference measurement conditions for the known maximum permissible errors $\pm\Delta_{\text{MPE},dm}$ of the instrument readings is calculated by the expression:

$$u_{dm,ref}\left(pH\right)=\frac{\Delta_{\text{MPE},dm}}{\sqrt{3}}. \tag{8}$$

For the value of ±0.05 pH units from Table 1, the standard uncertainty associated with the measurement by the instrument under reference conditions is:

$$u_{dm,ref}\left(pH\right)=\frac{\Delta_{MPE,dm}}{\sqrt{3}}. \tag{9}$$

Similarly, we calculate the component of the standard uncertainty due to the inaccuracy of the conversion function of the measuring electrodes under reference conditions. Here, $\pm\Delta_{\text{MPE},el}$ should be used (Table 1) and then the corresponding component of the standard uncertainty is:

$$u_{el,ref}\left(pH\right)=\frac{0.02\ pH}{\sqrt{3}}\approx 0.0115\ pH. \tag{10}$$

The uncertainty of electrode calibration with buffer solutions depends on the uncertainty $u\left(pH_{cal}\right)$ of the pH_{cal} values of the calibration solutions and on the non-compliance of the calibration conditions and the calibration procedure in the reference conditions. If the electrodes were calibrated under reference conditions, this uncertainty component is mainly determined by the uncertainty of the calibration solutions. In particular, if the maximum permissible error $\pm\Delta_{\text{MPE,cal}}$ (Table 1) of the pH_{cal} values of the calibration solutions is known, then, also assuming a uniform distribution, the corresponding component of the standard ~~measurement~~ uncertainty due to electrode calibration is:

$$u_{cal}\left(pH\right)=u\left(pH_{cal}\right)=\frac{0.01\ pH}{\sqrt{3}}\approx 0.0058\ pH. \tag{11}$$

5. Problems of estimating uncertainty components from influencing quantities

In fact, as mentioned earlier, pH measurements are measurements in which a large number of influencing factors should be taken into account. Table 2 shows the main influencing values, reference and operating conditions, and influence factors during pH measurements using a pH meter -150M with EKS-10610/7 electrodes [16], [17], [18].

Table 2: Influencing values, reference and operating conditions and influence factors (as a fraction of the basic maximum permissible error) during *pH* measurements using a *pH* meter -150M with electrodes ЕКС-10610/7 [16], [17], [18]

№	Influenced quantity	Operating conditions	Reference conditions	Sensitivity coefficient c_i
1	Temperature θ_m measuring medium (solution) under automatic temeperature correction	from -10°C to 100°C	from 15°C to 25°C	$c_{\theta m}=1.5$
2	Outside temperature θ_{out} : for 10°C deviation from the reference range	from 5°C to 40°C	from 15°C to 25°C	$c_{\theta out}=1.5/10\ ^{o}\text{C}$
3	Outside relative humidity H_{rel}	from 90% to 25°C	30%÷80%	$c_H=2.0$
4	Device power supply voltage U_{ps}	from 198 V to 242 V	(207÷235) V	$c_{Ups}=1.0$

5	Resistance R_{me} of measuring electrode: the basic value of $R_{b.me}$ =500 MΩ	from 0 to 1000 MΩ	0 MΩ	c_{Rme} =1.0/500 MΩ
6	Resistance R_{re} of reference electrode: the basic value of $R_{b.ce}$ =10 kΩ	from 0 to 20 кΩ	0 кΩ	c_{Rre} =1.0/10 kΩ
7	AC voltage U_{re} (of 50 Hz frequency) in the circuit of the reference electrode	from 0 to 50 mV	0 mV	c_{Ure} =1.0/50 mV
8	DC voltage U_{s-g} in circuit of measuring solution - ground:	from -1.5 V to+1.5 V	0 V	c_{Ug-g} =1.0/1.5 V

Note 1: According to GOST 29322-92 in the current edition (2014) [19] for a 230V network, the maximum deviations (both positive and negative) in Ukraine should not exceed 10% of the nominal value, i.e. from 207 to 253 volts.

Note 2: Since the pressure value during *pH* measurements is almost always within the reference range of 84 to 106.7 kPa, the impact of this component of uncertainty is not assessed.

In Ukrainian national metrological practise [20], as a legacy from the previous system, normalisation and calculation of the uncertainty caused by an influence quantity v within the work area are most often carried out as a product of the corresponding influence factor on the standard uncertainty $u_{ref}(X)$ of the measurement under reference conditions. In this case, two options are used mainly. In the first case, the influence factor is constant; that is, the standard uncertainty component is calculated using a simple expression.

$$u_v(X)=c_v\cdot u_{ref}(X) \tag{12}$$

and does not depend on the actual value of the influencing quantity in the working area of values.

In the second case, the sensitivity coefficient has the dimension of sensitivity to the normalised deviation $\Delta v_{ref}=\left|v_{op}-v_{ref}\right|$ of the value of the quantity from the edge of the reference range v_{ref}:

$$c_{v,1}=\frac{c_v}{\Delta v_{ref}}. \tag{13}$$

Then, to calculate the corresponding uncertainty component, the deviation value Δv of the influencing quantity new from the edge of the reference range should be determined, and the standard uncertainty component is calculated by the expression:

$$u_v\left(X\right)=c_{v,1}\cdot\Delta v\cdot u_{ref}\left(X\right)=c_v\cdot\frac{\Delta v}{\Delta v_{ref}}\cdot u_{ref}\left(X\right). \tag{14}$$

In certain cases, the sensitivity factor has a sensitivity dimension to the so-called base value of the influencing quantity.

Analysing Table 2, we can note that the coefficients of influence of one part of the influencing quantities are constant, i.e., they do not take into account the actual deviation of the influencing quantity from the reference range. This applies, for example, to the temperature θ_m of the measuring medium (water) with automatic thermal compensation, the relative humidity of the environment, and the supply voltage of the device U_{ps}. For other influencing quantities, the respective influence factors take into account the corresponding normalised or reference value of the influencing quantity. In these cases, the actual value of the influencing quantity must be known to calculate the standard uncertainties.

As noted above, the manufacturers of the measuring instruments mostly provide only the values of the influence factors, as in Table 2, but do not provide their uncertainties. However, it is known that even physical constants are characterised by uncertainty. Obviously, the values of the influence coefficients given in Table 2 are approximate, i.e., they also have uncertainty. GUM [12] draws attention to this situation. In particular, Section G.4 of [12] argues that the nonstatistical estimate of the standard uncertainty, i.e., the Type B method, is largely subjective, with values derived from scientific judgement based on the totality of available information. Often, the values that determine the uncertainty are themselves characterised by uncertainty of even a few tens of percent [12]. This approach to [12] is used to determine the so-called effective number of degrees of freedom. In this regard, based on [12], we will assume that the influence coefficients have a relative standard uncertainty of about 25-30%.

However, the value of an influential quantity is never known exactly. When measuring the influencing quantity, there is always a standard uncertainty of the measurement. Therefore, given the above, the first method of normalisation of (12) should take into account the uncertainty of the sensitivity coefficient, i.e., the standard uncertainty should be calculated using the expression:

$$u_v(X)=\sqrt{c_v^2+u^2(c_v)}\cdot u_{ref}(X)=c_v\sqrt{1+u_{rel}^2(c_v)}\cdot u_{ref}(X), \tag{15}$$

where $u_{rel}(c_v)$ is the relative standard uncertainty of the coefficient c_v.

In the second method of normalising (14), in addition to the uncertainty of the coefficient, the uncertainty of the influencing quantity should also be taken into account, i.e.:

$$u_v(X)=c_v\sqrt{1+u_{rel}^2(c_v)}\cdot\frac{\Delta v_{dev}\sqrt{1+u_{rel}^2(v)}}{\Delta v_{ref}}\cdot u_{ref}(X). \tag{16}$$

where $u_{rel}(v)$ is the relative standard uncertainty of the measured value *v*. This uncertainty can be estimated based on the characteristics of the instrument concerned, for example, the accuracy class, the measuring limit, and its indication. In some cases, it is estimated by calculation, based on an analysis of the measurement conditions or data from previous measurements.

It should be noted that, in certain cases, a seemingly paradoxical situation may arise when estimating the uncertainty components of the influential quantities. For example, let the width of the range of deviation of the influential quantity from the reference range be given as v_R. If the influential quantity is not measured, then only the expected value of the influential quantity, which is in the middle $v_\partial/2$ of this range, with possible deviations $\pm v_R/2$, is guided, then, assuming a uniform distribution and, for simplicity, neglecting the uncertainty $u_{rel}(c_v)$, in (16) we have:

$$u_v(X)\approx c_v\cdot\frac{\Delta v}{2\cdot\Delta v_{ref}}\sqrt{1+\frac{1}{3}}\cdot u_{ref}(X)=c_v\cdot\frac{\Delta v}{\sqrt{3}\cdot\Delta v_{ref}}\cdot u_{ref}(X). \tag{17}$$

On the other hand, if you want to improve the accuracy of measurements and for this purpose measure the influencing quantity and find that its value is close to the limit values: $|v|\approx v_{\lim}$. Then, even with a negligibly small standard measurement uncertainty of the influential quantity ($u(v)\to 0$), according to (16), the standard uncertainty of this influential quantity is:

$$u_v(X)\cong c_v\cdot\frac{\Delta v}{\Delta v_{ref}}\cdot u_{ref}(X), \tag{18}$$

which in $\sqrt{3}$ is larger than the standard uncertainty (17) without measuring this influential variable.

A priori, a one-sided triangular distribution of the deviation of the influencing quantity, for example, temperature, in a certain direction from the reference region [12] is more likely. Then in (17), instead of $\sqrt{3}$ there will be $\sqrt{6}$, i.e.:

$$u_v(X)=c_v\cdot\frac{\Delta v}{\sqrt{6}\cdot\Delta v_{ref}}\cdot u_{ref}(X). \tag{19}$$

Therefore, if the measured value of the influencing quantity is close to the limit values: $|v| \approx v_{\lim}$, then the resulting standard uncertainty will be greater $\sqrt{6}$ than the standard uncertainty without the measurement of the influencing quantity. Even if the value of the influence quantity is greater than approximately $0.4v_{\partial}$, the standard uncertainty will still be greater than the standard uncertainty without measuring the influence quantity.

The paradox is that in order to reduce the uncertainty, an additional measurement of the influencing quantity was performed, i.e., to reduce its uncertainty, but as a result, the measurement uncertainty component of this influencing quantity increased. The same effect can occur if additional research is performed to determine the actual value of the influence coefficient.

This situation can be explained by the fact that by assuming a uniform, triangular, or other distribution of the impact value (or the value of the impact coefficient) within the boundary values, we are performing an imaginary randomisation of these values, i.e. we assume that they are random. And the uncertainty estimate found with this approach is as expected when using a given type of measuring instrument under typical measurement conditions. This expected uncertainty can be called a priori. However, in a particular measurement, the value of the influencing quantity takes on a specific value (similarly, for a particular measuring instrument, the influence coefficient has a specific (though possibly unknown) value), and therefore the actual uncertainty of the measurement result when using a particular measuring instrument under specific conditions may differ from the expected one.

In general, to estimate the uncertainty caused by the influence of a quantity on the reading of a measuring instrument, one should proceed from a mathematical model:

$$\vartheta(v) = c_v \cdot v\,. \tag{20}$$

In this model, the influence coefficient c_v has a certain value c_k with a standard uncertainty $u(c_v)$, and the influencing quantity v has a value v_k with a standard uncertainty $u(v)$. Then, after performing the correction for systematic bias, the correction $p_k = -c_k v_k$, according to the requirements of the [12] and assuming the independence of the influence factor and the influencing quantity, the component of the standard uncertainty of the measurement due to this influencing quantity should be calculated by the expression:

$$u_v^2(X) \approx \sqrt{c_k^2 \cdot u^2(v) + v_k^2 u^2(c_v) + u^2(c_v) \cdot u^2(v)}\,. \tag{21}$$

Another factor that is not taken into account when estimating uncertainty components from influencing quantities is the influence of the time factor, i.e. changes in the properties (drift, "ageing") of measuring transducers, instruments, etc. after the last calibration. Unfortunately, manufacturers of pH measuring instruments do not provide any information on this issue.

6. Quantifying uncertainty from influencing quantities

The actual measurement conditions (including the values of the influencing quantities) are presented in Table 3. Standard measurement uncertainties of the influencing quantities will be evaluated using the known maximum permissible errors in the following analysis. The last two influencing quantities (AC voltage in reference electrode circuit and DC voltage in the water-ground circuit) are characterised by the so-called a priori uncertainty, i.e. calculated.

Table 3: Actual values of influencing quantities (pH measurement conditions)

№	Influence quantity	Operating conditions
1	Temperature θ_m measuring medium (solution) under automatic temeperature correction	13°C ±0.5°C
2	Outside temperature θ_{out}	29.0°C ±0.5°C
3	Outside relative humidity H_{rel}	70%±5%
4	Device power supply voltage U_{ps}	(226.0 ± 1.0) V

5	Resistance R_{me} of measuring electrode	≈750 MΩ
6	Resistance R_{re} of reference electrode	≈9 kΩ
7	AC voltage U_{re} (of 50 Hz frequency) in the circuit of the reference electrode	≈15 mV
8	DC voltage U_{s-g} in circuit of measuring solution - ground:	≈0.30 V

The temperature of test water $\theta_{\mathrm{m}} = (13 \pm 0.5)^{o}C$ (Table 3) is outside of the reference range $\theta_{\mathrm{ref}} = (20 \pm 5)^{o}C$, i.e. from 15ºC up to 25ºC. Therefore due to the 1st line of table 2, from which coefficient $c_{\theta_m} = 1.5$ (with neglected uncertainty), the standard uncertainty due to the deviation of the test water temperature from reference range is:

$$u_{\theta_m}(pH) = c_{\theta_m} \cdot u_{dm,ref}(pH) = 1.5 \cdot 0.0288 \text{ pH} = 0.0432 \text{ pH} . \tag{22}$$

The ambient (outside) temperature is measured: $\theta_{\mathrm{out}} = (29 \pm 0.5)^{o}C$ (Table 3) is outside of reference range $\theta_{\mathrm{ref}} = (20 \pm 5)^{o}C$, and temperature deviation is $\Delta\theta_{\mathrm{out}} = 29^{o}C - 25^{o}C = 4^{o}C$. Assuming triangle distribution inside MPE=±0.5°C, which causes standard uncertainty of temperature $u(\theta_{\mathrm{out}}) = 0.5^{o}C / \sqrt{6} \approx 0.20^{o}C$ or relative standard uncertainty is $u_{rel}(\theta_{\mathrm{out}}) = 0.20^{o}C / 4^{o}C \approx 0.05$. This component of standard uncertainty can be neglected. According 2nd line of Table 2, from which coefficient $c_{\theta_{out}} = 1.5/10^{o}C$ (with neglected uncertainty) after substitution these values to (16) the standard uncertainty caused by deviation of the ambient temperature deviation from reference range is:

$$u_{\theta_{out}}(pH) = c_{\theta_{out}} \cdot \Delta\theta_{out} \cdot u_{dm,ref}(pH) = \frac{1.5}{10^{o}C} 4^{o}C \cdot 0.0288 \,\text{pH} = 0.0173 \,\text{pH} . \tag{23}$$

Because ambient humidity H_{rel}=70 % (Table 3) not deviate from the reference: 30%÷80%, therefore the component of standard uncertainty of ambient humidity deviations is not determined, i.e.:

$$u_H(\text{pH}) = 0 . \tag{24}$$

The supply voltage is (226.0± 1.0) V (Table 3) and reference range is (207 ÷253) V. Thus, the supply voltage is within the reference range, and for this reason, the component of the standard uncertainty due to the deviation of the device supply voltage is determined, i.e:

$$u_{Ups}(\text{pH}) = 0 . \tag{25}$$

The resistance of measuring electrode is $\mathrm{R_{me}} \approx 750 \ \mathrm{M\Omega}$ (Table 3). According to 5th line of Table 2 the sensitivity coefficient c_{Rme} =1.0/500 MΩ for base value 500 MΩ. Therefore, the standard uncertainty component due to the effect of the value of the resistance of the measuring electrode is:

$$u_{Rme}(\text{pH}) = c_{Rme} \cdot \frac{\mathrm{R_{me}}}{\mathrm{R_{b,me}}} \cdot u_{el,ref}(\text{pH}) = 1.0 \cdot \frac{750\mathrm{M\Omega}}{500\mathrm{M\Omega}} \cdot 0.0115 = 0.0173 \,\text{pH} . \tag{26}$$

The resistance of reference electrode is $\mathrm{R_{re}} \approx 9 \ \mathrm{k\Omega}$ (Table 3). According to 6th line of Table 2 the sensitivity coefficient c_{Rre} =1.0/10 kΩ for the base value 10 kΩ. Therefore, the standard uncertainty component due to the effect of the auxiliary electrode resistance value is:

$$u_{Rre}(\text{pH}) = c_{Rre} \cdot \frac{\mathrm{R_{re}}}{\mathrm{R_{b,re}}} \cdot u_{el,ref}(\text{pH}) = 1.0 \cdot \frac{9\mathrm{k\Omega}}{10\mathrm{k\Omega}} \cdot 0.0115 = 0.0104 \,\text{pH} . \tag{27}$$

The alternating voltage of frequency 50 Hz in the circuit of the reference electrode is $\mathrm{U_{re}}$ ≈15 mV. For the limited value of 50 mV (7th line of Table 2) the sensitivity coefficient is 1.0/50 mV, so the standard uncertainty component due to the influence of the AC voltage in the reference electrode circuit is:

$$u_{Ure}(\mathrm{pH}) = c_{Ure} \cdot \frac{\mathrm{U_{re}}}{\mathrm{U_{re,lim}}} \cdot u_{el,ref}(\mathrm{pH}) = 1.0 \cdot \frac{15\ \mathrm{mV}}{50\ \mathrm{mV}} \cdot 0.0115 = 0.0035\ \mathrm{pH} \tag{28}$$

The DC voltage in the circuit test solution - ground is $\mathrm{U_{s-g}} = 0.30\ \mathrm{V}$ (Table 3). For the limited value of ±1.5 V (8th line of Table 2) the sensitivity coefficient is c_{Ug-g} =1.0/1.5 V 1, so the standard uncertainty component due to the influence of the DC voltage in the test solution - ground circuit is:

$$u_{Us-g}(\mathrm{pH}) = 1.0 \cdot \frac{\left|\mathrm{U_{s-g}}\right|}{1.5\ \mathrm{V}} \cdot u_{el,ref}(\mathrm{pH}) = 1.0 \cdot \frac{0.3\ \mathrm{V}}{1.5\ \mathrm{V}} \cdot 0.0115 = 0.0023\ \mathrm{pH} \tag{29}$$

When calculating the total standard uncertainty of the technical result of the pH measurement of water, we assume that the uncertainty components are not mutually correlated, since they are caused by different factors, so the total (composite, combined) standard uncertainty of the *pH* measurement result is equal to the square root of the sum of the squares of all the components found above, i.e:

$$u_c(\mathrm{pH}) = \sqrt{\begin{array}{l} u_s^2(\mathrm{pH}) + u_{cal}^2(\mathrm{pH}) + u_{dm,ref}^2(\mathrm{pH}) + u_{nel,ref}^2(\mathrm{pH}) + u_{\theta m}^2(\mathrm{pH}) + u_{\theta out}^2(\mathrm{pH}) + \\ + u_H^2(\mathrm{pH}) + u_{Ups}^2(\mathrm{pH}) + u_{Rme}^2(\mathrm{pH}) + u_{Rre}^2(\mathrm{pH}) + u_{Ure}^2(\mathrm{pH}) + u_{Us-g}^2(\mathrm{pH}). \end{array}} \tag{30}$$

Since all the components of the uncertainty from the influencing quantities are normalised relative to the uncertainty of the digital meter and measuring electrode under reference conditions, the combined standard uncertainty (28) can be written in a different form:

$$u_c(\mathrm{pH}) = \sqrt{\begin{array}{l} u_s^2(\mathrm{pH}) + u_{cal}^2(\mathrm{pH}) + u_{dm,ref}^2(\mathrm{pH}) \cdot \left[1 + c_{\theta m}^2 + c_{\theta out}^2 \frac{\Delta\theta_{\mathrm{out}}^2}{\Delta\theta_{\mathrm{ref}}^2} + c_H^2 + c_{Ups}^2 \right] + \\ + u_{el,ref}^2(\mathrm{pH}) \cdot \left[1 + c_{R\text{вв}}^2 \frac{\mathrm{R_{me}^2}}{\mathrm{R_{b,me}^2}} + c_{Rre}^2 \frac{\mathrm{R_{re}^2}}{\mathrm{R_{b,re}^2}} + c_{Ure}^2 \frac{\mathrm{U_{re}^2}}{\mathrm{U_{re,lim}^2}} + c_{Up-\text{з}}^2 \frac{\mathrm{U_{s-g}^2}}{\mathrm{U_{s-g,lim}^2}} \right] \approx 0.0644\ \mathrm{pH} \end{array}} \tag{31}$$

The expanded uncertainty $U_p(pH)$ of the technical pH measurement is calculated as the product of the combined standard uncertainty $u_c(\mathrm{pH})$ calculated above by the coverage factor k_p for a given confidence level *p*:

$$U_p(pH) = k_p \cdot u_c(pH). \tag{32}$$

Since the number of non-zero uncertainty components is 10 (two components are equals to zero: $u_H(\mathrm{pH}) = 0$ and $u_{Ups}(\mathrm{pH}) = 0$) and components of standard uncertainty have approximately similar values and are independent, the value of coverage factor can be taken as the corresponding quantile of the normal distribution [12] , i.e. for $p = 0.95$ $k_{0.90} \approx 1.96$ [12].

The calculated components are recorded in the *pH* measurement uncertainty budget table (Table 4).

Table 4. Uncertainty budget for water *pH* measurement.

N	Quantity, parameter, *q*	Quantity value	Type. (A or B)	PDF *p(q)*	Sensitivity coef. c_i	Stand. uncert. *u(q)*, pH
1	Solution heterogeneity ν_{pH}	± 0.06 pH	B	Triangle	1.0	0.0238
2	Electrode calibration, $\mathrm{pH_{cal.}}$, $\mathrm{MPE_{cal}}$, $\Delta_{cal,lim}$	± 0.01 pH	B	Uniform	1.0	0.00577
3	Electrode (reference conditions), $\mathrm{MPE_{el}}$, $\Delta_{\mathrm{el,ref,lim}}$	±0.02 pH	B	Uniform	1.0	0.0115
4	Digital meter (reference conditions), $\mathrm{MPE_{dm}}$, $\Delta_{\mathrm{dm,ref,lim}}$	±0.05 pH	B	Uniform	1.0	0.0288

5	Temperature of measuring solution	$\theta_m = 27^{o}C$ $\theta_{ref,lim}$=25^{o}C	B	Uniform	1.5	0.0432
6	Outside temperature	$\theta_{out} = 29^{o}C$, $\theta_{ref,lim}$=25^{o}C $\Delta\theta_{out}$ =4^{o}C	B	Uniform	1.5/10^{o}C	0.0173
7	Relative humidity	H=70 %, $H_{ref,lim}$=80 %	B	Uniform	1.0	0
8	Power supply.	(226.0±1.0) V $U_{ps.lim}$=207 V÷253 V	B	Triangle	1.0	0
9	Measuring electrode resistance o	R_{re}=750^{o}MΩ, $R_{b.re}$=500^{o}MΩ	B	Uniform	1.0	0.0173
10	Reference electrode resistance	R_{me}=9^{o}kΩ, $R_{b.me}$=10^{o}kΩ	B	Uniform	1.0	0.0104
11	AC voltage in circuit of reference electrode	U_{re}=15 mV $U_{re,lim}$=50 mV	B	Triangle	1.0	0.0035
12	DC voltage in circuit solution - ground	U_{s-g}=0.3 V $U_{s.g,lim}$=1.5 V	B	Triangle	1.0	0.00192
13	Combined standard uncertainty					0.0644
14	Expanded uncertainty(p=0,95, $k_{0,95}$=1,96)					0.126 pH
15	Relative combined standard uncertainty					0.915%
16	Effective number degrees of freedom, ν_{eff}					33
17	Expanded coefficient (coverage factor), k_p					2.035
18	Refined value of expanded uncertainty (p=0.95, ν_{eff}=33, k_p=2.035)					0.131 pH
19	Relative expanded uncertainty					1.86%
20	Result of measurement (short presentation,,): pH=(7.04±0.13) pH, p = 95, k_p=2.035					1.86%

7. Conclusion

Based on the analysis of the measurement conditions performed and the evaluation of uncertainty, we can confirm that pH measurements of drinking water refer to measurements in which multiple components of uncertainty must be taken into account.

These are measurements in which one of the important components is the uncertainty associated with the test object itself, namely, the uncertainty caused by the heterogeneity of the pH of different samples of drinking water under test from the same source.

The second important component of pH measurement uncertainty is due to the inaccuracy of the measurement tools (digital meter and electrodes) directly involved in the measurements.

In addition, there are a large number of uncertainty components in these measurements from the interactions of influencing quantities. Among them are influences from: temperature of tested water and outside temperature, humidity of air, voltage supply (in these measurements, the values of relative humidity of the air and value of voltage supply were within reference limits), values or resistances of measuring and reference electrodes, AC voltage in circuit of reference electrode and DC voltage in circuit test water – ground.

As a result of the evaluation of the uncertainty in the measurement of drinking water pH, the relative expanded uncertainty (confidence level 0.95) was found to be about 1.9%. This value can be accepted. In measurements with significant impact of influencing quantities and therefore required correction of their impact, because the correction is never perfect, for correct estimation of the uncertainty caused by these influences, in addition to the values of sensitivity coefficients, it is necessary to have the values of their uncertainty. Of course, the measurement uncertainty of the influencing quantities must also be estimated.

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