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Estimation of uncertainty at reference buffer solution certification

The national standard of the pH scale is the primary standard of the Republic of Kazakhstan, which confirmed its equivalence with international comparisons, namely, key comparisons of APMP QM-R19 (2014) and pilot comparisons of COOMET 655/EN/15 (2017). The standard implements the primary method of pH measurements using cells without transfer (Harned cells) with hydrogen and silver chloride electrodes. This cell is characterized by high reproducibility of measurement results. The state reference materials (SRM), which are widely used by laboratories at verification of measuring instruments and internal quality control, are certified with this standard. SRM of pH are the accurate samples of chemicals dissolved in 1 kg of bidistilled deionized water with a specific electrical conductivity of not more than 2·10–4 Cm/m at a temperature of 20 °C. The paper presents an estimation of uncertainty of certified pH values of CRM-standard buffer solutions in the range 9.010–9.280 pH. Determination of the pH of solutions is an indirect type of measurement. The reference pH value is determined from the results of measurements of electromotive force, temperature, pressure and other parameters.

Keywords: measurement uncertainty, state standard samples, pH buffer solutions, primary state standard, international comparisons, electromotive force, standard potential.

Introduction

Uncertainty estimation was performed according to [1] using the basic provisions [2]. In general, the combined standard uncertainty of the certified value of pH CRM is evaluated by the equation:

$$u_c^2\left(A\right) = u_{char}^2 + u_h^2 + u_{stab}^2 , \tag{1}$$

where u_{char} is the uncertainty associated with characterization of certified values; u_h is the standard uncertainty of homogeneity; u_{stab} is the standard uncertainty of long-term instability.

Certified values of the pH CRM as an activity of hydrogen ions expressed in units of pH have been obtained on the state standard of the pH scale. The scientific novelty and purpose of this paper is to assess the measurement capabilities of the State scientific metrological center for further transfer of the pH measurement units and calibration of working standards.

Method

Estimation of solutions pH was carried out as an indirect measurement. The reference value of pH was determined from the results of measurements of the electromotive force (EMF), temperature, pressure and other parameters.

Results and discussion

The entire procedure of determining the pH of reference buffer solutions based on the measurement of the EMF of the cell and has been nominally divided into three stages. The first stage includes the estimation of standard silver chloride electrode potential. Standard silver chloride electrode potential $E^0_{\mathrm{Ag/AgCl}}$ is determined by measuring the EMF of the Harned cells Ag|AgCl|HCl (0.01M)| H_2 Pt [3] using the formula:

$$E^0_{\mathrm{Ag/AgCl}} = E + \frac{2RT\ln 10}{F}\left(\lg(m_{\mathrm{HCl}}) + \lg(\gamma_{\pm\mathrm{HCl}}) + 0.25\lg\frac{p^0}{p_{\mathrm{H_2}}}\right), \quad (2)$$

where E is the measured voltage in V; R is the universal gas constant, which is equal to (8.314510 ± ± 0.000070) J×mol^{-1}×K^{-1}; T is the thermodynamic temperature, K; F is the Faraday constant, which is equal to (9.648530 ± 0.00002)×10^4 C×mol^{-1}; m_{HCl} is the HCl molality in the solution; $\gamma_{\pm\mathrm{HCl}}$ is the molality activity coefficient of chloride ions; P^0 is the normal atmospheric pressure of 101.325 kPa.

Equation (1) is a measurement model equation in determining of a standard silver chloride electrode $E^0_{\mathrm{Ag/AgCl}}$.

The main components of the uncertainty [4] are as follows:

– the measurement of the EMF of the electrode E;

– the measurement of the temperature T;

– the molality concentration of the solution of HCl, m_{HCl};

– the hydrogen partial pressure $P_{\mathrm{H_2}}$;

– the coefficient of ion activity $\mathrm{Cl^-}$ $\gamma_{\pm\mathrm{HCl}}$.

Uncertainties associated with R and F were insignificant and not taken into account during calculating the combined standard uncertainty. Standard silver chloride electrode potential was determined as $E^0_{\mathrm{Ag/AgCl}}$ = = 0.222107 V with a standard uncertainty $u(E^0_{\mathrm{Ag/AgCl}}) = 8.26\cdot10^{-5}$ V.

The second stage includes the determination of the function of acidity $p(\alpha_{\mathrm{H}}Y_{\mathrm{Cl}})$ and the limit of the function of acidity $p(\alpha_{\mathrm{H}}Y_{\mathrm{Cl}})^0$. At the second stage EMF, the E of nine Harned cells, has been measured, these cells are filled with the reference buffer solution, whose $pH(X)$ has been determined. These nine cells have been divided into three groups, each containing three cells. The difference between the groups is in the concentration of the alkali metal chloride added to the buffer solution. Usually the following molality of chloride ions is used: m_{Cl}=0.005; 0.010; 0.015 mol/kg.

Values of function of acidity $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$ in 3 groups of cells have been obtained from the measured EMF and previously determined $E^0_{\mathrm{Ag/AgCl}}$:

$$p(\alpha_{\mathrm{H}}\gamma_{\mathrm{Cl}}) = \frac{\left(E - E^o_{\mathrm{Ag/AgCl}}\right)F}{RT\ln 10} + \lg m_{\mathrm{Cl}} + 0.5\lg\left(\frac{p^0}{p_{\mathrm{H_2}}}\right). \quad (3)$$

Equation (3) is the measurement model equation for estimate of the function of acidity. The main components of uncertainty in estimation acidity function $p(\alpha_{\mathrm{H}}\gamma_{\mathrm{Cl}})$ are:

– the estimated value $E^0_{Ag/AgCl}$;

– the determination of the EMF of the electrode E;

– the determination of the temperature T;

– the molality concentration of the solution of HCl m_{HCl};

– the hydrogen partial pressure P_{H_2}.

Estimates of all the major components have been identified at the first stage and are shown in Tables 1 and 2.

Limit of the function of acidity was specified equal to $p(\alpha_{\mathrm{H}}Y_{\mathrm{Cl}})^0$= 9.23980 with a standard uncertainty $u(\alpha_{\mathrm{H}}Y_{\mathrm{Cl}}) = 1.48\cdot10^{-3}$.

Stage 3 includes calculation of the certified value of the standard sample $pH(X)$

$$pH(X) = p\left(a_{\mathrm{H}}\gamma_{\mathrm{Cl}}\right)^0 + \lg\gamma^0_{\mathrm{Cl}};$$

$$\lg\gamma^0_{\mathrm{Cl}} = \frac{A\sqrt{I}}{1+1.5\sqrt{I}},$$

where A is the Debye-Hückel constant, I is the ionic strength of the buffer.

Estimates of all the main components identified in the first stage are given in Tables 3 and 4.

Table 1

Estimation of input values of uncertainty

Influencing quantity	Estimated uncertainty
Measured value of EMF, E = 0.463320 V	$u_B(E)=\frac{\text{error of the multi meter from the certificate}}{\sqrt{3}}$=1.2010^{-5} V
The temperature of measurement, T = 298.153 K	$u(E)$=1.1010^{-2} K (specified in the certificate at the thermometer)
Molality of the HCl solution, mol/kg	$u(m_{\text{HCl}})$=1.2010^{-5} mol/kg (specified in the certificate of analysis on a solution)
The partial pressure of hydrogen, P_{H2}	$u(P_{H_2})$=5.0 Pa (determined by the accuracy of measurement of atmospheric pressure)
Molality activity coefficient of chloride ions, $\gamma_{\pm HCl}$	$u(\gamma_{\pm\text{HCl}}) = 9.3\cdot10^{-4}$ (from the IUPAC data)

Table 2

Uncertainty budget at determination of the capacity of the standard silver chloride electrode $E^0_{\text{Ag/AgCl}}$

Quantity x_i	Value x_i	Unit	Standard uncertainty $u(x_i)$	Sensitivity factor c_i	Unit	Contribution of the uncertainty $c_i{\cdot}u(x_i)$	Unit
E	0.463320	V	$1.20\cdot10^{-5}$	1	–	$1.2\cdot10^{-5}$	V
T	298.153	K	$1.10\cdot10^{-2}$	$\frac{2R\ln 10}{F}\left(\begin{matrix}\lg(m_{\text{HCl}})+\lg(\gamma_{\pm\text{HCl}})+\\+0.25\lg\frac{p^0}{p_{\text{H}_2}}\end{matrix}\right)=$ $=8.1\cdot10^{-4}$	V/K	$-8.89\cdot10^{-6}$	V
m_{HCl}	0.01	mol/kg	$1.2\cdot10^{-5}$	$\frac{2RT}{Fm_{\text{HCl}}}=5.14$	V·kg/mol	$6.17\cdot10^{-5}$	V
P_{H_2}	96686.0	Pa	5.0	$-\frac{2RT}{FP_{\text{H}_2}}=-1.33\cdot10^{-7}$	V/Pa	$-6.65\cdot10^{-7}$	V
$\gamma_{\pm\text{HCl}}$	0.9042	mol/kg	$9.3\cdot10^{-4}$	$\frac{2RT}{F\gamma_{\pm\text{HCl}}}=5.68\cdot10^{-2}$	V·kg/mol	$5.29\cdot10^{-5}$	V
$E^0_{\text{Ag/AgCl}}$	0.222107	V				$8.26\cdot10^{-5}$	V

Table 3

Uncertainty budget for the estimate of function of acidity $p(\alpha_H Y_{Cl})^0$

Size x_i	Value x_i	Unit	Standard uncertainty $u(x_i)$	Sensitivity factor c_i	Unit	Contribution of the uncertainty $c_i{\cdot}u(x_i)$	Unit
1	2	3	4	5	6	7	8
E	0.904029	V	$1.20\cdot10^{-5}$	$\frac{F}{RT\ln(10)}=16.9$	1/V	$2.03\cdot10^{-4}$	–
$E^0_{\text{Ag/AgCl}}$	0.222107	V	$8.26\cdot10^{-5}$	$-\frac{F}{RT\ln(10)}=-16.9$	1/V	$-1.40\cdot10^{-3}$	–
T	298.152	K	$1.1\cdot10^{-2}$	$-\frac{(E-E^0_{\text{Ag/AgCl}})F}{RT^2\ln(10)}=-3.86\cdot10^{-2}$	1/K	$-4.25\cdot10^{-4}$	–

Continuation of Table 3

1	2	3	4	5	6	7	8
m_{HCl}	0.005	mol/kg	2.010^{-6}	$\frac{1}{m_{\mathrm{HCl}}\ln(10)}=86.86$	kg/mol	$-1.74\cdot10^{-4}$	–
$P_{\mathrm{H_2}}$	96457.0	Pa	5.0	$-\frac{0.5}{P_{\mathrm{H_2}}\ln(10)}=-2.25\cdot10^{-6}$	1/Pa	$-1.13\cdot10^{-5}$	–
$p\left(a_{\mathrm{H}}\gamma_{\mathrm{Cl}}\right)^0$	9.23980					$1.48\cdot10^{-3}$	–

Table 4

Uncertainty budget for the determination of acidity function $p(\alpha_{\mathrm{H}}Y_{\mathrm{Cl}})^0$

Size x_i	Value x_i	Unit	Standard uncertainty $u(x_i)$	Sensitivity factor c_i	Contribution of the uncertainty $c_i\cdot u(x_i)$
$p\left(a_{\mathrm{H}}\gamma_{\mathrm{Cl}}\right)^0$	9.23980	–	$1.48\cdot10^{-3}$	1	$1.48\cdot10^{-3}$
$\lg\gamma^0_{\mathrm{Cl}}$	–0.05960	–	$0.58\cdot10^{-5}$	1	$0.58\cdot10^{-5}$
pH(*X*)	9.1802				$1.48\cdot10^{-3}$

Thus, the certified value of the standard sample is determined as *pH*(*X*) = 9.1802 with the standard uncertainty $u_{char}= 1.48\cdot10^{-3}$.

Stability estimation of CRM is carried out within six months according to the [5].

The obtained data and calculations are shown in Table 5.

Table 5

The results of stability test of CRM pH = 9.18

Time, *n*	Current value, *Xn*	Value of difference, *dn*	$\alpha\cdot dn$	$(1-\alpha)\cdot U$	*Un*	Swing, *R*
0	9.1802	0.0000	0.0000	0	0	
1	9.1808	0.0006	0.0002	0	0.0002	0.0006
2	9.1818	0.0016	0.0005	0.0001	0.0006	0.0010
3	9.1811	0.0009	0.0003	0.0004	0.0007	–0.0007
4	9.1809	0.0007	0.0002	0.0005	0.0007	–0.0002
5	9.1804	0.0002	0.0001	0.0005	0.0005	0.0005
6	9.1815	0.0013	0.0004	0.0004	0.0008	–0.0011

The standard uncertainty from the instability was calculated according to [1].

Average moving range is as follows:

$$\overline{R} = 0.00022,\ S_D = 0.89\times\overline{R} = 0.89\times0.00022 = 0.000193;$$

$$S_a = \frac{S_D}{\sqrt{\sum_{i=1}^{n} t_i^2}} = \frac{0.000193}{\sqrt{1^2+2^2+3^2+4^2+5^2+6^2}} = 0.0000202\,;$$

$$u_{stab} = 0.0000202\times7 = 0.0001415 = 0.14\cdot10^{-3}.$$

Measurement performed for an estimation of the uncertainty on account of in homogeneity, had pointed, that contribution of u_h was insignificant and it was not taken into account to combined standard uncertainty.

Combined standard uncertainty of certified value of the reference buffer solution of 1th category is estimated using equation (1):

$$u_c\left(A\right) = \sqrt{u_{char}^2 + u_{stab}^2} = \sqrt{\left(1.48\cdot10^{-3}\right)^2 + \left(0.14\cdot10^{-3}\right)^2} = 1.4910^{-3}\,.$$

Extended standard uncertainty is:

$$U(A) = k\cdot u_c(A) = 2\cdot1.49\cdot10^{-3} = 2.98\cdot10^{-3} \approx 0.003.$$

Certified value of the pH state certified reference materials, standard buffer solution 1 category, will be equal to (9.1802 ± 0.003) pH at $k = 2$ for 95 % confidence level. Currently work to further improve the state standard is underway [6, 7].

Conclusions

Measurements of pH are influenced by the number of factors. The main contribution to the measurement uncertainty is made by the potential of the chlorine-silver electrode.

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Эталондық буферлік ерітіндіні аттестаттау кезіндегі белгісіздікті бағалау

pH шкаласының Мемлекеттік эталоны Қазақстан Республикасының бастапқы эталоны болып табылады, ол өзінің халықаралық салыстырмалармен баламалылығын растады: APMP QM-R19 (2014) негізгі салыстырмаларымен және COOMET 655/EN/15 (2017) Пилоттық салыстырмаларымен. Эталон сутекті және хлоркүмісті электродтары бар тасымалсыз (Харнед ұяшықтары) ұяшықтарды қолдана отырып, pH өлшеудің бастапқы әдісін жүзеге асырады. Бұл ұяшық өлшеу нәтижелерінің жоғары жаңғыртылуымен сипатталады. Эталон сондай-ақ өлшеу құралдарын тексеру және сапаны ішкі бақылау кезінде зертханалар кеңінен қолданатын мемлекеттік стандартты үлгілерді (ГСО) әзірлеуге мүмкіндік береді. pH ГСО-20 ºC температурада меншікті электрөткізгіштігі $2\cdot10^{-4}$ См/м аспайтын бидистилденген деионизацияланған судың 1 кг-да ерітілген химиялық заттардың дәл ілімін білдіреді. Жұмыста 9.010–9.280 pH диапазонындағы стандартты буферлік ерітінділердің pH CRM аттестатталған мәндерінің белгісіздігін бағалау ұсынылған. Ерітінділердің pH — анықтау-өлшеудің жанама түрі. pH эталондық мәні электр қозғаушы күштің, температураның, қысымның және басқа да параметрлердің өлшеу нәтижелерінен анықталады. Эталондық электрхимиялық ұяшықтың ЭҚК өлшеулерінің дұрыстығы сутекті және хлоркүмісті электродтардың көрсеткіштеріне тәуелді.

Кілт сөздер: өлшеулердің белгісіздігі, мемлекеттік стандартты үлгілер, pH буферлік үйлесімдер, бастапқы мемлекеттік эталон, халықаралық салыстырулар, электрқозғаушы күш, стандартты әлеует.

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Оценка неопределенности при аттестации эталонного буферного раствора

Государственный эталон шкалы pH является первичным эталоном Республики Казахстан, который подтвердил свою эквивалентность международными сличениями: ключевыми сличениями APMP QM-R19 (2014) и пилотными сличениями COOMET 655/EN/15 (2017). Эталон реализует первичный метод измерений pH с применением ячеек без переноса (ячеек Харнеда) с водородным и хлорсеребряными электродами. Данная ячейка характеризуется высокой воспроизводимостью результатов измерений. На эталоне аттестуются государственные стандартные образцы (ГСО), которые широко используются лабораториями при поверке средств измерений и внутреннем контроле качества. ГСО pH представляют собой точные навески химических веществ, растворенные в 1 кг бидистиллированной деионизированной воды с удельной электрической проводимостью не более $2 \cdot 10^{-4}$ См/м при температуре 20 ºС. В работе представлена оценка неопределенности аттестованных значений pH CRM — стандартных буферных растворов в диапазоне 9,010–9,280 pH. Определение pH растворов — косвенный вид измерений. Эталонное значение pH определяется из результатов измерений электродвижущей силы, температуры, давления и других параметров.

Ключевые слова: неопределенность измерений, государственные стандартные образцы, буферные растворы pH, первичный государственный эталон, международные сличения, электродвижущая сила, стандартный потенциал.

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