Procedure of sample preparation for international and interlaboratory comparisons in the field of the pH measuring of borate buffer solution

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Abstract. In the paper is described the preparation method of buffer solution for interlaboratory and international comparisons. This technique was developed by scientists of All-Russian Scientific Research Institute of Physicotechnical and Radio Engineering Measurements during the preparation of samples for international comparisons in the field of measuring the hydrogen index of borate buffer solution. According to the measurement results, the offered method allows to prepare the homogeneous and stable buffer solutions.

Hydrogen index (pH) is a fundamental physical and chemical value that characterizes the acid-base properties of liquid media and solutions. pH measurement is the most common method of monitoring the normalized indexes in the production processes of the main industries and agriculture (pharmaceuticals, food production, beverages and juices, livestock products, chemical industry). It should be noted that pH measurement is also important for the control of high purity substances in petrochemicals, water treatment, as well as in the ecological monitoring of environmental water locations.

In practice, to measure the pH various types of pH meters are used, which have typical uncertainties from 0.03 to 0.5. The pH meters are required periodic the calibration and graduation with buffer solutions - pH working standards.

The pH State Primary Standard numbered GET 54 has been established for metrological support of the pH-measurement in Russia since early 90es of the 20th century. The standard reproduces, conserves and transfers the pH value in the range from 1 to 12 at temperatures from 0 °C to 95 °C, non-excluded systematic measurement error is ± 0.0017 at the temperature of 25 °C [1].

In 2019, the laboratory of All-Russian Scientific Research Institute of Physicotechnical and Radio Engineering Measurements (VNIIFTRI) carried out an upgrading of the GET 54-2011. The standard is
the principle of the Russian state hierarchy scheme for pH measuring instruments and ensures the unity of measurements of the hydrogen ion activity in aqueous solutions in the expanded range of the pH scale.

According to the results of the upgrading, the metrological characteristics of the pH primary standard have been established [2, 3]:

- the primary standard reproduces the pH value of the activity of hydrogen ions in aqueous solutions in the range of pH values from 1 to 12 with an standard deviation of the measurement result not exceeding 0.001 for 10 independent measurements at a temperature of 25 °C , the non-excluded systematic error does not exceed 0.0017,

- the primary standard reproduces the pH value of the activity of hydrogen ions in aqueous solutions in the range of pH values from 0.01 to 1.0 with an standard deviation of the measurement result not exceeding 0.0015 for 10 independent measurements at a temperature of 25 °C, the non-excluded systematic error does not exceed 0.02;

- the standard uncertainty of measuring the pH of the activity of hydrogen ions in aqueous solutions, in the range of pH values from 1 to 12:
  - evaluated by type A is 0.001;
  - evaluated by type B is 0.0007;
  - the combined standard uncertainty is 0.0012;
  - the expanded uncertainty is 0.0024 (confidence interval is 95% and coverage factor k = 2),

- the standard uncertainty of measuring the pH of the activity of hydrogen ions in aqueous solutions, in the range of pH values from 0.01 to 1.0:
  - evaluated by type A is 0.0015;
  - estimated by type B is 0.0083;
  - the combined standard uncertainty is 0.0084;
  - the expanded uncertainty is 0.0168 (confidence interval is 95% and coverage factor k = 2).

The laboratory takes part in the international comparisons within the framework of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) to confirm its calibration and measurements capability in the pH measurement area. As well as, when the authorized providers confirmed the laboratory competence order the samples (buffer solutions) the laboratory prepares it for them to organize the interlaboratories comparison on pH measuring.

What is need to prepare the samples? Let’s consider our expertise for the solution with pH about 9.2.

The samples were prepared for a comparison of pH measurements at temperature of 15 °C, 25 °C, 37 °C and optionally at 5 °C and 50 °C.

To begin with, it is necessary to prepare the needed chemical reagents: the salt of sodium tetraborate 10-water should be got to a constant weight. For that, it is necessary to place the crushed salt in a quartz bowl and place it in a desiccator over saturated potassium bromide for about 1 month. To control the weight, a little sodium tetraborate is placed in a porcelain crucible, placed in the same desiccator and periodically weighed used analytical weight. The substance is considered ready for further use when the weight of the sample stops changing. Distilled water for the preparation of buffer solutions must comply with GOST R 58144-2018 [4] or another equal international standard.

After readiness of reagents, 3.8065 g of the sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was dissolved per one kilogram of deionized water to prepare the total volume of batch 60 L of the comparison solution. Thus, we prepared the borate buffer with pH value of around 9.2 and the mass fraction of water in the solution $w(\text{H}_2\text{O}) = 0.9965$. 
The ready solution was bottled and packed. Before using, the bottles were washed in an ultrasonic bath for about 45 minutes. Then they were dried. After that, to bottle the buffer solution into polyethylene terephthalate bottles with volume of 500 ml, to close the lids tightly with a control ring. After that, all samples were numbered and weighed 3 times during the week. The mass of the bottled samples is permitted to vary within $\pm 1\%$. When the all samples were weighed and their mass were within the permissible range, they were packed in zip-lock bags, and the bags with the sample sealed. The packages were also labeled the same number like as the samples inside.

The next step, the samples were studied on homogeneity and stability. The homogeneity and stability during whole period the conducting the comparison measurements were confirmed by the primary Harned cell method.

The homogeneity of the samples was studied before the shipment of samples. The results are given in the Table 1.

Tab.1. Results of study on the homogeneity of the prepared buffer solution with pH ~9.2. The expanded uncertainties were evaluated for coverage factor $k = 2$.

| Date of measurement | Bottle No. | $p$H value | $U(k=2)$ |
|---------------------|------------|------------|----------|
| July 5, 2019        | 10         | 9.2180     | 0.0030   |
| July 5, 2019        | 3          | 9.2179     | 0.0031   |
| July 5, 2019        | 60         | 9.2182     | 0.0030   |
| July 5, 2019        | 26         | 9.2178     | 0.0030   |
| July 5, 2019        | 35         | 9.2185     | 0.0031   |
| July 5, 2019        | 55         | 9.2177     | 0.0030   |

According to the study results, given in the Table 1, the pH values at 25 °C had the standard deviation equal to no more 0.0031 for studied in random six bottles. In that way, the prepared buffer solution was quite homogeneity to use it as the comparison sample.

The stability of the samples was studied using the primary Harned cell method in the period from July 2019 to January 2020. The results of the study are shown in the Table 2.

Tab.2. Results of study on the stability of the prepared buffer solution with pH ~9.2. The expanded uncertainties were evaluated for coverage factor $k = 2$.

| Date of measurement          | $p$H value | $U(k=2)$ |
|------------------------------|------------|----------|
| July 5, 2019                 | 9.2180     | 0.0030   |
| July 23, 2019                | 9.2168     | 0.0030   |
| September 25, 2019           | 9.2185     | 0.0031   |
| October 14, 2019             | 9.2187     | 0.0030   |
| November 19, 2019            | 9.2204     | 0.0030   |
| December 17, 2019            | 9.2157     | 0.0031   |
| January 18, 2020             | 9.2183     | 0.0030   |

According to the study results, given in the Table 2, standard deviation was no more $\pm 0.0031$. Therefore, the prepared buffer solution could be considered as a stable sample for a period of comparisons.

Thus, according to the study results, the method allows to prepare the homogeneous and stable borate buffer solutions for conducting the international and interlaboratory comparisons.
References:
[1] ГОСТ 8.120-2014 Государственная система единства измерений. Государственная поверочная схема для средств измерений pH.— М.: Стандартинформ, 2016.— 6 с. (GOST 8.120-2014 State system of measurement uniformity. State verification scheme for measuring instruments of pH.— M.: Standartinform, 2016. — p. 6.)
[2] Prokunin S V et al 2020 Improvement of metrological support of methods and means for determining the hydrogen index in aqueous solutions // Reference materials in measurements and technologies: Abstracts of the IV International Scientific conference, St. Petersburg, December 01–03, 2020. - St. Petersburg: Federal State Unitary Enterprise "All-Russian Scientific Research Institute of Metrology named after D.I. Mendeleev" pp. 90-91 (in Russian)
[3] Prokunin S V 2021 Methods for measuring the hydrogen index in the strongly acidic region // Almanac of modern metrology No. 1 (25) pp. 89-95 (in Russian)
[4] ГОСТ Р 58144-2018 Вода дистиллированная. Технические условия.— М.: Стандартинформ, 2019.— 10 с. (GOST R 58144-2018 Distilled water. Specifications.— M.: Standartinform, 2019. — p. 10.)