We consider the results of work done at GMNTs VNIIFTRI based on a high-precision apparatus to create a Russian state primary standard for pH. We present the results of measuring the pH values of buffer solutions (primary standards for pH) and comparison of standards of VNIIFTRI and PTB (Germany).

In conformance with the plan for state standardization of the Russian Federation, in 1997 it was proposed to implement a new interstate standard "The pH scale for aqueous solutions" to replace GOST 8.134–74 [1]. The new version of the standard, developed at GNMTs VNIIFTRI, is based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) [2]. The new standard raises the precision level for the pH values of the standards (standard solutions), reproducing the pH scale in the interval 0-14 at a temperature of 0-100°C.

Accordingly, for reproduction and dissemination of the pH scale, the need arose to create a primary state standard, including a measuring apparatus and a set of pH standards (a number of buffered solutions with pH values assigned to them). This work is also important because after the breakup of the USSR, the previous standard was at the Isari NPO [Scientific-Industrial Association] (Georgian Republic).

A high-precision apparatus was created and certified in 1993 at VNIIFTRI for metrological assurance for the Russian Federation in the area of pH measurements. Currently, work has been completed on creating a state primary standard for pH; in 1995, a comparison of the VNIIFTRI and PTB (Germany) standards was done.

The pH value (hydrogen ion exponent) is defined as the negative log (base 10) of the activity of hydrogen ions in solution:

\[ \text{pH} = -\log a_w \]  

(1)

This is only a conceptual definition, since Eq. (1) includes the activity of the hydrogen ions \( a_w \), which cannot be unambiguously measured. So in practice, pH is measured using standard buffer solutions (in the terminology of the new version of GOST 8.134–74, working standards for pH), the ensemble of which forms a series of reference points for a practical pH scale for aqueous solutions.

In such a method for specifying the scale for determining the pH value of some analyte solution \( X \), the electromotive forces (emfs) \( E(X) \) and \( E(S) \) are measured for each of two cells I and II connected by a liquid bridge, containing respectively the analyte solution \( X \) and the pH standard \( S \):

I) reference electrode \( \text{KCl (saturated solution)} \parallel \text{solution } X \parallel \text{H}_2(\gamma, p = 1 \text{ atm})\parallel \text{Pt}; \)

II) reference electrode \( \text{KCl (saturated solution)} \parallel \text{pH standard } S \parallel \text{H}_2(\gamma, p = 1 \text{ atm})\parallel \text{Pt}. \)

The pH value of the solution \( X \), \( \text{pH}(X) \), is related to the pH value of the standard \( S \), \( \text{pH}(S) \), as follows:

\[ \text{pH}(X) = \text{pH}(S) + \frac{E(S) - E(X)}{(RT/F)\times 10^b}. \]  

(2)

where \( R \) is the universal gas constant; \( T \) is the thermodynamic temperature; \( F \) is the Faraday constant.
In conformance with the new version of GOST 8.134—74, a solution of potassium hydrogen phthalate \( \text{KHC}_8\text{H}_4\text{O}_4 \) with molarity 0.05 moles/kg is used as the standard reference material (SRM) for pH.

The procedure for assignment of pH values is based on the method recommended by IUPAC [2, 3] and using electrochemical cells III without transference:

\[
\text{Pt} \mid \text{H}_2 (g, p = 1 \text{ atm}) \mid \text{SRM}, \text{Cl}^- \mid \text{AgCl} \mid \text{Ag} ;
\]

\[
E = E^0 - \frac{RT}{F} \ln \left( m_a m_o \gamma_a \gamma_o \right)
\]

where \( m_a \) and \( m_o \) are the molarities of the hydrogen ions and chloride ions in solution; \( \gamma_a \) and \( \gamma_o \) are the activity coefficients of the hydrogen ions and chloride ions; \( m^0 \) is the molar concentration of hydrogen ions in the standard state, 1 mole/kg (actually a normalized coefficient, making the argument of the logarithm dimensionless); \( E^0 \) is the standard emf of the cell with hydrogen and silver chloride half-cells (since, by definition, the standard potential of the hydrogen electrode is equal to zero at all temperatures, \( E^0 \) corresponds to the standard value of the silver chloride electrode).

The value of \( E^0 \) is determined based on measurements of the emf of cell IV:

\[
\text{Pt} \mid \text{H}_2 (g, p = 1 \text{ atm}) \mid \text{HCl (0.01 moles/kg)} \mid \text{AgCl} \mid \text{Ag}
\]