GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

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Water quality -- Determination of pH value -- Glass electrode method

水质 pH 值的测定

玻璃电极法

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1 Scope of application

1.1 This method is applicable to the determination of the pH value of drinking water, surface water and industrial wastewater.

1.2 The color, turbidity, colloidal substance, oxidizing agent, reducing agent and high salinity of water do not interfere with the determination; however, in the strong acidic solution with pH <1, there is so-called "acid error", which can be determined according to the acidity; in the alkaline solution with pH>10, due to the existence of a large amount of sodium ions, the error is generated; therefore, the reading is relatively low, which is commonly referred to as "sodium error". For the methods of eliminating the "sodium error", in addition to use the specially-made electrode of “low sodium error”, it can also adopt the standard buffer solution which is similar to the pH value of the solution under test, in order to calibrate the instrument.

The temperature can affect the electric potential of the electrodes and the ionization balance of the water. It shall be noted that the compensation device of the adjusting instrument should be consistent with the temperature of the solution, and the temperature error of the standard buffer solution between the sample to be measured and the calibrating instrument should be within ± 1°C.

2 Definitions [1]

The pH is defined from the operation. For solution X, it should measure the galvanic cell's:

reference electrode | KCl concentrated solution || solution X |H_2| Pt

electromotive force E_X. Replace the solution X, whose pH(X) is unknown, into the standard

[1] This definition is cited from p.151 of GB 3100-3102-82 *Quantities and units*.

pH solution S, and measure the battery's electromotive force ES, then,

$$pH(X) = pH(S) + (Es - Ex) F / (RTln10)$$

Therefore, the defined pH is the dimensionless quantity.

pH has no theoretical significance. the definition is the practical definition. However, within the limited range of the dilute aqueous solution whose amount-of-substance concentration is less than 0.1mol·dm^3, when it is neither strong acidity nor the strong alkalinity (2 < pH < 12), then it has the followings according to the definition:

$$pH = -\log_{10}[c(H^+)y / (mol \cdot dm^3)] \pm 0.02$$

In the formula, c(H^+) represents the amount-of-substance concentration of the hydrogen ion (H^+). y represents the activity coefficient of the typical 1-1-valence electrolyte in the solution.

3 Principle

The pH value is obtained by measuring the electromotive force of the battery. This battery is usually composed of that the saturated calomel electrode is acted as the reference electrode AND the glass electrode is acted as the indicator electrode. At the temperature of 25°C, if the solution changes 1 pH unit, the change of the potential difference will be 59.16 mV. Hereby, it will be indicated by the way of pH read directly on the instrument. The temperature difference has the compensation device on the instrument.

4 Reagents

4.1 Preparation method of the standard buffer solution (abbreviated as standard solution)

4.1.1 Mass of the reagent and distilled water

4.1.1.1 In the analysis, unless otherwise stated, it requires to use the analytic reagent or the guaranteed reagent. When purchasing the bagged pH standard substances which have been approved by the National Institute of Metrology of China, they can be used with reference to the specifications.

4.1.1.2 The distilled water which is used in the preparation of the standard solution shall meet the following requirements: boiled and then cooled down; the electrical conductivity is less than 2×10^{-6}S/cm[2]; pH of the distilled water should be 6.7~7.3.

4.1.2 When measuring the pH, according to the three possible conditions -- the water sample can present to acidity, neutrality and alkalinity -- the following three standard

[2] The unit of electrical conductance is Siemens which is denoted by the symbol of "S". 1S = 1Ω^{-1}.

9.3 It must be noted that between the inner electrode of the glass electrode and the bulb AND between the inner electrode of the calomel electrode and the ceramic core, there must not have air bubbles, in order to prevent the open circuit.

9.4 The liquid level of the saturated potassium chloride solution in the calomel electrode must be higher than the mercury body. It should have little potassium chloride crystal at the room temperature, in order to ensure the saturation of the potassium chloride solution, however, it is important to note that the potassium chloride crystal should not be too much, in order to prevent from blocking the access of the solution to be tested.

9.5 When measuring the pH, in order to reduce the dissolution or volatilization of the carbon dioxide from the air and the water sample, it should not open the bottle of water sample in advance before measuring the water sample.

9.6 If the surface of glass electrode is contaminated, it is necessary to carry out treatment. If it is attached with the scaling of inorganic salt, it can be dissolved by the warm diluted hydrochloric acid; for the insoluble scaling such as calcium and magnesium, they can be dissolved by EDTA-Na_2 solution. If there is oil contamination, it can use acetone for cleaning. After the electrode is treated according to the above method, it shall be immersed in the distilled water for one day-night before use. Pay attention to avoid treating the electrode with anhydrous ethyl alcohol and dehydrating detergent.

10 Test Report

The test report shall include the followings:

a. Date, time and place of the sampling;

b. Preservation method of the sample;

c. Date and time of determining the sample;

d. The temperature when measuring the sample;

e. The result of the determination (The pH should adopt the one which is nearest to 0.1 pH unit. If there is special requirement, the number of digits of the significant figures for the result can be determined according to the requirements and the accuracy of the instrument);

f. Other situations which require explanations.

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