JJG

NATIONAL METEROLOGICAL VERIFICATION

SPECIFICATION OF THE PEOPLE'S REPUBLIC OF CHINA

JJG 119-2018

Laboratory pH meters

实验室 pH（酸度）计

Issued on: December 25, 2018 **Implemented on: June 25, 2019**

Issued by: State Administration for Market Regulation

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Verification regulation of laboratory pH meters

1 Scope

This Regulation applies to the initial verification, subsequent verification, in-use inspection, for laboratory pH (acidity) meters AND laboratory general-purpose ion meters that can be used as pH (acidity) meters.

2 Normative references

This Regulation cites the following documents:

GB/T 11165-2005 pH Meter

GB/T 20245.2-2013 Expression of performance of electrochemical analyzers - Part 2: pH value

IUPAC: 2002 Measurement of pH. Definition, Standards and Procedures

OIML R54:1981 (E) pH Scale for Aqueous Solutions

For dated references, only the dated version applies to this Regulation; for undated references, the latest edition (including all amendments) applies to this Regulation.

3 Overview

A laboratory pH (acidity) meter (hereinafter referred to as a pH meter) is an electrochemical analytical instrument, which is used to measure the pH of an aqueous solution. The pH meter is mainly composed of an electric meter AND a measuring electrode. The electric meter part includes impedance converter, amplifier, positioning regulator, slope regulator, temperature compensator, display, etc. The measuring electrode includes indicating electrode and reference electrode. The indicator electrode of the composite electrode is mostly a glass electrode; the reference electrode is often called the internal reference electrode.

A pH meter measures the pH of a solution, using a comparative method. The measurement principle is as follows: a battery is composed of an indicator electrode, a reference electrode, a pH standard buffer solution; the electrometer measures the battery's electromotive force E_S; the pH standard value pH_S is input. After calibrating the pH meter, replace it with the solution to be tested and the same pair of electrodes,

6.4.8 Indication error caused by input impedance

Connect the pH meter and the calibrator, according to the circuit in Figure 1. Disconnect the calibrator's high resistance. The pH meter selects the pH measurement mode. Adjust the temperature compensation to 25 °C (or a certain intermediate temperature point). Adjust the calibrator, so that it outputs a signal, which is equivalent to ($pH_D + 6$). Record the pH meter's indication value, pH_1. Connect to high resistance (when the resolution of the display unit is 0.001, connect to 1 GΩ high resistance; for other resolutions, connect to 3 GΩ high resistance). Adjust the calibrator, so that its output signal is pH_D. Adjust the pH meter, so that the pH indication value is 7 (or the pH meter's equipotential pH value). Adjust the calibrator, to make it output the signal of ($pH_D + 6$) again. Record the pH meter's indication value pH_2. Repeat the above operation three times. Use the formula (7), to calculate the indication error, ΔpH_R, which is caused by the input impedance.

$$\Delta\, pH_R = \frac{|\overline{pH_2} - \overline{pH_1}|}{2} \tag{7}$$

Where:

$\overline{pH_1}$、$\overline{pH_2}$ - Respectively, the average pH value 3 measurements, before and after high resistance access.

When testing the input signal (pH_D - 6), by the same method, the indication error, $\Delta pH'_R$, which is caused by the input impedance, takes the larger of ΔpH_R and $\Delta pH'_R$ as the verification result of this item.

6.4.9 Approximate equivalent input impedance

Take the larger median value of ΔpH_R and $\Delta pH'_R$ in 6.4.8. Use the formula (8) or formula (9), to calculate the equivalent input impedance r or r' of the electric meter. If ΔpH_R and $\Delta pH'_R$ are both zero, substitute half of the resolution of the display unit of pH meter into the formula, for calculation.

$$r = \frac{3R}{\Delta\, pH_R} \tag{8}$$

$$r' = \frac{3R}{\Delta\, pH'_R} \tag{9}$$

Where:

R - The high resistance of the calibrator, Ω.

6.4.10 Indication error caused by temperature compensation

6.4.10.1 Indication error caused by manual temperature compensation

Connect the pH meter and the calibrator, according to the circuit in Figure 1. Disconnect the calibrator's high resistance. The pH meter selects the pH measurement mode. Adjust the temperature compensation, to a temperature other than 25 °C. Including the upper and lower limit temperatures of the temperature compensation function, there are no less than 5 temperature points to be verified. At each verification point, adjust the calibrator, so that it outputs a signal equivalent to (pH_D + 6) at the temperature. Record the value of the pH meter. Repeat the measurement 2 times. Calculate the indication error ΔpH_T, which is caused by temperature compensation, according to formula (10).

$$\Delta\, pH_T = \frac{1}{2} \times [\overline{pH} - (7 - pH_D + pH_S)] \tag{10}$$

Where:

$\overline{pH}$ - The average pH value of pH meter in 2 measurements;

pH_D - Equipotential pH value of the calibrator;

pH_S - The standard value of the calibrator.

6.4.10.2 Indication error caused by automatic temperature compensation

Connect the pH meter and the calibrator, according to the circuit in Figure 1. Disconnect the calibrator's high resistance. The pH meter selects the pH measurement mode. Put the thermometer and pH meter temperature probe, into the constant temperature water tank. Adjust the temperature of the constant temperature water tank, to a temperature other than 25 °C. Select not less than 5 temperature points uniformly, in the range of (5 ~ 60) °C. At each verification point, adjust the calibrator, to output a signal equivalent to (pH_D + 6), at the temperature (standard temperature of the thermometer). Record the indication value of pH, temperature, temperature indications of the electric meter. Repeat the measurement 2 times. Calculate the indication error, ΔpH_T, which is caused by temperature compensation, according to formula (10).

6.4.11 Temperature measurement error of temperature probe

Calculate the temperature measurement error, ΔT, of the pH meter's temperature probe at different temperature points, according to the pH meter's temperature indication value and the thermometer temperature's indication value, which are recorded in 6.4.10.2, according to formula (11). Take the largest absolute value of ΔT, as the verification result of this item.

$$\Delta T = \overline{T} - \overline{T}_S \tag{11}$$

Where:

$\overline{T}$ - The average value of the two temperature measurements of the pH meter's temperature probe, °C;

$\overline{T_S}$ - The average value of 2 temperature measurements of the thermometer, °C.

6.4.12 Repeatability of indication value of electric meter

Connect the pH meter and the calibrator, according to the circuit in Figure 1. Disconnect the calibrator's high resistance. The pH meter selects the pH measurement mode. Adjust the temperature compensation to 25 °C (or some intermediate temperature point). Adjust the calibrator, to output a signal equivalent to (pH_D + 3) at this temperature. Connect a 1 GΩ high resistance. Record the pH_i of the pH meter, after the pH meter is stable. Repeat the above operation 6 times. Calculate the repeatability s_{pH} of the electric meter's indication value, according to the formula (12).

$$s_{pH} = \sqrt{\frac{\sum_{i=1}^{n} (pH_i - \overline{pH_{DJ}})^2}{n-1}} \qquad (12)$$

where:

$\overline{pH_{DJ}}$ - The average pH value of 6 measurements;

n - The number of measurements, n = 6.

6.4.13 Indication error of instrument

Select (3 ~ 5) kinds of standard solutions in Table A.1 of Appendix A. Place them in a constant temperature water tank, at a constant temperature. Under normal operating conditions of the pH meter, use a standard solution to calibrate it. THEN, measure another standard solution, which is not used in the verification. Repeat the above operation 6 times. Calculate the pH meter's indication error ΔpH_S, according to formula (13). The pH meter's verification shall try to choose a method with high accuracy; the pH difference, between the verification solution and the solution to be measured, should not exceed 3.

$$\Delta pH_S = \overline{pH} - pH_{SS} \qquad (13)$$

Where:

$\overline{pH}$ - The average value of six measurements of the standard solution to be tested;

pH_{SS} - The pH value of the standard solution.

6.4.14 Repeatability of instrument's indication value

Take the 6 measurement data in 6.4.13. Calculate the measurement repeatability of the pH meter, s'_{pH}, according to formula (14).

$$s'_{pH}=\sqrt{\frac{\sum_{i=1}^{n}(pH_i-\overline{pH})^2}{n-1}} \qquad (14)$$

Where:

pH_i - The measured value of the standard solution to be tested;

$\overline{pH}$ - The average value of six measurements of the standard solution to be tested;

n - The number of measurements, n = 6.

6.5 Processing of verification results

6.5.1 A pH meter, that meets both general technical requirements and measurement performance requirements, is a qualified instrument. The pH meter, that has passed the verification, is issued with a verification certificate. The verification results and instrument level of each item shall be given on the verification certificate.

6.5.2 For a pH meter, that is in use AND after repair, if the electrical meter's verification meets the requirements of the Regulations, BUT when the pH meter with original electrode is beyond the requirements of the Regulation, in case of the verification of the whole machine, the inspection unit can choose a new electrode for re-verification. After the electrode is replaced, if the whole machine is verified as qualified, it is still a qualified instrument, AND a verification certificate is issued.

6.5.3 When the pH meter cannot meet the requirements of this level, it is allowed to downgrade for use. Descending to the next level must meet the requirements of that level of pH meter. If the minimum requirements of the verification Regulations are still not met, after the downgrade, THEN the instrument is unqualified, a notice of verification results shall be issued, AND the unqualified items shall be indicated.

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