

B. GENERAL TESTS

pH Determination

pH is measured using a pH meter of a glass electrode. pH fundamentally represents the value of hydrogen ion activity in solutions. It is defined by the equation given below. This value well accords with the logarithm of the reciprocal of hydrogen ion concentration in dilute solutions.

$$\text{pH} = \text{pH}_s + \frac{E - E_s}{2.3026 RT/F},$$

where pH_s = pH value of a pH standard solution,

E = electromotive force (volt) on the combination of glass and reference electrodes in a sample solution; the constitution of the cell is expressed by the following:

glass electrode | sample solution || reference electrode

E_s = electromotive force (volt) on the combination of glass and reference electrodes in a pH standard solution, the constitution of the cell is expressed by the following:

glass electrode | pH standard solution || reference electrode

R = gas constant,

T = absolute temperature,

F = Faraday constant.

The values of $2.3026 RT/F$ (volt) at various temperatures are as follows:

Temperature of solution	2.3026 RT/F	Temperature of solution	2.3026 RT/F
5°C	0.05519	35°C	0.06114
10°C	0.05618	40°C	0.06213
15°C	0.05717	45°C	0.06313
20°C	0.05817	50°C	0.06412
25°C	0.05916	55°C	0.06511
30°C	0.06015	60°C	0.06610

Hereinafter in the Monographs, such a specification as “pH 6.0–7.5 (1.0 g, 20 ml of water)” indicates that the pH of the solution is 6.0–7.5, when determined on the solution prepared by weighing accurately 1.0 g of the test substance and dissolving in 20 ml of water.

Preparation of pH Standard Solution pH standard solutions are used as

B. GENERAL TESTS

standards of pH. Use the water, directed below, to prepare the pH standard solutions.

Distill purified water, boil the distillate for more than 15 minutes to expel carbon dioxide, and cool in a container fitted with a carbon dioxide-absorbing tube (soda lime). Store the pH standard solutions in hard glass or polyethylene bottles. As the pH value may change during storage for a long period, usually use acidic standard solutions within 3 months, and use basic standard solutions within 1 month under storage in containers fitted with a carbon dioxide-absorbing tube (soda lime).

Oxalate pH Standard Solution Reduce potassium tetraoxalate for pH determination to a fine powder, and dry in a desiccator. Weigh 12.71 g exactly, and dissolve in water to make exactly 1,000 ml.

Phthalate pH Standard Solution Reduce potassium hydrogen phthalate for pH determination to a fine powder, and dry at 110°C to constant weight. Weigh 10.21 g exactly, and dissolve in water to make exactly 1,000 ml.

Phosphate pH Standard Solution Reduce monopotassium phosphate for pH determination and anhydrous disodium phosphate for pH determination to fine powders, and dry at 110°C to constant weight. Weigh 3.40 g (0.025 mol) of monopotassium phosphate and 3.55 g of disodium phosphate exactly, and dissolve in water to make exactly 1,000 ml.

Borate pH Standard Solution Place sodium borate for pH determination in a desiccator (sodium bromide moistened with water), and allow to stand to constant weight. Weigh 3.81 g exactly, and dissolve in water to make exactly 1,000 ml.

Carbonate pH Standard Solution Dry sodium hydrogen carbonate for pH determination in a desiccator to constant weight, and weigh 2.10 g exactly. Dry sodium carbonate for pH determination at 300 to 500°C to constant weight, and weigh 2.65 g exactly. Mix both, and dissolve in water to make exactly 1,000 ml.

Calcium Hydroxide pH Standard Solution Reduce calcium hydroxide for pH determination to a fine powder, transfer 5 g into a flask, add 1,000 ml of water, shake well, maintain the temperature at 23–27°C, saturate thoroughly, and filter the supernatant at the same temperature. Use the clear filtrate (about 0.02 mol/l).

The pH values of these pH standard solutions at various temperatures are shown in the table below. pH values at temperatures not indicated in the table are calculated from the value in the table by the interpolation method.

pH Meter A pH meter generally comprises a detecting unit consisting of a glass electrode and a reference electrode, and an indicating unit for indicating the pH value corresponding to the electromotive force detected. The indicating unit usually has dials for zero point adjustment and temperature compensation, and some have a dial for sensitivity adjustment.

When the pH value is tested five times by the procedure below for one of the above pH standard solutions, the reproducibility of the meter should be within ± 0.05 .

B. GENERAL TESTS

Wash well the detecting unit with water at each measurement.

pH values of pH standard solutions

Temperature	Oxalate pH Standard Solution	Phthalate pH Standard Solution	Phosphate pH Standard Solution	Borate pH Standard Solution	Carbonate pH Standard Solution	CalciumHydroxide pH Standard Solution
0°C	1.67	4.01	6.98	9.46	10.32	13.43
5°C	1.67	4.01	6.95	9.39	10.25	13.21
10°C	1.67	4.00	6.92	9.33	10.18	13.00
15°C	1.67	4.00	6.90	9.27	10.12	12.81
20°C	1.68	4.00	6.88	9.22	10.07	12.63
25°C	1.68	4.01	6.86	9.18	10.01	12.45
30°C	1.69	4.01	6.85	9.14	9.97	12.30
35°C	1.69	4.02	6.84	9.10	9.93	12.14
40°C	1.70	4.03	6.84	9.07		11.99
50°C	1.71	4.06	6.83	9.01		11.70
60°C	1.73	4.10	6.84	8.96		11.45

Procedure Immerse the glass electrode previously in water for several hours. Start the measurement more than 5 minutes after switching on. Rinse well the detecting unit with water, and blot the water gently with a piece of filter paper. When the pH meter is adjusted at one pH value, rotate the temperature compensation dial to set to the temperature of the pH standard solution, immerse the detecting unit in the pH standard solution which has a pH near that of the sample solution, and after more than 2 minutes, adjust the zero point adjustment dial so that the reading of the pH meter is set to the pH of the pH standard solution indicated in the table for that temperature. When the pH meter is adjusted at two different pH values, rotate the temperature compensation dial to set to the temperature of the solutions, usually immerse the detecting unit in Phosphate pH Standard Solution, adjust the pH by means of the zero point adjustment, and proceed in the same manner as described above, with the pH standard solution which has a pH value near that of the sample solution, by means of a sensitivity adjustment dial or a temperature compensation dial irrespective of the temperature of the pH standard solution.

Wash well the detecting unit with water, and blot the water gently with a piece of filter paper. Immerse the detecting unit in the sample solution, and read the pH value.

Notice on Procedure (1) Structures and procedures of pH meters are different in details according to pH meters.

(2) Because solutions, when their pH values are higher than 11 and they contain alkali metal ions, have large measurement errors, use an electrode with less alkali error, and make any necessary correction.

(3) It is desirable that the temperature of the sample solution is the same as that of the pH standard solution.