

High-End Ion-Selective Composite Electrode Operation Manual

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1. Introduction

This operation manual describes the preparation, operation, and maintenance methods of ion-selective composite electrodes (ISE), including routine analytical test methods, electrode performance, and relevant introductions to electrode theory. Ion-selective composite electrodes can quickly, simply, accurately, and economically measure the concentration of corresponding ions in aqueous solutions, as well as the content of corresponding ions in food and pharmaceuticals.

Note: The water hardness composite electrode, also known as a divalent ion electrode, is an ion-selective electrode with the same response characteristics to calcium ions and magnesium ions. It has almost identical response curves for calcium ions and magnesium ions. It can quickly, simply, accurately, and economically measure the total amount of calcium and magnesium in aqueous solutions.

BestLab Ion-Selective Composite Electrode

BestLab integrates a reference electrode and an indicator electrode. The composite electrode requires a small volume of solution, reducing the generation of waste. The built-in washable reference liquid junction avoids diaphragm clogging and provides fast, stable readings. This composite electrode is equipped with a standard BNC interface and can be used on all ion meters/potentiometers compatible with BNC interfaces.

2. Required Equipment

- 1st Ion meter/pH meter with BNC connector, such as Leici PXSJ-226 ion meter, PXS-270 ion meter, or ion meters/pH meters from other brands compatible with BNC;
- 2nd Stirrer;
- 3rd Volumetric flasks, graduated cylinders, beakers, pipettes (plastic utensils are recommended for measuring sodium ions);
- 4th Distilled water or deionized water;
- 5th Electrodes and reagents.

3. Electrode and Measurement Setup

3.1 Electrode Preparation

- 1st Take the ion-selective composite electrode out of the packaging box;

- 2nd Insert the nozzle of the ion-selective composite electrode filling solution bottle into the filling hole on the electrode, and add a small amount of reference solution. Invert the electrode to wet the O-ring, then return the electrode to the vertical position;
- 3rd Hold the electrode shaft with one hand, press the electrode cap with your thumb, and discharge a few drops of filling solution to wet and clean the liquid junction;
- 4th Release the electrode cap. If the electrode housing cannot return to its original position, check if the O-ring is wet, and repeat steps 2 to 4 until the electrode housing returns to its original position;
- 5th Add filling solution to the electrode filling hole;
- 6th Immerse the electrode in a 10–3mol/L target ion standard solution (100 ppm (as CaCO₃) for water hardness) and soak for 2 hours to activate.
- 7th Due to its different structure, the sodium ion electrode only needs to have reference solution added to the filling hole, and no other operations are required. In addition, the sodium ion electrode needs to be soaked in the activation solution for more than 8 hours.

Note:

- Add filling solution before use every day. The liquid level of the filling solution should be at least 2.5 cm higher than the liquid level of the sample in the beaker to ensure an appropriate flow rate.
- The copper ion composite electrode should not be soaked in the solution for a long time; it is recommended to store it dry if not used for more than 4 hours.
- The copper ion composite electrode may be affected by external light; it is recommended to use it in an environment with stable light intensity.

![[Figure 1. Schematic Diagram of the Ion-Selective Composite Electrode]](Note: Figure 1 shows the structure including electrode cap, spring, cable, O-ring, electrode housing, filling hole, reference cell, internal electrode, reference lead, and sensitive component)

![[Figure 2. Schematic Diagram of the Sodium Ion Composite Electrode]](Note: Figure 2 shows the structure including lead, electrode, filling hole, BNC cable interface, blue sodium ion composite electrode filling edge, filling plug, ceramic liquid junction, electrode measuring end, sensitive glass bulb, and electrode protection cap/bottle)

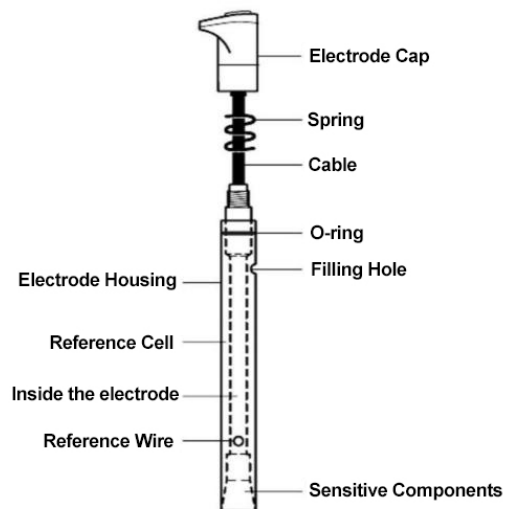


Figure 1 Structural diagram of ion composite electrode

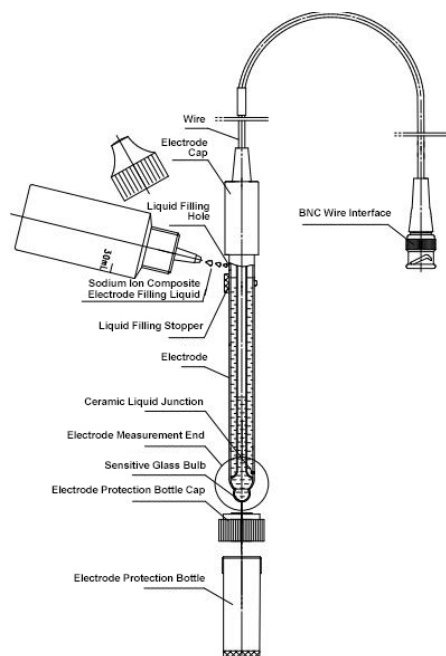


Figure 2 Schematic diagram of the structure of sodium ion composite electrode

3.2 Checking Electrode Performance (Slope)

This method can quickly test the slope of the electrode. The slope is the change in electrode potential when the target ion concentration changes by 10 times. Detecting the electrode slope can easily confirm the electrode status, thereby ensuring measurement accuracy.

- 1st If the electrode is stored empty, handle it according to the method described in 3.1 before testing;
- 2nd Connect the electrode to the ion meter/pH meter and set the instrument to mV mode;
- 3rd Add 100 mL of deionized water and 2 mL of the ionic strength adjuster (ISA) matching the corresponding electrode to a 150 mL beaker, and turn on the stirrer for stirring;
- 4th Rinse the electrode with deionized water, then place it in the solution prepared in step 3);
- 5th Take 1 mL of 0.1 M target ion standard solution (for water hardness composite electrode: 1 mL of 10000 ppm (as CaCO_3) water hardness standard solution), add it to the beaker, and maintain a stable stirring rate. When the potential reading stabilizes, record the electrode potential $E_1\text{mV}$;
- 6th Continue to add 10 mL of the same concentration of ion standard solution to the beaker, and keep the stirring rate unchanged. When the potential reading stabilizes, record the electrode potential $E_2\text{mV}$;

When the temperature of the test solution is between 20-25°C, the potential difference between E_1 and E_2 should be 54-60 mV for monovalent ion electrodes and 25-30 mV for divalent ion electrodes. If the potential difference is not within this range, refer to Chapter 7 for troubleshooting.

3.3 Sample Requirements

The electrode housing of the ion-selective composite electrode is made of epoxy resin and can only be used in aqueous solutions (except for the sodium ion composite electrode with a glass housing; however, since the glass bulb is easily contaminated by organic solvents, the electrode performance will decrease to varying degrees after use in organic solvents, including slower response and reduced range). Samples shall not contain organic solvents. The temperature of the test solution must be below 40°C (below 80°C for sodium ion composite electrodes and below 50°C for lead ion composite electrodes).

When $\text{pH} > 6$, copper ions will form copper hydroxide precipitates. If necessary, acidify the sample with 1 mol/L HNO_3 .

Samples and standard solutions should be measured and calibrated at the same temperature. In all analytical steps, the corresponding ionic strength adjuster must be added to samples and standard solutions before measurement (for sodium ion composite electrode measurement, the pH of samples and standard solutions must be adjusted to >10 with diisopropylamine (ISA VII) before measurement).

3.4 Serial Dilution

The best method for preparing standard solutions is serial dilution. Serial dilution refers to diluting the initially prepared standard solution using a volumetric flask to obtain the second standard solution. Then dilute the second standard solution to prepare the third standard solution, and so on until the required standard solutions are obtained.

Generally, the concentration between adjacent levels is 10 times.

3.5 Measurement Tips

- 1st Stir standard solutions and samples at the same stirring speed.
- 2nd Use fresh standard solutions for calibration.
- 3rd Rinse the electrode with deionized water between measurements and shake off water droplets to avoid cross-contamination of samples. Do not scratch the sensitive component of the electrode forcefully.
- 4th For more accurate measurement, standard solutions and samples must be at the same temperature.
- 5th To eliminate measurement errors caused by heat generated by the magnetic stirrer, place a small piece of thermal insulation material between the magnetic stirrer and the beaker, such as polystyrene foam or cardboard.
- 6th Calibrate the electrode every two hours. Immerse the electrode in a fresh, lowest-concentration calibration standard solution. If the reading exceeds 2% (4% for water hardness electrodes and calcium ion electrodes), re-calibrate the electrode.
- 7th When the electrode is immersed in the solution, check if there are bubbles attached to the sensitive surface of the electrode. If there are bubbles, remove them by repeatedly immersing the electrode in the solution.

8th For sample solutions with very high ionic strength (>0.1 M), prepare standard solutions with a background composition similar to the sample for calibration.

9th If the electrode has measured some complex or viscous samples, or if the electrode response becomes slow, empty the external reference solution and clean the liquid junction with deionized water. After emptying the residual deionized water inside the electrode, refill it with fresh external reference solution. Press the electrode cap to allow several drops of external reference solution to flow through the liquid junction, then replenish the external reference solution to the appropriate height.

10th For samples with very high alkalinity of water hardness and calcium ion solutions, adjust the pH of the sample to below 11 before adding the ionic strength adjuster.

11th If the electrode response is slow, it may be due to the accumulation of precipitates on the sensitive component. Polish the electrode with a polishing strip to restore electrode performance. Cut a 2.5 cm long polishing strip and polish the sensitive component of the electrode in a rotating manner for about 30 seconds. Before use, clean the electrode and soak it in the standard solution for 5 minutes. (This step is only for salt membrane and crystal membrane electrodes)

- **Salt membrane electrodes:** Chloride ion composite electrode, bromide ion composite electrode, iodide ion composite electrode, lead ion composite electrode, copper ion composite electrode.
- **Crystal membrane electrodes:** Fluoride ion composite electrode.

Notes for tetrafluoroborate ion electrode:

Store the electrode in a 10–2mol/L or 100 ppm tetrafluoroborate standard solution during measurement intervals.

Notes for sodium ion composite electrode:

The main material of the electrode measuring end is glass; confirm that the test solution will not damage the electrode measuring end before measurement.

Notes for fluoride ion composite electrode:

For sample solutions with very high acidity or alkalinity, adjust the pH of the sample to the range of 5-6 before adding TISAB.

4. Electrode Storage and Maintenance

4.1 Electrode Storage

For measurement intervals and short-term storage, the electrode can be soaked in a 10–3mol/L target ion standard solution (water hardness electrode can be soaked in a 100 ppm water hardness standard solution, and sodium ion composite electrode can be soaked in an activation solution). Do not add ionic strength adjuster to the solution to avoid evaporation and crystallization.

If the electrode is stored for more than one week, drain the internal solution of the electrode and rinse the reference cell with distilled water. Store the electrode dry (for sodium ion electrode, add 1-2 mL of reference filling solution to the electrode protection bottle, and seal and store the sensitive bulb with the electrode protection bottle and cap).

The copper ion composite electrode should be stored dry. If not used for more than 4 hours, it is recommended to store it dry.

4.2 Rinse the Liquid Junction

If the contact area between the electrode housing and the internal conical sensitive component is clogged by samples or precipitates, rinse the area with reference filling solution or distilled water.

- 1st Hold the electrode with one hand and press the electrode cap with your thumb until the electrolyte in the reference cell is drained.
- 2nd Add distilled water to the electrode and press the electrode cap until the distilled water in the reference cell is drained.
- 3rd Add fresh reference solution to the filling hole. Press the electrode cap to drip out several drops of filling solution, then refill the lost filling solution.

4.3 Activation of the Sensitive Membrane

When the PVC membrane electrode is exposed to high-concentration interfering ions, the performance of the sensitive membrane will degrade, such as slower response and reduced slope. In such cases, first soak the electrode in deionized water for 1 hour, replace the external reference filling solution, and then soak it in a 0.01 M target ion standard solution for 2 hours (water hardness electrode: soak in a 1000 ppm water hardness standard solution for 8 hours) to restore electrode performance. If the above operations cannot restore electrode performance, replace the electrode sensitive membrane.

The sensitive surfaces of salt membrane and crystal membrane electrodes will age slowly, causing potential drift, poor repeatability, and longer response time for low-concentration samples. Polishing the sensitive surface with the attached polishing strip can repair the electrode. Similarly, if the sensitive surface is corroded or contaminated by chemicals, polish the electrode surface as follows:

- 1st Cut a 2.5 cm long polishing strip.
 - 2nd Hold the electrode with the sensitive surface facing up.
 - 3rd Moisten the sensitive surface with a few drops of distilled water.
 - 4th Place the rough side of the polishing strip downward and gently press it against the sensitive surface.
 - 5th Rotate the electrode for about 30 seconds.
 - 6th Rinse the electrode with distilled water, then soak it in a 100 ppm or 10–3mol/L ion standard solution for 10 minutes.
- Soak the fluoride ion electrode in a 100 ppm or 10–3mol/L ion standard solution for 2 hours.

4.4 Replacement of the Sensitive Membrane

After a period of use, the PVC sensitive membrane will experience slower response and reduced slope. If performance cannot be restored through sensitive membrane activation, replace it with a new sensitive membrane.

Replacing the sensitive membrane:

- 1st First, drain the reference filling solution and clean the reference cell with deionized water;
- 2nd Hold the electrode housing, rotate the electrode cap, and loosen the electrode cap and spring assembly from the electrode along the electrode wire;
- 3rd Push the inner tube from above to pull the sensitive membrane out of the housing;

4th Gently unscrew the sensitive head from the electrode shaft and install a new sensitive head;

5th Reassemble the electrode.

Cleaning and repair of sodium ion composite electrode:

During use, the glass sensitive bulb is easily contaminated by the solution, leading to decreased electrode performance. The following methods can be used for cleaning and repair:

1st **Inorganic contamination:** Immerse the electrode measuring end in 0.1 mol/L HCl or EDTA solution for 15 minutes.

2nd **Organic contamination:** Immerse the electrode measuring end in absolute ethanol (or a solvent capable of dissolving the organic substance) for 15 minutes.

3rd **Oil adhesion:** Immerse the electrode measuring end in a weakly alkaline detergent for 15 minutes.

4th **Protein precipitation:** Immerse the electrode measuring end in a 1% pepsin hydrochloric acid solution (HCl concentration: 0.1 mol/L) for 15 minutes.

Gently shake the electrode during soaking to accelerate the surface cleaning process. After taking out the electrode, rinse it with deionized water and soak it in the electrode activation solution for 8 hours to activate.

5. Analytical Methods

Direct Calibration Method

The procedure is simple and suitable for measuring most samples. Only one instrument is needed to measure various samples. First, calibrate with a series of standard solutions, then obtain the ion concentration of the sample by comparing the potentials of the sample and the standard solutions. The corresponding ionic strength adjuster must be added to all solutions to ensure that the sample and standard solutions have similar ionic strengths.

Adopt the direct calibration method when:

- Potassium ion concentration > 10–5mol/L,
- Calcium ion concentration > 10–5mol/L,
- Water hardness concentration > 10 ppm,
- Ammonium ion concentration > 10–5mol/L,
- Tetrafluoroborate concentration > 1 ppm or 10–5mol/L,
- Nitrate ion concentration > 10–4mol/L (1.4 ppm as nitrogen),
- Sodium ion concentration > 10–5mol/L (0.23 ppm Na),
- Fluoride ion concentration > 2×10–5mol/L (0.38 ppm F),

- Chloride ion concentration > 10–4mol/L (3.55 ppm Cl),
- Bromide ion concentration > 5×10–6mol/L (0.4 ppm Br),
- Iodide ion concentration > 1×10–6mol/L (0.13 ppm I),
- Copper ion concentration > 10–6mol/L,
- Lead ion concentration > 10–5mol/L (or 2 ppm),
- Perchlorate ion concentration > 10–6mol/L.

Low-Concentration Calibration Method

This method is suitable for solutions with low ionic strength that do not contain complexing agents for the target ion and cannot meet the requirements of the direct calibration method. At least three-point calibration is required to compensate for the non-linear response of the electrode at this concentration.

For solutions with low ion concentration but high ionic strength, prepare standard solutions with a composition similar to the sample before measurement using this method. For accurate measurement, note the following:

- Longer stabilization time is required for measuring low-concentration samples.
- The stirring speed of standard solutions and samples should be the same.
- Add a low-concentration ionic strength adjuster to standard solutions and samples.
- Use plastic utensils when measuring low-concentration ions.

5.1 Direct Calibration Method

Test Preparation

1st Prepare the electrode according to the Electrode Preparation chapter;

2nd Connect the electrode to the instrument;

3rd Prepare at least two solutions with a 10-fold concentration difference (using the serial dilution method), and keep the standard solutions and samples at the same temperature. Calibrate the hydrogen ion-selective electrode with pH 4.00 and pH 9.18 electrode standard solutions.

Test Procedure

- 1st Measure 100 mL of the lower-concentration standard solution and 2 mL (10 mL for ammonium ion electrode ISA, 1 mL for sodium ion electrode ISA) of the corresponding electrode's ionic strength adjuster into a 150 mL beaker (for fluoride ion electrode standard solution test: measure 50 mL of the lowest-concentration fluoride ion standard solution and 50 mL of TISAB II into a 150 mL beaker; for lead ion standard solution test: measure 50 mL of the lowest-concentration standard solution and 50 mL of methanol-formaldehyde solution into a 150 mL beaker, then add 2 mL of ISA VI solution), and stir the solution thoroughly.
- 2nd Rinse the electrode with deionized water, blot dry, and immerse it in the lowest-concentration standard solution. After the reading stabilizes, record the potential value and the corresponding standard solution concentration.
- 3rd Measure 100 mL of the higher-concentration standard solution and 2 mL (10 mL for ammonium ion electrode ISA, 1 mL for sodium ion electrode ISA) of the corresponding electrode's ionic strength adjuster into another 150 mL beaker (for fluoride ion standard solution test: measure 50 mL of the higher-concentration fluoride ion standard solution and 50 mL of TISAB II into another 150 mL beaker; for lead ion standard solution test: measure 50 mL of the higher-concentration standard solution and 50 mL of methanol-formaldehyde solution into a 150 mL beaker, then add 2 mL of ISA VI solution), and stir the solution thoroughly.
- 4th Rinse the electrode with deionized water, blot dry, and immerse it in the higher-concentration standard solution. After the reading stabilizes, record the potential value and the corresponding standard solution concentration.
- 5th Use semi-logarithmic graph paper to plot the calibration curve with potential value as the ordinate and standard solution concentration as the logarithmic abscissa.
- 6th Measure 100 mL of the sample and 2 mL (10 mL for ammonium ion electrode ISA, 1 mL for sodium ion electrode ISA) of the corresponding electrode's ionic strength adjuster into a clean 150 mL beaker (for fluoride ion sample test: measure 50 mL of the fluoride ion sample solution and 50 mL of TISAB II into a clean 150 mL beaker; for lead ion test: measure 50 mL of the sample and 50 mL of methanol-formaldehyde solution into a 150 mL beaker, then add 2 mL of ISA VI), and stir the solution thoroughly.

7th Rinse the electrode with deionized water, blot dry, and immerse it in the sample. After the reading stabilizes, record the potential value.

8th Calculate the sample concentration using the calibration curve obtained in step 5.

When the sample volume is small, a smaller amount of sample can be used for testing. For fluoride ion testing, add TISAB II at a 1:1 ratio; for lead ion testing, maintain the ratio of sample solution to methanol-formaldehyde solution to ISA VI at 50:50:2; for other electrode tests, add the ionic strength adjuster at a 50:1 ratio (10:1 for ammonium ion electrode).

5.2 Low-Concentration Calibration Method

Test Preparation

- 1st Prepare the electrode according to the Electrode Preparation chapter;
- 2nd Connect the electrode to the instrument;
- 3rd Prepare Low-Level ISA: Take 20 mL of ISA and dilute it to 100 mL with deionized water.

Test Procedure (Ion-Selective Composite Electrode Test)

- 1st Measure 100 mL of deionized water and 1 mL of Low-Level ISA into a 150 mL beaker.
- 2nd Rinse the electrode with deionized water, immerse it in the beaker, and stir thoroughly.
- 3rd Refer to the steps in the table below to add the corresponding volume of 10–3mol/L (or 100 ppm) ion standard solution. After each addition, record the stable potential (mV) reading.

Table 1. Low-Concentration Measurement Calibration Curve

Step	Sample Addition Volume (mL)	Concentration (mol/L) ⁿ	Concentration (ppm) [□]
1	0.1	1.0×10 ⁻⁶	0.1
2	0.1	2.0×10 ⁻⁶	0.2
3	0.2	4.0×10 ⁻⁶	0.4
4	0.2	6.0×10 ⁻⁶	0.6
5	0.4	9.8×10 ⁻⁶	1.0

ⁿ Continuously add 10–3mol/L ion standard solution; □

Continuously add 100 ppm ion standard solution.

1st Plot the graph on semi-logarithmic graph paper with potential value as the ordinate and concentration value as the logarithmic abscissa. Use fresh standard solutions every day to draw a new calibration curve.

2nd Measure 100 mL of the sample and 1 mL of Low-Level ISA into a clean 150 mL beaker. Rinse the electrode with deionized water, blot dry, and immerse it in the sample solution.

3rd After thorough stirring, record the stable potential (mV) reading.

4th Calculate the sample concentration using the measured potential value based on the low-concentration calibration curve.

When the sample volume is small, a smaller amount of sample can be used for testing (step 5). Add Low-Level ISA at a 100:1 ratio during testing.

6. Electrode Performance

6.1 Electrode Slope

The slope of the straight line obtained by plotting electrode potential against ion concentration on semi-logarithmic graph paper.

6.2 Response Time

The response time of the electrode (reaching 99% of the stable potential) varies depending on the solution concentration. Measuring high-concentration solutions takes a few seconds, while measuring solutions close to the electrode's lower limit takes several minutes.

6.3 Temperature Influence

Temperature changes affect the electrode potential, so the temperature difference between the sample and the standard solution shall not exceed $\pm 1^{\circ}\text{C}$ (2°F). When measuring samples with an ion concentration of 10–3mol/L (100 ppm for water hardness), a temperature change of 1°C will cause a measurement error of 2% (4% for calcium ion and water hardness electrodes). Since the dissolution equilibrium of the reference electrode changes slowly with temperature, the absolute potential of the reference electrode also changes slowly with temperature. As with the influencing factor "S" in the Nernst equation, the slope of the ion electrode changes with temperature. The theoretical slope values of potassium ion, ammonium ion, nitrate ion, tetrafluoroborate ion, and sodium ion electrodes at different temperatures are shown in Table 2. The theoretical slope values of calcium ion, copper ion, lead ion, and water hardness electrodes are shown in Table 3. If the temperature changes, both the instrument and the electrode need to be recalibrated.

Table 2. Theoretical Slope vs. Temperature

Temperature ($^{\circ}\text{C}$)	Theoretical Slope (mV)
0	54.2
10	56.2
20	58.2
25	59.2
30	60.1
40	62.1

Table 3. Theoretical Slope vs. Temperature

Temperature ($^{\circ}\text{C}$)	Theoretical Slope (mV)
0	27.1
10	28.1
20	29.1
25	29.6
30	30.1
40	31.1

As long as the electrode reaches equilibrium with the temperature, PVC membrane electrodes can be used at 0 to 40°C, and salt membrane electrodes can be used at 0 to 80°C. If the sample temperature differs significantly from room temperature, the equilibrium time should be at least 1 hour.

6.4 Electrode Service Life

Under normal use, the service life of the ion-sensitive membrane (PVC) is approximately 6 months. The actual service life is affected by various factors such as the nature of the sample solution, the type and concentration of interfering ions, test temperature, and test intensity.

7. Troubleshooting

Problems can be identified by following systematic steps. To facilitate problem detection, the entire measurement system can be divided into five aspects: (1) Instrument, (2) Electrode, (3) Standard Solution, (4) Sample, (5) Analytical Method.

7.1 Instrument

Problems caused by the instrument are the easiest to solve. Check the instrument operation according to the steps in the instrument's operation manual.

7.2 Electrode

- 1st Thoroughly rinse the electrode with deionized water (thoroughly activate the sodium ion electrode with activation solution).
- 2nd Check the electrode performance according to the steps in Checking Electrode Performance (Slope).
- 3rd If the above checks fail, refer to the Measurement Tips chapter. Polish the electrode membrane according to the Measurement Tips chapter.
- 4th Repeat the steps in Checking Electrode Performance (Slope) to check the electrode performance.

5th If the stability and slope of the electrode pass the checks but measurement problems still exist, the sample solution may contain interfering substances or complexing agents, or the measurement method may be incorrect. Refer to the Standard Solution, Sample, and Analytical Method chapters.

6th Before replacing the faulty electrode or if there is no additional electrode for testing, carefully review the operation manual and confirm the following:

- The electrode has been correctly prepared.
- Appropriate filling solution, ISA, and standard solutions are used.
- The sample is measured correctly.
- Refer to the Troubleshooting Checklist chapter.

7.3 Standard Solution

The accuracy of measurement results largely depends on the quality of the standard solution. When problems occur, fresh standard solutions must be used to resolve the issue more quickly. Many incorrect results are caused by contaminated standard solutions, incorrect dilution, poor quality of distilled water, or errors in concentration calculation.

The best method for preparing standard solutions is serial dilution. Dilute the initial standard solution using a volumetric flask to prepare the second standard solution. Continue to dilute the second standard solution to prepare the third standard solution, and so on until the required concentration of standard solutions is obtained.

7.4 Sample

If the electrode and instrument can normally measure standard solutions but cannot measure the sample solution, check if the sample contains interfering substances, complexes, or substances that affect the electrode response or cause physical damage to the electrode. Try to determine the composition of the sample. Refer to the Sample Requirements, Temperature Influence, Interfering Substances, and pH Requirements chapters.

7.5 Analytical Method

Check if the analytical method is appropriate. The direct calibration method is not always applicable. If the sample contains a large amount of complexes, the known addition method is the best choice. If the sample viscosity is high, the sample addition method can solve this problem. If measuring low-concentration samples, follow the steps of the low-concentration calibration method. Also, confirm that the concentration of the measured ion is within the electrode's detection limit.

If the problem persists, check the operating steps. Refer to the Measurement Tips and Analytical Method chapters to confirm that the appropriate analytical method is followed.

7.6 Troubleshooting Checklist

Phenomenon	Possible Cause	Solution
Reading out of range or measuring range	Instrument malfunction	Refer to the instrument operation manual
	Incorrect electrode connection	Unplug the electrode and reinstall it
	No reference filling solution added	Add the correct reference filling solution to the filling hole
	Bubbles on the sensitive component	Re-immerses the electrode in the solution to remove bubbles
	Electrode not immersed in the solution	Immerse the electrode in the solution
Noise or unstable readings (irregular, rapid)	Static electricity	Wipe the plastic parts of the instrument/titrator with a cleaning agent
	Instrument malfunction	Troubleshoot the instrument
Phenomenon changes)	Instrument or stirrer not properly grounded	Ground properly
	Bubbles on the sensitive component	Re-immerses the electrode in the solution to remove bubbles
	Ionic strength adjuster not used	Use the recommended ionic strength adjuster
Drift (unidirectional slow change in readings)	Temperature difference between sample and standard solution	All solutions must be at the same temperature
	Contamination or corrosion of the sensitive component	Polish the sensitive component (see Measurement Tips)
	Incorrect electrode filling solution used	Use the recommended reference filling solution
Low slope or no slope	Contaminated or incorrectly prepared standard solution	Prepare fresh standard solution
	Ionic strength adjuster not used	Use the recommended ionic strength adjuster
	Electrode malfunction	Refer to Troubleshooting
	Contamination	Activate and repair in

Phenomenon	Possible Cause	Solution	Phenomenon	Possible Cause	Solution
Calibration curve is correct, but readings are inaccurate	or corrosion of the sensitive component	10–2mol/L standard solution			- Copper ion electrode: 10–3mol/L=63.5mg/L - Lead ion electrode: 10–3mol/L=207mg/L
	Incorrect scale ratio on semi-logarithmic graph paper	Plot potential values on the ordinate. Plot 10-fold concentration values on the logarithmic abscissa			
	Signal error	Confirm that the recorded potential values are correct		Complexing agents in the sample	Use the known addition method or titration method, or decompose the complexes
	Incorrect standard solution	Prepare fresh standard solution			
	Incorrect unit used	Use the correct conversion factor: - Potassium ion electrode: 10–3mol/L=39mg/L - Calcium ion electrode: 10–3mol/L=40mg/L - Water hardness electrode: 10–3mol/L=100ppm as CaCO ₃ - Ammonium ion electrode: 10–3mol/L=17mg/L - Nitrate ion electrode: 10–3mol/L=62mg/L - Tetrafluoroborate ion electrode: 10–3mol/L=87mg/L - Sodium ion electrode: 10–3mol/L=23mg/L - Fluoride ion electrode: 10–3mol/L=19mg/L - Chloride ion electrode: 10–3mol/L=35.5mg/L - Bromide ion electrode: 10–3mol/L=79.9mg/L - Iodide ion electrode: 10–3mol/L=126.9mg/L			

8. Electrode Parameters

Concentration Range

- Potassium ion composite electrode: 1×10^{-6} mol/L to 1 mol/L
- Calcium ion composite electrode: 5×10^{-7} mol/L to 1 mol/L
- Water hardness composite electrode: 1×10^{-5} mol/L to 1 mol/L (1 ppm to 100000 ppm, as CaCO_3)
- Ammonium ion composite electrode: 1×10^{-6} mol/L to 1 mol/L
- Nitrate ion composite electrode: 1×10^{-5} mol/L to 1 mol/L
- Tetrafluoroborate ion composite electrode: 7×10^{-6} mol/L to 1 mol/L (0.61-86800 ppm)
- Sodium ion composite electrode: 1×10^{-7} mol/L to saturation
- Fluoride ion electrode: 10^{-6} mol/L to saturation
- Chloride ion electrode: 5×10^{-5} mol/L to 1 mol/L
- Bromide ion electrode: 2×10^{-6} mol/L to 1 mol/L
- Iodide ion composite electrode: 1×10^{-7} mol/L to 1 mol/L
- Copper ion composite electrode: 1×10^{-7} mol/L to 0.1 mol/L
- Lead ion composite electrode: 1×10^{-6} mol/L to 0.1 mol/L
- Perchlorate ion composite electrode: 5×10^{-6} mol/L to 0.1 mol/L
- Hydrogen ion electrode: pH 2 to pH 12

pH Range

- Potassium ion composite electrode, calcium ion composite electrode, water hardness composite electrode, ammonium ion composite electrode, nitrate ion composite electrode, tetrafluoroborate ion composite electrode: pH 2.5-11
- Fluoride ion electrode: pH 5-7 (at 10^{-6} mol/L (0.02 mg/L F^-))
- Hydrogen ion electrode: pH 2-12
- Chloride ion electrode: pH 2-12
- Bromide ion electrode: pH 0-14
- Iodide ion composite electrode: pH 0-12

- Copper ion composite electrode: pH 2-12
- Lead ion composite electrode: pH 4-7
- Sodium ion composite electrode: pH 6-12
- Perchlorate ion composite electrode: pH 4-10

Temperature Range

- PVC membrane electrodes: 0 to 40°C
- Sodium ion composite electrode and salt membrane composite electrode: 0 to 80°C

Repeatability

- $\pm 2\%$
- Note: Calcium ion composite electrode, water hardness composite electrode: $\pm 4\%$