

Ion-selective electrodes (ISE)



Manual

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1 Introduction

1.1 General

Inspect the delivery immediately upon receipt:

- Check the delivery against the delivery note to ensure completeness.
- Check the product for damage.
- If the delivery is incomplete or damaged, contact your regional Metrohm representative.



NOTE

Defective sensors must be sent back for warranty processing within two months (starting from the day of delivery).

If the defect is proven to be due to a material or manufacturing defect, the electrode is replaced at no charge. Transport costs are borne by the customer.

1.2 Design of ion-selective electrodes (ISE)

1.2.1 Electrodes with crystal membrane

Examples: Cu^{2+} crystal membrane electrodes, F^- crystal membrane electrodes



1 Protective cap
can be removed and an electrode cable can be connected

2 Ground-joint sleeve SGJ 14/15, movable
slide all the way up for sample changer applications

3 Sensor surface

2 Measuring



CAUTION

- Do not touch the sensor surface with your fingers.
- Do not leave the electrode standing in distilled water.
- Do not rub the electrode dry after rinsing.
- Avoid any contact of polymer membrane electrodes (e.g. Na^+ , K^+ , Ca^{2+} , NO_3^-) with organic solvents. Crystal membrane electrodes may be used in organic solvents (acetone, methanol, benzene) for short periods of time.
- Protect the Cu electrode against direct sunlight and do not use it in environments with changing illumination (the electrode is light-sensitive).
- The Pb electrode must not be used in solutions containing acetate (interferences with the membrane material).

2.1 Preparing the electrodes

The ion-selective electrode must be prepared in the following cases:

- Prior to first-time use
- After prolonged pauses
- Between precipitation titrations

2.1.1 Crystal membrane electrodes

F⁻ electrodes

Clean the sensor surface with a strongly alkaline detergent such as Deco-nex universal or also with toothpaste.

Do **not** clean with the polishing set!

All other crystal membrane electrodes (6.0502.XXX electrodes: Ag^+ , Cu^{2+} , Pb^{2+} , Cl^- , Br^- , I^- , CN^- , S^{2-})

Clean with the 6.2802.000 polishing set. Put powder on the polishing pad, moisten and polish the sensor surface using light pressure.



NOTE

One polishing set may be used for only one ISE type. If various ion-selective electrodes are to be polished, then one dedicated polishing set should be reserved for each ISE type.

2.1.2 Polymer membrane electrodes

Separate polymer membrane electrode
(e.g. Na^+ , Ca^{2+})

Rinse the electrode with distilled water.

Combination polymer membrane electrode

The combined ion-selective electrode (ISE) is ready for direct use in most samples and requires no special preparation.

Combination polymer
membrane electrode
 Ca^{2+}

The electrode is shipped with $c(\text{NH}_4\text{NO}_3) = 1 \text{ mol/L}$ (6.2327.000) as reference electrolyte. This reference electrolyte contains no chloride that could interfere in applications with parallel chloride titrations.

If necessary, e.g. for direct potentiometric measurements, $c(\text{KCl}) = 3 \text{ mol/L}$ can also be used as reference electrolyte. Metrohm recommends not using $c(\text{NH}_4\text{NO}_3) = 1 \text{ mol/L}$ again in an ISE that has been filled with $c(\text{KCl}) = 3 \text{ mol/L}$ as a reference electrolyte, because traces of chloride could lead to mixed potentials.

Combination polymer
membrane electrode
 NO_3^-

The electrode contains $c(\text{KCl}) = 3 \text{ mol/L}$ (6.2308.020) as reference electrolyte.

Combination polymer
membrane electrode
 K^+

The electrode contains $c(\text{CH}_3\text{COOLi}) = 1 \text{ mol/L}$ (6.2328.000) as reference electrolyte.

2.1.3 Glass membrane electrodes

6.0501.100 Na⁺ electrode: Place in a solution of $c(\text{NaCl}) = 1 \text{ mol/L}$ for several hours.

2.2 Titration

Ion-selective electrodes are well-suited for potentiometric titrations. The resulting titration curves are usually S-shaped and can be evaluated well in automatic titration systems.

For application advice on working with ion-selective electrodes, please go to www.metrohm.com.

2.3 Direct measurement with calibration

The ion activity in the sample is interpolated by means of a calibration curve. Establish the calibration curve with standard solutions. The expected ion activity in the sample should lie in the mid-concentration range of the standard solutions.

Since the concentration of an ion is usually to be determined (rather than its ion activity), perform measurements at a fixed ionic strength. The ionic strength is measured in an ISA (Ionic Strength Adjuster) solution or a TISAB (Total Ionic Strength Adjustment Buffer) solution. ISATISAB solutions have a high ionic strength so that the various contributions of the measuring ion to the ion strength can be ignored. The TISAB solution also buffers the pH value.



NOTE

Measure samples and calibration standards under identical measuring conditions. The temperature of the standard solutions and the sample solutions should be the same as far as possible, and the temperature should vary as little as possible during measurements.

- In order to guarantee reliable results, periodically execute a control measurement with a calibration standard (e.g. daily).
- Establish a new calibration curve if the deviation is deemed unacceptable.

2.4 Standard addition / standard subtraction

In the standard addition method, a defined quantity of the ion to be determined is added to a known volume of the sample (in multiple steps). Normally, ISA/TISAB solutions are used in this process. The unknown concentration can be calculated from the resulting potential differences between the sample and the sample with added standard solution. This calculation is performed automatically by modern ion meters.

The volume of the added standard solutions should not exceed 25% of the sample volume, and the concentration of the standard solutions should be as high as possible (in order to be able to rule out errors due to dilution effects). The potential differences between the increments should be constant and amount to at least 10 mV. Avoid temperature differences between the standard solution and the sample solution.

In the standard subtraction method, a solution that eliminates the ion to be determined is added (complexation or precipitation). Apart from that, the same conditions apply as for standard addition. However, this method is rarely used.

2.5 Cleaning the electrode

- 1 Rinse the electrode with distilled water after each measurement or titration.
- 2 Check whether the measurement surface of the electrode is clean.



NOTE

The surface must be kept clean at all times before the measurement.



CAUTION

- **Never** treat electrodes in ultrasonic baths, as they may be damaged by such a treatment.
- Do not clean polymer membrane electrodes with organic solvents, as they attack and irreversibly destroy the polymer.

2.6 ISA/TISAB solutions

The following table gives examples for possible ISA/TISAB solutions:

| Measuring ion | ISA/TISAB | For 100 mL of solution | Remarks |
|---------------------|---|------------------------|--|
| Ag ⁺ | KNO ₃ 1 mol/L | 10.11 g | |
| Br ⁻ | KNO ₃ 1 mol/L | 10.11 g | |
| | or | | |
| | NaNO ₃ 2 mol/L | 17.00 g | |
| Ca ²⁺ | KCl 1 mol/L | 7.46 g | |
| Cl ⁻ | KNO ₃ 1 mol/L | 10.11 g | |
| | or | | |
| | KNO ₃ | 5.06 g | |
| | Ammonium acetate | 3.85 g | |
| | Glacial acetic acid | 2.8 mL | |
| | or | | |
| | NaNO ₃ 2 mol/L | 17.00 g | |
| CN ⁻ | NaOH 0.1 mol/L | 0.40 g | S ²⁻ interferes. |
| Cu ²⁺ | KNO ₃ 1 mol/L | 10.11 g | |
| F ⁻ | NaCl | 5.84 g | Set to pH 5.5 using c(NaOH) = 8 mol/L (AB-082). |
| | Glacial acetic acid | 5.75 mL | |
| | Trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid monohydrate (CDTA, Komplexon IV) | 0.45 g | |
| | | | |
| I ⁻ | KNO ₃ 1 mol/L | 10.11 g | |
| | or | | |
| | NaNO ₃ 2 mol/L | 17.00 g | |
| K ⁺ | NaCl 0.1–1 mol/L | 0.584–5.844 g | AB-134 |
| Na ⁺ (G) | Tris(hydroxymethyl)aminomethane [(HOH ₂ C) ₃ CNH ₂] 1 mol/L | 12.11 g | Set to between pH 8 and pH 10 using HNO ₃ (AB-083). |
| | or | | |
| | Triethanolamine | 7.50 mL | |

| Measuring ion | ISA/TISAB | For 100 mL of solution | Remarks |
|------------------------------|--|--|--|
| Na ⁺ (P) | CaCl ₂ 1 mol/L | 14.70 g CaCl ₂ ·2 H ₂ O | AB-083 |
| NO ₃ ⁻ | [(NH ₄) ₂ SO ₄] 1 mol/L or [Al ₂ (SO ₄) ₃] 0.1 mol/L | 13.21 g 3.42 g | |
| Pb ²⁺ | NaClO ₄ ·H ₂ O 1 mol/L | 14.05 g | At low Pb ²⁺ concentrations, set to between pH 5 and pH 9 |
| S ²⁻ | NaOH 2 mol/L | 8.00 g | pH ≥ 13 |

Abbreviations used:

AB: Metrohm Application Bulletin

Na⁺ (G): Glass membrane electrode

Na⁺ (P): Polymer membrane electrode

The pH value of the solution is adjusted to pH 5.5 with $c(\text{NaOH}) = 8 \text{ mol/L}$.

3 Storing electrodes

| Electrode | Type | Storage | |
|------------------------------|------|---|------------------------------------|
| | | For short periods | For longer periods |
| Ag ⁺ | C | dry | dry, with protective cap |
| Br ⁻ | C | KBr 0.1 mol/L | dry, with protective cap |
| Ca ²⁺ | P | CaCl ₂ 0.01 mol/L | dry, in the storage vessel*) |
| Cl ⁻ | C | NaCl 0.1 mol/L | dry, with protective cap |
| CN ⁻ | C | dry, with protective cap | dry, with protective cap |
| Cu ²⁺ | C | Cu(NO ₃) ₂ 0.1 mol/L | dry, with protective cap |
| F ⁻ (separate) | C | NaF 0.1 mol/L | dry, with protective cap |
| F ⁻ (combined) | C | NaF 0.1 mol/L | Reference electrolyte, KCl 3 mol/L |
| I ⁻ | C | KI 0.1 mol/L | dry, with protective cap |
| K ⁺ | P | KCl 0.1 mol/L | dry, in the storage vessel*) |
| Na ⁺ (G) | G | NaCl 0.1 mol/L | dry, in the storage vessel |
| Na ⁺ (P) | P | dry | dry, in the storage vessel |
| NO ₃ ⁻ | P | KNO ₃ 0.01 mol/L | dry, in the storage vessel*) |
| Pb ²⁺ | C | dry | dry, with protective cap |
| S ²⁻ | C | dry | dry, with protective cap |

*) A small amount of residual moisture (deionized water) on the electrode helps keep the reference electrode operational.

Abbreviations used:

G: Glass membrane electrode

C: Crystal membrane electrode

P: Polymer membrane electrode

4 Troubleshooting

The following malfunctions could occur:

- Measuring signal is unstable
- Sluggish response time ("running" measured value)
- Insufficient electrode slope
- Shifting of the electrode zero point ($E(0)$)
- Reduced linearity range

These problems may arise with the reference electrode or the ion-selective electrode.

4.1 Problems with the reference electrode

- Is sufficient bridge electrolyte filled in?
- Are there any air bubbles in the bridge electrolyte?
- Loosen the ground-joint diaphragm and clean it in order to increase the bridge electrolyte flow.
- Is the electrode cable screwed on and plugged in correctly?
- Is the electrode cable defective?
- Did you wait long enough after exchanging the bridge electrolyte?

4.2 Problems with the ion-selective crystal membrane electrode

- Polishing the sensor surface according to *Chapter 2.1.1, page 3*.
- Eliminating or masking electrode poisons (*see chapter 4.6, page 12*).
- Is the electrode cable screwed on and plugged in correctly?
- Is the electrode cable defective?
- The sensor surface might be destroyed. Use a new electrode.

4.3 Problems with the ion-selective polymer membrane electrode

- The combined electrode must not be stored in reference electrolyte, as this may cause the ionophore to leach out quickly.
- Do not use any organic solvents.
- Other components that could destroy the sensor surface must be eliminated from the sample.
- Eliminating or masking electrode poisons (*see chapter 4.6, page 12*).
- Is the electrode cable screwed on and plugged in correctly?
- Is the electrode cable defective?
- The sensor surface might be destroyed. Use a new electrode.
- The electrode might be too old (ionophore leached out). Use a new electrode.

4.4 Application-related problems

- Has the sensor been conditioned long enough?
- Did you wait until the measuring signal was stable before reading off the values?
- Are the ISA/TISAB solutions fresh?

4.5 Checking the electrode

1 Measure $c(\text{measuring ion}) = 10^{-4} \text{ mol/L}$ standard solution and write down the potential.

2 Measure $c(\text{measuring ion}) = 10^{-3} \text{ mol/L}$ standard solution and write down the potential.

3 Calculate the change of potential with the 2 previously measured potentials:

For monovalent ions this value has to be at least 47.3 mV at 25 °C (80% of the theoretical slope)

For divalent ions this value has to be at least 23.7 mV at 25 °C (80% of the theoretical slope)

If the respective value cannot be reached, the electrode needs to be replaced.

| Measuring ion | Interferences |
|----------------------|--|
| Pb ²⁺ (C) | Ag ⁺ , Hg ²⁺ and Cu ²⁺ must be absent. Fe ³⁺ and Cd ²⁺ interfere if their concentration is higher than the concentration of the measuring ion. |
| S ²⁻ (K) | Hg ²⁺ must be absent. Proteins should also be absent. |

Abbreviations used:

(G): Glass membrane electrode

(P): Polymer membrane electrode

(C): Crystal membrane electrode

5 Technical specifications

5.1 Measured data

| Electrode | Measuring range [mol/L] | Reproducibility | pH range | Temperature range [°C] | Membrane resistance [MΩ] | Reference resistance [kΩ] |
|------------------------------|--------------------------------------|-----------------|---------------------|------------------------|--------------------------|---------------------------|
| Ag ⁺ | 1·10 ⁻⁷ –1 | ±2% | 2–8 | 0–80 | ≤ 1 | – |
| Br ⁻ | 1·10 ⁻⁶ –1 | ±2% | 0–14 | 0–50 | ≤ 0.1 | – |
| Ca ²⁺ (separate) | 5·10 ⁻⁷ –1 | ±4% | 2–12 | 0–40 | 1–6 | – |
| Ca ²⁺ (combined) | 5·10 ⁻⁷ –1 | ±4% | 2–12 | 0–40 | 1–6 | < 10 |
| Cl ⁻ | 1·10 ⁻⁵ –1 | ±2% | 0–14 | 0–50 | ≤ 0.1 | – |
| CN ⁻ | 8·10 ⁻⁶ –10 ⁻² | ±2% | 10–14 ^{*1} | 0–80 | ≤ 0.1 | – |
| Cu ²⁺ | 1·10 ⁻⁸ –10 ⁻¹ | ±4% | 2–12 ^{*2} | 0–80 | ≤ 1 | – |
| F ⁻ (separate) | 1·10 ⁻⁶ –sat. | ±2% | 5–7 | 0–80 | 0.15–0.2 | – |
| F ⁻ (combined) | 1·10 ⁻⁶ –sat. | ±2% | 5–7 | 0–40 | 0.1–0.2 | 5 |
| I ⁻ | 5·10 ⁻⁸ –1 | ±2% | 0–14 | 0–50 | ≤ 0.1 | – |
| K ⁺ | 1·10 ⁻⁷ –1 | ±2% | 2.5–11 | 0–40 | 10–20 | < 10 |
| Na ⁺ (G) | 1·10 ⁻⁵ –1 | ±2% | 5–9 | 0–80 | ≤ 300 | – |
| Na ⁺ (P) | 5·10 ⁻⁶ –1 | ±2% | 2–12 | 0–40 | 3–20 | – |
| NO ₃ ⁻ | 1·10 ⁻⁶ –1 | ±2% | 2.5–11 | 0–40 | 1–8 | < 10 |
| Pb ²⁺ | 1·10 ⁻⁶ –10 ⁻¹ | ±4% | 4–7 | 0–80 | ≤ 1 | – |
| S ²⁻ | 1·10 ⁻⁷ –1 | ±2% | 2–12 | 0–80 | ≤ 1 | – |

Abbreviations used:

G: Glass membrane electrode

C: Crystal membrane electrode

P: Polymer membrane electrode

*1: HCN is present at $\text{pH} < 10$

*2: recommended $\text{pH} \leq 6$

5.2 Service life of polymer membrane electrodes

The service life of the electrode is limited. The average service life in regular laboratory use is approx. half a year. This value greatly depends on the application used and on the maintenance of the electrode.

The service life is also shortened if the electrode is not used, i.e. only kept in storage.

Measures to reduce the decrease in service life:

- Do not purchase stocks of electrodes for future use.
- Do not store electrodes unused for long periods.
- Instructions for storage: (*see chapter 3, page 9*)



NOTE

Metrohm recommends performing regular checks of stored electrodes:
(*see chapter 4.5, page 11*)

Glossary

Activity coefficient

The activity coefficient γ_i is a measure for the nonideal behavior of a solution. It can be calculated approximately and is valid up to about $c < 0.1$ mol/L. The activity coefficient depends on the solvent, the temperature, the ionic strength and the effective size of the hydrated ion.

Ag/AgCl reference system

The reference system consists of silver, silver chloride and a KCl solution, usually $c(\text{KCl}) = 3$ mol/L.

Calibration curve

The calibration curve shows the measured potential U as a function of the logarithm of the ion activity. The following diagram shows the calibration curve of a fluoride ISE (note the negative slope of the calibration curve, which is due to the ion charge z of $\text{F}^- = -1$):

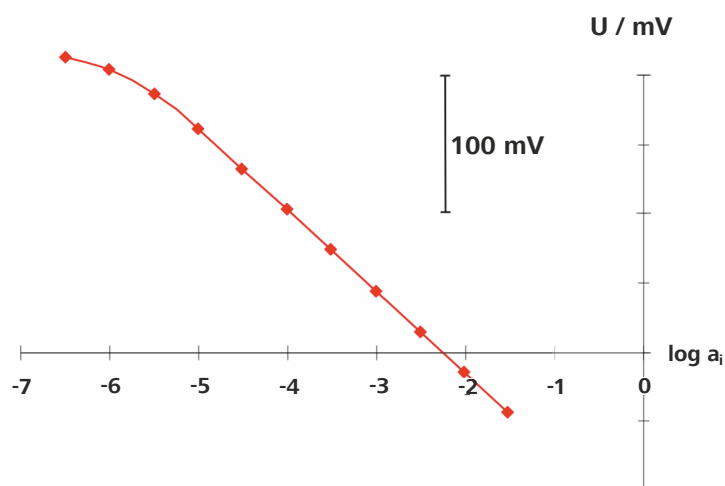


Figure 1 Calibration curve of a fluoride ISE

For low ion concentrations, the curve is nonlinear, which means that in this range the electrode responds not only to the measuring ion but also to interfering ions (e.g. to OH^- for the fluoride ISE).

To counterbalance this non-linear effect in the lower concentration range, we recommend calibrating over a smaller area.

Cross-sensitivity

See interfering ions.

Double-junction electrode

Electrode which contains another electrolyte solution (so-called bridge electrolyte solution) between the sample solution and the reference system. For an example of a double-junction electrode, LL ISE Reference 6.0750.100

Electrode slope

The potential U of ion-selective electrodes depends on the activity a_i of free ions in the solution. This relation is described by the Nernst equation as follows:

$$U = U_0 + \frac{2.303 \cdot R \cdot T}{z_i \cdot F} \cdot \log a_i = U_0 + U_N \cdot \log a_i$$

U_0 : Standard potential of the measuring chain

R : Gas constant ($8.31441 \text{ JK}^{-1}\text{mol}^{-1}$)

T : Absolute temperature

z_i : Charge of the measuring ion i (including sign)

F : Faraday constant ($96,484.56 \text{ Cmol}^{-1}$)

a_i : Activity of the measuring ion

U_N : Nernst slope

The electrode slope depends on the charge of the ion (including its sign) as well as on the temperature.

| Ion charge | Slope | Example |
|------------|---------|--|
| + 2 | 29.58 | Ca^{2+} |
| + 1 | 59.16 | K^+, Na^+ |
| – 1 | – 59.16 | $\text{Br}^-, \text{Cl}^-, \text{F}^-$ |
| – 2 | – 29.58 | S^{2-} |

Electrolyte solution

Solution with electric conductivity.

ISA

This abbreviation stands for **I**onic **S**trength **A**djuster and designates a solution with high ionic strength that maintains the ionic strength of a sample solution at a constant level.

[illegible]

Ion activity, ion concentration

$$a_i = y_i \cdot c_i$$

A measure for interionic interactions in a solution. The ionic strength I depends on the concentration c_i and the charge z_i of the ions:

$$I = \frac{1}{2} \cdot \sum_i c_i \cdot z_i^2$$

This abbreviation stands for **T**otal **I**onic **S**trength **A**djustment **B**uffer and designates a buffer solution with high ionic strength that maintains the ionic strength of a sample solution as well as its pH value at a constant level. TISAB solutions are mainly used for measurements using calibration curves.

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