Metrohm
Ion analysis

CH-9101 Herisau/Switzerland
E-Mail info@metrohm.com
Internet www.metrohm.com

Ion-selective electrodes (ISE)

Manual

Teachware
Metrohm AG
Oberdorfstrasse 68
CH-9101 Herisau
teachware@metrohm.com

Although all the information given in this manual has been checked with great care, errors cannot be entirely excluded. Should you notice any mistakes please inform the author at the address given above.

Table of contents

1 Introduction

1.1 Assembly of ion-selective electrodes

1.1.1 Electrodes without exchangeable tip

Concerning:

- Ca^{2+} and Na^{+} polymer membrane electrodes (Note: The Na^{+} glass electrode looks like a pH glass electrode).
- All crystal membrane electrodes (Ag^{+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, F^{-}, Cl^{-}, Br^{-}, I^{-}, CN^{-}, SCN^{-}, S^{2-})

Screw off protection cap and screw on electrode cable
for suitable electrode cables see *page 50*

Movable sleeve SGJ 14/15
Move SGJ sleeve up completely for Sample Processor applications

Sensor surface, **don't touch with your fingers!**

~~1.1.2 Electrodes with exchangeable tip~~

Concerning:

- K^+, NO_3^- and BF_4^- polymer membrane electrodes

Screw off protection cap and screw on electrode cable
for suitable electrode cables see *page 50*

Movable sleeve SGJ 14/15
Move SGJ sleeve up completely for Sample Processor applications

Electrode tip with flat packing
screw to electrode shaft, tighten with fingers only

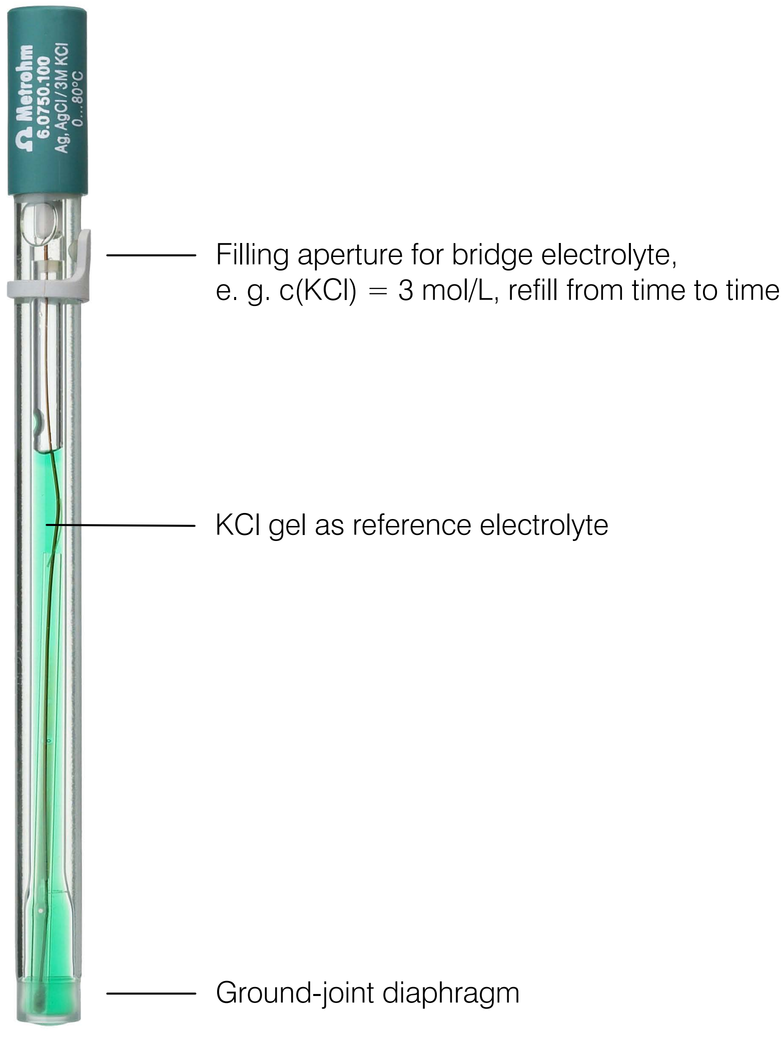
Electrode tip

Sensor surface, **don't touch with your fingers!**

1.2 Reference electrode

A separate reference electrode is necessary for measurements with ion-selective electrodes. For this purpose we recommend the LL ISE Reference 6.0750.100. The LL ISE Reference is insensitive to contamination due to its fixed ground-joint diaphragm. Another advantage are the low-noise measurement signals. The LL ISE Reference is filled with KCl (c = 3 mol/L) as reference as well as bridge electrolyte.

If K^+ or Cl^- interfere (e. g. because it is the measuring ion or because of cross sensitivity), the LL ISE Reference must be filled with a suitable bridge electrolyte, e. g. KNO_3, NaCl or NH_4Cl.



2 Measurements

> ***Attention!***
> *Don't touch the sensor surface with your fingers!*
> *Don't leave the electrode in dist. water for longer periods of time. Dry the electrode carefully after rinsing with a soft paper cloth.*
> *Don't use or rinse polymer membrane electrodes (Na^+, K^+, Ca^{2+}, NO_3^-, BF_4^-) with organic solvents.*
> *Crystal membrane electrodes may be used in organic solvents (acetone, methanol, benzene) for short periods of time.*
> *Protect the Cu^{2+} electrode against direct solar radiation and don't use it in changing light situations (it is light sensitive).*
> *The Pb electrode must not be used in solutions containing acetate (interferences with the membrane material).*

2.1 Preparing electrodes

Ion-selective electrodes should be prepared before the first usage, after longer pauses and between precipitation titrations.

2.1.1 Crystal membrane electrodes

F^--Electrode 6.0502.150: Polish sensor surface with tooth paste or liquid soap. **Never use the polishing set!**

Other crystal membrane electrodes (electrodes 6.0502.XXX: Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, Cl^-, Br^-, I^-, CN^-, SCN^-, S^{2-}: Polish with the 6.2802.000 polishing set; put powder on the polishing support, moisten and polish sensor surface pressing slightly.

2.1.2 Polymer membrane electrodes

Concerning the electrodes 6.0504.XXX (K^+, NO_3^-, BF_4^-):

Screw the electrode tip onto the shaft. Tighten it with your finger only, never use a tool. Take care that the flat packing fits correctly, see *page 31*. Leave the electrode during 15 minutes in dist. water, then another 30 minutes in a solution of the corresponding measuring ion ($c = 10^{-2}$ mol/L)

Na^+ electrode 6.0508.100, Ca^{2+} electrode 6.0508.110: Rinse the electrode with dist. water and dry it with a soft paper cloth.

2.1.3 Glass membrane electrodes

Na^+ electrode 6.0501.100: Leave the electrode in a solution of NaCl ($c = 1$ mol/L) for several hours.

2.2 Titrations

Ion-selective electrodes can easily be used for potentiometric titrations. The resulting titration curves are usually S-shaped. They can be evaluated with automatic titrators.

Metrohm offers application tips for titrations with ion-selective electrodes:

- Application Bulletins No. 14, 101, 125, 140, 143, 181, 182, 235. Application Bulletins are free of charge and can be ordered at Metrohm.
- Application Notes T-7, T-24, T-29, T-66, T-69. Application Notes can be printed from the Internet (www.metrohm.com).

2.3 Direct measurements with calibration

The ion activity is interpolated by means of a calibration curve. The calibration curve is established with standard solutions. The expected ion activity of the sample should be within the range of the calibration curve.

The requested analytical answer is usually the concentration of a substance (and not its activity). Measurements are therefore executed at fixed ionic strength. The ionic strength is fixed with a TISAB solution (Total Ionic Strength Adjustment Buffer). TISAB solutions have such a high ionic strength that the contributions of the measuring ion can be neglected. Most of the time, the pH value is fixed as well.

> ***Note!***
> *Carry out the measurements of the samples and the calibration standards at identical measuring conditions. They also must have the same temperature!*
>
> *A calibration standard should be measured periodically (e. g. daily) in order to guarantee reliable results. A new calibration should be carried out if a non-tolerable potential difference is detected.*

Metrohm offers application tips for direct measurements with calibration using ion-selective electrodes:

- Application Bulletins No. 82, 83, 85. Application Bulletins are free of charge and can be ordered at Metrohm.
- Application Note I-3. Application Notes can be printed from the Internet (www.metrohm.com).

2.4 Standard addition/-subtraction

This method is based on adding a defined quantity of the measuring ion to a known initial volume of the sample (poss. several increments). The sample solution is usually buffered. The unknown concentration of the sample is calculated from the resulting potential differences. This calculation is executed automatically by modern ion meters.

The volume of added solutions should not exceed 25 % of the sample volume. The concentration of the standard solution should be as high as possible in order to avoid errors due to dilution. If several increments are added, the potential differences between the increments should be about constant.

The standard subtraction method uses the same principle as above. Instead of adding a defined quantity of the measuring ion, the solution contains a substance which eliminates the measuring ion (complexation or precipitation). Apart from that the same conditions are valid as for standard addition. However, this method is rarely used.

Metrohm offers application tips for standard addition methods:

- Application Bulletins No. 82, 83, 85. Application Bulletins are free of charge and can be ordered at Metrohm.
- Application Note I-1, I-5, I-6, I-7, I-8, I-9, I-10. Application Notes can be printed from the Internet (www.metrohm.com).

2.5 ISA/TISAB solutions

The following table gives examples for ISA/TISAB solutions:

Measuring ion	*ISA/TISAB*	*For 100 mL solution*	*Remarks*
Ag^+	$c(KNO_3)$ = 1 mol/L	10.110 g	
BF_4^-	$c[(NH_4)_2SO_4]$ = 2 mol/L	26.427 g	
Br^-	$c(KNO_3)$ = 1 mol/L or $c(NaNO_3)$ = 2 mol/L	10.110 g 16.999 g	
Ca^{2+}	c(KCl) = 1 mol/L	7.455 g	
Cd^{2+}	$c(KNO_3)$ = 1 mol/L	10.110 g	
Cl^-	$c(KNO_3)$ = 1 mol/L or KNO_3 Ammonium acetate Glacial acetic acid or $c(NaNO_3)$ = 2 mol/L	10.110 g 5.06 g 3.85 g 2.8 mL 16.999 g	
CN^-	c(NaOH) = 0.1 mol/L	0.400 g	Interference with S^{2-}
Cu^{2+}	$c(KNO_3)$ = 1 mol/L	10.110 g	
F^-	NaCl Glacial acetic acid Trans-1,2-Diamino-cyclohexane-N,N,N,N-tetraacetic acid monohydrate (CDTA, Komplexon IV)	5.84 g 5.75 mL 0.45 g	AB 82
I^-	$c(KNO_3)$ = 1 mol/L or $c(NaNO_3)$ = 2 mol/L	10.110 g 16.999 g	
K^+	c(NaCl) = 1 ... 0.1 mol/L	5.844 … 0.584 g	
Na^+ (G)	Trishydroxymethyl aminomethane $c[(HOH_2C)_3CNH_2]$ = 1 mol/L or triethanolamine	12.114 g 7.5 mL	Set to pH = 8 ... 10 with HNO_3 AB 83
Na^+ (P)	$c(CaCl_2)$ = 1 mol/L	14.702 g $CaCl_2 \cdot 2\,H_2O$	AB 83
NO_3^-	$c[(NH_4)_2SO_4]$ = 1 mol/L or $c[Al_2(SO_4)_3]$ = 0.1 mol/L	13.213 g 3.421 g	
Pb^{2+}	$c(NaClO_4 \cdot H_2O)$ = 1 mol/L	14.046 g	Set to pH = 5 ... 9 for low Pb^{2+} conc.

Measuring ion	*ISA/TISAB*	*For 100 mL solution*	*Remarks*
S^{2-}	c(NaOH) = 2 mol/L	7.999 g	pH ≥ 13
SCN^{-}	$c(KNO_3)$ = 1 mol/L or Acetate buffer pH = 6, $c(CH_3COO^-)_{tot}$ = 1 mol/L	10.110 g	

Abbreviations:
AB: Metrohm Application Bulletin
Na^+ (G): Glass membrane electrode
Na^+ (P): Polymer membrane electrode

3 Maintenance

3.1 Storage

Elec-trode	*Type*	*Storage* *for shorter periods*	*for longer periods*
Ag^+	C	dry	dry, with protection cap
BF_4^-	P	$c(NaBF_4) = 0.01$ mol/L	screw off electrode tip and store it in the original tube
Br^-	C	$c(KBr) = 0.1$ mol/L	dry, with protection cap
Ca^{2+}	P	$c(Ca(Cl)_2) = 0.01$ mol/L	dry, with protection cap
Cd^{2+}	C	$c(Cd(NO_3)_2) = 0.1$ mol/L	dry, with protection cap
Cl^-	C	$c(NaCl) = 0.1$ mol/L	dry, with protection cap
CN^-	C	dry	dry, with protection cap
Cu^{2+}	C	$c(Cu(NO_3)_2) = 0.1$ mol/L	dry, with protection cap
F^-	C	$c(NaF) = 0.1$ mol/L	dry, with protection cap
I^-	C	$c(KI) = 0.1$ mol/L	dry, with protection cap
K^+	P	$c(KCl) = 0.1$ mol/L	screw off electrode tip and store it in the original tube
Na^+	G	$c(NaCl) = 0.1$ mol/L	dry
Na^+	P	dry	dry, with protection cap
NO_3^-	P	$c(KNO_3) = 0.01$ mol/L	screw off electrode tip and store it in the original tube
Pb^{2+}	C	dry	dry, with protection cap
S^{2-}	C	dry	dry, with protection cap
SCN^-	C	dry	dry, with protection cap

Abbreviations:
C: Crystal membrane electrode
G: Glass membrane electrode
P: Polymer membrane electrode

3.2 Troubleshooting

The following problems may occur:

- Measured signal is unstable
- Sluggish response time ("running" measured value)
- Electrode slope too low
- Electrode zero point (E(0)) not correct
- Reduced linearity range

These problems can occur on account of the reference or the ion-selective electrode.

Problems with the reference electrode

- Is the quantity of the bridge electrolyte enough?
- Are there air bubbles in the bridge electrolyte?
- Open and clean the ground-joint diaphragm. Is the flow through the diaphragm OK after cleaning?
- Is the electrode cable correctly plugged in?
- Is the electrode cable defective?

Problems with the ion-selective crystal membrane electrode

- Polish the sensor surface with the polishing set.
- Exception: The sensor surface of the F^- electrode is polished with tooth paste or liquid soap.
- Avoid electrode poisons, see also *page 40*. Electrode poisons must be precipitated or masked.
- Is the electrode cable correctly plugged in?
- Is the electrode cable defective?
- The sensor surface may be destroyed. Use new electrode.

~~Problems with the ion-selective polymer membrane electrode~~

- Don't use organic solvents!
- Any other components which may destroy or contaminate the sensor surface must be eliminated.
- Avoid electrode poisons, see also *page 40*. Electrode poisons must be precipitated or masked.
- Is the electrode cable correctly plugged in?
- Is the electrode cable defective?
- The sensor surface may be destroyed. Use new electrode tip or new electrode.

- The electrode may be too old (ionophore leached out). Use new electrode tip or new electrode.

3.3 Interfering ions

The following table shows the concentrations of interfering ions in mol/L which produce an error of app. 10 %.

Measuring ion	*Interferences*
Ag^+	Hg^{2+} must be absent. Proteins should also be absent.
BF_4^-	$c(NO_3^-) < 5 \cdot 10^{-3}$; $c(SO_4^{2-}) < 0.2$; $c(ClO_4^-) < 5 \cdot 10^{-7}$; $c(F^-) < 0.6$; $c(CH_3COO^-) < 0.2$; Precipitate halides with silver sulphate.
Br^-	Hg^{2+} must be absent. $c(OH^-) < 3 \cdot 10^4 \cdot c(Br^-)$; $c(Cl^-) < 4 \cdot 10^2 \cdot c(Br^-)$; $c(I^-) < 2 \cdot 10^{-4} \cdot c(Br^-)$; $c(S^{2-}) < 10^{-6} \cdot c(Br^-)$; $c(CN^-) < 8 \cdot 10^{-5} \cdot c(Br^-)$; $c(NH_3) < 2 \cdot c(Br^-)$; $c(S_2O_3^{2-}) < 20 \cdot c(Br^-)$
Ca^{2+}	$c(Na^+) < 0.26$; $c(Pb^{2+}) < 5.3 \cdot 10^{-6}$; $c(Fe^{2+}) < 6.7 \cdot 10^{-5}$; $c(Zn^{2+}) < 2.6 \cdot 10^{-6}$; $c(Cu^{2+}) < 6.7 \cdot 10^{-5}$; $c(Mg^{2+}) < 8.3 \cdot 10^{-3}$
Cd^{2+}	Ag^+, Hg^{2+} and Cu^{2+} must be absent. Fe^{3+} and Pb^{2+} interfere if their concentration is higher than the concentration of the measuring ion.
Cl^-	Hg^{2+} must be absent. $c(OH^-) < 80 \cdot c(Cl^-)$; $c(Br^-) < 3 \cdot 10^{-3} \cdot c(Cl^-)$; $c(I^-) < 5 \cdot 10^{-7} \cdot c(Cl^-)$; $c(S^{2-}) < 10^{-6} \cdot c(Cl^-)$; $c(CN^-) < 2 \cdot 10^{-7} \cdot c(Cl^-)$; $c(NH_3) < 0.1 \cdot c(Cl^-)$; $c(S_2O_3^{2-}) < 10^{-2} \cdot c(Cl^-)$
CN^-	S^{2-} and Ag^+ complexing substances have to be absent. $c(Cl^-) < 10^6 \cdot c(CN^-)$; $c(Br^-) < 5 \cdot 10^3 \cdot c(CN^-)$; $c(I^-) < 10^{-1} \cdot c(CN^-)$
Cu^{2+}	Ag^+, Hg^{2+} and S^{2-} must be absent. Cl^-, Br^-, I^-, Fe^{3+}, and Cd^{2+} interfere if their concentration is higher than the concentration of the measuring ion.
F^-	$c(OH^-) < 10^{-1} \cdot c(F^-)$
I^-	Hg^{2+} must be absent. $c(Cl^-) < 10^6 \cdot c(I^-)$; $c(Br^-) < 5 \cdot 10^3 \cdot c(I^-)$; $c(S^{2-}) < 10^{-6} \cdot c(I^-)$; $c(CN^-) < 0.4 \cdot c(I^-)$; $c(S_2O_3^{2-}) < 10^5 \cdot c(I^-)$
K^+	$c(Na^+) < 5 \cdot 10^{-1}$; $c(TRIS^+) < 0.1$; $c(Li^+) < 1$; $c(NH_4^+) < 3.3 \cdot 10^{-3}$; $c(Cs^+) < 1 \cdot 10^{-4}$; $c(H^+) < 1 \cdot 10^{-2}$
Na^+ glass	$pH > (pNa+4)$; $c(Li^+) < 5 \cdot 10^{-2}$; $c(K^+) < 0.1$; $c(Rb^+) < 3$; $c(NH_4^+) < 3$; $c(Ag^+) < 3 \cdot 10^{-7}$
Na^+ polymer	SCN^- and organic lipophile ions (e. g. acetate) should be absent. $c(K^+) < 0.15$; $c(Li^+) < 1$; $c(Ca^{2+}) < 1$; $c(Mg^{2+}) < 1$; $c(NH_4^+) < 1$; $c(H^+) < 1$
NO_3^-	$c(Br^-) < 7 \cdot 10^{-4}$; $c(NO_2^-) < 7 \cdot 10^{-4}$; $c(SO_4^{2-}) < 1$; $c(Cl^-) < 2.5 \cdot 10^{-2}$; $c(F^-) < 1$; $c(CH_3COO^-) < 0.1$

Measuring ion	*Interferences*
Pb^{2+}	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-}	Hg^{2+} must be absent. Proteins should also be absent.
SCN^-	$c(OH^-) < 10^2 \cdot c(SCN^-)$; $c(Cl^-) < 20 \cdot c(SCN^-)$; $c(Br^-) < 3 \cdot 10^{-3} \cdot c(SCN^-)$; $c(I^-) < 10^{-6} \cdot c(SCN^-)$; $c(S^{2-}) < 10^{-6} \cdot c(SCN^-)$; $c(CN^-) < 7 \cdot 10^{-3} \cdot c(SCN^-)$; $c(S_2O_3^{2-}) < 0.13^3 \cdot c(SCN^-)$

Na^+ (glass): Glass membrane electrode
Na^+ (polymer): Polymer membrane electrode

4 Appendix

4.1 Technical data

4.1.1 Measuring data

Electrode	*Type*	*Measuring range [mol/L]*	*Repeat-ability*	*pH range*	*Temp. range [°C]*	*Membrane resistance [MΩ]*
Ag^{+}	C	$1 \cdot 10^{-7}$ ... 1	± 2 %	2 ... 8	0 … 80	≤ 1
BF_4^{-}	P	$7 \cdot 10^{-6}$ ... 1	± 2 %	2.5 … 11 (pH ≥ 5.5 recommended, because the glass of the reference electrode is corroded by acidic BF_4^{-} solutions)	0 ... 40	1 ... 5
Br^{-}	C	$5 \cdot 10^{-6}$ ... 1	± 2 %	0 … 14	0 … 50	≤ 0.1
Ca^{2+}	P	$5 \cdot 10^{-7}$ ... 1	± 4 %	2 … 12	0 … 40	1 … 4
Cd^{2+}	C	$1 \cdot 10^{-7}$ ... 10^{-1}	± 4 %	2 … 12 (pH ≤ 7 recommended)	0 … 80	≤ 1
Cl^{-}	C	$5 \cdot 10^{-5}$ ... 1	± 2 %	0 ... 14	0 ... 50	≤ 0.1
CN^{-}	C	$8 \cdot 10^{-6}$ ... 10^{-2}	± 2 %	10 … 14 (HCN is formed at pH < 10)	0 ... 80	≤ 30
Cu^{2+}	C	$1 \cdot 10^{-8}$ ... 10^{-1}	± 4 %	2 … 12 (pH ≤ 6 recommended)	0 … 80	≤ 1
F^{-}	C	$1 \cdot 10^{-6}$ ... sat.	± 2 %	5 ... 7	0 … 80	0.15 ... 0.2
I^{-}	C	$5 \cdot 10^{-8}$ ... 1	± 2 %	0 ... 14	0 ... 50	≤ 0.1
K^{+}	P	$1 \cdot 10^{-6}$ ... 1	± 2 %	2.5 ... 11	0 ... 40	10 ... 20
Na^{+}	G	$1 \cdot 10^{-5}$ ... 1	± 2 %	5 ... 9	0 … 80	≤ 300
Na^{+}	P	$1 \cdot 10^{-6}$ ... 1	± 2 %	3 ... 12	0 … 40	< 50
NO_3^{-}	P	$7 \cdot 10^{-6}$ ... 1	± 2 %	2.5 ... 11	0 … 40	1 … 5
Pb^{2+}	C	$1 \cdot 10^{-6}$ ... 10^{-1}	± 4 %	4 ... 7	0 … 80	≤ 1
S^{2-}	C	$1 \cdot 10^{-7}$ ... 1	± 2 %	2 … 12	0 … 80	≤ 1
SCN^{-}	C	$5 \cdot 10^{-6}$ ... 1	± 2 %	2 … 10 (pH ≤ 4 recommended)	0 … 50	≤ 0.1

4.1.2 Response time

For 99 % of the final value ≤ 1 min

4.1.3 Dimensions, immersion depth

Type of electrode	*Minimum immersion depth*	*Shaft length*	*Shaft diameter*	*Shaft material*
C	1 mm	123 mm	12 mm	EP
G	20 mm	125 mm Length from SGJ: 86 mm	12 mm	Glass
P	1 mm	123 mm	12 mm	EP/PVC

Abbreviations:
G: Glass membrane
C: Crystal membrane
P: Polymer membrane
EP: Epoxy resin
PVC: Polyvinyl chloride

4.1.4 Working life of polymer membrane electrodes

Concerning electrodes 6.0504.XXX, 6.0508.XXX for Ca^{2+}, K^+, Na^+, NO_3^-, BF_4^- and electrode tips 6.1205.XXX.

Average working life at normal laboratory use app. ½ year

The chemical properties of the ion-exchange material embedded in the membrane limit the storage. Do therefore not stock up on these electrodes and store them for too long!

4.2 Glossary

Activity coefficient

The activity coefficient y_i is a measure for the non-ideal 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. The following table shows some activity coefficients in aqueous solutions at 25 °C as a function of the ionic strength I and the actual size k of the hydrated ion.

k: Actual size of the hydrated ion	I = 0.001	I = 0.01	I = 0.1
Monovalent ions			
9 e. g. H^+	0.967	0.913	0.826
6 e. g. Li^+, $(C_2H_5)_4N^+$, $C_6H_5COO^-$	0.966	0.907	0.796
5 e. g. $(C_2H_5)_3NH^+$, $CHCl_2COO^-$	0.965	0.904	0.783
4 e. g. Na^+, $(CH_3)_4N^+$, HCO_3^-, $H_2PO_4^-$, CH_3COO^-	0.965	0.902	0.770
3 e. g. K^+, Ag^+, NH_4^+, OH^-, F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, ClO_4^-, NO_3^-	0.965	0.899	0.754
Bivalent ions			
8 e. g. Be^{2+}, Mg^{2+}	0.872	0.690	0.445
6 e. g. Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}	0.870	0.676	0.401
5 e. g. Ba^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, CO_3^{2-} $(COO)_2^{2-}$	0.869	0.668	0.377
4 e. g. SO_4^{2-}, $S_2O_3^{2-}$	0.867	0.661	0.351
Trivalent ions			
9 e. g. Al^{3+}, Fe^{3+}, Cr^{3+}	0.737	0.443	0.178
4 e. g. PO_4^{3-}	0.726	0.394	0.095

Ag/AgCl reference system

The Ag/AgCl reference system consists of silver, silver chloride, and a KCl solution, usually c(KCl) = 3 mol/L. The standard reference potential at 25 °C for this system is 207.0 mV.

Calibration curve

The calibration curve shows the measured potential U as a function of the logarithm of the ion activity. The diagram below shows the calibration curve of a F^- electrode (note the negative slope of the curve which is due to the ion charge z of $F^- = -1$!):

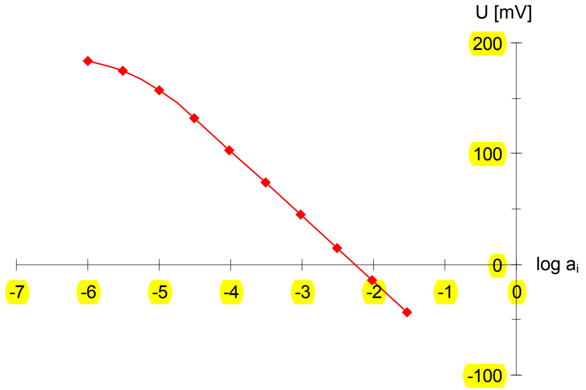


Fig. 1: Calibration curve of a fluoride electrode

For low activities, the curve is non-linear which means that the electrode responds not only to the measuring ion (F^-) but also to interfering ions (e. g. to OH^- for the F^- electrode).

Cross-sensitivity

See interfering ions.

Double junction electrode

Double junction electrodes have another electrolyte (so-called bridge electrolyte) between the sample solution and the reference system. An example of a double junction electrode is given on *page 32*.

Electrode slope

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

$$U = U_0 + \frac{2.303 \cdot R \cdot T}{z_i \cdot F} \cdot \log a_i = U_0 + U_N \cdot \log a_i \quad (1)$$

U_0: Standard potential of the measuring assembly
R: Gas constant (8.31441 $JK^{-1}mol^{-1}$)
T: absolute temperature
z_i: Charge of measuring ion i (including sign)
F: Faraday constant (96'484.56 $Cmol^{-1}$)
a_i: Activity of measuring ion
U_N: Nernst slope

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

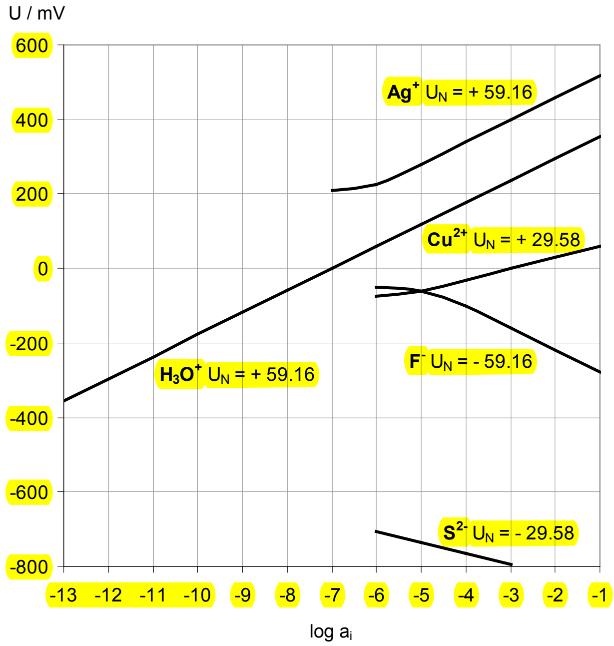


Fig. 2: Dependence of the electrode potential U on the ion activity a for different types of ions at 25 °C

Electrolyte

Solution with electric conductivity.

Interfering ions

Ion-selective electrodes often respond to other ions besides the measuring ion (cross-sensitivity). The lower the concentration of the measuring ion, the greater the interference of such ions. This results in a non-linear calibration curve for low concentrations of the measuring ion.

Ion activity, ion concentration

As the ion concentration c_i rises, equations describing the behavior of solutions loose their validity. These equations are again valid for the ion activity by introducing the activity coefficient y_i. Activity a_i and concentration c_i of the ion i in solutions containing only free ions are related as follows:

$$a_i = y_i \cdot c_i \qquad (2)$$

Ion-selective electrodes respond only to ion activities. For low concentrations, the activity coefficient $y_i \cong 1$, which means that concentration and activity are equal.

Ionic strength

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

$$I = \frac{1}{2} \cdot \sum_i c_i \cdot z_i^2 \qquad (3)$$

TISAB

TISAB is the abbreviation of **T**otal **I**onic **S**trength **A**djustment **B**uffer. A TISAB solution is a buffer solution with high ionic strength, which fixes the ionic strength of a sample solution as well as its pH value. TISAB solutions are important for direct measurements using calibration curves.

4.3 Warranty

The warranty on our products is limited to defects that are traceable to material, construction or manufacturing error which occur within 12 months from the day of delivery. In this case the defects will be rectified in our workshops free of charge. Transport costs are to be paid by the customer.

For day and night operation the warranty is limited to 6 months.

Glass breakage in the case of electrodes or other parts is not covered by the warranty. Checks which are not a result of material or manufacturing faults are also charged during the warranty period. For parts from outside manufacturers, insofar as these constitute an appreciable part of our instrument, the warranty stipulations of the manufacturer in question apply.

With the regard to the guarantee of accuracy the technical specifications in this manual are authoritative.

Concerning defects in materials, construction or design as well as the absence of guaranteed features the purchaser has no rights or claims except those mentioned above.

If damage of the packaging is evident on receipt of a consignment or if the goods show signs of transport damage after unpacking, the carrier must be informed immediately and a written damage report demanded. Lack of an official damage report releases Metrohm from any liability to pay compensation.

If any instruments and parts have to be returned then the original packaging should be used if at all possible. This applies above all to instruments and electrodes. Before embedment in wood shavings or similar material the parts must be packed in a dustproof package (for instruments the use of a plastic bag is essential). If open assemblies are included that are sensitive to electromagnetic voltages (e. g. data interfaces, etc.) then these must be returned in the associated original protective packaging (e. g. conductive protective bag). (Exception: assemblies with a built-in voltage source belong in non-conductive protective packaging).

For damage which arises as a result of non-compliance with these instructions no warranty responsibility whatsoever will be accepted by Metrohm.

4.4 Ordering numbers and accessories

4.4.1 Ion-selective electrodes

Order no.	*Description*
6.0504.130	BF_4^-, Polymer membrane electrode
6.0502.100	Br^-, Crystal membrane electrode
6.0508.110	Ca^{2+}, Polymer membrane electrode
6.0502.110	Cd^{2+}, Crystal membrane electrode
6.0502.120	Cl^-, Crystal membrane electrode
6.0502.130	CN^-, Crystal membrane electrode
6.0502.140	Cu^{2+}, Crystal membrane electrode
6.0502.150	F^-, Crystal membrane electrode
6.0502.160	I^-, Crystal membrane electrode
6.0502.180	Ag^+, Crystal membrane electrode
6.0504.110	K^+, Polymer membrane electrode
6.0501.100	Na^+, Glass membrane electrode
6.0508.100	Na^+, Polymer membrane electrode
6.0504.120	NO_3^-, Polymer membrane electrode
6.0502.170	Pb^{2+}, Crystal membrane electrode
6.0502.180	S^{2-}, Crystal membrane electrode
6.0502.190	SCN^-, Crystal membrane electrode

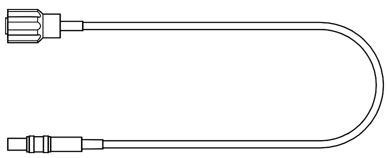
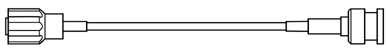
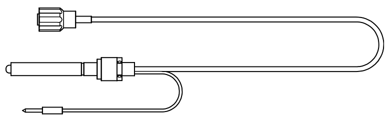
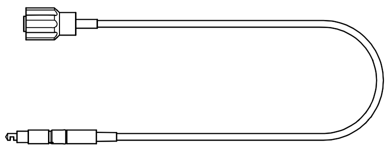
The reference electrode and electrode cables have to be ordered separately, see below.

4.4.2 Reference electrodes

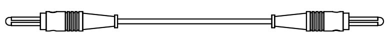
Order no.	*Description*
6.0750.100	LL ISE Reference Ag/AgCl reference electrode with fixed ground-joint diaphragm, bridge electrolyte c(KCl) = 3 mol/L, length 133 mm, with Metrohm socket B
  6.0726.107 6.0726.117	Ag/AgCl reference electrode with ground-joint diaphragm, filled with c(KCl) = 3 mol/L, with Metrohm socket B Length 86 mm Length 125 mm
  6.0726.100 6.0726.110	Ag/AgCl reference electrode with ground-joint diaphragm, without electrolyte, with Metrohm socket B Length 86 mm Length 125 mm

4.4.3 Electrode cable

For ISE electrodes

Order no.	*Description*
 6.2104.020 6.2104.030 6.2104.040	Plug type F Length 1 m Length 2 m Length 3 m 
6.2104.090	Plug type BNC, 1 m 
6.2104.010	Plug type US, 1 m 
6.2104.130	Plug type Radiometer, 1 m 

For reference electrodes

Order no.	*Description*
 6.2106.020 6.2106.060 6.2106.050	Plug type B Length 1 m Length 2 m Length 3 m 

4.4.4 Electrode tip

Order no.	*Description*
	Spare part for polymer membrane electrodes with separate electrode tip
6.1205.020	K^+
6.1205.030	NO_3^-
6.1205.040	BF_4^-

4.4.5 Ion standards

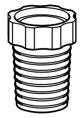
250 mL, c(ion) = 0.1000 ± 0.0005 mol/L

Order no.	*Description*
6.2301.000	KBr ion standard
6.2301.010	NaCl ion standard
6.2301.020	$Cu(NO_3)_2$ ion standard
6.2301.030	NaF ion standard
6.2301.040	KI ion standard
6.2301.050	$Pb(ClO_4)_2$ ion standard
6.2301.060	KCl ion standard
6.2301.070	$CaCl_2$ ion standard
6.2301.080	KNO_3 ion standard

4.4.6 Electrolytes

Order no.	*Description*
6.2313.000	Electrolytic solution c(KCl) = 3 mol/L, 1000 mL
6.2308.020	Electrolytic solution c(KCl) = 3 mol/L, 250 mL
6.2310.000	Electrolytic solution $c(KNO_3)$ = sat., 250 mL

4.4.7 Miscellaneous

Order no.	*Description*
6.2802.000	Polishing set for crystal membrane electrodes Already included in delivery for Cd^{2+} and Pb^{2+} crys- tal membrane electrodes
6.1236.020 6.1236.050	Sleeve SGJ14/15, PP Sleeve SGJ14/15, PE 

5 Index