USER'S MANUAL – COPPER ION SELECTIVE ELECTRODE ECl-01

Characteristic and usage

The polycrystalline chloride electrode type ECl-01 is designed for direct measurements of activity or concentration of chlorine (Cl^-) ions in aqueous solutions and also in many water-organic mixtures. The measurements may be done in two ways, by direct measurement or using any of the techniques based on the growth of Cl ion concentration in the sample.

This electrode may be specially useful in comprehensive potentiometric titration, used as a indicator of the end point of titration Quite good stability enables using the electrode in different kinds of analysers used for continuous controlling and measuring of Cl^- ions.

The typical applications of the Cl electrode are chloride measurements in industrial sewage, all kinds of water in food products and biological samples etc.

Electrode Reaction

Measuring the chloride ions concentration is based on measuring the difference between the measuring and the reference electrodes, which immersed in the measured or sample solution create a measuring link. Changes in the Cl^- ion concentration in the solution cause changes of the ECl electrode potential what is equal to changes of the electromotive force (EMF) measured by ion or pH meter. The dependence between the Cl electrode potential and the Cl ions concentration usually is
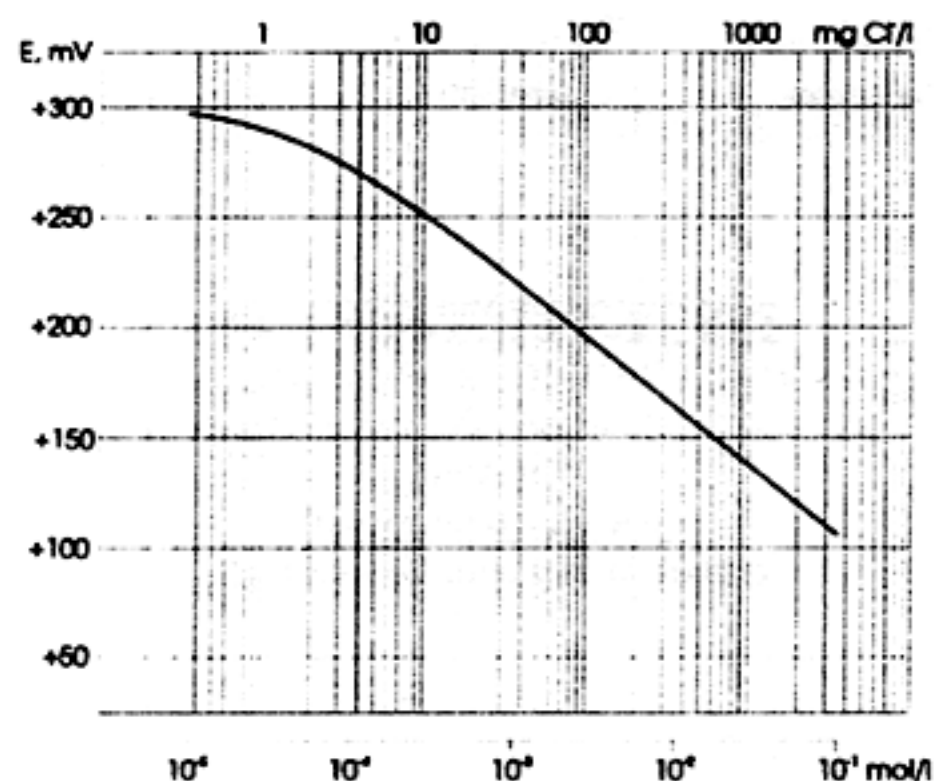
Graph 1. Characteristic of the Chloride electrode type ECl-01.

showed in graphical form called a electrode characteristic curve. Typical characteristic of the Cl electrode, determined on KCl sample solution in relation with RL-100 reference electrode is showed on the graph 1.

To make the changes of the electrode potential proceed according to Nernst's law, it is necessary to stabilise on the equal level the ion strength and the pH level in the sample and measured solutions, it is done by introducing equal portions of electrolyte which is not interfering the electrode work. One may use saturated sodium nitrate solution with addition of acetic acid, which stabilises the pH of solutions on optimal level.

Interference

Important interference may be created by ions which are able to create with the membrane material a difficult to dissolve precipitates, this are S^{2-}, J^-, Br^-, substances which create soluble complex compounds like CN^-, $S_2O_3^{2-}$, NH_3, or reducing substances like for example compounds of photographic developers.

The S^{2-} ions may be removed from the solution by their boiling away from earlier acidified sample and next absorbing the produced hydrogen sulphide in a zinc or cadmium acetate. There is also possibility of direct precipitating in the solution in form of zinc or cadmium sulphide. The cyanides may be bound with use of Cu^{2+} ions into strong complex $[Cu(CN)_4]^{2-}$. The influence of NH_4 may be eliminated by making the measurements in pH range below 7, in which it exists in the NH_4 form.

The reducing substances have to be tentatively oxidised (ex. using HNO_3 or H_2O_2). In case of simultaneous existing bromide and iodide ions in the solution the satisfying results may be obtained by titration of each of this ions and next the chloride ions with use of $AgNO_3$.

In this case it is important to change the chloride electrode to sulphide/silver electrode resistant to contamination with Br^- and J^- ions.

Reference electrode

When choosing the reference electrode it is necessary to take into consideration the conditions and methodology of carrying the measurements. For measurements in laboratory it is advised to use the RL-100 electrode (AgCl) or RL-200 (calomel) equipped with electrolytic bridge. In case of measurements in industrial conditions (ex. in continuous measurements or in samples under increased pressure),it is advised to use reference electrodes RP-100 or RP-200.

Methodology of making the measurements

The described below methodology concerns the measurements in laboratory conditions in range 1 to 1000 mg Cl^-/l.

General notices

a) Before starting the measurements it is necessary to bring the temperature of sample and measured solutions to the surrounding (ex. room) temperature.
b) The sample and measured solutions should have similar pH value and ionic strength.
c) Solutions with high Cl ions concentration, exceeding 1000 mg Cl^-/l (0,028 mol/l) before the measurement should be diluted.
d) Between the measurements the electrodes should be carefully washed in distilled water, it is very important not to bring the contaminants from one sample to another.
e) Before the measurements it is necessary to remove the strongly interfering ions.

Preparing the electrode for the measurements

Few hours before starting the measurements, it is advised to immerse the electrode in the KCl solution with concentration about 0,01M (0,75 g/l) KCl. This conditioning enables obtaining better reaction time and improves electrode potential.

The reference electrodes RL-100 and RL-200 are delivered with the outer chamber filled with saturated KCl solution. When starting work with new RL100 or RL-200 electrode it is necessary to take off a protective ring from it's end, holding the socket unscrew the outer

chamber, pour out the electrolyte (KCl), wash it with deionized water. Fill in the chamber with protective electrolyte, leaving an air bubble (about 1 cm^3) As a protective solution a 1M KNO_3, $NaNO_3$ or saturated K_2SO_4. After filling screw in the chamber into the socket.

Measuring link

a) prepare few solutions which differ one from another in the concentration 10 times. It is done by diluting with deionized water the concentrated sample solution. Next to each 100 ml of the sample solution add 2 ml of ion strength stabilising solution, it should include in 1000 ml 425 g $NaNO_3$ and 29 ml of ice cold acetate acid, next stir it accurately.

b) Connect the chloride and reference electrodes to the meter prepared for mV measurement or to ion meter.

c) Wash the electrodes with deionized water and next immerse them in the sample solutions (stirred) starting with the one with lowest concentration. After placing the electrode in each of the solutions read and write down the value of the EMF electromotive force. Remember about the order of immersing in solutions and washing the electrodes between each measurement.

d) According to gathered data prepare the curve placing on the vertical axis the measured values and on the horizontal one the values of the sample solutions.

Using the concentration curve

a) prepare the measured solution by adding to it the ion strength stabilising solution. Add this same volume of the solution 2 ml / 100 ml of the solution.

b) Connect the electrodes with the mV meter and prepare it for mV measurement or connect it with ion meter.

c) Wash the electrodes with deionized water and place them in the measured solution.

d) After stabilisation read and write down the value.

e) Using the earlier prepared curve read the value of Cl^- ion concentration in the measured sample, which responds to the measured mV value. (Electromotive force)

Maintenance of the electrode

The chloride electrode ECl-01 practically does not require any maintenance, beside protecting the membrane surface against contaminating. Strongly contaminated electrode should be washed in water with detergent (ex. washing up liquid) or with right organic solvent. Membrane contaminated with interfering ions may be regenerated by polishing it with very fine sand paper (600) and next polished with paste made of aluminium oxide placed on felt.

Storing the electrode

During short breaks between the measurement (ex. night) the electrode may be stored in 0,01M KCl or NaCl solution. The electrode **shouldn't** be stored in the deionized water. Different kinds of Ion selective electrodes can't be stored in this same solution, due to risk of contaminating the chloride membrane. During longer breaks between the measurements the electrode should be stored dry ex. in the box delivered by the manufacturer.

During short breaks in measurements the reference electrodes RL-100 and RL-200 should be rather stored unscrewed, placing the inner link in KCl solution and the outer chamber in the protective electrolyte. In case of longer breaks between measurements the outer chamber should be filled with saturated KCl solution and screwed together, the junction should be protected with the rubber ring and whole electrode placed it in the box.

Technical Data

Measuring Range	$5 \times 10^{-5} \div 1$ mol Cl^-/l (pCl$^-$)
	$1.8 \div 35.500$ mg Cl^-/l (ppm Cl^-)
Sensitivity	56 ± 3 mV/pCl$^-$
Acceptable pH range	$2 \div 11$ (direct measurement)
Optimal pH range	$3 \div 7$
Temperature range	$0 \div 80°C$
Membrane resistance	$5 \div 50$ kΩ
Reaction time	$30 \div 60$ s
Selectivity	S^{2-} even trace cause interference
Coefficient	$J^- = 10^{-5}$
	$S_2O_3^{2-} = 80$
	$Br^- = 10$
	$OH^- = 0,03$
Durability	12 months of work in standard laboratory conditions
Dimensions	
- Diameter	12 mm
- Length	120 mm
Cable length	approx. 1 m
Connector	BNC-50