1. Potential of electrodes

1.a. Halide and nitrate ion selective electrodes

The main component of the halide ion selective electrode (ISE) is the membrane from insoluble AgX monocrystalline compound, where X is a halide. The membrane separates two solutions containing the anions X^- of the activities a_1 and a_{X^-}.

Inner solution X^-	membrane	Outer solution X^-
(a_1)	AgX	(a_{X^-})

The membrane potential E_M is given by relationship:

$$E_M = C + \frac{RT}{nF} ln \frac{a_1}{a_{X^-}} = C + \frac{2{,}303\,RT}{nF}\log a_1 - \frac{2{,}303\,RT}{nF}\log a_{X^-} \qquad (1.1.)$$

where $n = 1$ is the number of transmitted electrons, C is electrode constant. The symbols R, T, F have the usual meaning. The halide activity a_1 of the inner solution is determined by the electrode filling solution and it is constant in contrary to outer halide activity a_{X^-}. Both activities can be replaced by the molarities of the anions at low concentrations *(<0.01M*).

The theoretical dependence of the electrode membrane potential of is linear function of $\log a_{X^-}$ in the outer solution (eqn (1.1.). The slope of the dependence is:

$$\frac{dE_M}{d(\log a_{X^-})} = -2{,}303\, {}^{RT}\!/_{F} = -0{,}059V \qquad (1.2.)$$

This value is called Nernst's electrode response. The response is *-59mV* at standard (*25°C)* and ideal conditions. The real response may deviate for real electrode. The **Figure 1** shows the dependence of the electromotive voltage (EMV) of a cell composed of a chloride ISE and a reference calomel electrode that are immersed in a solution of KCl.

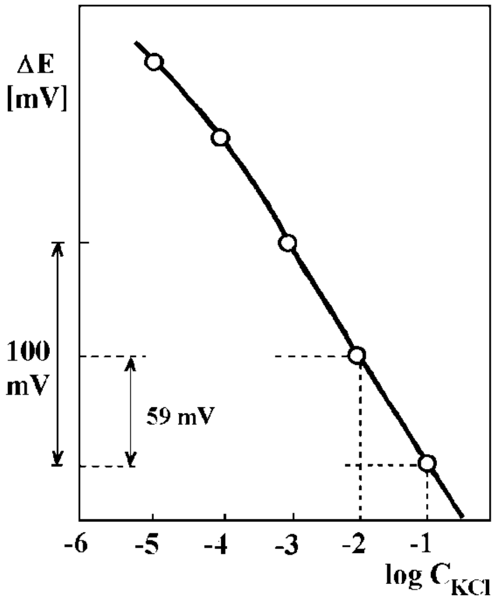

Figure 1: Calibration curve ($\log a_{X^-} = \log c_{Cl^-} = \log c_{KCl}$) of chloride ISE in electrochemical cell with a reference electrode.

The constant inner activity of the chlorides can be achieved by submerging the silver wire coated with *AgCl* in water. The solubility product constant of the *AgCl* is $P_{AgCl} = a_{Ag^+} \cdot a_{Cl^-} = 10^{-10}$ at *25°C.* It means that $a_1 = a_{Cl^-} = a_{Ag^+} = 10^{-5}$ if the ideal solution exists and other ions are not present. The disadvantage of this design is that the membrane response error occurred if low chloride concentrations (see **Figure 1**) is measured in outer solution because chloride ions are transported across the membrane from the inner to the outer solution. This disadvantage can be removed if the inner solution is $0.1M\ KCl$ thus $a_1 = a_{Cl^-} = 10^{-9}$, the value C in eqn (1.1.) changes to $C^{`}$ (but remains constant) and the potential of chloride ISE is given by relationship:

$$E_{Cl} = C^{`} - \frac{2{,}303\ RT}{F}\log a_{Cl^-} \qquad (1.3.)$$

The presence of the other halogens (iodides, bromides) dissolved in the outer solution disrupts selectivity of the chloride ISE:

$$E_{Cl} = C^{`} - \frac{2{,}303\ RT}{F}\log(a_{Cl^-} + K_{Br}a_{Br^-} + K_I a_{I^-}) \qquad (1.4.)$$

where $K_{Br} = P_{AgCl}/P_{AgBr}$ (or $K_I = P_{AgCl}/P_{AgI}$) is the selectivity ratio of Br^- (or I^-) anion for the chloride ISE.

The chloride ISE will be damaged if the relationship $a_{Br^-} > a_{Cl^-}(P_{AgBr}/P_{AgCl})$ (or $a_{I^-} > a_{Cl^-}(P_{AgI}/P_{AgCl})$) valid because $AgBr$ (or AgI) deposes on the surface of the $AgCl$ membrane. The electrode behave as bromide (or iodide) ISE after that event. Therefore, the measurement of the chloride concentration using chloride ISE in iodide (bromide) solutions is avoided. On the other hand, iodide ISE can be used to measure chloride and bromide concentrations because the electrode is completely regenerated after consequent measurement in the iodide solution.

Measurement with halide ISEs and their properties. The halide membrane electrodes are mainly used for so-called direct potentiometry, whereby the concentration of halides is obtained from the measured EMN. The cell is made up of a membrane ISE and a reference electrode. The concentration is determined from the knowledge of the calibration curve in **Figure 1**. All silver halide membrane ISEs react to halide anions as well as loose silver cations with Nernst response, thus the least soluble Ag_2S membrane ISE is preferable for silver determination. The potentiometric measurements with halide ISEs disrupt both anions forming less soluble silver salt than membrane material (eg S^{2-}), and anions forming soluble silver complexes (CN^-, SCN^-). Reducing agents cancel the halide measurement if they reduce AgX to Ag (see principle of chemical photography).

Halide ISEs have a large internal resistance (similar to a glass electrode), their potential in the solution stabilizes within 3 to 6 minutes. As a reference, we use a calomel electrode and we connect the calomel electrode to the measured solution using a salt bridge filled by KNO_3 solution. The EMV of the cell can be measured with a pH or Ion meter. Typically, the combined ISEs are used. The combined ISE includes membrane ISE, salt bridge and reference electrode in one sensor. The halide ISEs used to be stored in *KX* electrolyte (chloride in saturated KCl), if we do not measure.

Nitrate ISE. The inner solution of this electrode forms a solution of *[tris-(1,10-phenanthroline)]nickel(II) nitrate* in *2,4-dinitrophenyl n-octyl ether* solvent. The membrane is made polyvinyl chloride (*PVC*). Determination of nitrate ions is disrupted by ions: $\mathrm{ClO^{4-}}$, $\mathrm{ClO^{3-}}$ and $\mathrm{I^-}$. The reference electrode is the calomel electrode without the salt bridge with KNO_3. The nitrate ISE used to be stored in $5\cdot10^{-2}M\ KNO_3$.

TASK: Measure the calibration curve of the combined nitrate membrane ion selective electrode. Determine the NO_3^- concentration in an unknown sample (drinking water, beverages, milk, etc.). Determine the Nernst's response of the used electrode in linear section of the calibration graph and compare it with the theoretical response.

8.a-b

úloha

Laboratory aids and chemicals: combined ISE, Ion meter capable of mV readings, *2* beakers *(100 cm^3)*, scale pipettes (*25, 10* and *5 cm^3*), *9* volumetric flasks *(50 cm^3)*, storage solution, NO_3^- stock solutions: *1M; 0.1M; 0.05M; 0,01M; 10^{-3}M* a *10^{-4}M.* Sample (drinking water).

Instructions: Get acquainted with the use of the pH meter in mode mV reading. Assemble, if needed, the electrochemical cell: ISE | measured solution | salt bridge | reference solution | reference electrode. Combined ISE cell is assembled from the manufacturer so that then can be immersed directly in the measured solution.

1. **Preparation of standard solutions.** Using a stock NO_3^- solutions, prepare calibration solutions in volumetric flasks with the following concentrations: *$1\cdot10^{-2}$; $5\cdot10^{-3}$; $2.5\cdot10^{-3}$; $1\cdot10^{-3}$; $5\cdot10^{-4}$; $2.5\cdot10^{-4}$; $1\cdot10^{-4}$; $5\cdot10^{-5}$; $1\cdot10^{-5}$M.*
2. **Preparation of combined electrode.** Clean the electrode with distilled water and place it in a Teflon crucible with distilled water. Insert the stirrer. Switch the instrument and mix on. Pour out the water after about 2 minutes of mixing. Repeat the cleaning several times until the EMV ranges in interval ± 10mV.
3. **Calibration.** Pour the weakest calibration solution into a dry Teflon crucible. Mix about *3 min*, switch the stirrer out, note the ENV of the electrode in *mV*. Measure other calibration solutions in the same way, from the weakest to the more concentrated.
4. **Sample measurement.** Prepare the electrode according to point **2**. Measure the EMV of the cell with the sample. Determine an unknown concentration of NO_3^- using calibration graph.

Report: Tabule 1: for each standard solution: NO_3^- concentration c, $log(c)$, EMV. **Calibration graph 1:** dependence of the *EMV* on *log(c)*. **Next:** EMV of the sample and its concentration in (*mg* of NO_3^-*)*/dm^{-3} unit. Experimental Nernst's response of the used electrode.