

## 16. Quantitative volumetric analysis with conductometric detection of the end point

**Conductometry** is an electroanalytical method involving the measurement of electrolytic conductivity which value changes with the change of the concentration of ions in solution. Electrolytic conductivity of the solution is due to an electric charge transfer by cations (positive ions) and anions (negative ions) under the influence of an external electric field. The migration of ions under the influence of the electric field depends on several factors:

- ion mobility - limited by the size and charge of ions and solvent type,
- temperature - has a major influence on the viscosity of the solution, and therefore the mobility of the ions. When the temperature increases the viscosity of the solution decreases and the conductivity increases. Also the dissociation constants depend on the temperature. Therefore, the measurement should be carried out at a constant temperature or changes in temperature should be compensated taking into account the so-called temperature coefficients,
- concentration of the electrolyte - in solution of low concentration the increase of conductivity is the result of the increase in ion concentration. In electrolyte solution of high concentration the conductivity initially increases with increasing concentration and then decreases (Fig. 1),
- the presence of other ions.

Conductometer measures the so-called **specific conductivity** ( $S \cdot \text{cm}^{-1}$  or  $\Omega^{-1} \cdot \text{cm}^{-1}$ ), which is given by:

$$\kappa = l/Rs$$

where:  $l$  - is the distance between the electrodes [m],  $s$  - electrodes surface [ $\text{m}^2$ ],  $R$  - resistance of the conductor (solution) [ $\Omega$ ].

The unit of conductivity is the Siemens,  $S = \Omega^{-1}$ . The ratio  $l / S$  [ $\text{cm}^{-1}$ ], is denoted as  $k$  and called **electrolytic cell constant**.

**Conductometric titration** is based on the observation of changes in conductivity of the solution titrated. These changes result from the conversion of a specific ion mobility, the mobility of ions other than the ions originally present in the solution. The end point of the titration is determined from the break point in the system plotted  $\kappa = f(V_{\text{titrant}})$ .

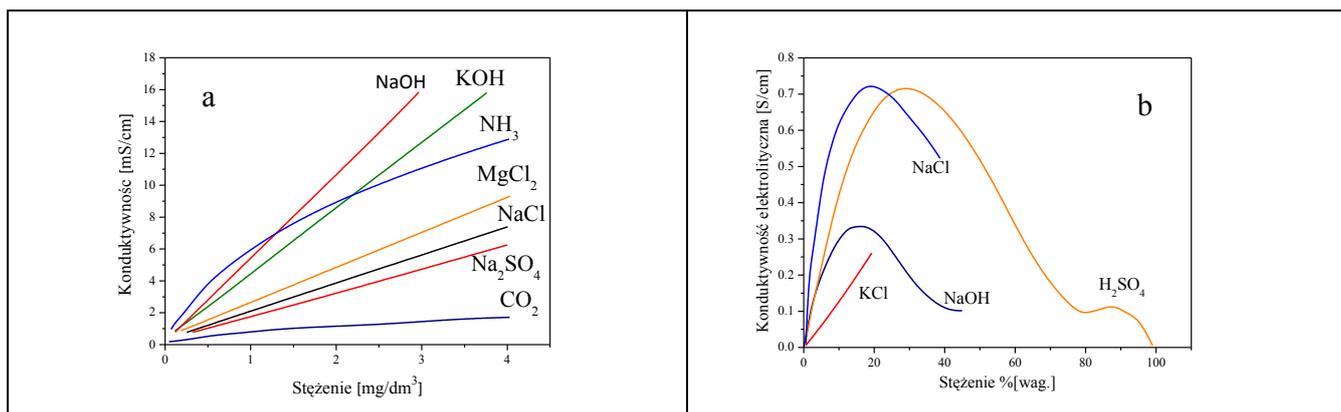


Fig. 1. The dependence of conductivity on the concentration of electrolytes in aqueous solutions (a) dilute, (b) concentrated.

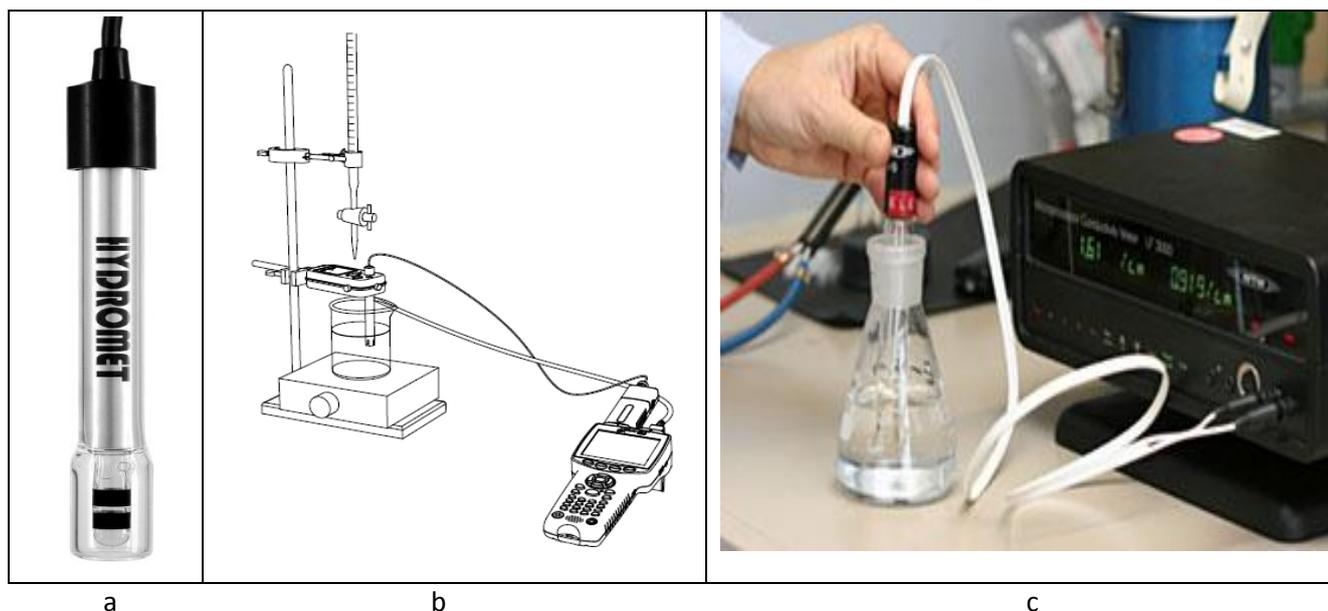


Fig. 2. (a) The conductometric sensor for measurement of electric conductivity of an aqueous solution (electrolyte) in laboratory conditions. The sensor electrodes are made of platinum coated with platinum black to reduce polarization phenomena occurring in the samples with high conductivity<sup>1</sup>, (b) a typical set of conductometric titration, (c) The conductometric sensor during operation<sup>2</sup>.

The aim of this analysis is quantitative volumetric analysis by conductometric titration.

#### Chemicals and apparatus

- standard solutions of NaOH (0.1 M) and NH<sub>4</sub>NCS (0.05 M)
- solid (dried) NaCl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> for preparation titrants by weighing
- conductometer with sensor
- conductometric vessel
- magnetic stirrer with magnetic stir bar
- 500 cm<sup>3</sup> volumetric flask; 50 cm<sup>3</sup> burette

#### PROCEDURE

1. Dilute the obtained (unknown) solution in the conductometric vessel to ca. 40 cm<sup>3</sup>
2. Place the conductometric vessel on a magnetic stirrer, put in the magnetic stirring bar. Close the vessel using Teflon cover.
3. Immerse the conductometric sensor in the solution and install the burette with respective titrant.
4. Read the conductivity (stirring is off).
5. Add 1 cm<sup>3</sup> of titrant from a burette, stir for ca. 30 sec after each addition. Read the conductivity ( $\kappa_R$ ) (stirring off). Repeat this point until the end of experiment.
6. Titration should be finished when at least 40 ml of titrant was added.
7. The results of the titration collect in the table, listing the volumes of added titrant (cm<sup>3</sup>) and the corresponding conductivity values.
8. Turn off conductometer, rinse and protect the conductometric sensor and the magnetic bar, wash the burette and glassware used.

<sup>1</sup> <http://www.hydromet.com.pl>

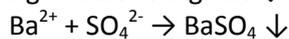
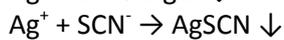
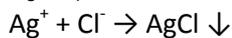
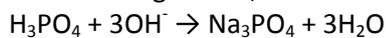
<sup>2</sup> <http://www.clas.clariant.com>

## CALCULATIONS AND REPORT

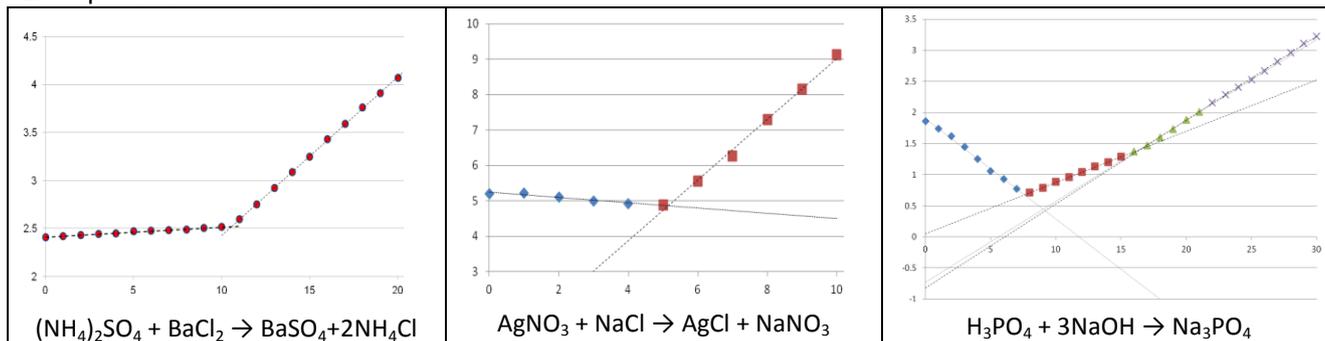
1. Calculate the correction in accordance with the formula  $p = (V_1 + V_2) / V_1$   
where:  
 $p$  - the correction to change of the volume;  
 $V_1$  - volume of solution before titration;  
 $V_2$  - volume of the titration reagent added.
2. Calculate the corrected conductivity value ( $\kappa_c$ ) from the formula  $\kappa_c = \kappa_R \cdot p$
3. Draw the conductometric titration curves for each titration in the system  $\kappa_c = f(V_{\text{titrant}})$ .
4. Determine graphically the end-point of each titration.
5. Calculate the mass of analyte in obtained solution.

$V_{\text{titrant}} [\text{cm}^3]$	Read conductivity ( $\kappa_R$ )	Correction ( $p$ )	Corrected value of conductivity ( $\kappa_c$ )

**Note:** among others, students may perform analyses based on reactions



Examples of titration curves:



Sources:

Cygański A.: „Metody elektroanalityczne”, Wyd. 2, Warszawa, WNT 1995, rozdz. 2.1, 2.2, 2.3, 2.6.