Chapter 1

Introduction

The knowledge of phenomena that take place in automatic controlled plants is very important[1]. Almost all of the automatic controlled systems possess therefore at least one sensor[2], which transforms a non-electrical quantity to an electrical one. Very often such a sensor may be a very simple one; however, its accuracy is not good in this situation. To improve the feature, specialized converters are added, very often supported by a microprocessor-based unit. The microprocessor is needed because the complexity of the mathematical model of physico-chemical phenomena grows with increasing accuracy which is required.

Nowadays, electronic devices (such as measuring amplifiers, analogue to digital converters, microprocessor systems) are still very rapidly developed. On the other hand, progress in physico-chemical sciences allows for the application of the better mathematical models. As a consequence, it leads to an enhancement of the measurement quality.

Potentiometry is the field of the electro-analytical chemistry in which potential is measured under the conditions of no current flow[3]. It is based on the electrical signal arising between two electrodes immersed in a sample solution created a galvanic cell[4] (Figure 1.1). First of these electrodes is an ion-selective electrode (ISE), which is the measuring electrode; the second one is a reference electrode [2, 48]. The measured potential may then be used to determine the analytical quantity of interest, *i.e.* the concentration of some component of an analysed solution[3]. The potential of the ISE against the reference electrode changes *vs.* ion activity in the sample solution. Observation of the potential changes between both electrodes is an essence of potentiometry, which is a very simple and useful electro-analytical method [66].

The output value of the ISE is potential, which is described by using the phase boundary potential model [4, 67]. It has the following arguments: ion activities in the probe, potentiometric selectivity coefficients, temperature and cell constant (Chap. 2.3.1). Ion activity is a theoretical quantity, directly immeasurable, related by the activity coefficient to molality.

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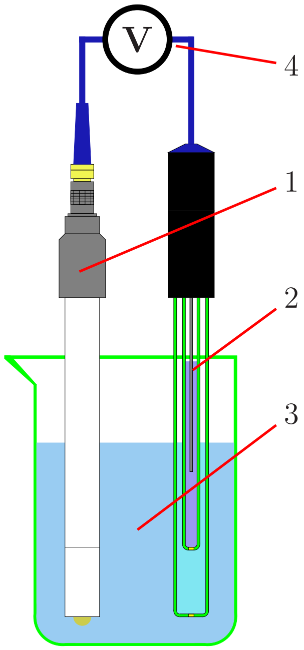
[1] `http://www.professionalpasta.it/dir_3/3_techno/3_dry_/chap_5_1.htm`

[2] Hong Kong IGDS 2000, Industrial Control, `http://www.ee.polyu.edu.hk/staff/eencheun/WebSubject2/chapter0.htm`

[3] `http://www.chemistry.adelaide.edu.au/external/soc-rel/content/potentio.htm`

[4] `http://www.dekker.com/servlet/product/DOI/101081EEPT120003778`



1. Ion-selective electrode
2. Reference electrode
3. Sample of interest
4. Voltmeter

Figure 1.1 The simplest measuring system with an ion-selective electrode.

The molality determines an amount of dissolved component in the given mass of solvent. The next physical quantity is molarity, related to molality by density of solution and atom masses of used components. The electric potential of measuring electrode is measured with respect to a reference electrode. In turn, the potential of the reference electrode should be unchanged against the solution potential. Due to existing liquid-junction potential (on the junction), the value of which is a function of concentrations of electrolytes in both sides of the junction, the potential of the reference electrode is not constant.

In practice, simplifications occur very often. The potential of the measuring electrode is described with the use of the Nikolsky–Eisenman or Nernst equation. Activity coefficient, which should be characterised by very complex Pitzer model [75] or mean spherical approximation (MSA) [96], is very often simplified to another models or even equate to unity. Also frequently, there is no conversion between molarity and molality and the liquid-junction potential is omitted. As a consequence, these simplifications lead to errors, which values are dependent on the used measuring range. The total concentration of given species is sometimes directly measured by using ISEs. It is a wrong approach because by using ISEs only an activity of dissociated ions (not chemically bonded) are measured.

In the multi-component potentiometric analyses, values of concentrations of many ions are determined by using several ISEs simultaneously and performing only one ion-selective measurement. Due to limited membrane selectivity, the potential of ISE (sensitive to a particular ion) is determined not only by the activity of this ion (primary ion) but also by activities of another ions (interfering ions) that are present in the solution. If the analysed quantity is not activity but concentration of given ion then the matrix effect caused by other species is even more visible. It occurs because both activity coefficient of determined ion as well as density of the solution depend on all components present in the solution. Due to complicated mathematical models of the phenomena describing the quantities, the very complex mathematical transformations are required to determine the ion concentration, so very often the only way is a numerical approximation of coefficients that describe these models.

One of the most important operations is determination of calibration parameters of the electrodes. The operation is divided into two steps: 1) conducting the calibration experiments; 2) determining the parameters based on performed measurements. The first step can be expensive due to a large number of measurements (particularly in the measurements made by using several ISEs) and consumption of the chemical reagents. For this reason, the proper preparation of the experiments and measurement methodology is very important. The second step is mathematically complex and more attention should be paid to the errors, which may appear during the numerical approximations of the parameters. Almost always the measuring range, in which the measurements are performed, is known. It is very important because the calibration process is dependent on the range – the calibration points and the measuring points should be possibly close each other.

The last but not the least important is the measurement uncertainty. It is a parameter that characterizes the dispersion of measuring results. The parameter should be attributed to the measurand, *i.e.* concentration, mass, potential or a selectivity coefficient [36].

The title of the dissertation is: "Characterisation of Measurement Errors Caused by Model Simplifications of Physico-Chemical Phenomena in Multi-Component Potentiometric Analysis". It means that the subjects of the work are:

(1) multi-component potentiometric analysis,
(2) models of physico-chemical phenomena having place in the analysis,
(3) mathematical simplifications of the phenomena and
(4) measurement errors arising from the simplifications.

Above written subjects have already been briefly described. In the place, therefore, the thesis can be stated.

The goal of the thesis is to verify the validity of the following statement:

"It is possible to establish the required accuracy of the determination of values of coefficients that describe influences of interfering matrix in the potentiometric multi-component measurement,

depending on the applied measuring range and on the assumed measurement uncertainty.”

It will be impossible to analyse all possible cases during the work. Therefore some assumptions/limitations will be made:

(1) Each measurement is made in the steady state and is characterised by a given uncertainty.

Due to the dynamics features, the value of an ISE’s potential does not change immediately after the change of ion activity. The potential gradually achieves the exact value. It is assumed in the dissertation that the measurement is made when the potential changes within the range described by the uncertainty.

(2) Each measurement is made at constant temperature.

Temperature influences on many electrochemical phenomena, therefore parameters describe electrodes are temperature-dependent. Analysis of the influences is very broad task. In the literature, the value of many parameters are commonly determined at 25°C. In the dissertation, also the same temperature is chosen.

(3) All electrolytes are totally dissociated.

Using ion-selective electrodes it is only possible to measure activities of dissociated ions. If the electrolyte is not totally dissociated then the ratio of free to total species concentration should be used to combine activities with concentrations and then the mathematical descriptions become more complex.

(4) The pH of probes equals to 7.

At 25°C the neutral pH is 7. At this pH the H^+/OH^- equilibrium is achieved. For common strong electrolytes, such as NaCl and KCl, the ratio of free to total species concentration is near 1.

In this thesis, the following four main contributions will be made:

(1) automation of the calibration process of ISEs in order to reduce the costs of the operation;
(2) elaboration of an algorithm that approximates the calibration parameters, has negligible numerical errors and allows for determination of the ISE’s model parameters;
(3) determination of the useful range of an ISE in which the measurement uncertainties are assumed;
(4) determination of values of additional errors arising from the simplification of the physico-chemical models.

The outlook of the dissertation is as follows: The most important information concerning the chemical sensors, especially the ion-selective electrodes, their applications, advantages and types, information concerning the definitions of the electrochemical quantities, models of physico-chemical phenomena that have placed during multi-component potentiometric analysis, the calibration methods of ISEs as well as the uncertainty and error evaluation will be presented in Chap. 2. Basing on the knowledge, there are placed in Chap. 3 all descriptions, derivations, results and discussions of works made by the content author and connected with the thesis. There are nine chapters describing different problems. Each chapter ends with summary. General conclusions are placed in Chap. 4. Manufacture's data and a project of a divice are placed in appendixes.

In order to avoid unreadable charts, descriptions of thesi coordinate axes will not be placed in most cases on the figures but below ones.