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A PRACTICAL APPROACH TO ION SELECTIVE ELECTRODES PERFORMANCE IN STATIC AND DYNAMIC CONDITIONS

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Abstract – The paper presents a practical approach to ion selective electrodes (ISE). The behaviour of Pb^{+2} ISE (ELIT8231) and Cd^{+2} ISE (ELIT8241) for pure (only Cd^{+2} or Pb^{+2}) and mixed solutions (Cd^{+2} and Pb^{+2}) in static and dynamic conditions is studied. The pH variation of ISE test solution is considered in order to perform the pH correction of the ISE potentiometric selectivity coefficient determined under static conditions using a neural network processing structure. The dynamic test is performed in order to evaluate sensor's transient response and time constant as well as ion interference and pH influence on sensor's output. The experimental set-up is expressed by a multisensor virtual measurement system that acquires the voltage of the sensor channels, controls the ISE dynamic test and performs the data processing using a software implemented in LabVIEW.

Keywords: ion selective electrodes, virtual instrument, neural processing

1. INTRODUCTION

Ion-selective electrodes (ISE) are analytical tools that allow the determination of a large number of ions concentrations in a wide range [1]. These sensors, mostly of the solid-state type, find wide application in medical, environmental and industrial analysis. Examples of such solid state ISEs are the NASICON membranes sensors [2] and the PVC membrane sensors [3]. Two of the main characteristics of ISEs are the extremely high output impedance (1-100M Ω) and limited selectivity expressed by the fact that ISE often exhibit a response to other ions. The degree of ISE selectivity is expressed by the potentiometric selectivity coefficient ($K_{A,B}^{pot}$) [4] that depends on primary and interference ions concentrations and on pH and temperature.

This paper presents the measuring system and static and dynamic experimental results obtained for Cd^{+2} and Pb^{+2} ISEs under different temperature, pH and ion concentrations.

2. ISE STATIC AND DYNAMIC CHARACTERISATION SYSTEM

The ISE experimental set-up (Fig. 1) comprises a sensor block, a conditioning block, a pump block and an

acquisition block. The sensor block includes one of two ISEs associated with Cd^{+2} and Pb^{+2} ion concentration measurement, a pH sensor (ISI11) and a ON401 thermistor temperature sensor. The conditioning block (CB) includes two high input impedance operational amplifiers (MAX 419) that avoid the ISE and pH sensor polarization due to the current, four programmable gain instrumentation amplifier (AD524) and the thermistor conditioning circuit based on a LM324. Sensor channels are connected to a PC plug-in 12bit data acquisition board (PCI-MIO-16E-4).

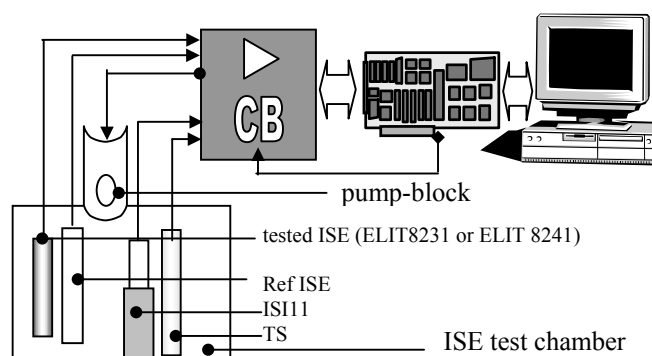


Fig. 1. Experimental set-up for ISE static and dynamic characterisation

The dynamic characterisation of ISE is based on a pump-based system that assures the injection of the test solution in the ISE test chamber [4].

3. ISE STATIC CHARACTERISATION

This paragraph refers to ISE selectivity characterisation in static conditions. For that purpose different concentration of the primary ions and pH variation of the tested solutions are considered. The delivered data for the studied ISEs is acquired and processed by a virtual system using a LabVIEW developed program.

3.1. Selectivity -static characterisation

For cadmium ISE static characterisation, ISE channel signals are acquired for different calibration conditions: concentration of $C_{Cd^{+2}} \in [0.14; 10]$ ppm; concentration of $C_{Pb^{+2}} \in [0.14; 10]$ ppm; $pH \in [5; 9]$. Firstly are measured the ISE delivered voltages for ion pure solution and for different values of pH. Adding interfering Pb^{+2} ions, the sensor

response follows the Nicolsky Einsman equation:

$$E = E_0 + \frac{2.3 \cdot R \cdot T}{z_A \cdot F} \cdot \log \left(a_A + K_{A,B}^{pot} \cdot a_B \frac{z_A}{z_B} \right) \quad (1)$$

which includes the potentiometric selectivity coefficient $K_{A,B}^{pot}$ that will be determined using the two mixed solution method [5]. In (1), $E-E_0$ represents the electrode voltage response, a_A and a_B represent the activity values for primary and interfering ion, T is the absolute temperature, z_A and z_B are the charges of primary and interfering ions and R and F are, respectively, the gas and the Coulomb constants. Thus, for the Cd^{+2} ISE, the acquired voltages for Cd^{+2} pure solution (without Pb^{+2}) and Cd^{+2} and Pb^{+2} mixed solution are used to obtain the $K_{Cd,Pb}^{pot}$ using the following relation:

$$K_{A,B}^{pot} = a_A \left(e^{\frac{\Delta E}{R \cdot T} \cdot z_A \cdot F} - 1 \right) / a_B \frac{z_A}{z_B}$$

$$\Delta E = E_{A+B} - E_A \quad (2)$$

where A is related to the primary ion pure solution (Cd^{+2} only) and B concerns the mixed solution of primary and interfering ions (Cd^{+2} and Pb^{+2}). Interchanging the meanings of A and B, and using the appropriated values, relation (2) can be used to determined the static (30 minutes stabilisation) potentiometric selectivity coefficients for ELIT8231 and ELIT8241. pH values of the used solution are also taken into account. Results for ELIT8231 static selectivity are shown in Fig. 2.

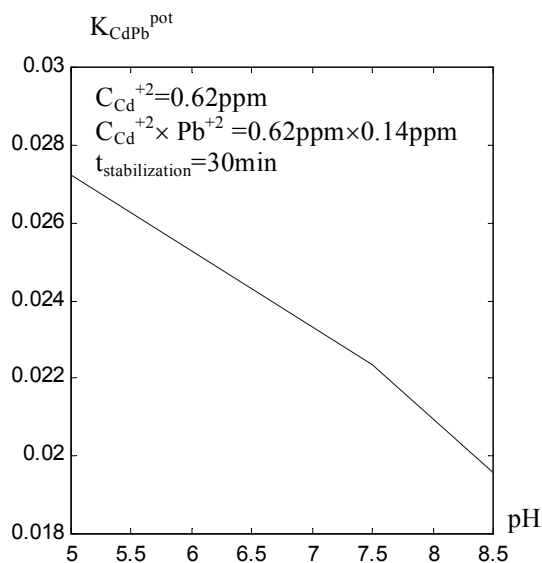


Fig. 2. The evolution of $K_{Cd,Pb}^{pot}$ for Cd ISE for different values of pH

Analysing Fig. 2 it can be underlined that the potentiometric selectivity coefficient is strongly dependent on pH. Thus, for a variation of pH between 5 and 8.5 the $K_{Cd,ISE}^{pot}$ varies some 40%. Similar results are obtained for Pb^{+2} ISE case. Taking into account the above-mentioned results, a pH correction structure of the ISE static selectivity is proposed.

3.2. pH correction structure

In order to perform the pH correction of the static selectivity, a two inputs - one output MLP neural network

(MLP-NN) is designed and implemented [6]. The MLP-NN inputs are $K_{A,B}$ calculated using the relation (2) and the value of the pH measured with the pH sensor. The network output is the potentiometric selectivity coefficient for $pH=7$.

4. DYNAMIC CHARACTERISATION

For ISE dynamic characterisation, a set of pure and mixed solutions are considered in order to obtain the following ISE characteristics:

- response time and transient response,
- drift,
- reproductibility

4.1. ISE-Response time and transient response

We use the definition of ISE response time as the length of time that elapses between the instant at which the considered ISE (Cd^{+2} ISE and Pb^{+2} ISE) and the reference electrode are brought into contact with the sample solution (Cd^{+2} or Pb^{+2} pure solutions or Cd^{+2} and Pb^{+2} mixed solutions) and the first instant at which the slope of the delivered voltage ($E-E_0$) against time becomes equal to 0.1 mV/min.

In order to obtain the ISE response time the sensors were preconditioned. Thus for ELIT8241 was used the cadmium standard solution, traceable to SRM from NIST ($Cd(NO_3)_2$ in HNO_3 2 mol/l) 1000mg/l \approx 1000 ppm Cd^{+2} while for ELIT8231 was used the lead standard solution, traceable to SRM from NIST ($Pb(NO_3)_2$ in HNO_3 2mol/l) 1000mg/l \approx 1000 ppm Pb^{+2} . The preconditioning time was 72 h.

For ISE response time experiment, pH and temperature experimental settings were $pH=5$ and $T=25^\circ C$. These values were measured within the experiment time interval ($t \in [0,10]$ min) using the pH and temperature measurement channels.

The ISE response times of pure solutions of Cd^{+2} and Pb^{+2} were determined. The used ion concentrations and the response time values are presented in Table I.

Table I – Cd^{+2} and Pb^{+2} ISE response time

Ion	ion concentration [ppm]	Response time [min]
Cd⁺²	5	2
	7	3
	9	3
	10	4
	100	5
Pb⁺²	5	3
	7	3
	9	4
	10	4
	100	5

Analysing Table I, it can be underlined that ISEs response times depend on ion concentration and is less than 10 min for concentration included in the interval 0-100ppm.

The ISE transient response was obtained using the acquisition capabilities of the ISE characterisation system and the acquisition software developed in LabVIEW. As an

example it is presented in Fig. 3 the Cd⁺² ISE transient response for C_{Cd⁺²}=7ppm.

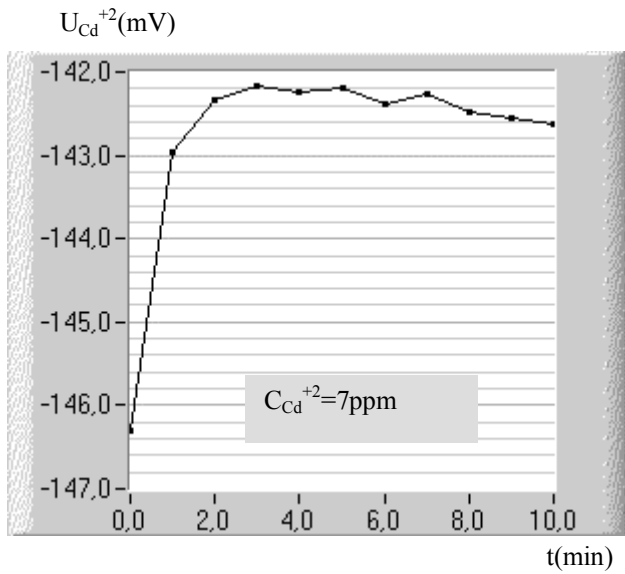


Fig. 3. Cd⁺² ISE transient response

For the lower concentration near the ISE detection level (0.1 ppm for ELIT8253 and ELIT8243) the ISE transient behaviour is the one shown in Fig. 4.

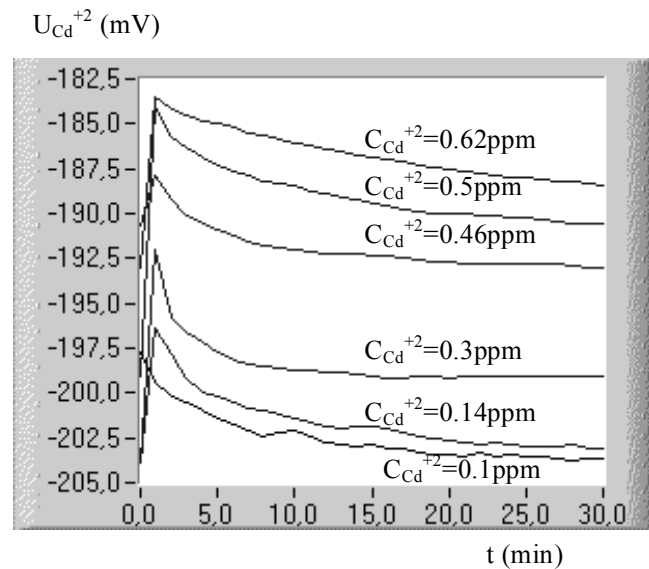


Fig. 4. The U_{Cd⁺²} versus time evolution for low values of Cd⁺² concentration and for pH=5.2 and T=22.5°C

The presence of the interference ions (Pb⁺² ions) in the Cd⁺² ISE testing solution or vice-versa implies the modification of Cd⁺² ISE transient response. Fig. 5 shows results obtained for the transient response of Cd⁺² ISE. The fact that different curves are obtained for different values of the interference ion (Pb⁺²) reveals poor selectivity of the Cd⁺² ISE.

In what the response time (τ_{ISE}) is concerned, no strong dependence on interfering ion concentration was detected,

τ_{ISE} being included in the [3 ;5] min time interval. The τ_{ISE} was determined based on LabVIEW derivative function. A graphical representation of $\frac{dU_{Cd^{+2}}}{dt}$ represents an easier way to express the τ_{ISE} evolution (Fig. 6).

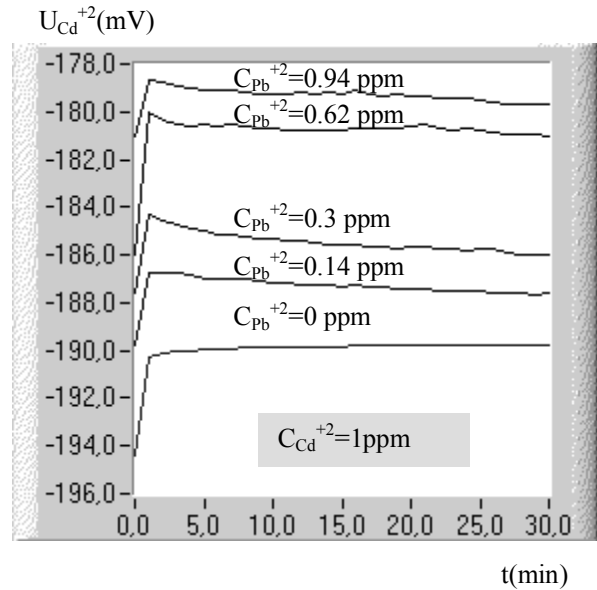


Fig. 5. The U_{Cd⁺²} versus time evolution for low value of Cd⁺² concentration and Pb⁺² interfering ions. Experimental conditions: pH=8.5, T=26.7°C

$$\left(\frac{dU_{Cd^{+2}}}{dt}\right) \leq 0.1 \text{ mV/min}$$

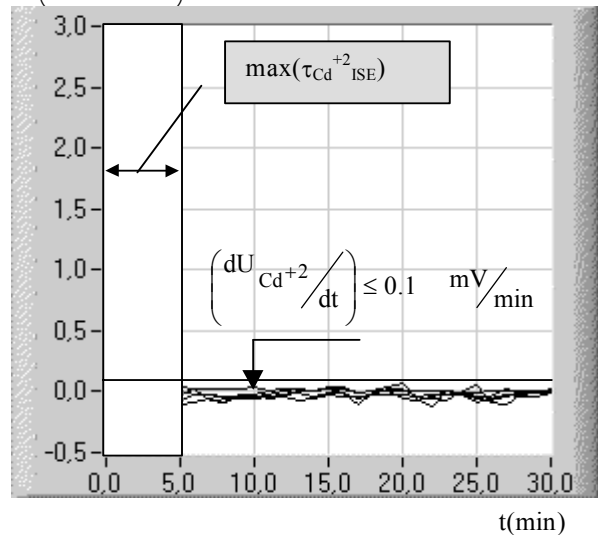


Fig. 6. The derivative U_{Cd⁺²} versus time evolution for low concentrations of Cd⁺² primary ions and Pb⁺² interfering ions

In Fig. 6 one can observe that the Cd⁺² ISE response time is less than 5 min, value that characterises the studied ISE for pure solutions (Table I).

Graphs of Figs 4 and 5 show change with time in the ISE potential difference (U_{Cd⁺²}) and different values of difference for initial potential difference U_{Cd⁺²} or U_{Pb⁺²} that corresponds to unionised cleaning water. Such observations justify attention to ISEs drift and reproducibility.

4.2. ISE-drift

The ISE drift is defined as the slow non-random change with time in the potential difference of the ion-selective reference electrode cell containing a solution of constant composition and temperature [7].

The determination of drift was made for Cd⁺² and Pb⁺² ISE for a 20 min time period and for different constant concentrations of the measured ions. The used ISE drift formula is []:

$$d_{ISE} = \frac{\sum_i (t_i - \bar{t}) \cdot (U_{ISE_i} - \overline{U_{ISE}})}{\sum_i (t_i - \bar{t})^2} \Big|_{t_i \geq \tau_{ISE}} \quad (3)$$

where t_i represents the instant time, \bar{t} the time average, $\overline{U_{ISE}}$ the average of ISE channel acquired voltage for $t_i \geq \tau_{ISE}$ (τ_{ISE} - response time). The drift evolution for Cd⁺² and Pb⁺² ISEs for mixed solutions is presented in Fig. 7.

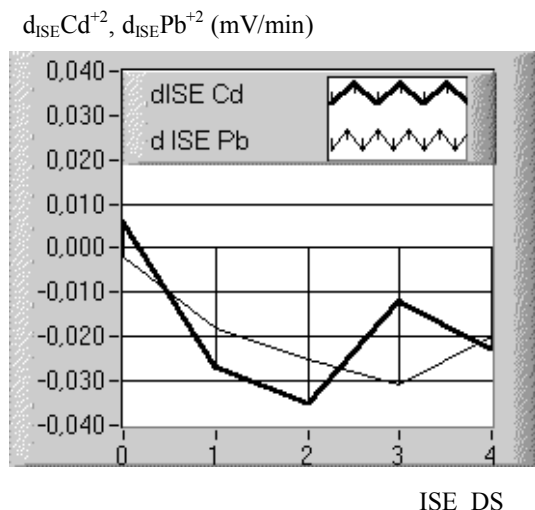


Fig. 7. The evolution of Cd⁺² and Pb⁺² ISE drift

In Fig. 7 each ISE_DS value identifies a set of values used for drift determination for above mentioned heavy metal sensors. The C_{Cd⁺²} and C_{Pb⁺²} of ISE DS are presented in Table II.

As it is presented in Fig.7 the maximum drift levels are comparable for Cd⁺² and Pb⁺² and did not give information about the influence of interfering ions.

Table II -Values of drift test set

ISE drift test	ISE_DS	C _{Cd⁺²} (ppm)	C _{Pb⁺²} (ppm)
Cd ⁺² ISE	0	1	0.00
	1	1	0.14
	2	1	0.30
	3	1	0.62
	4	1	0.94
Pb ⁺² ISE	0	0.00	1
	1	0.14	1
	2	0.30	1
	3	0.62	1
	4	0.94	1

4.3. ISE-reproducibility

Cd⁺² and Pb⁺² ISE response curves obtained for pure and mixed solutions underline the electrodes memory effect (EME). The EME occurs if, after the concentration has been changed and restored to its original value, a different value of potential difference is observed. The reproducibility of the electrode will consequently be poor. Thus, in ISE based measurements a systematic error component caused by EME occurs. The value of the error depends on the difference between the current ion concentration and the concentration of the solution in which the electrode was previously immersed [8]. In order to diminish this effect, a cleaning procedure is implemented. The main steps of that procedure are:

- ISE rinsing - the electrodes are rinsed by spraying with a jet of deionised water,
- ISE soaking - the electrodes are soaked in deionised water for 1 min (and then dried to prevent dilution of sample) before every measurement.

The cleaning procedure is implemented using the pump-block associated with the ISE test chamber. Electrodes drying can be performed automatically using heated air jet generated by an additional ventilator.

Several results that present the electrode reproducibility are presented in Fig. 8.

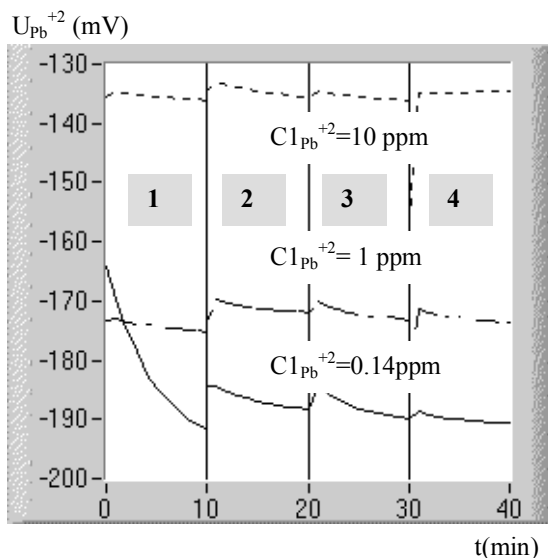


Fig. 8. Dynamic response of Pb⁺² ISE for step changes in concentration of Pb⁺² ion

Results presented in Fig. 8 refer to the dynamic response of the Pb⁺² ISE when submitted to the following 4 period two-step concentrations:

- C_{Pb⁺²} = 0 ppm - C_{Pb⁺²} = 0.14ppm (solid curve),
- C_{Pb⁺²} = 0 ppm - C_{Pb⁺²} = 1ppm (dashed curve),
- C_{Pb⁺²} = 0 ppm - C_{Pb⁺²} = 10ppm (dotted curve)

The graphs were obtained using the effective measured data and do not include the interleave cleaning times (1 min interval).

As it can be observed, U_{Pb⁺²} presents small variations from period to period of the same concentration, which underline the electrode memory effect. On the other hand the starting point differs from period to period revealing ISE's poor reproducibility. The reproducibility deviation

level for ISE and for different tests was evaluated using the following formula:

$$RD_{ISE} = \frac{\sigma_{U_{SP}}}{U_{SP}} \cdot 100[\%] \quad (4)$$

where $\sigma_{U_{SP}}$ represents the standard deviation of the first value of ISE voltage when the sensor is immersed in the solution characterised by C_{ISE} of primary ions. For the particular Pb^{+2} sensor and for the dynamical tests of Fig. 8, values of reproducibility deviation were 8.3% for the $C_{Pb^{+2}}=0.14ppm$ case, 2.4% for the $C_{Pb^{+2}}=1ppm$ case and 7.5% for $C_{Pb^{+2}}=10ppm$ case.

5. CONCLUSION

In this paper the interference phenomenon of ISE based PVC membranes under static and dynamic conditions was studied. As additional disturbance quantity the pH of the solution was considered and a neural network correction of the potentiometric selectivity coefficient was designed and implemented. Referring to the experimental set-up, a virtual system with ISE dynamic test capability was designed and implemented.

Dynamic tests conducted on cadmium and lead electrodes showed that their response time is of some 3 to 5 minutes depending on concentration levels. On the other hand, and because they exhibit drift and poor reproducibility, ISEs usage is difficult and requires special care and processing of experimental data to obtain meaningful measurements.

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