



INCREASING ION SELECTIVE ELECTRODES PERFORMANCE USING NEURAL NETWORKS

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Abstract: *This paper reports the implementation of a neural processing structure as a component of an intelligent measuring system that uses ion selective electrodes (ISEs) as sensing elements of heavy metal ions (Pb⁺², Cd⁺²) concentration. The neural network (NN), designed and implemented to reduce errors due to ion interference and to pH and temperature variations, is of the multiple-input multiple-output Multilayer Perceptron (MLP-NN) type. The NN is a component of a virtual instrument that includes a PC laptop, a PCMC data acquisition board with associated conditioning circuits and the specific ISE sensors. A practical approach concerning the optimal neural processing solution (number of NN structures, number of neurons, neuron transfer functions) to increase the performance of low cost ISEs is presented. Results are presented to evaluate the performance of the NN intelligent ISE system and to discuss the possibility of transferring the acquisition and processing task to a low cost acquisition and control unit such as a microcontroller.*

Keywords: *intelligent measuring systems, signal conditioning, neural networks.*

1. INTRODUCTION

Ions of heavy metals, such as lead and cadmium, are an undesired presence in river waters. The monitoring of its concentration requires the utilization of measuring systems often based on ion selective sensors (ISE). Glass electrodes ISEs are characterized by fragility, temperature dependent sensitivity and limited selectivity [1]. All these limitations make their use unsuitable for permanent field measurements required for continuous river water quality monitoring. Other groups of ISEs are solid-state crystal membrane sensors, such as NASICON, and PVC membranes, such as ELIT, which detect the ions (i.e. Pb⁺², Cd⁺², Hg⁺²) in aqueous solutions [2][3].

These types of ISEs are robust enough to permit its field utilization. However, most of them have ion-selective membranes that allow transit of more than one type of ions. Methods to increase the selectivity of this type of sensors are reported in the literature and are based on multivariable modeling techniques applied to reduce the interference effects. Solutions in the multivariable modeling area use both the fuzzy system [4] and neural networks [5][6] to perform the

modeling of sensor with non-linear characteristics and multiple influence factors.

2. ISE SYSTEM: ISE PRESENTATION AND MODELING

The present work proposes a ISE pH and temperature sensor based unit that includes an intelligent processing of sensors information in order to measure the lead and cadmium ions concentration with better accuracy, reducing the errors caused by temperature, pH variation and ion interference ions. The data sensor fusion based on NNs [7][8] is the main technique used in the present case.

Ion sensing part of the system includes an ISE for lead ions, an ISE for cadmium ions and a reference electrode.

The potential of lead and cadmium ISEs depends on the Pb⁺² and Cd⁺², respectively, and is given by Nernst equation:

$$E = E_0 + \frac{2.3 \cdot R \cdot T}{Z \cdot F} \cdot \log(a_x) \quad (1)$$

where: E_0 - reference electrode potential, R - constant of gases, T - absolute temperature, Z - charge on the ion with sign, F - Faraday constant, a_x - activity of the measured ion, X .

Due to the dependence of E on temperature, a temperature sensor is included in the system to allow the on-line correction of ISE characteristics with temperature.

The activity of each ISE depends on the concentration of the main ions (Pb^{+2} for Pb-ISE or Cd^{+2} for Cd-ISE) but also on the presence of other ions in the analyzed medium (i.e. river water). In these conditions the Pb-ISE and Cd-ISE output voltages are expressed by Nikolsky-Eiseman equations:

$$E_{Cd^{+2}} = E_0 + \frac{2.3 \cdot R \cdot T}{Z \cdot F} \cdot \log \left(a_{Cd^{+2}} + \sum k_{Pb, X_i}^{pot} \cdot a_{X_i Z_i} \right) \quad (2)$$

$$E_{Pb^{+2}} = E_0 + \frac{2.3 \cdot R \cdot T}{Z \cdot F} \cdot \log \left(a_{Pb^{+2}} + \sum k_{Cd, X_i}^{pot} \cdot a_{X_i Z_i} \right)$$

where $a_{Pb^{+2}}$ $a_{Cd^{+2}}$ are the Pb^{+2} and Cd^{+2} activities, k_{Pb, X_i}^{pot} and k_{Cd, X_i}^{pot} represent the potentiometric selectivity coefficients of the ISE considered electrodes for different interfering ions, Z_i are the charge number of the interfering ions, and R the constant of gases. The potentiometric selectivity coefficient defines the ability of an ion-selective electrode to distinguish a particular ion from others [9]. Ion activity is proportional to concentration. Thus, in the particular case of Pb^{+2} and Cd^{+2} , activities are expressed by:

$$a_{Pb^{+2}} = \gamma_1 \times C_{Pb^{+2}} \quad ; \quad a_{Cd^{+2}} = \gamma_2 \cdot C_{Cd^{+2}} \quad (3)$$

where γ_1 and γ_2 are the activity coefficients that depend on the ionic strength of the measured solution and $C_{Pb^{+2}}$ and $C_{Cd^{+2}}$ are the concentrations of lead and cadmium, respectively.

Taking into account the complexity of ISE sensors, a global characterization using neural networks is a solution to consider.

3. ISE SYSTEM: HARDWARE

The ISE sensors are part of a virtual instrument designed and implemented to measure the ion concentration in the river water. Sensors used are ELIT8231 and ELIT8241, specific ISE for Pb^{+2} and Cd^{+2} , and a double junction lithium acetate ELIT003 as the reference electrode (Fig.1).

Considering that the used sensors are potentiometric, the electrode polarization due to the current should be avoided. For this purpose a conditioning circuit with two 1,2μA Max, single-supply MAX406 operational amplifiers (AO1 and AO2) is implemented. AO1 and AO2 output voltages are acquired using two analog differential inputs (ACH0 and ACH8 for V_{Pb} ISE and ACH1 and ACH9 for V_{Cd} ISE) of a PC notebook plugged-in data acquisition board (PCMCIA DAQ6022).

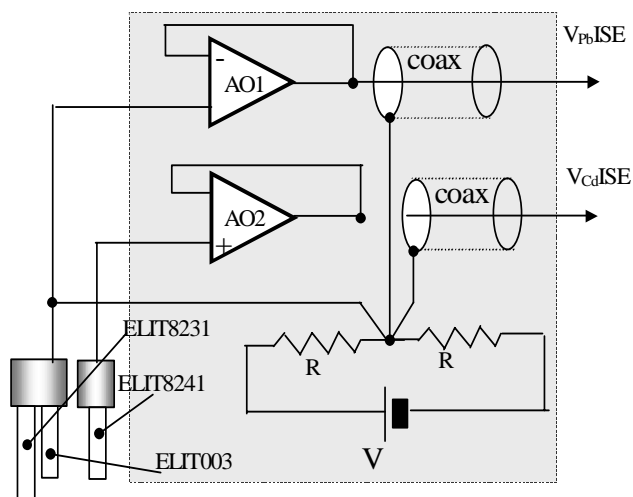


Fig. 1. ISEs conditioning block.

Referring to the temperature conditioning circuit, a LM324 based controlled current source is implemented in order to obtain a voltage signal V_T linearly dependent on the resistance variations of an ON401 thermistor. The injected current is 0.2mA in order to prevent self-heating effects.

The value of concentration's pH is also an important parameter that influences ISEs output, namely for low values of ion concentrations. Fig. 2 shows the effects of pH variation on the concentration measurement in the particular case of Cd^{+2} ion measured with ELIT8241. In the figure, $V_{ISE, Cd}$ expresses Cd^{+2} ion sensor acquired voltage, pH represents the value of pH measured with ISI model 11 pH sensor and Δe_{pXCd} represents the $pXCd^{+2}$ absolute errors obtained for different pH values. The Δe_{pXCd} error is defined by the following relation:

$$\Delta e_{pXCd} = \left| \frac{pX_{Cd^{+2}} \Big|_{pH=pH_i} - pX_{Cd^{+2}} \Big|_{pH=5}}{pX_{Cd^{+2}} \Big|_{pH=5}} \right| \cdot 100 [\%] \quad (4)$$

where

$$pXCd^{+2} = -\log_{10} (C_{Cd^{+2}}) \quad (5)$$

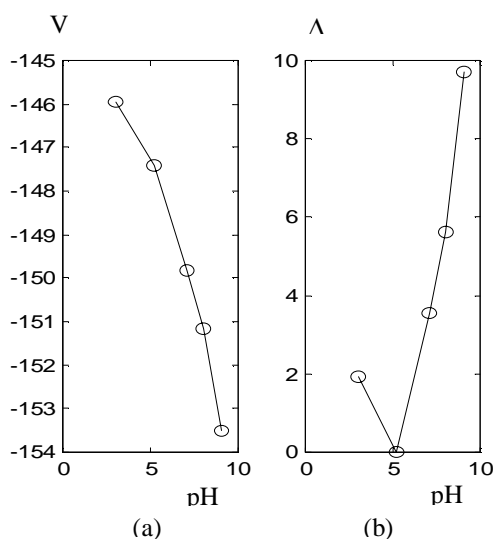


Fig. 2. pH influence on Cd+2 measurement using ELIT8241 sensor (pH ∈ [3,9] and pXCd ∈ [4,7].
 (a) sensor's output voltage, VCd-ISE versus pH for pXCd+2=5; (b) pX absolute errors versus pH.

Thus, the pH of the tested solution is measured using the ISI11 pH transducer that delivers a voltage included in 0-300mV interval for pH=[1-10]. After conditioning, the voltage signal corresponding to pH is digitized using the DAQ.

Fig. 3 shows the overall hardware and its interface with the software component of the measuring system.

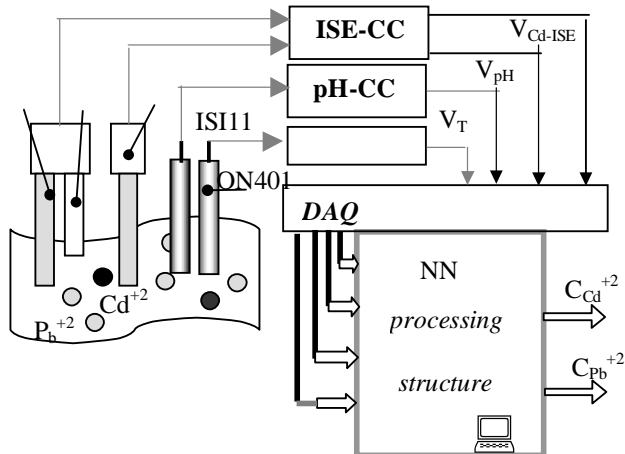


Fig. 3. The ISE based virtual instrument for Pb²⁺ and Cd²⁺ ion concentration measurement.

4. ISE SYSTEM: SOFTWARE

The software components of the virtual system are related with the acquisition and filtering of V_{Pb-ISE}, V_{Cd-ISE}, V_{pH}, V_T and with the neural processing of the

acquired voltages in order to obtain the accurate values of Pb²⁺ and Cd²⁺ ions concentration with compensation of temperature, pH and interfering ion effects.

Data acquisition and filtering are performed using a set of LabVIEW functions. Acquisition sampling rate is f_s=10kS/s. For each sampling set corresponding to Δt_i=1s acquisition time, average voltages V_{ISE_Cd²⁺}^{avg}, V_{ISE_Pb²⁺}^{avg}, V_{T^{avg}}, V_{pH^{avg}} are calculated in order to increase the signal to noise ratio (SNR). The time interval between two acquisition times is set at τ_i=1min. Different Cd²⁺ and Pb²⁺ based solutions (C_{Cd²⁺} and C_{Pb²⁺} = [0.14;10]ppm) with different pH (3÷9) values and temperature (T=[273-303]K) are considered in order to obtain the corresponding sensor voltage responses used to train and test the neural network (NN) processing structure design. The main blocks included in the NN processing structure are the NN temperature sensor-processing block (NN-T), the NN pH sensor-processing block (NN-pH) and the NN-ISE processing block (NN-ISE) all of them expressed by multilayer perceptron neural networks (Fig. 4).

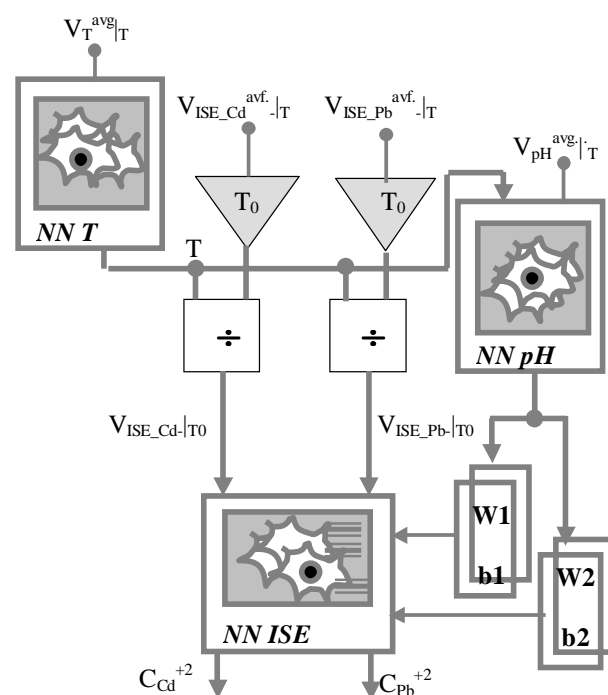


Fig. 4. The NN processing structure.

4.1 NN temperature sensor processing block

The NN-T performs temperature (T) calculation of the aqueous solution under test using the V_{T^{avg}} acquired

voltage. The main characteristics of the considered neural networks are:

- type - multilayer perceptron, single input, single output;
- number of layers - 3 layers (input layer, hidden layer, output layer);
- number of neurons - 1 in the input layer, 2 to 10 in the hidden layer, 1 in the output layer;
- neuron transfer functions – linear, for output neurons (f_{output}), tansigmoid [10], for hidden neurons (f_{hidden}).

The weights ($W1, W2$) and biases ($b1, b2$) of the NN are obtained using the Levenberg Marquardt algorithm [11] for an imposed training stop condition expressed by the sum square error value, SSE_{STOP} . The training and testing sets correspond to 273 to 303K-temperature interval.

In the training phase a data set including half of the 48 pairs of V_T and temperature experimentally obtained is used to design the neural network Taking into account the capabilities of the Matlab NN training implemented program, a study concerning the $n_{hidden}(SSE_{STOP})$ characteristic is performed. A graphical expression of the above mentioned characteristic is presented in Fig. 5. As shown in the figure, for $n_{hidden}>9$ neurons the test error (e_t) defined as:

$$e_t = \max |o_{NNi} - o_{testi}|_{i=1...M} \quad (6)$$

where o_{NNi} is the NN output value and the o_{testi} represents the test NN target value is ten times greater than the e_t calculated for $2 \leq n_{hidden} \leq 9$ case. The training stop condition for both situations is $SSE_{STOP}=0.005$. Considering as the aim of the NN design the higher accuracy of numerical linearization and, at the same time, the reduction of NN number of neurons, the possible solutions for temperature linearization are presented in Table 1.

Table 1. NN-T architecture and performances

n_{hidden}	SSE_{STOP}	$e_t(K)$
5	0.00005	0.13
6	0.0005	0.21
7	0.0001	0.21

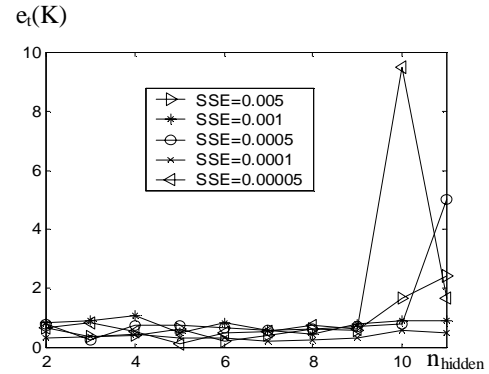


Fig. 5. The evolution of test error e_t for different NN-T architectures and training stop conditions.

4.2 NN pH sensor processing block

Referring to the NN-pH architecture, a two inputs and one output structure is used [12]. Its main characteristics are: (a) number of layers - 3 layers (input layer, hidden layer, output layer); (b) number of neurons - 2 in the input layer (corresponding to T and V_{pH}^{avg}), 10 to 40 tansigmoid hidden neurons, 1 linear output neuron.

In the NN-pH training phase a 2×20 input matrix (P_{pH}), including the normalised values of temperature and V_{pH} , and 1×20 target matrix (T_{pH}), including the temperature compensated pH normalised values, are used. The network is trained using the Levenberg-Marquardt algorithm and a stop condition expressed by $SSE_{STOP} \leq 1E-4$.

Results of the network testing for different number of neurons in the hidden layer are summarized in Fig. 6. Analysing the figure it can be underlined that the best approximation of 2D pH characteristics is obtained for $n_{hidden}=45$ and the corresponding weights and biases are implemented in LabVIEW for on line extraction of temperature compensated pH value.

4.3. NN ISE processing block

After having the temperature and the temperature corrected pH values, the first natural solution to obtain the concentration of metals taking into account not only those two quantities but also ion cross interference on sensors output voltage using a neural network, is to convert sensors voltage from temperature T to temperature T_0 at which data is obtained in laboratory and then to implement a three input, two output neural network whose inputs are those converted values and the temperature corrected pH value and whose outputs are metal concentrations.

This solution is not however considered. In fact, the problem faced of finding a 2 dimensional solution in a 3 dimensional space using neural networks is only well or fairly solved if the network is trained using a large set of input values, that is to say, if the region of training finely covers the region where solutions are. In the absence of such a set, and similarly to the NN pH sensor-processing block, the NN ISE processing block uses a *two input single output* multilayer perceptron but whose weights and biases are a function of the temperature corrected pH value (Fig. 4). The main characteristics of the network are:

- type - two-inputs-two outputs multilayer perceptron;
- number of layers - 3 layers (input layer, hidden layer, output layer);
- number of neurons - 2 in the input layer (corresponding to the voltage acquired on the temperature channel, 10 to 50 tansigmoid neurons in the hidden layer, 2 linear on the output layer.

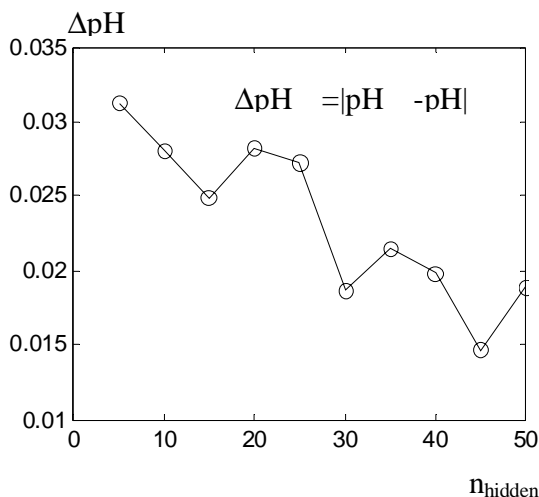


Fig.6. The evolution of ΔpH_{NN} versus number of neurons of the NN-pH hidden layer.

The neural network training set is composed by several pairs of input \mathbf{P}_{ISE}^{pHi} (2×36) and target \mathbf{T}_{ISE}^{pHi} (2×36) matrices each pair corresponding to a pH value (pH_i) of the ISEs calibration solution. \mathbf{P}_{ISE}^{pHi} includes the pairs of $V_{Cd_ISE|T_0}$ and $V_{Pb_ISE|T_0}$ values acquired from the ISE channels in the laboratory conditions (T_0) and ISE calibration phase. The target matrix is expressed by the concentration of the Cd^{+2} and Pb^{+2} ions in the measured solution. In order to reduce errors, the NN-ISE is designed using voltages and ion concentration values corresponding to two ion concentration ranges, $C_{Cd}^{+2}, C_{Pb}^{+2} \in [0.14; 1]$ ppm, $C_{Cd}^{+2}, C_{Pb}^{+2} \in [0.14; 10]$ ppm.

The designed NN-ISE operates with the $V_{Cd_ISE|T_0}$ and $V_{Pb_ISE|T_0}$ obtained from the measured $V_{Cd_ISE|T}$ and $V_{Pb_ISE|T}$ using the following relations.

$$V_{ISE_Cd}|_{T_0} = V_{ISE_Cd}|_T \cdot \frac{T_0}{T} \quad (7)$$

$$V_{ISE_Pb}|_{T_0} = V_{ISE_Pb}|_T \cdot \frac{T_0}{T}$$

where T represents the temperature of the measured solution and T_0 is the temperature at which training and testing values are obtained

The used training algorithm is Levenberg Marquardt and the stop condition is $SSE_{STOP} = 0.001$. In order to obtain an optimal solution in terms of ISE characteristics modeling accuracy, different NNs with different number of hidden neurons are trained and tested, the final structure being represented by 2 input neurons, 20 tansigmoid-hidden neurons and 2 linear output neurons.

RESULTS AND DISCUSSION

After the NNs are designed in Matlab, on line data processing is fully implemented in LabVIEW. Thus, weights and biases of NN-T, NN-pH and NN-ISE stored in files are directly accessed according to the acquired voltage on the T, pH, ISE_Cd and ISE_Pb channels and used as factors and terms involved in matrices multiplication that lead to C_{Cd}^{+2} and C_{Pb}^{+2} values.

The designed neural network based system is tested on-line for different solutions characterized by different concentrations of Cd^{+2} and Pb^{+2} ions included in [0.1;1] ppm and [0.1;10] ppm. The temperature and pH of the tested solutions correspond to typical river water conditions: $pH=5.2$ and $T=293$ K. Results are presented in Fig.7 and Fig.8 and reveal the concentration absolute errors are smaller than 0.01 ppm for the 0 to 1 ppm scale and 0.1 ppm for 0 to 10 ppm scale that, which represent less than 1% of full scale in both cases.

In order to evaluate the advantage of the NN utilization in the presented application, errors with NN processing (NN T, NN-pH and NN-ISE) are compared with errors without correction.

Ignoring temperature correction, ion concentration measurement errors are about 6% when the temperature of the ISE is in the 278 K to 303 K interval. Using the above presented *temperature scaling* technique, and considering that the errors associated with temperature measurement are about

0.2 K, system's errors negligible since they are reduced to some 0.05%.

In what concerns pH and ion interference correction, ELIT sensor manufacturers indicates only that under particular conditions (one single type of ion, pH=3-7, activity coefficient>0.98), the concentration value obtained has an error of some 5%. In our case, only with two ions present and concentrations between 0.1 and 10 ppm, the error of concentration evaluation neglecting interference effects and thus using (1) is much higher reaching some 500% (for an interference concentration 10 times greater than the primary ion concentration). This fact renders useless this type of sensors in applications where several ions are simultaneously present in the medium under measurement without some sort of post data processing. As can be seen in Fig. 7 and Fig. 8, this error is reduced with the proposed data fusion method to 1% in the worst case ((0.1 ppm/10 ppm)×100),

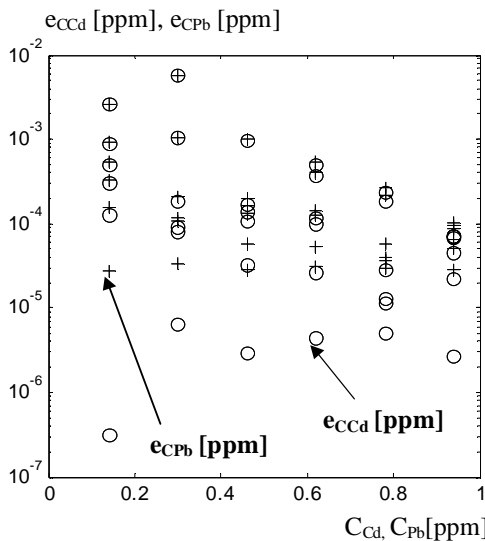


Fig. 7. Concentration error (eC) versus concentration for low concentrations of Cd+2 and Pb+2 ions. + - Pb; o - Cd.

6. CONCLUSION

The ISE based system proposed increases the performance of ion selective electrodes used for heavy metal concentration measurement compensating the effects of interfering ions, of temperature and pH variations using additional sensors and adequate neural processing structures.

In what acquisition of sensors output voltages is concerned, a microcontroller with a 12 bits analog-to-

digital converter can be used instead of the PC plugged-in data acquisition board.

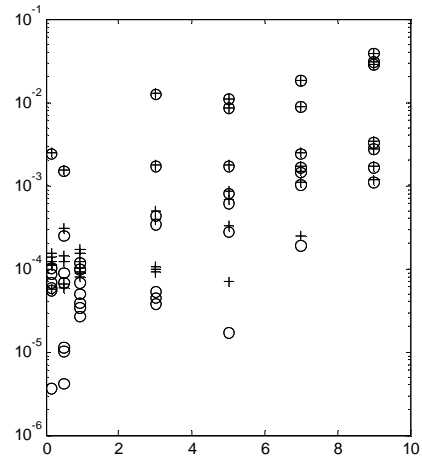


Fig. 8. Concentration error (eC) versus concentration for high concentrations of Cd+2 and Pb+2 ions. + - Pb; o - Cd.

A practical approach concerning the dependencies between the NNs performance and the number of processing units was performed in order to evaluate the relationship between the performance and the NN implementation complexity. The conclusion obtained is that after NN optimization, the proposed solution can be easily implemented also in a microcontroller. The possibility of microcontroller usage both for data acquisition and processing tasks is very attractive for field measurements and monitoring applications.

Also, the flexibility of the system permits to add new ISEs to the system without important changes of system's hardware and of increase of system's software complexity.

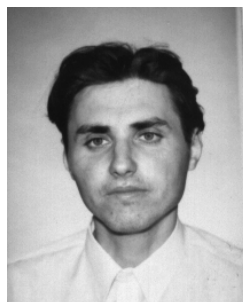
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REFERENCES

- [1] P. Fabry, J. Gros, J. Million-Brodaz, "NASICON, an ionic conductor for solid-state Na⁺ selective electrode", *Sensors and Actuators*, 15 (1988) 33-49.

- [2] P. Fabry, E. Siebert, C. Gondran, A. Attari, H. Khireddine, "De nouvelles céramiques conductrices pour capteurs ioniques potentiométriques", *Science Technique Technologie* 24, (1993), 30-37
- [3] Nico 2000. Ltd-"Operating Instructions for ELIT Ion-selective Electrodes", Nico 2000 Publishing.
- [4] M. Heniche, M. Attari, F. Boudjena, "Reducing the effects of temperature and K^+ activity in sodium measurement by mean of a fuzzy logic system", *Proc. IMEKO-TC4, Naples, Italy, (1998)*, pp.602-606.
- [5] O. Postolache, P. Girão, M. Pereira, "Neural Network in Automatic Measurement System: State of Art and New Research Trends", *Proc. IEEE - IJCNN'2001, Washington DC, vol. 3-4, (2001)*, pp.2310-2315.
- [6] C. Alippi, V. Piuri, F. Scotti, "A Methodology to Solve Performance/Complexity Trade-off in RBF Neural Networks", *Proc. IEEE International Workshop on Virtual and Intelligent Measurement System, Annapolis, USA, (2000)*, 147-150.
- [7] L. Jain, N. Martin, *Fusion of NN, Fuzzy Sets, and Genetic Algorithms - Industrial Applications*, CRC Press, Washington DC, (1998).
- [8] David L. Hall and James Llinas (Editors), *Handbook of Multisensor Data Fusion, The Electrical Engineering and Applied Signal Processing Series*, CRC Press LLC, Boca Raton (FL), (2001).
- [9] IUPAC Compendium of Chemical Terminology 2nd Edition 1997
- [10] P. V. Venvilainen, H. Ihalainen, "Estimating the Activation Functions of an MLP-Network", *Proc. IMEKO World Congress, Vol. IX, pp.359-364, Wien, 2000*.
- [11] S. Haykin, *Neural Networks - A Comprehensive Foundation*, Prentice Hall, (1999).
- [12] O. Postolache, M. Pereira, P. Girão, M. Cretu and C. Fosalau, "Application of neural structures in water quality measurements", *Proc. IMEKO World Congress, Wien, Oct. 2000, vol. IX, pp.353-358*.



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