

APPLICATION OF INVERSE PROBLEM ALGORITHM FOR ESTIMATION OF ION MIXTURE COMPOSITION

M. JANICKI, M. DANIEL, A. NAPIERALSKI
TECHNICAL UNIVERSITY OF ŁÓDŹ, POLAND

KEYWORDS: CHEMFET, Membrane selectivity, Inverse problem, Multiple ion concentration estimation

ABSTRACT: The paper deals with the problem of ion mixture composition determination using the CHEMICALLY Modified Field Effect Transistor (CHEMFET), which is closely related to the conventional Metal-Oxide-Semiconductor device. The main difference between the devices is the construction of the gate structure, where the traditional metal electrode is replaced by some special polymer membrane sensitive to concentration of ions in an electrolyte flowing over the gate. The numerical simulations presented in this paper, concern the problem of the ion mixture composition estimation from noisy sensor measurements for given membrane selectivity coefficients values. The estimation accuracy is improved employing the function specification algorithm dedicated for solving different kinds of inverse problems. This algorithm can be easily implemented as a digital filter. Additionally, some considerations on the choice of the optimal algorithm parameter values are included.

INTRODUCTION

The pollution of the natural environment is nowadays one of the major problems in industrialised countries. Thus, as a follow-up to the Kyoto agreement, the idea of the sustainable development, allowing economical growth and technological progress while protecting the environment, has been conceived and consequently included into the government policies in many countries, including the European Union. The main goal of these actions is to induce in citizens growing consciousness and understanding of the necessity of environmental care. One of the ways of implementing the sustainable growth policy is the creation of networks dedicated for continuous monitoring of environment pollution.

The particular research presented in this paper is a part of a larger international project, supported by the EU 5th Framework Programme, aimed at the creation of a water pollution monitoring system as described in [1]. The project is currently in the last year of its realization. The sensors designed and manufactured in the frames of the project activities are to be integrated with a data acquisition unit. The pre-processed measurement data will be transmitted from the field posts to a water quality monitoring station where, according to sensor indications, appropriate actions will be taken. The sensors are not sensitive only to a single ion, thus special techniques must be used so as to assure good quality of obtained estimates and immunity to errors. The next section of the paper will provide some basic information on the principles of CHEMFET operation and problems related to the limited device selectivity. Next, based on the numerical simulations, the possibility of improving the accuracy of obtained ion concentration estimates employing inverse problem algorithms will be demonstrated. In particular, the problem of the choice of the algorithm parameters will be discussed in detail.

CHEMFET DESCRIPTION

Operation Principle

Basically, CHEMFETs are Metal Oxide Semiconductor FETs (MOSFETs) in which the standard gate is replaced by some more complex structure, shown in Figure 1, sensitive to the concentration of different ions. This gate consists of the reference electrode and the gate dielectric (a composite of silicon oxide and nitride in the case considered here) between which an analysed electrolyte flows. The sensitivity to particular ions is achieved by covering the dielectric with ion-selective membranes and a PolyHEMA hydrogel, which contains an intrinsic electrolyte of known composition and stabilizes the sensor operation [2].

The electrolyte flowing over the gate closes the electric gate-source circuit and the ion concentration influences the gate potential, which in turn modifies the transistor threshold voltage. Thus, the ion concentration exercises electrostatic control over the drain-source current.

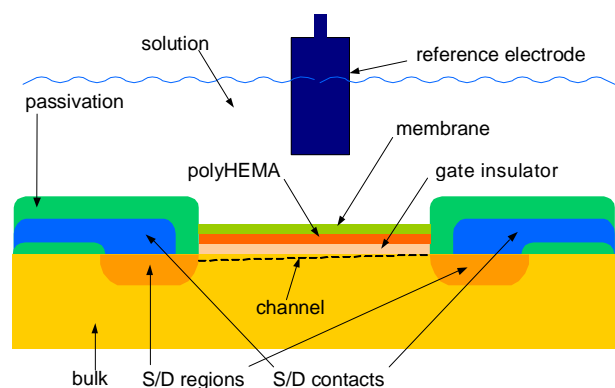


Figure 1: Cross-section of CHEMFET structure

CHEMFETs are operated in the constant drain current mode. Then, the change of the drain current due to the variation of the ion concentration is compensated for by application of external voltage to the gate. Therefore, the device sensitivity is usually expressed as the gate potential change per decade of ion concentration.

Membrane Selectivity

One of the problems encountered during measurements of ion concentration with CHEMFET sensors is related to the limited selectivity of the device membrane. Namely, the membrane potential varies not only with the concentration of the main ion to be detected, but also it is dependent on the concentration of some other ions, called disturbing or interfering ions.

There exist two different approaches to the modelling of the phenomena occurring in the device membrane, the physical approach and the empirical one. In this paper, the authors focus only on the empirical model, but this does not limit the scope of the presented considerations because both approaches are to some extent equivalent and produce similar results. According to the empirical model, the membrane potential changes ΔV in presence of various univalent ions in the analysed solution can be expressed by the following equation derived from the well-known Nikolski-Eisenman equation [3]:

$$\Delta V = 2.303 \frac{RT}{F} \log[a_i + \sum_{j \neq i} k_{ij} a_j] \quad (1)$$

where:

F – Faraday constant [C]; R – gas constant [J/Kmole];
 T – absolute temperature [K]; a – ion activities [mole];
 i, j – ion indices; k – selectivity coefficients;

The curves resulting from the above equation obtained for two different selectivity values and five different disturbing ion activities pK_d are plotted in Figure 2. As can be seen from the figure, due to the presence of disturbing ions, the ideal curve flattens out for certain concentrations of the main ion and as the result the sensor becomes insensitive to the main ion at its low concentration values.

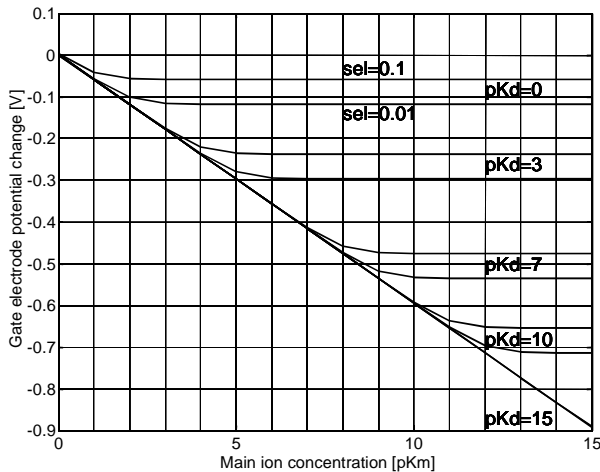


Fig. 2. Gate potential dependence on ion concentration for different selectivity values.

The exact location of the bending point on the curve, and consequently the usable measurement range, are determined both by the membrane selectivity and the concentration of disturbing ion pK_d . For example, when the concentration of the disturbing ion is equal to 7, the measurement range of the main ion concentration pK_m is between 0 and 7 or 8, depending on the membrane selectivity. The impact, which this phenomenon has on the results of ion mixture composition analysis, will be discussed in the following section.

The selectivity coefficient k is the relative selectivity to an interfering ion j with respect to the main ion i . For example, if the value of the coefficient is equal to 0.1, the presence of the interfering ions in the concentration ten times higher than the concentration of the main ion causes exactly the same change of the sensor threshold voltage. The values of the selectivity coefficients are usually given in the logarithmic scale. Then, the above coefficient value of 0.1 equals -1 . Similarly, the cation activities a_K are given in the units of pK which are equal to $-\log_{10}(a_K)$. Another issue which has to be commented on is the difference between the ion activity a and the ion concentration c . Both these quantities are directly related through the ionic strength of the solution. Since, for small size ions and lower ion activities, they are almost equal, in the later presented simulations it was assumed that the activity was equal to the concentration.

NUMERICAL EXPERIMENT

The numerical experiments presented in this section were carried out in order to investigate the possibility of estimating the composition of ion mixture in the presence of measurement errors. For the experiment, it was assumed that there were three types of sensors monitoring the concentration of potassium, sodium and ammonium. The corresponding selectivity coefficient values for the PSX membrane, given in Table 1, were provided by the research group of Prof. Brzózka from Warsaw University of Technology. The hypothetical variations of ion concentrations in time assumed in the numerical experiment for each of the three cations are represented by black lines in Figure 3.

Then, knowing the concentration of each cation and the selectivity coefficient values for each membrane, the sensor responses in time were computed based on Equation 1. Next, some noise was introduced into the sensor responses so as to investigate the immunity of ion concentration estimation to the measurement errors. The standard deviation of the noise added to the original values ranged from 1 mV to 20 mV. Both the exact (black lines) and the corrupted sensor responses noise (grey lines) are presented in the Figure 4.

TABLE 1 - Logarithms of selectivity coefficients.

Interfering ion:		K ⁺	Na ⁺	NH ₄ ⁺
Main ion:	K ⁺	0.000	-2.564	-1.688
	Na ⁺	-1.479	0.000	-1.662
	NH ₄ ⁺	-0.483	-1.799	0.000

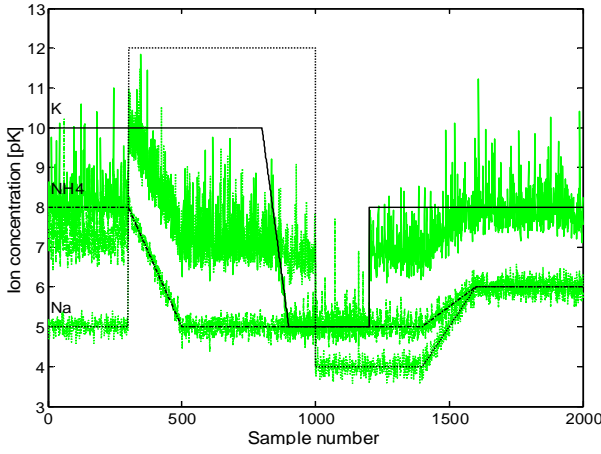


Fig. 3: Original and estimated ion concentrations
- noise standard deviation 10 mV.

Examining in Figure 4 the changes of the gate potential of the individual sensors, it is clearly visible that all the sensors respond quite strongly to high concentrations of interfering ions. This is particularly noticeable for the sodium sensor, which at low sodium concentration responds strongly to the change in the ammonium concentration.

One-step Estimates

The next step of the experiment was to compute the ion activity estimates from the noisy sensor responses. For the estimation purposes, Equation 1 was transformed to the matrix form given in the following equation:

$$K A = 10 \frac{\Delta V F}{2.3RT} \quad (2)$$

K is the sensitivity coefficient matrix containing ones on the diagonal and adequate sensitivity coefficients outside the diagonal. A is a vector of unknown ion activities. The right hand side of the equation is the pre-processed vector of the sensor gate voltage changes ΔV . Thus, in order to determine the activities of each particular ion based on the measured potential changes, it is enough to invert the sensitivity coefficient matrix K and consequently compute the unknown ion activity matrix A . The so-called one-step ion activity estimates obtained through the simple inversion of the sensitivity matrix both for the exact (black lines) and noisy data (grey lines) are presented in Figure 3.

The ion activity values estimated from the exact data are equal to the arbitrary ones originally assumed for the simulation. This proves that in the case of errorless input data it is possible to obtain accurate estimates of ion concentration values. On the contrary, the results produced for the erroneous input data are inaccurate and the estimation error increases significantly for low ion concentration values. This is due to the fact that, because of the limited membrane selectivity, when the concentration of the main ion is low, sensors become sensitive to the interfering ions. As a result, the sensors follow rather the changes in the concentrations of the disturbing ions instead of the one of the main ion.

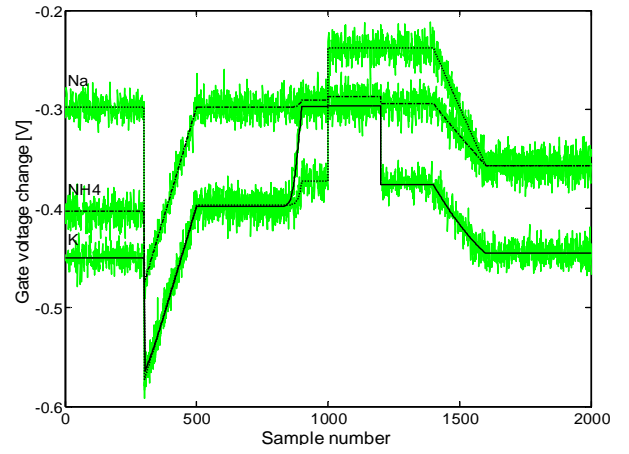


Fig. 4: Exact and noisy gate potential responses
- noise standard deviation 10 mV.

Filtered Estimates

The quality of the obtained estimates can be improved to some extent introducing into the system redundant information. This could be done by placing additional sensors or averaging a certain number of consecutive measurements. Then, instead of the simple inversion of the square selectivity matrix K , the so-called pseudo inverse matrix of the rectangular selectivity matrix has to be computed. The general formula to determine the pseudo inverse sensitivity matrix K^{-1} , derived from the least mean squares method, can be expressed by the following equation [4]:

$$K^{-1} = (K^T * K)^{-1} * K^T \quad (3)$$

The exact form of the sensitivity matrix depends on the choice of the particular estimation algorithm. There exist a large variety of such algorithms, but generally they can be divided into two groups; the adaptive algorithms and the specialised algorithms for solving inverse problems. For the simulations presented here, the function specification algorithm, belonging to the latter group of algorithms, has been chosen.

The function specification algorithm is based on the assumption that the variation with time of the unknown quantity to be estimated has some functional form. The simplest and the most commonly used version of the algorithm assumes that r consecutive measured samples are equal, i.e. the functional form is constant. In the sequential estimation, the unknown values of the ion concentration are determined successively with each new arriving data. These values are found in each iteration knowing the current sensor indication and $r-1$ "future" measurements. The estimation accuracy can be further improved introducing additional sensors. Then, the activity of each ion can be computed using the following formula [5]:

$$\hat{a}_k = \frac{\sum_{i=1}^r \sum_{j=1}^J s_{ji} \Delta V_{j,k+i-1}}{\sum_{i=1}^r \sum_{j=1}^J s_{ji}^2} \quad (4)$$

where:

J - number of sensors; ΔV - gate voltage change;
 \hat{a} - estimated ion activity; r - number of future values;
 i, j - series indices; k - sampling instant;
 s - inverse membrane selectivity;

Based on Equations 3-4, during simultaneous estimation of p unknown ion activities, the vector \hat{a} containing the estimates of the activities can be found at each sampling instant k using Equation 5. This equation was derived under the assumption that r consecutive measured samples are equal. Additionally, it was assumed that all the chemical processes in the membrane at the sampling instants are in equilibrium, i.e. that the sensor response to the change of ion concentration has stabilized [6].

$$\hat{A}_k = ((KI)^T KI)^{-1} * (KI)^T * \Delta V \quad (5)$$

where:

$$K = \begin{bmatrix} k_1 & 0 & 0 & \dots & 0 \\ k_2 & k_1 & 0 & \dots & 0 \\ k_3 & k_2 & k_1 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ k_r & k_{r-1} & k_{r-2} & \dots & k_1 \end{bmatrix}$$

A - $[p \times 1]$ unknown ion activities vector;
 I - $[r \times p]$ vector of r identity matrices;
 ΔV - $[r \times 1]$ pre-processed potential change vector;
 k - $[J \times p]$ selectivity coefficient sub-matrices;

The above presented form of the function specification algorithm was employed for improving the quality of the previously obtained one-step activity estimates. Different values of parameters were explored in the simulations so as to find the best possible configuration. Namely, the estimates were found for different number of sensors (up to 5 of each kind) or variable number of averaged samples (up to 20). Additionally, both space and time averaging was applied at the same time with 3 sensors of each kind and 10 samples averaged. The measures of the algorithm effectiveness were the mean value and the standard deviation of the difference between the actual value of the ion concentration and the estimated one.

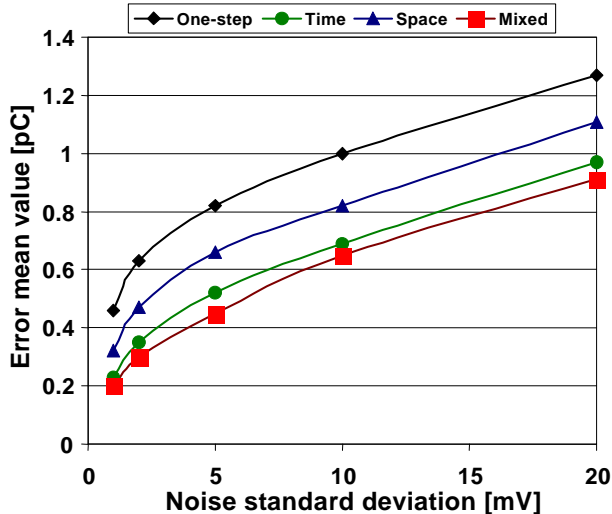


Figure 5: Estimation error mean value.

The obtained estimation error mean values and standard deviation in function of the input noise for one of the sensor are presented in Figures 5-6 respectively. The number of sensors and averaged samples correspond to the ones mentioned in the paragraph. Additionally, they are compared to the values obtained previously without any averaging. The results obtained for other sensors were similar, so due to the limited size of the publication they will not be presented here.

The application of the function specification algorithm undoubtedly improved the accuracy of the estimates reducing both the mean value and the standard deviation of the estimation error through the averaging process. The original values of the mean and the deviation in the case of the one step-estimates for 20mV input noise, which corresponds to 0.4 decade of ion concentration, amounted to 1.3 decade estimate error. The introduction of additional sensors improved the estimation quality reducing the error mean value to 1.1 decade of ion concentration. Much better results were obtained owing to the time averaging, when the error mean value dropped down to 0.95 decade. The best results were obtained in the case when both additional sensors and multiple values were used. Then, the error mean value was brought down to 0.9 decade (70 % of its original value). From the figures, it can be concluded that the numbers of sensors and future values should not be too large since the improvement in accuracy is insignificant in comparison to the computational complexity. Instead, it is better to use a mixed approach combining the space and time averaging.

The general conclusion however is that the errors seem to be unacceptably high in all cases. The cause for this can be determined examining Figures 7-9, which show the mixed filtered estimates (black lines) compared with the exact values and the one-step estimates (grey lines) for all the considered cations. It can be concluded from the figures that, due to the limited membrane selectivity, the obtained estimation results are far from the actual values but only for low concentrations of the main ion. Consequently, the practical estimation range is limited to the ion concentrations higher than 10^{-8} mole/l unless some extremely selective membranes are developed.

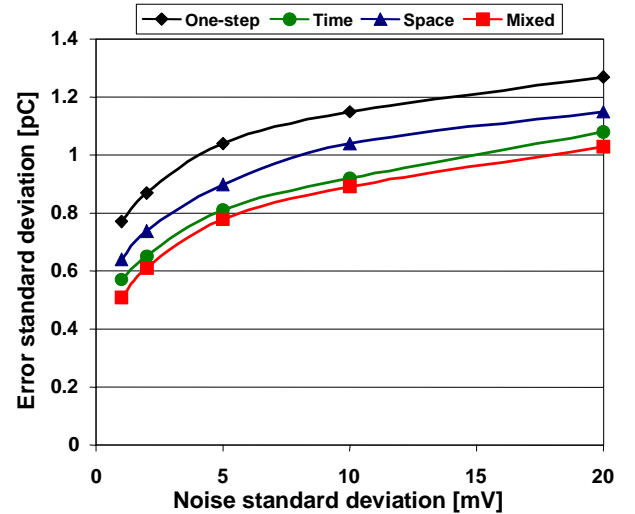


Figure 6: Estimation error standard deviation.

Digital Filter Realisation

The particular problem described here is linear when all the considered ions are univalent. Then, the function specification algorithm can be easily implemented in the form of a digital filter. This approach is computationally efficient and seems to be particularly suited for on-line water pollution monitoring purposes.

The filter coefficients can be determined directly from the algorithm as appropriate sensitivity coefficients. For the full description of the filter coefficient derivation method, refer to [5]. Another possibility is to employ the Kalman filter as described in [7].

The most important advantage of the digital filter approach is that some of the nonlinearities occurring in the real cases, such as the temperature dependence of CHEMFET parameters or selectivity coefficients, can be easily accommodated during the iterative updates of filter coefficients.

CONCLUSIONS

This paper presented the most important problem related to the water pollution monitoring using the CHEMFET sensors. Namely, the particular problem discussed here is due to the imperfect selectivity of sensor membranes, which limits significantly the practical measurement range. The presented numerical experiments confirmed the fact that such sensors are vulnerable to the presence of interfering ions.

The function specification algorithm might be relatively efficient tool for improving the quality of estimates. Employing this algorithm, both the mean value and the standard deviation of the estimation error can be limited in two ways: by averaging subsequent ion concentration measurements or by introducing additional sensors. Both techniques can be applied simultaneously.

The averaging of measured values increases the delay between the occurrence of the ion concentration change and its detection. On the other hand, the introduction of additional sensors increases the computational effort and consequently the estimation time. Therefore, for the on-line estimation of ion concentration, the function specification algorithm combining both averaging techniques to reduce the measurement error influence is suggested.

Although the application of some specialised algorithms can alleviate the problem a bit, but certainly it is not a perfect solution. Definitely, the main limitation of the estimation accuracy constitutes the poor membrane selectivity. Currently, since the estimates obtained for high ion activities are quite accurate, CHEMFETs can be used efficiently only for the detection of contaminant alarm levels. Decisively, in order to improve further the estimate quality the research should be focused on the development of some more selective membranes.

The digital filter approach renders possible the design of an ion concentration monitoring unit, containing a digital filter implementing the function specification algorithm and some additional logic circuitry, which can be integrated within a single IC.

THE AUTHORS

Professor Andrzej Napieralski, Dr. Marcin Janicki and Dr. Marcin Daniel are with Department of Microelectronics and Computer Science, Technical University of Łódź, Politechniki 11, 93-590 Łódź, Poland.
E-mail: napier, janicki, daniel@dmcs.p.lodz.pl

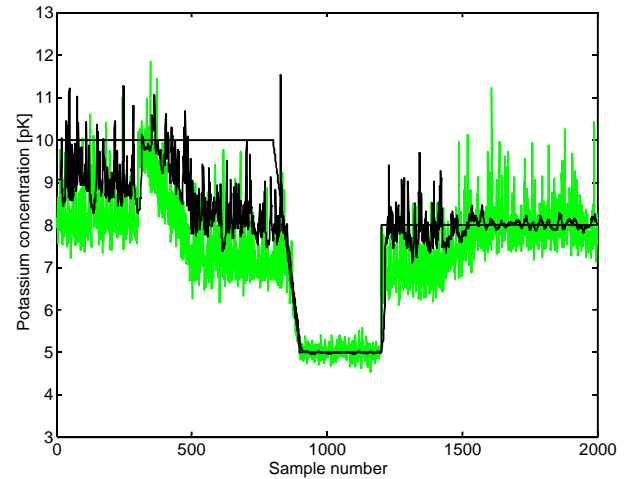


Figure 7: Potassium concentration estimates.

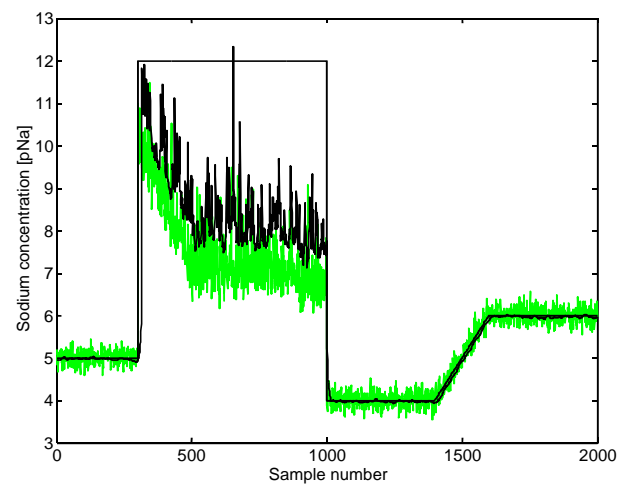


Figure 8: Sodium concentration estimates.

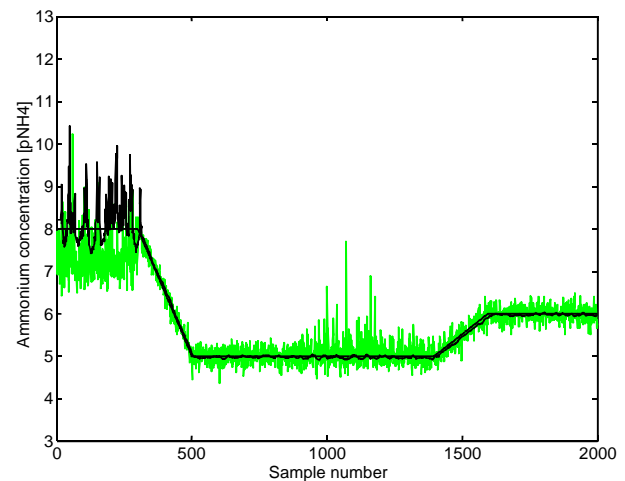


Figure 9: Ammonium concentration estimates.

ACKNOWLEDGEMENTS

This research was supported by the 5th Framework Programme project SEWING – ‘System for European Water monitorING’, IST–2000–28084.

The authors would like to extend their gratitude to all the SEWING partners, especially to the team of Prof. Z. Brzózka, from the Institute of Chemistry at the Warsaw University of Technology, for providing the authors with the values of selectivity coefficients.

REFERENCES

- [1] M. Szermer, M. Daniel, A. Napieralski, Design and Modelling of Smart Sensor Dedicated for Water Pollution Monitoring, Proc. of the 2003 NANOTECH Conference, San Francisco, USA, 23-27 February 2003, Vol. 1, pp. 110-114
- [2] M. Daniel, M. Szermer, M. Janicki, A. Napieralski, Modeling and Practical Verification of the Ionophore Based Chemically Modified Field Effect Transistor, Proceedings of the 2004 NANOTECH Conference, Boston, MA, USA, 7-11 March 2004, Vol.1, pp. 438-442
- [3] M. Daniel, M. Janicki, W. Wroblewski, A. Dybko, Z. Brzózka, A. Napieralski, Ion selective transistor modelling for behavioural simulations, Proc. of the International Conference on Automation in Water Quality Monitoring AutMoNet, 19-20 April 2004, Vienna, Austria, pp. 37-44
- [4] Å. Björck, G. Dahlquist, Numerical Methods, Prentice-Hall Int., New York, 1974
- [5] J.V. Beck, B. Blackwell and C.R. St. Clair Jr., Inverse Heat Conduction - Ill-posed Problems, John Wiley & Sons Inc., 1985.
- [6] M. Janicki, M. Zubert, A. Napieralski, Application of Inverse Problem Algorithms for Integrated Circuit Temperature Estimation, Microelectronics Journal, Vol. 30, November 1999, pp. 1099-1107
- [7] S. Haykin, Adaptive filter theory, Prentice-Hall International, New Jersey, USA, 1996