Flow-injection analysis of multiconponent liquids with multisensor detection

Ipatov, Andrei

Publication date:
2001

Citation for published version (APA):
Ipatov, A. (2001). *Flow-injection analysis of multiconponent liquids with multisensor detection*. Roskilde Universitet. http://rudar.ruc.dk/handle/1800/450

Roskilde University Center

Andrei Ipatov

FLOW-INJECTION ANALYSIS OF MULTICOMPONENT LIQUIDS WITH MULTISENSOR DETECTION

Scientific advisers:
Ass. Prof. John Mortensen, Roskilde University Center (Denmark)
Dr. Andrey Legin, St. Petersburg University (Russia)

Scientific consultant:
Prof. Yuri Vlasov, St. Petersburg University (Russia)

Roskilde
2001

TABLE OF CONTENTS

INTRODUCTION. 4

1. LITERATURE REVIEW 9

1.1. Flow-injection analysis. 9

1.2. Multisensor systems, "electronic tongue" 11

1.2.2 Mathematical data processing methods for multisensor analysis 15

1.3. Choice of industrial objects for FIMS application: control of flue gas from incinerators 21

2. EXPERIMENTAL 24

2.1. Flow - injection multisensor system 24

2.2. Reagents and model solutions 32

2.3. Design of mobile prototype of FIMS 33

2.4. Experiments on incinerators: Vestforbranding (Copenhagen) and ZSO (St. Petersburg) 33

2.5. Mathematical methods for experimental design and data processing 36

3. EXPERIMENTAL RESULTS AND DISCUSSION. 40

3.1. Development of flow - injection multisensor system 40

3.1.1. Choice of the sensors for the analysis of multicomponent solutions 40

3.1.2. Sensors with solid inner contact: analytical characteristics and their comparison with sensors with liquid filling solution 45

3.1.3. Choice of optimum parameters of the flow-injection analysis 50

3.2. Development of flow-injection multisensor system for determination of heavy metal cations: Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr(VI) 56

3.3 Development of flow-injection multisensor system for determination of inorganic anions: SO_4^{2-}, Cl^-, NO_3^-. 62

3.4. Flue gas control 65
3.4.1. Determination of the content of heavy metals in real gas samples 69
3.4.2. Determination of the content of HCl, nitrogen and sulphur oxides in the flue gas from the incinerator 73

4. CONCLUSIONS 76

REFERENCES 79

APPENDIX1. 84

APPENDIX 2. 85

APPENDIX 3. 87

APPENDIX 4. 89

APPENDIX 5. 95

APPENDIX 6. 96

APPENDIX 7. 97

APPENDIX 8. 99

INTRODUCTION.

Development of simple, inexpensive and rapid methods of determination of various components in liquid and gaseous exhausts of industrial enterprises is an urgent task. A perspective direction to solve this task is an elaboration of new ways of control based on combinations of modern methods of the analysis, which are well developed, convenient in practice, but are used separately. Such analytical methods, which could be fruitfully combined together, are flow-injection analysis (FIA) and analysis with chemical sensors and sensor systems (arrays). Utilization of flow-injection analysis allows computerizing of measurements, sampling and sample treatment and also minimizing amount of reagents. The analysis is performed under identical conditions and in short time.

Application of chemical sensors to industrial analysis is highly attractive method but measurements with sensors in multicomponent solutions are hindered by typical difficulties such as poor selectivity of many commercially available discrete sensors. However, recently a new approach has been developed, the so-called “electronic tongue”, based on application of arrays of non-selective (non-specific, poorly selective) sensors and multi dimensional mathematical methods for processing of results of measurements with such arrays (multivariate analysis, artificial neural networks, etc.). Utilization of an array of non-specific sensors (multisensor system) as a detector together with appropriate software opens an opportunity to make simultaneous analysis of several components without preliminary separation or masking of interfering species. Thus, the development and application of new method based on combination of FIA and “electronic tongue” multisensor system for simultaneous determination of content of various substances in complex liquids is an actual and promising scientific task. In the present work we have been concerned with development of flow-injection system with sensor array detection for analysis of heavy metal ions and inorganic anions in multicomponent solutions.

Waste incineration plants near big cities can be potentially dangerous source of environmental hazards. Flue gas from modern incinerators passes through several steps of cleaning, but none of the cleaning methods can guarantee absolute purity of the waste going to the environment. On-line flue gas composition is controlled continuously with respect to content of HCl and SO_2 by spectrophotometry. However, determination of the content of heavy metals in flue gas is being performed only in laboratory, usually with the help of atomic absorption spectroscopy (AAS). The complexity of AAS instrumentation (and similar methods), requirement of highly skilled operator and high price of the analysis is a significant problem. Therefore, the analysis of heavy metal content in the flue gas is performed on periodic basis and it has to be carried out only two times per year according EEC regulations. Consequently, there is no real-time information available about the actual content of heavy metals in the flue gas. In the present work we studied an opportunity to apply our newly developed approach (FIA + sensor array) to analysis of flue gas on site. This is an urgent practical task demanded both by industry and controlling authorities.

Thus the objective of the present study is to develop a method of flow-injection analysis of solutions with multisensor detection for simultaneous determination of several components and to develop and to test a mobile prototype of flow-injection multisensor system (FIMS). FIMS is supposed to be applied at incinerators to perform rapid quasi on-line analysis of heavy metals and other toxic substances, e.g. acidic oxides in the flue gas after it absorption in a special solution.

The main content of this thesis has been published in the international reviewed journals and has been presented at several international conferences devoted to analytical, sensor and environmental topics. The list of relevant publications follows:

1. Y.G. Vlasov, Y.E. Ermolenko, V.V. Kolodnikov, A.V. Ipatov, S. Al-Marok, A mercury sensor for flow- and batch-injection analysis, in Proc. of Intern. Conf. “Chemical Sensors ’94 IMCS”, Rome, 11-14 July, 1994.-Vol.1.-p.405-408.
2. Y.G. Vlasov, Y.E. Ermolenko, V.V. Kolodnikov, A.V. Ipatov, S. Al-Marok, Chloride-selective electrode with flow-injection analysis for determination chloride-content in natural water, in Proc. of the Russian Symposium "Flow-Injection Analysis", Moscow, IONC RAS, 1994, p. 27.
3. Y.G. Vlasov, Y.E. Ermolenko, V.V. Kolodnikov, A.V. Ipatov, S. Al-Marok, A mercury sensor for flow- and batch-injection analysis, Sensors and Actuators, Chemical B 24-25, 1995, pp. 317-319.
4. A. Ipatov, Yu. G. Vlasov, A. Legin and J. Mortensen, Chalcogenide Ion-selective Electrodes and Flow-Injection, in Proc. of 6th Intern. Symposium on kinetics in analytical chemistry, Chalkidiki, Greece, 16-19 September, 1998.
5. J. Mortensen, A. Legin, A. Rudnitskaya, A. Ipatov, Yu. Vlasov, A Sensor Array Flow-injection System for Multicomponent Analysis of Liquids, in Proc. of Intern. Conf. Eurosensors XIII, The Hague, The Netherlands, 12-15 Sept., 1999, pp. 937-940.
6. J. Mortensen, K. Hjuler, A. Legin, A. Rudnitskaya, A. Ipatov, Yu. Vlasov, in Proc. of CEM99 (Control Emission Monitoring) Conference, 6-9 Sept. 1999, Warwick University, Coventry, UK.
7. A. Legin, A. Rudnitskaya, A. Ipatov, Yu. Vlasov, J. Mortensen, K. Hjuler, J., Flow-injection Analysis with multisensor system used for measuring heavy metal ion content in incinerating plant smokes, Appl. Chem. (Russian), 1999, Vol. 72, No. 4, pp. 633-636.

8. J. Mortensen, A. Legin, A. Ipatov, A. Rudnitskaya, Yu. Vlasov, K. Hjuler, A flow injection system based on chalcogenide glass sensors for the determination of heavy metals, Anal. Chim. Acta, 2000, V.403, N1-2, pp.273-277.
9. A. Legin, A. Rudnitskaya, A. Ipatov, Yu. Vlasov, J. Mortensen, Flow-injection analysis of multicomponent liquids, in Proc. of the 2nd Russian Symposium "Flow-Injection Analysis", Moscow, IONC RAS, 1999, p. 42.
10. J. Mortensen, A. Legin, A. Rudnitskaya, A. Ipatov, Yu. Vlasov, A flow-injection system on the principles of ”electronic tongue” for multicomponent analysis of liquids, in Proc. of the 8th Intern. Symposium on flow analysis, Warsaw, Poland, 25-29 June 2000.
11. J. Mortensen, A. Legin, A. Rudnitskaya, A. Ipatov, Yu. Vlasov, A flow-injection system for multicomponent analysis of liquids on the principles of ”electronic tongue”**,** 10th Russian-Japan Joint Symposium on Analytical Chemistry, Moscow and St.Petersburg, Russia, 20-28 August, 2000.
12. J. Mortensen, A. Legin, A. Rudnitskaya, A. Ipatov, S. Makarychev-Mikhailov, Yu. Vlasov, A flow-injection system based on the principles of ”electronic tongue” for multicomponent analysis of liquids In Proc. of Intern. Conf. Eurosensors XIV, August 27-30, 2000, Copenhagen, Denmark, p.193-194.

The reprints of the most important and detailed papers are attached to this thesis.

Main scientific tasks to be developed and studied in the present thesis:

1. Method of simultaneous determination of multiple components in solution based on combination of flow-injection analysis and multisensor potentiometric system with non-specific sensors and computer assisted signal processing by multivariate analysis and/or pattern recognition methods.
2. Method and procedure of simultaneous determination of content of heavy metals (Cu^{2+}, Pb^{2+}, Cd^{2+} etc.) in multicomponent solution with the help of FIMS.
3. Method and procedure of simultaneous determination of content of inorganic anions (Cl^-, SO_4^{2-}, NO_3^-) in multicomponent solution with the help of FIMS.
4. Feasibility study enabling control of composition of flue gas from incinerators by absorption of the gas in liquid with subsequent analysis by using FIMS.

1. LITERATURE REVIEW

1.1. Flow-injection analysis.

The opportunity of automation of the analysis plays an important role in the choice of analytical method. The automation allows to make human work more productive and to avoid routine operations. From this point of view flow-injection analysis has the special advantage. Initially injection method was applied as automatic variant of the analysis in separate containers. This approach strongly increased productivity in comparison with hand-made analysis, but the first pieces of the equipment were complex. Development of modern technology in industry and computers gave a new impact to the development of FIA. Now there are different flow-injection analysers available for laboratory and industrial use. The typical sample volume in them is within the limits from several μdm^3 up to 1 cm^3. An opportunity to carry out the analysis several hundreds times per hour is very important also. Computer software allows quick processing of the data and gives result of measurements in the form convenient for the researcher or user. At present time over 10 thousand works devoted to FIA and its applications are published. There are several periodic international conferences and symposiums, such as International conference on Flow analysis, International conference on Flow-injection analysis, etc. Furthermore, a number of computer databases allow finding technique, methodology and fields of application of flow-injection analysis [1,2].

Current situation in FIA throughout the world is described thoroughly in the books and reviews of Hansen and Ruzicka [3-5]. Papers [6,7,8] are devoted to the history of development, theory and detection methods in FIA and also a wide range of applications is described. The reviews [9,10] are devoted to new modifications of FIA - sequential injection analysis (SIA) and bead injection (BI). The principles of these methods of the analysis and also spheres of there application (biomonitoring, monitoring of sewage, analysis of petroleum and objects containing radionuclides, monitoring of pharmaceutical productions) are described.

In case of industrial process control, chemical process control, etc., it is important that the manipulatory steps in the analytical chain can be carried out in aggressive solution, with small quantities of analytes without losing of reagents, etc. All the system parameters in FIA can be readily optimized, controlled and adjusted to ensure the best performance and highest available precision [11].

Since recently a tendency is observed towards development of electrochemical methods of detection in FIA. Electrochemical detectors, especially chemical sensors of different types display serious advantages in comparison with widespread photometric ones: relative simplicity, low cost, wide range of concentrations and quick response. There are numerous different modifications of flow cells for electrochemical detectors: from conventional ones, used for direct potentiometry, up to elaborated devices, where the sensitive layer is deposited onto the surface of internal channel and is actually a part of the tube. However, application of electrochemical sensors in flow-injection systems for industrial analysis still comes across many difficulties.

It is possible solve some of these problems with the help of new approach based on application of non-specific sensor systems ("electronic tongue") and mathematical methods of pattern recognition and multivariate analysis.

1.2. Multisensor systems, "electronic tongue"

1.2.1. Examples of multisensor systems for the analysis of multicomponent solutions

Application of multisensor systems for the analysis of liquids obtained recently increasing development [12]. Multisensor system consisting of non-specific sensors with the data processing by pattern recognition and multivariate analysis methods for simultaneous determination of multiple components were named "electronic tongue" in 1995 [13].

First multisensor systems consisted of small number (3-4) of ion-selective sensors (electrodes). Various methods of the data processing were applied to deal with the output produced by these systems.

Simultaneous determination of concentration of NH_4^+, Ca^{2+}, K^+, Na^+ ions in solutions in a wide concentration range was described in [14]. A set of modified Nikolski equations was used to fit response of the sensor array.

Otto and Thomas [15] choose multiple linear and partial least squares regressions to produce calibration model, which was based on two parameters in the extended Nikolski equation. E_j^0 and K_j, where E_j^0 – the standard electrode potential for j -electrode, K_j - selectivity factor of j-electrode to analyte *k* in presence of an interfering ion *l*. This work demonstrated the opportunity of determination of Ca^{2+}-, Mg^{2+}-, K^+-, Na^+- ions at concentration levels characteristic for biological cells (millimoles per liter). The advantage of application of partial least squares regression to data processing from the sensor array is shown in comparison with common least squares method. Sensor array included glass sodium-selective electrode, PVC electrode selective to potassium and calcium ions and custom made

Ca^{2+}, Mg^{2+} selective electrodes. Sensor array and partial least squares regression for data processing ensured concentration determination of Ca^{2+} and Mg^{2+} ions with an average error about7 %.

Beebe K. etc. suggested a nonlinear regression technique [16] for processing of signals from an ion-selective electrode array. It was assumed that the shape of electrode response is unknown a-priori and could be considered as changeable parameter during experiment. It was stated that stability and reproducibility of sensor responses are necessary characteristics for such an analytical technique. Simultaneous determination of Na^+ and K^+ ions was possible with errors 0.9 % and 3.4 %, respectively.

A new non-parametric multivariate regression method was introduced in [17]. This method allows to carry out calibration of sensor system without information about functional form of dependence between concentrations and sensor responses. The method was applied to the data processing from ion-selective sensor array for determination of Na^+ and K^+ ions. Sensor responses were described by a set of extended Nernst equations:

$E_{ij}=E_j^0+S_j *log(C_{iNa}+K_j *C_{iK})$.

Average errors of Na^+ and K^+ ions detection were 0.4 % and 5.3 % respectively.

Application of artificial neural networks for the processing of the signals from sensor array is discussed in [18]. Simultaneous determination of concentration of Ca^{2+} and Cu^{2+} ions was carried out with the help of calcium, copper and pH-selective electrodes. The errors of determination were not more than 8 %. For simultaneous determination of K^+, Ca^{2+}, NO_3^- and Cl^- ions sensor array included corresponding ion-selective electrodes and pH-glass electrode. Average errors of determination were about 6 % and the poorest precision (for K^+ and NO_3^-) was within 20%.

Response from flow-injection system including sodium, potassium and calcium ion-selective electrodes as detectors is described in [19]. Back-propagation artificial neural network was applied for data processing. The influence of a number of parameters on results were investigated such as: number of iterations during net training and application and role of various factors in FIA, e.g. drift of baseline, change of the shape and height of peak, etc. Neural networks demonstrated ability to be trained and applied to identify components with the help FIA. About 44 of 56 combinations of ion test samples were classified correctly. Chalcogenide glass materials sensitive to heavy metal ions were suggested in [20-22] with the aim to develop and study "electronic tongue" multisensor systems. More than 30 various materials were applied as sensors and optimal sensor arrays were investigated.

Quantitative determination of cations of heavy metals (Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}) in concentration range 10^{-7}-10^{-4} mol/dm^3 and inorganic anions (Cl^-, F^-, SO_4^{2-}) in aqueous solutions with the help of multisensor systems is described in [12,23]. Artificial neural networks for processing of sensor array response ensured nice precision with the following average analytical errors: 2.3 % - Cl^-, 1.3 % - F^-, 8.5 % - SO_4^{2-}, 0.6 % - Cu^{2+}, 4.3 % - Pb^{2+}, 6.7 % - Cd^{2+}, 11.0 % - Zn^{2+}.

Influence of membrane composition on its cross-sensitivity was studied in [20,22]. Over 30 chalcogenide glass membranes of various composition were evaluated and it was shown that most of the sensors display sufficient cross-sensitivity to use them in sensor arrays. A set of empirical parameters was offered to estimate cross-sensitivity of sensors [12,22]: S_{av} - average ion slope, F - non-selectivity factor, K - reproducibility factor.

The parameters of cross-sensitivity are calculated using the following formulas:

$$\mathbf{S_{av}} = \frac{1}{\mathbf{n}}\sum_{\mathbf{i}} \mathbf{S_i} \qquad (1.1),$$

Where S_i - sensor response slope in solution of *I*- ion, *n* - number of ions.

$$F = \frac{S_{av}}{s^2} \qquad (1.2),$$

Where s^2 - variance of average slope value.

$$K = \frac{1}{n}\sum_{i} \frac{S_i}{s_i^2} \qquad (1.3),$$

Where s_i^2 – variance of sensor response slope in solution of *I*- ion.

Average slope S_{av} is the most significant cross-sensitivity parameter. The value of S_{av} higher than 20 was considered as acceptable for application of the sensor in an array of electronic tongue. Such sensors are considered to be non-specific. Non-selectivity factor describes the “smoothness” of sensitivity distribution. F value lower than 0,1 corresponds to “too selective” sensor that is sensitive mainly to its primary ion. Sensor with $F=2$ and higher display reasonable sensitivity to several ions from chosen set. Reproducibility factor *K* describes reproducibility of sensor response in solution of all ions of interest. $K > 2$ corresponds to acceptable reproducibility of sensor behaviour for multisensor applications. Therefore, the following values of cross-sensitivity parameters: $S_{av}>20$, $F>0,2$, $K>2$ were found acceptable for non-specific sensors. Cross-sensitivity estimation method appears to be universal enough and applicable to different potentiometric chemical sensors. Method of cross-sensitivity evaluation will be used further in present work to choose materials for sensor array of FIMS.

1.2.2 Mathematical data processing methods for multisensor analysis

Application of sensor systems for multicomponent analysis requires special mathematical methods for processing of complex experimental data [24-26]. Measurements in this case are made not with discrete sensors but with an array of sensors with different compositions and properties e.g. cross-sensitivity. Sensor responses (potentials vs. standard reference electrode) in analysed solutions are registered. All sensors of array should be in identical conditions during measurements. Resulting experimental data represent a set of variables, which contain information about different solution constituents. Sometimes this data set can be big enough, e.g. it can include responses of 20 sensors in 30 multicomponent solutions, each containing at least 5 chemical components. Multivariate data analysis techniques proved to be very useful in the case when more then one variable is considered. In quantitative analysis multivariate calibration methods are applied to produce calibration model when dependent variable or variables (concentrations of analytes) is a function of several explanatory variables (responses of sensors). Multivariate calibration is performed with a set of calibration solutions, which should be as close as possible in composition to solutions to be analysed in the future. Calibration solutions can contain various ionic and neutral organic and inorganic components depending on the task. During calibration process mathematical model for adequate representation of experimental data is elaborated. Calibration process consists of determination of parameters of this model(s). After calibration the multisensor system can be used for prediction of analyte concentration in unknown samples.

Various multivariate calibration methods can be applied for multisensor system data processing.

Multiple linear regression (MLR).

The MLR is linear and parametric method and can be used when components of a complex signal are known or can be adequately estimated [25,26]. Thus, it is supposed that complex signal R_i is a linear combination of individual components and can be expressed as follows:

$$R_i=\beta_{1i}p_1+\beta_{2i}p_2+\ldots+\beta_{ni}p_n+\varepsilon_I \qquad (1.4)$$

Where β_{1i} - coefficient (molar ratio) of *j*-component, which has influence on R_i; p_j - signal obtained from pure j-component; ε_I - error.

For n components the equation (1.1) can be written in the matrix form:

$$R= P\beta + \varepsilon \qquad (1.5)$$

If P and R are known, it is possible to estimate β using least squares criterion.

Multiple linear regression may fail in some cases. First, the number of variables can be larger than the number of samples as it frequently happens in practical tasks. In this case the system is overdefined and the unique solution could be not found. Another requirement for application of MLR is that variables should not be collinear, i.e. they must be not correlated. Collinearity in the data can lead to unstable solutions. Thus, another multivariate calibration techniques should be used to handle collinear and noisy data. One of the most powerful methods in this case is partial least squares regression (PLS), which is also referred to as Projection to Latent Structures.

Partial least squares regression (PLS)

Application of PLS [27-29] allows to obtain stable solution (calibration model) in the cases when other regression techniques fail. PLS is one of the most generalised regression techniques since it can perform particularly well on collinear and noisy data, as well as handle the data where number of variables is bigger then that of samples. Another feature of PLS is favourable signal-to-noise ration, which is achieved by data decomposition into structured and noisy parts. In contrast to other techniques the number of response variables (Y-variables) can be more then one and generally is not limited.

Partial Least Squares Regression is a bilinear modelling method where information in the original explanatory variables (X matrix) is projected onto a small number of underlying ("latent") variables called PLS components. The Y-variables are actively used in estimation of the "latent" variables to ensure that the first components are those that are the most relevant for precise prediction of the Y-variables. Resulting calibration model usually use smaller number of components in comparison with other regression methods, and these components are more easily interpreted.

The most important feature of PLS is that decomposition of X matrix is guided by the structure of Y matrix and vice versa. First, Y-scores are calculated and then used as starting score values for X matrix decomposition. After scores and loadings (called weights in PLS) for X matrix are calculated, X-scores are used as starting point for Y matrix decomposition, i.e. X scores are taken instead of Y scores in the beginning of calculation. Therefore X and Y scores are interchanged until they converge. As a result, final PLS model would include only that part of variance (information) from X matrix, which is correlated with Y matrix. Resulting PLS model can be described as follows:

$$\begin{aligned} X &= \sum_{A} T \cdot P' + E \\ Y &= \sum_{A} U \cdot Q' + F \end{aligned} \qquad (1.6)$$

where T and U are scores, P and Q are loadings and E and F are errors for X and Y matrix, respectively, A is a number of PLS components used in the model.

Decision on now many components to include in the model is based on validation results. Validation is a necessary part of calibration process, which also helps to estimate prediction error in determination of concentration of unknown samples.

PLS components are used to construct traditional regression equation:

$$\mathrm{Y} = \mathrm{B} \cdot \mathrm{X}, \qquad (1.7)$$

where B is a vector of regression coefficients.

This equation is used for component concentration prediction in unknown samples.

Regression coefficients B are calculated as follows:

$$\mathrm{B} = \mathrm{W}(\mathrm{P}' \cdot \mathrm{W})^{-1}\mathrm{Q}', \qquad (1.8)$$

where W is X loading weights.

Artificial neural network (ANN).

Artificial neural networks are computational algorithms based on analogy with learning and memory functioning in brain [30-33]. Network performance can be described by the following characteristics: processing units called neurons, order of their connection in the network (topology) and algorithm of network training. Associative neural networks are most often used in chemical applications. Networks of this type are capable, after an adequate training, to transfer the data from input space to output one. Both spaces and transition between them are defined during training process, during which input and output data sets are presented to network and its parameters are changed consequently. After training the network has ability to make "associations", i.e. to interpolate within defined spaces. The most widespread network of this type is the so-called feed-forward or back-propagation neural network [32].

The model of processing unit – an artificial neuron is shown in Fig. 1. Neuron receives a number of inputs and produces only one output signal. Each input signal X_i to neuron is connected to the weight factor or connection strength w_i. The behaviour of the neuron itself is described by two functions: input net function and activation function *f (net).* The input function computes a single input value (stimulus) from assembly of input signals and their associated weights. The activation function calculates the activation (output) value of the neuron as a function of the current net input. The activation function can take the previous activation value into account when deriving a new activation value, thus giving the neuron a time-dependent behaviour.

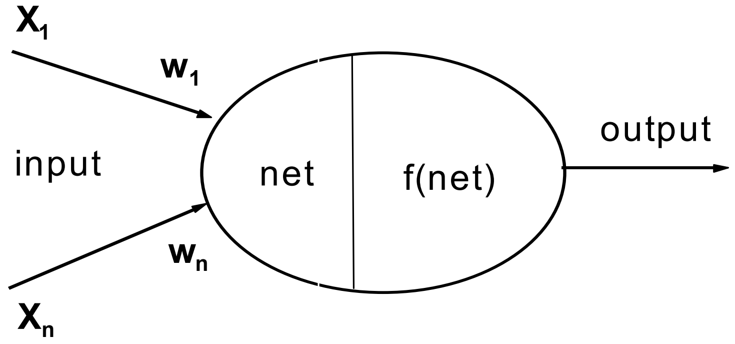


Fig. 1. Model of an artificial neuron.

Input function in feed-forward neural net is often a weighted summation of input signals.

$$\mathrm{net} = \sum_i x_i w_i \qquad (1.9)$$

Activation function may have different forms; most often it is non-linear smooth function such as, e.g. sigmoid one:

$$f(\mathrm{net}) = \frac{1}{1 + e^{-\mathrm{net}}} \qquad (1.10)$$

The network is usually organised in layers and has an input layer, at least one processing or hidden layer and the output layer. The input layer receives the external information; the output layer provides for response of the network to the set of input signals. There may be one or more hidden layers, which together with non-linear activation function gives the network its non-linear modelling capability [32].

Feed-forward neural network produces non-linear model, capable to map an input space to an output space. Performance of the network with the given topology is determined by a set of weights, which are defined during training and would not change afterwards. Thus, the aim of network training is the search for such set of weights, which would make the network to yield correct output signals for each sample from the given training set. During training the weights are optimised iteratively using a set of examples (samples) – the so-called control data set [31-34]. The aim of optimisation is to minimise the errors of output signals. This is done by comparing actual network output with desired one. After training the network can be applied, depending on the task, for prediction of component concentrations or class membership for new (unknown) samples.

The choice of the data processing methods in the present study was based on the available literature and previous expertise of the author and coworkers. PLS is one of the most widespread and successful methods in multivariate analysis. Previously, dealing with the data processing from the sensor systems, different multivariate methods were assessed such as multilinear regression (MLR), principal component regression (PCR) and some others. Usually, the best or one of the best fits was produced using PLS. For this reason PLS has been chosen as an adequate example of the multivariate analysis technique for the present study, to process the data from flow-injection multisensor system.

Similarly to the case of PLS, different types of artificial neural networks were studied and evaluated for the sensor array data processing earlier. It has been found that the best fit is commonly produced by a 3-layer back-propagation artificial neural network (BPNN) with adequate number of neurones, depending on the task and the data structure. Other types of ANN, such as radial basis function network, perception, general regression network, etc., were also assessed but did not give any advantages in comparison with BPNN for this kind of the data. Thus, BPNN was chosen as a typical ANN for the purpose of the present study.

1.3. Choice of industrial objects for FIMS application: control of flue gas from incinerators

Construction of waste combustion plants - incinerator began several decades ago. The first incinerators had primitive system of flue gas cleaning. Therefore, after certain time the content of toxic substances near plants exceeded permitted limits. For example, Cd content near incinerator of the first generation considerably exceeds limit threshold [35]. Nowadays both state authorities and public organisations pay attention to purity of exhausts from industrial plants, in particular from incinerators. The review [36] is devoted to the problem of mercury exhaust from incinerators. Various factors influencing mercury release and its mobility in different chemical forms are discussed in [37]. The presence of sulphur oxides in flue gases complicates gas cleaning by common filters (acid column) since mercury can be bound into insoluble chemical substances.

For this reason primary attention is paid now to the development of elaborated cleaning systems, which can cost up to 30 % of total factory cost. Large number of scientific publications is devoted to the study of influence of combustion technology on composition of the smoke (flue gas). In the last years significant attention is paid to the detection and cleaning of microamounts (picograms/м^3) of highly toxic organic compounds such as dioxines. The analysis of heavy metal content in ashes and in filtrates is done in [38,39]. It was found, that heavy metal content in fly ashes and filtrates depend not only on composition of burnt waste (garbage) but also on the size of particles and conditions of combustion. Various chemical reactions are studied, which can proceed depending on combustion temperature, rate of cooling of flue gases, technology details and accompanying substances present in flue gas. New absorbents and filters allow to increase significantly cleaning efficiency of flue gas [40-44] but still some heavy metals can be present in exhaust to atmosphere. Dependence of heavy metal vapour formation on combustion temperature is investigated in [45]. Temperature in the range 1000-1100^0 causes sharp increase of the content of Cd, Pb, Cu and Zn in the vapour (98-100 %). It is highly recommended that metal analysis in flue gas should be performed at least 2-3 times per month [40], however only dramatic reduction of analysis cost by available methods can make economically feasible several analyses per day.

Therefore literature analysis confirms that the ultimate purpose of the present study to develop an analytical device, which is capable to perform several analysis of flue gas per day is of highest practical impact.

2. EXPERIMENTAL

2.1. Flow - injection multisensor system

Flow-injection multisensor system (FIMS) comprised some standard elements commonly used in flow-injection analysis and the devices, which were developed for the first time in the present study. The system included the following parts: a computer-controlled three-channel peristaltic pump 110SR Ole Dich Instrumentmakers aps (range of flow rate from 1μdm^3/min to 1500 μdm^3/min), a device for automatic injection from Rheodyne, an injector from Altec with combined switch (manual or/and automatic) and connecting sockets from Upchurch. Teflon tubes (d=0.8 mm) were implemented in flow-injection system because solutions with various pH, including those of strong acids and bases, could be used.

The most crucial and novel element of FIMS, which was developed and studied in the present work was the flow cell specially designed for the sensor array applications.

The first experiments, at an earlier stage of FIMS development, were carried out with a cubic cell where each field of the cube has one sensor installed. The whole set-up was based on the wall-jet approach, well known for flow systems. The sensors were the standard chalcogenide glass ones with semi-spherical or flat membranes, incorporated into 10 or 12 mm diameter bodies with an outside screw. Thus, the cell included maximum 5 sensor (Cr, Pb, Cd, Cu, Fe) and a reference electrode. The inner diameter of the channel was about 2 mm and the shape of the channel was a broken line with a number of 90^o angles, after each next sensor.

The experiments in individual and mixed solutions with different combinations of components and concentration ranges were carried out in this cell. The overall ranges of component concentrations were as follows: dichromate potassium $5*10^{-4}$-$5*10^{-7}$ mol/l, lead nitrate $5*10^{-3}$-10^{-6} mol/l, cadmium chloride, $5*10^{-3}$-$5*10^{-7}$ mol/l and copper nitrate $5*10^{-4}$-10^{-6} mol/l. 0,01 M nitric acid was used as a background solution. The sample volume was changed in the range 50-500 μl. The flow rate was varied in the range 0,5 – 1,5 ml/min. The calibration measurements were carried out in individual ion solution as well as in various mixed solution.

An example of the results, obtained with this cell for lead, cadmium and chromium determination are shown in the Tabl.1 for the concentration range 10^{-3}-10^{-4} mol/l. One can see that the error of determination for lead and cadmium are big enough in this case (more than 100 %). The value of electrode slope (sensitivity) was from 50% to 90% of that measured under static conditions. Reproducibility of the results was in the range 10-20%. The relaxation time was in range from 50 sec (for low concentrations) and up to 10 min (for high concentration). High value of the relaxation time was probably related to the presence of some air bubbles but mainly to the presence of a “dead volume” zone near electrode surface, where only slow change of the solution after injection could occur. The detection limit for this cell under flow conditions was about 100 times worse than that for the same sensors in the static regime. The main suspected reason of the deterioration of the detection limit was the sensitivity of the sensors to high hydrogen concentration due to nitric acid background solution. The results of the calibrations were better, when the solutions were prepared on distilled water but not nitric acid. However, the design of the cell was still not a success.

For determination of multiple components in mixed solution the cell with more sensors was needed. Thus, we made the next cell of line construction with the channel inner diameter of 3 mm and of the overall sizes 2*2*15 cm.

The cell was made from a Plexiglas rod. The basic set-up was made for 6 sensors with an option to incorporate up to 10 sensors. The first experiments showed rather unstable sensor signals (more than 20% of peak magnitude variations) and high values of relaxation time. It was more than more than 10 min for solutions with the concentration in the range 10^{-4}-10^{-3} mol/l, for flow rate 0,5 ml/min and sample volume 0,1 ml.

Since all membranes still had spherical surface due to specific conditions of the synthesis of chalcogenide glasses it caused some problems about this set-up. It was practically impossible to solve the problem of air bubble penetration into the cell near the membranes, because it was very hard to maintain good hermetic tightening assembling all pieces of the construction together.

Therefore, we tried to construct the third cell, where sensitive membranes were glued into a plastic tube with the inner diameter of 3-5 mm. In this case the probability of air bubble penetration was much lower, because only part of the membrane was glued into the tube (6-8 mm^2), but not it's all surface (about 20-30 mm^2). In this set-up it was possible to use the tubes up to 20 cm long, which allowed to place up to 10-15 sensitive membranes. The dilution of the sample was significant in longer tubes. This cell had reasonable characteristics, but some problem arose when the cell contained more than 6-7 sensors. In this case the tube had too many holes and one must have used the set-up extremely carefully to avoid leakage, deformation or damages.

On other hand, in all three set-ups described above nitric acid was used as background solution. This also resulted in less reproducible results due to harsh conditions and significant influence of relatively high content of hydrogen ions on the sensor performance. Finally, it was decided to elaborate the procedure of measuring at “mild” pH values, e.g. in the acetic buffer. The acidic solution after the sampling was partly neutralised by sodium hydroxide and then sodium acetate was added. The resulted buffer had the pH from 4.5 to 5 and ensured very good conditions for long-term stable and reproducible sensor performance.

The determination of iron(III), chromium(VI) and mercury(II) must still be carried out in the pH range 0-2 due to specific features of chemistry of these elements such as pH ranges of stability of corresponding ions. Thus, it was finally suggested to divide sample into two part and to analyse one part without neutralisation (Cr, Fe, Hg) and another part in the acetic buffer (all other metal ions and anions).

The construction of the cell of the fourth generation is shown in Fig.2

The final version of the cell was made from a special sort of melted Plexiglas. It was not an accidental choice, because different materials were studied and it was found out for example, that extrusion Plexiglas is not chemically stable enough to be used as the cell material. The cells for various number of sensors (from 3 to 10) were made. The diameter of the internal channel of the cells was 1,4 mm. Since all parts of the cell and new configuration of sensors were made with high enough precision and accurate tightening it was possible to minimise the problems of bubbles and dead volumes. It was found that this was an optimal flow cell configuration, which allowed, together with using flat surface sensors in the specially designed bodies, a minimal dispersion of samples and reproducible results.

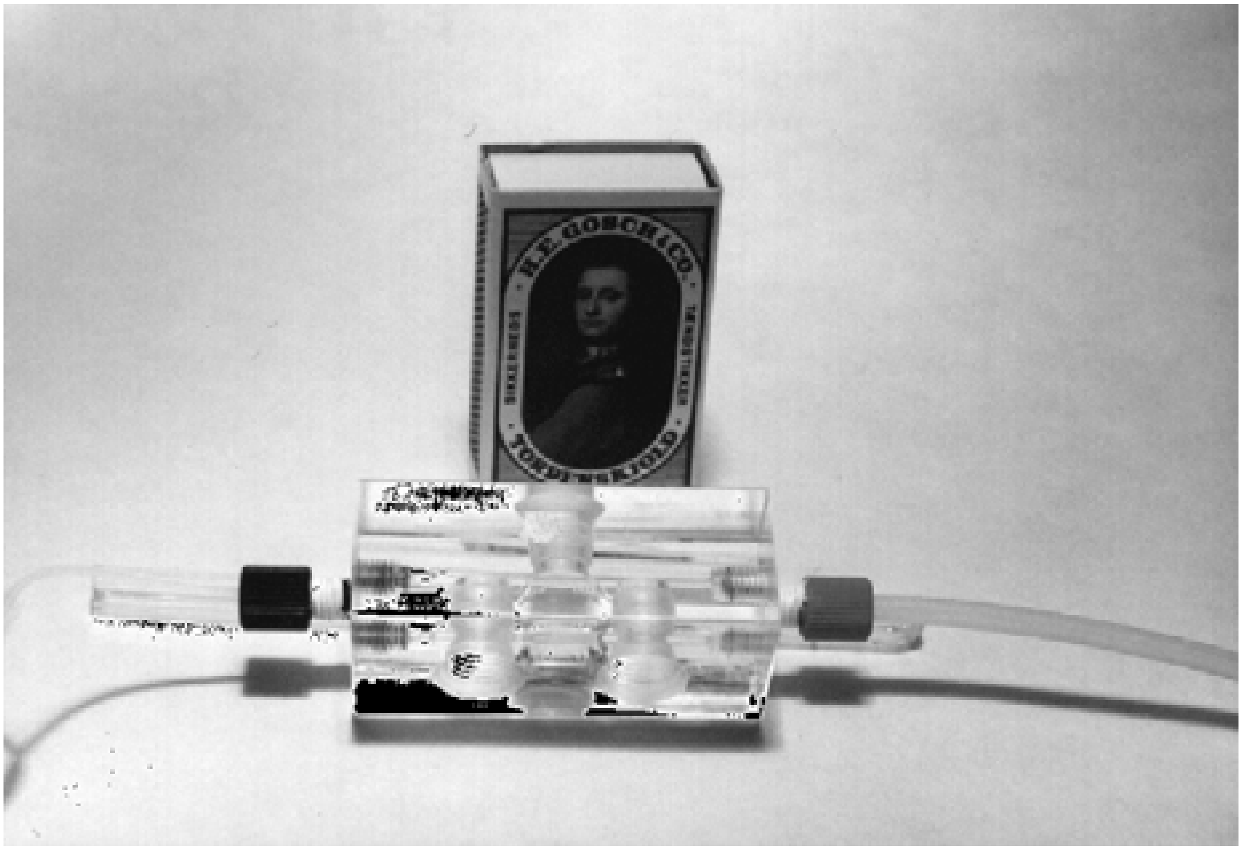


Figure 2. A flow cell for 3 sensors.

The synthesis of chalcogenide glasses is widely described elsewhere [46]. It was carried out in evacuated quartz ampoules from semiconductor pure components during 10-24 hours at 700-1000 K. Composition of each sensor was adjusted by addition of known amounts of different reagents, such as glass-formers As_2S_3, As_2Se_3, AsSe, AsTe, GeS_2, GeS, GeSe, Sb_2S_3, etc.; silver compounds Ag_2S, Ag_2Se, AgBr, AgI; different metal salts – CuI, CuBr, PbI_2, PbS, CdS, and other additives AsI_3, Ag_3SI, etc. Depending on combination and concentration of components it is possible to prepare a very wide number (hundreds and even thousands) of promising sensor compositions. This work was performed in the present study of the basis of preliminary expertise gained in the Laboratory of Chemical Sensor of St. Petersburg University.

Sensing materials for PVC based membranes were prepared by dissolving of known amounts of components (PVC, plastisizers, ionophores, neutral carriers, different additives) in an organic solvent (cyclohexanone or tetrahydrofurane) and drying of the resulted membrane at room condition for few hours. A metallic wire was glued to the membrane surface by a specially designed conductive material to produce all-solid-state without liquid filling inside, which is quite useful and convenient for relatively small sensors for FIA. All PVC sensor materials were purchased from Fluka in Selectofore grade. Typical examples of sensing material components are as follows: high molecular weight poly(vinyl chloride) (PVC); bis(2-ethylhexyl)sebacate (DOS) and 4-nitrophenyloctyl ether (*o*-NPOE) (plastisizers); tridodecylmethylammonium nitrate ($\mathrm{TDDMANO_3}$) (ionophore); nonactin or valinomycin (neutral carriers); potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB) (additive).

Crystalline and chalcogenide glass membranes were glued into sensor body with the help of epoxy resin, and PVC-based membranes were glued with PVC glue. The solid-sate sensors had mirror-flat surface, which was obtained by polishing them with abrasive paste (size particles – down to 0.5 micron). PVC membranes were made flat by pouring membrane cocktail on a flat glass surface of a Petri dish.

All sensors for FIMS were made with solid inner contact, including sensors based on PVC materials (Fig. 3).

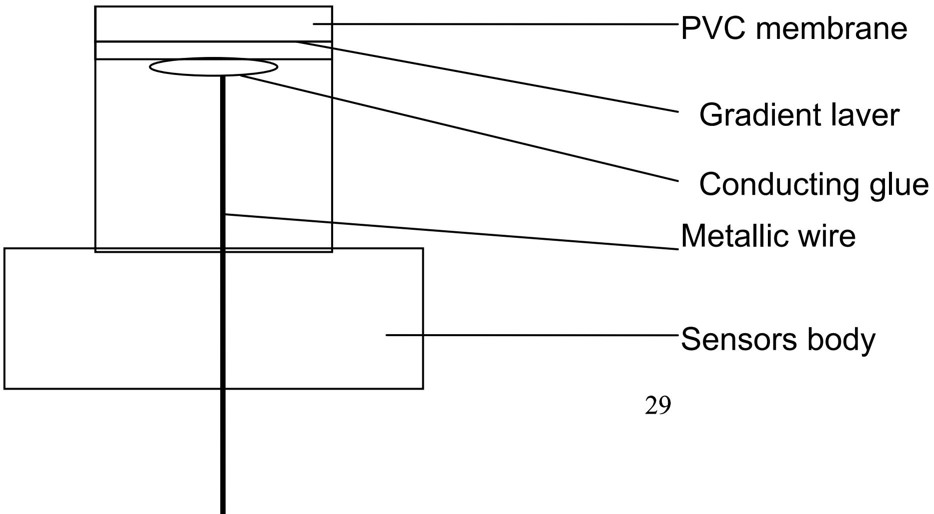


Figure 3. Design of PVC sensors with solid internal contact

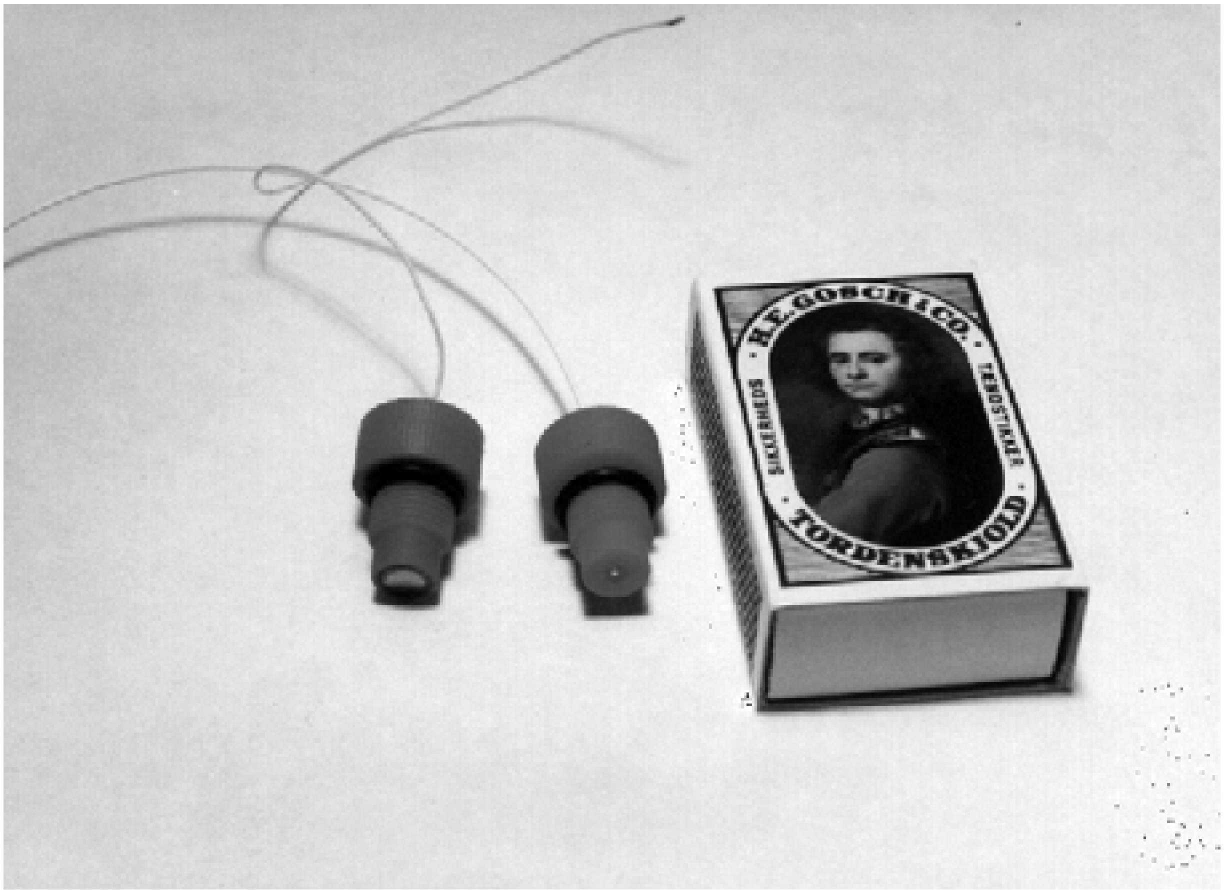
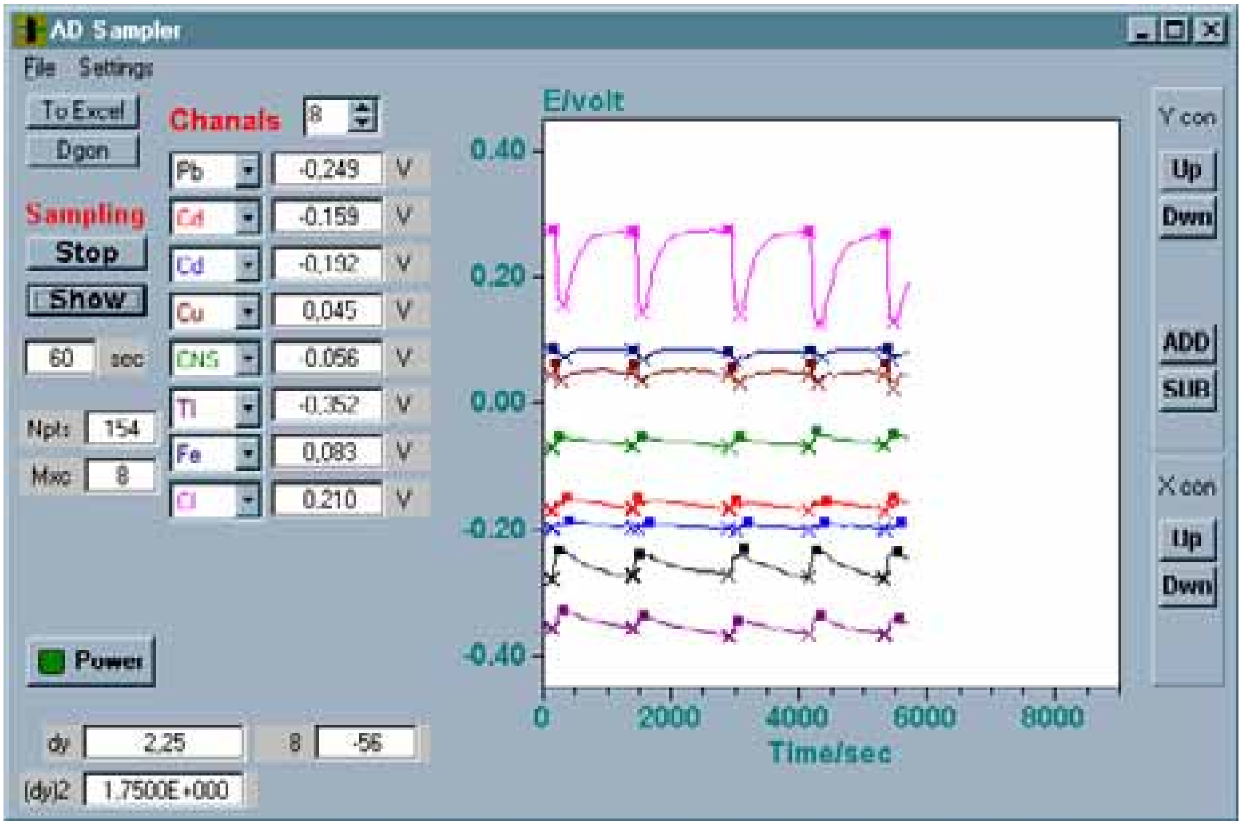


Figure 4. Sensors with solid internal contact used in FIMS.

Sensor bodies were specially developed and adjusted to flow cell. The bodies had small sizes and they were easily replaceable in the cell. The sensors for FIMS are presented in Fig. 4.

For data acquisition and management of flow-injection system hardware we made special computer software. The software was tested both on desktop and portable computers. Users interface of the software is shown in Fig. 5.



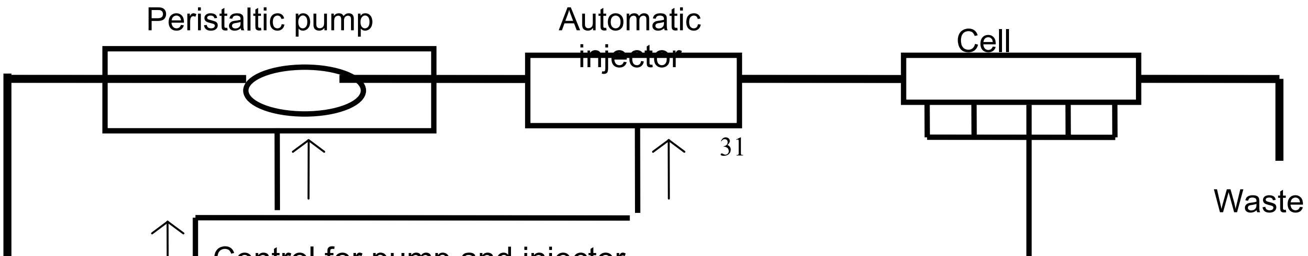
Chanals 8

Pb -0,249 V
Cd -0.159 V
Cd -0,192 V
Cu 0,045 V
CNS -0.056 V
Tl -0,352 V
Fe 0,083 V
Cl 0.210 V

60 sec
Npts 154
Mxo 8
dy 2,25
8 -56
(dy)2 1.7500E+000

Figure 5. The outlook of a screen with custom-made software interface for FIMS

The program showed the code name of sensors, potential values, rate of the drift for each sensor in real time and other data. The graphic plot of potential vs. time was also produced in real-time mode. The software allowed making automatically an injection, changing the flow rate, calculating parameters of sensor signals and producing the data file. Scheme of interaction of FIMS components is demonstrated in Fig. 6. The background solution was constantly pumped through the cell to stabilize the baseline. After an injection, the peak for each sensor was registered, the maximum height of the peak being calculated and written to the data file, which finally contained potential values of sensors for the baseline and magnitude of all peaks.



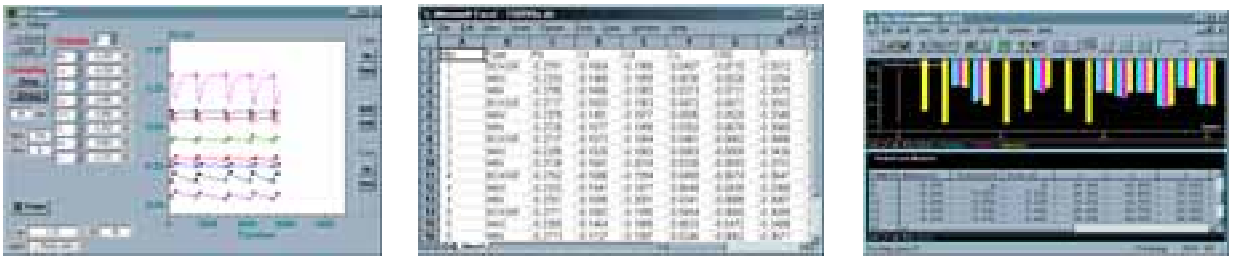


Figure 6. Schematic of FIMS operation

Different multivariate analysis methods (PLS, MLR, etc) were used for experimental data processing with the aim to produce an appropriate calibration model for given sensor array and set of analytes. After proper system calibration, determination of components concentration in unknown solutions composition was possible.

2.2. Reagents and model solutions

All chemicals for standard solution preparation were pro analysis from Merck. Stock solutions with concentration of 1 mM of the metal ions, preferably from their nitrate salts, were prepared in 1 M nitric acid. Cr(VI) solution was prepared from K_2CrO_4 in 1 M nitric acid. For anion determination, solutions of NO_3^-, SO_4^{2-}, Cl^- with concentration of 1M were prepared from their sodium salts. The model multicomponent solutions were prepared by addition of known amounts of concentrated standard solutions of appropriate components to fixed volume of distilled water.

2.3. Design of mobile prototype of FIMS

Besides experiments in the laboratory our work included development and testing of the system at incinerators. For this purpose the mobile prototype of FIMS (Fig. 7) was designed and assembled. All parts were placed in the box of standard industrial size, which can be combined together with other standard analyzers. A laptop computer was used for data acquisition and processing. The portable version of FIMS was used for measurements on incinerators Vestforbranding (Copenhagen) and ZSO (St. Petersburg).

Figure 7. Mobile prototype of FIMS.

2.4. Experiments on incinerators: Vestforbranding (Copenhagen) and ZSO (St. Petersburg)

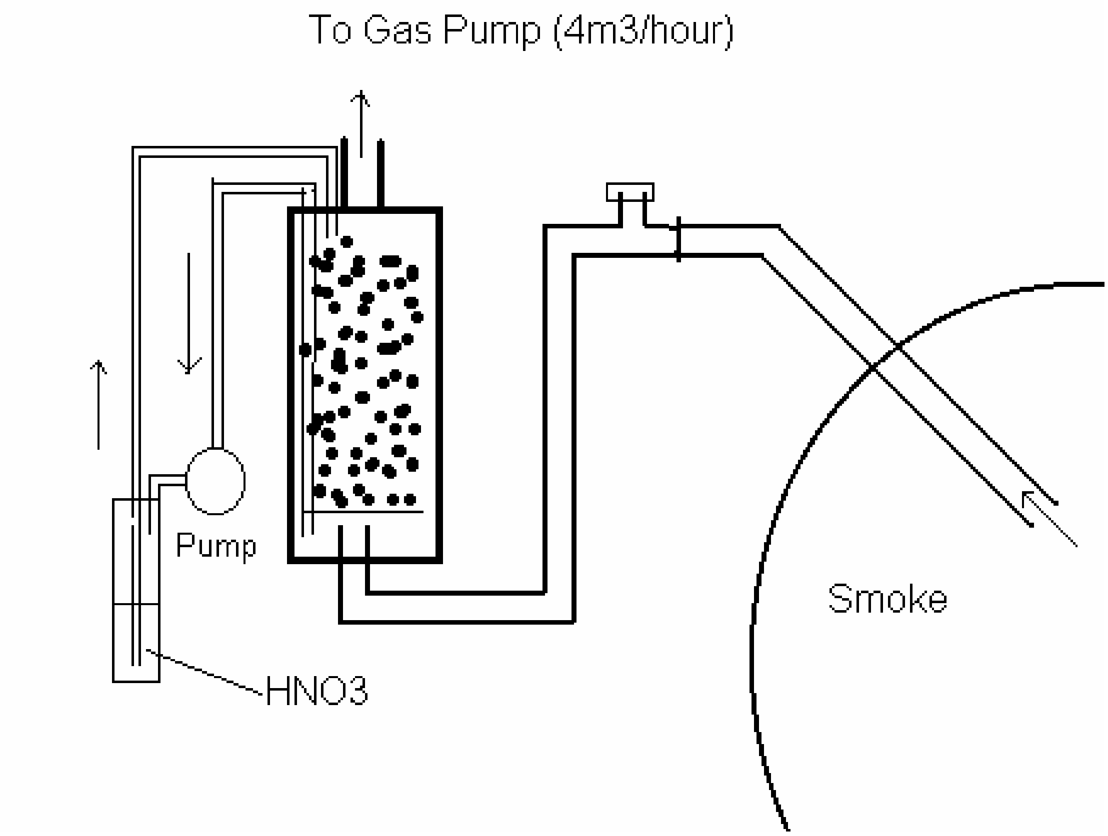


Figure 8. Scheme of column for heavy metal absorption from flue gas.

The task of present study did not include the development of a new method for gas sampling because the elaboration of an adequate heterogeneous sampling procedure is a very complicated and time-consuming problem. On the contrary, we used the standard well–defined and officially recommended sampling method and developed the FIMS on the basis on this standard gas sampling procedure.

The standard method of analysis of heavy metal content in gases (US-method EPA M.5, also accepted in EU), which is used on the incinerator in Denmark, assumes sampling by bubbling of flue gas through 400 ml of absorbing solution of nitric acid. The gas previously passes through the filter to collect large particles. The absorbing solution and filter (after its dissolution in 1M nitric acid) are analysed with the help of AAS. To omit operation of filter dissolving a modified design of absorbing column with enhanced absorbing capability shown in Fig. 8 was suggested.

Flue gas passes in this column through a volume filled up by an inert material with the large surface area (glass rings). Nitric acid circulates in the column against the gas flow. Such design is believed providing for high efficiency of absorption of heavy metals by the solution.

ZSO incinerator is a part of complex cleaning structures of wastewater from southern areas of St. Petersburg (about 60% of St. Petersburg area). At this plant the exuberant biomass (active silt) is combusted, which is formed during process of sewage cleaning by microorganisms. The deposit of sewage automatically enters the furnace after preliminary pressing with partial dehydration down to 72 % of water content (Fig. 9).

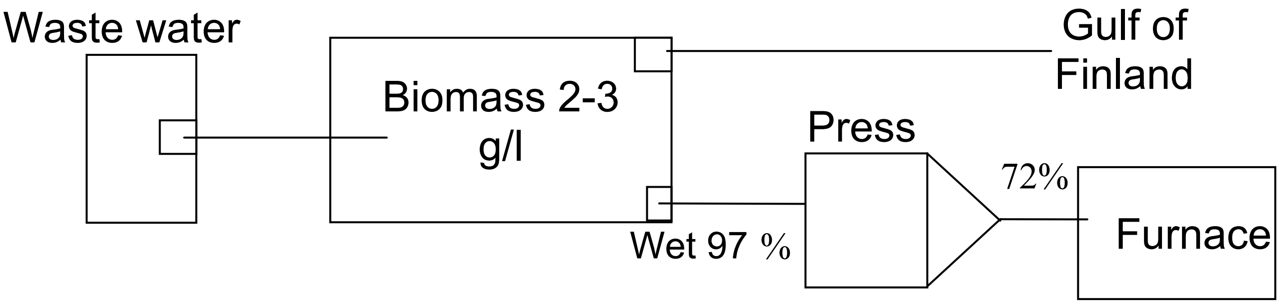


Figure 9. Scheme of cleaning process at ZSO (Bely Island, St. Petersburg).

At ZSO (St. Petersburg) FIMS was also connected to the standard sampling system with the standard pump, originally designed to take samples for the analysis of HCl and sulphur oxide content. For the purposes of the present study the gas passed through a 250-ml flask of nitric acid for the analysis of heavy metals, and through 40 ml volume of sodium hydroxide for determination of hydrochloric acid and oxides of nitrogen and sulphur.

The time of absorption depended of flue gas flow rate. At Vestforbranding the sampling time was 1-2 hours at the flow rate 1-4 m^3/h. At ZSO the sampling time was from 4 to 110 hours at flow rate 0,03 m^3/hours.

2.5. Mathematical methods for experimental design and data processing

One of the problems in quantitative analysis using the sensor arrays is the necessity to perform multicomponent calibration of the system. This calibration should take into account the variations of all targeted substances in all possible ranges of concentration.

The most intuitive approach to study all factors in this situation would be to vary the factors of interest in a full factorial design, that is, to try all possible combinations of substances and concentrations. This would work fine, except that the number of necessary runs or calibration solutions in the experimental measurements will increase geometrically. For example, if one want to study 7 component with 2 concentration, the necessary number of runs (calibration solutions) in the experiment would be 2**7 = 128. To study 10 component with 2 concentrations one would need 2**10 = 1024 runs in the experiment. Because a calibration with a big number of calibration solutions is time and labour consuming, fractional factorial designs are often used instead of full factorials. Fractional designs "sacrifice" interaction effects so that main effects may still be computed correctly, but they require much less runs (calibration solution) and more reasonable from the point of view of labour employed.

The general mechanism of generating fractional factorial designs, which was used in the present work, for example at 3 levels (3**(k-p) designs) (for 3 component) starts with a full factorial design, and then uses the interactions [47] of the full design to construct "new" factors (or blocks) by making their factor levels identical to those for the respective interaction terms (i.e., by making the new factors aliases of the respective interactions).

For example, consider the following 3**(3-1) factorial design:

3(3-1) fractional factorial design, 1 block , 9 calibration solutions**			
Standard Solution (run)	**Pb**	**Cd**	**Cu**
1	0	0	0
2	0	1	2
3	0	2	1
4	1	0	2
5	1	1	1
6	1	2	0
7	2	0	1
8	2	1	0
9	2	2	2

0, 1, 2 level for concentration of Pb^{2+}, Cd^{2+}, Cu^{2+}. (for example 10^{-5}, 10^{-4}, 10^{-3} mol/l)

The design is constructed by starting with the full 3-1=2 factorial design; those factors are listed in the first two columns (factors Pb^{2+} and Cd^{2+}). Factor Cu^{2+} is constructed from the interaction Pb^{2+}-Cd^{2+} of the first two factors. Specifically, the values for factor Cu^{2+} are computed as

$Cu^{2+} = 3 - mod_3 (Pb^{2+}+Cd^{2+})$

Here, $mod_3(x)$ stands for the so-called modulo-3 operator, which will first find a number y that is less than or equal to x, and that is evenly divisible by 3, and then compute the difference (remainder) between number y and x. For example, $mod_3(0)$ is equal to 0, $mod_3(1)$ is equal to 1, $mod_3(3)$ is equal to

0, $\mathrm{mod}_3(5)$ is equal to 2 (3 is the largest number that is less than or equal to 5, and that is evenly divisible by 3; finally, 5-3=2), and so on.

If we apply this function to the sum of columns Pb^{2+} and Cd^{2+} shown above, we will obtain the third column Cu^{2+}. This confounding of interactions with "new" main effects can be summarised in an expression:

$0 = \mathrm{mod}_3\ (A+B+C)$

If we look at the 3**(3-1) design shown earlier, we will see that, indeed, if you add the numbers in the three columns they will all sum to either 0, 3, or 6, that is, values that are evenly divisible by 3 (and hence: $\mathrm{mod}_3(A+B+C)=0$). Thus, one could write as a shortcut notation ABC=0, in order to summarise the confounding of factors in the fractional 3**(k-p) design.

The Taguchi robust design method is the one most similar to traditional techniques. Taguchi has developed a system of tabulated designs (arrays) that allow for the maximum number of main effects to be estimated in an unbiased (orthogonal) manner, with a minimum number of runs in the experiment. Latin square designs, 2**(k-p), 3**(k-p) designs, and Box-Behnken designs, etc., are also aimed at accomplishing this goal. In fact, many of the standard orthogonal arrays tabulated by Taguchi are identical to fractional two-level factorials, Plackett-Burman designs, Box-Behnken designs, Latin square, Greco-Latin squares, etc.

The optimisation, which we performed mainly in the way described above, permitted to carry out calibration using an incomplete (reduced) set of standard solutions without significant loss of accuracy of analysis. In our case the results of Taguchi optimisation coincided to those obtained using fractional algorithms.

Multiple linear regression (MLR), partial least squares (PLS) and artificial neural networks (ANN), namely back-propagation artificial neural network (BPNN), were applied for sensor array calibration.

Unscrambler 6.11 software was used to produce calibration models with the help of MLR and PLS. Data processing by ANN was carried out using Neural Solution 3.11.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Development of flow - injection multisensor system

3.1.1. Choice of the sensors for the analysis of multicomponent solutions

The right choice of sensors for the array is of crucial importance for successful work of multisensor flow-injection system. The flow-injection configuration of the cell implies some specific requirements on the number of sensors with respect to possible dispersion of the sample in the large detector. The choice of sensitive materials was based on the results obtained for sensors of similar composition under static conditions (no flow) in multicomponent solutions. It is possible to use the sensors based on the majority of known membrane materials in the flow-injection cells. In the present work various types of sensors (Table 1) for the multisensor detector for determination of Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr(VI) (CrO_4^{2-}, $Cr_2O_7^{2-}$), NO_3^-, SO_4^{2-}, Cl^- and their characteristics were investigated. . Sensitivity of sensors to different ions was studied in their individual solutions.

The determination of the detection limit is based on the experimental statistical approach. For discrete potentiometric chemical sensors for individual ion calibration we followed IUPAC recommendations, where the detection limit of an ion-selective electrode (chemical sensor) is defined as the concentration value, where the deviation of the electrode response from linearity (according the Nernst equation) at the room temperature is (59,15/z)*lg2, where z is the charge of the ion [48].

Table 1. Basic characteristics of the developed sensors.

Type of a sensor	Membrane composition	Detection limit, mg/l	pH range
Ag	Ag - As - Se	0,01	2 – 7
Cu	Cu – Ag – As – Se	0,006	1 – 7
Pb	PbI_2 - Ag_2S – As_2S_3	0,02	1 – 7
Cd	CdS - Ag_2S – As_2S_3	0,02	1 - 7.5
Tl	TlI - Ag_2S – As_2S_3	0,01	2 – 9
Cr(VI)	Cr–Ag-As–Se	0,15	0 – 2
Hg	AgBr – Ag_2S – As_2S_3	0,02	0 –2
Fe	Fe-Ge – Sb – Se	0,15	0 – 2
Cl	AgCl-Ag_2S	1	1 – 12
Anion 1	PVC(2)+DOP(1)+TDA_2CO_3(0,01m)+HE(0,02m))	5 (SO_4^{2-})	3 – 9
Anion 2	PVC(1)+DOP(1)+TDA_2CO_3(0,01m)+HE(0,01m)	4 (SO_4^{2-})	3 –9
NO_3^- (1)	TDA_2NO_3, DOP, PVC	0,6	2 – 10
NO_3^- (2)	TDA_2NO_3, DOP, PVC	0,6	2-10

DOP – Dioctylphtalate (plastisizer); TDA_2CO_3 - tetradecyl ammonium carbonate, TDA_2NO_3 - tetradecyl ammonium nitrate (anion exchanger); HE – hexyl ether trifluoroacetyl benzoic acide (neutral carrier).

The most important feature of sensors for multisensor system is cross-sensitivity, which is understood as sensitivity to as many components in solution as possible. Original method of sensor cross-sensitivity evaluation was elaborated earlier. Three empirical parameters for the description of cross-sensitivity were suggested: $S_{av.}$ - average slope, F - non-selectivity factor, K - reproducibility factor.

Table 2. Cross-sensitivity parameters of sensors in solutions of heavy metals (n=5, p=0.95).

Sensor	$S_i \pm \Delta S_i$ mV/pX^{z-}				$S_{av.}$ mV/pX^{z-}	K	F
	Cu^{2+}	Pb^{2+}	Cd^{2+}	H^+			
Pb(1)	75 ± 10	28 ± 2	22 ± 3	28 ± 6	38	2,9	0,1
Pb(2)	70 ± 8	27 ± 1	21 ± 3	30 ± 4	37	2,7	0,1
Cd(1)	52 ± 11	26 ± 2	26 ± 2	27 ± 4	33	9,1	0,1
Cd(2)	47 ± 7	27 ± 2	25 ± 2	25 ± 5	31	8,9	0,1
Cu	33 ± 2	9 ± 3	6 ± 3	25 ± 6	18	7,3	0,1
Ag	45 ± 8	20 ± 4	19 ± 5	28 ± 5	28	2,0	0,1
Tl	60 ± 10	16 ± 4	14 ± 5	26 ± 6	29	4,3	0,1
Fe	30 ± 2	29 ± 1	26 ± 1	23 ± 4	27	8,3	0.2
Cr	33 ± 2	10 ± 3	7 ± 3	25 ± 6	19	9,2	0,1
Hg	12 ± 2	2 ± 1	2 ± 1	10 ± 3	7	2,9	0,24

The higher is the value of all three parameter, the greater is cross-sensitivity of the sensor. The limit values of these parameters for the cross-sensitivity to heavy metals evaluation were determined earlier. If S_{av}. > 20, K > 2, F > 0,1 it is considered, that the sensor is cross sensitive enough to be included into multisensor system.

Several membranes with different ratio of components were synthesised for each type of sensors (Table 1) (more than 40 compositions totally). The sensors displaying the best parameters of cross-sensitivity were used for FIMS. The results of determination of cross-sensitivity parameters are summarised in the Tables 2 and 3.Sensors on the basis of chalcogenide glasses for the analysis of heavy metals in mixed solutions are shown in

Table 2. Characteristics of the sensors on the basis of PVC and crystalline materials for the analysis of inorganic anions in mixed solutions are shown in Table 3.

Table 3. Cross-sensitivity parameters of sensors in solutions of inorganic anions (n=5, p=0.95).

Sensor	$S_i \pm \Delta S_i$ mV/pX^{z-}				$S_{av.}$, mV/pX^{z-}	K	F
	NO_3^-	SO_4^{2-}	Ac^-	Cl^-			
Anion1	51 ± 5	22 ± 2	24 ± 4	36 ± 5	33	4	0,2
Anion2	32 ± 7	20 ± 2	15 ± 4	15 ± 3	21	3	0,2
Anion3	50 ± 9	17 ± 3	25 ± 3	29 ± 4	30	2	0,15
NO_3^-(1)	53 ± 2	11 ± 2	21 ± 3	33 ± 4	30	8	0,1
NO_3^-(2)	56 ± 2	13 ± 2	20 ± 3	30 ± 4	30	8	0,1
NO_3^-(3)	54 ± 2	15 ± 2	18 ± 3	28 ± 4	29	7	0,1
Cl^-	6 ± 2	1 ± 1	1 ± 1	57 ± 2	16	31	0,25

Most part of sensors (Table 2) corresponds to the above-mentioned criteria of cross-sensitivity and they can be used in the multisensor detector as non-specific sensors. Practically all sensors exhibit sensitivity to hydrogen ion concentration (pH). Therefore, to minimise pH influence the solutions were prepared on acetic buffer background (pH=4,6).

The experiments under static conditions showed that it is necessary to use not less than 8 sensors to determine the content of three components in mixed solutions with required accuracy. Thus, the array comprising the following 8 sensors based on chalcogenide glasses was used for the analysis of Cu^{2+}, Pb^{2+}, Cd^{2+} ions (mol %):

1. "Pb(1)" - $50PbI_2 - 20Ag_2S - 30As_2S_3$

2. “Pb(2)” - 25PbI$_2$ - 25Ag$_2$S - 50As$_2$S$_3$
3. “Cd(1)” - 15CdS - 42.5Ag$_2$S - 42.5As$_2$S$_3$
4. “Cd(2)” - 30CdS - 40Ag$_2$S - 50As$_2$S$_3$
5. “Cu” - 12.5Cu-12.5Ag-37.5As-37.5Se
6. “Ag” - 20Ag - 40As - 40Se
7. “Tl” - 30TlI - 35Ag$_2$S - 35As$_2$S$_3$
8. “Fe” - 2Fe - 32Ge - 33Sb - 33Se

For the analysis of Cr (VI) (CrO_4^{2-}, $Cr_2O_7^{2-}$), Hg (II) ions the following 3 sensors were used:

1. “Fe” - 2Fe - 32Ge - 33Sb - 33Se
2. “Cr(VI)” - 2.5Cr –22.5Cu -30As - 30Se
3. “Hg” - 60AgBr - 25Ag$_2$S - 15As$_2$S$_3$

The pH range of sensors for Cr (VI) (CrO_4^{2-}, $Cr_2O_7^{2-}$) and Hg (II) ions is pH=0-2. Therefore detection of these ions was carried out in solution without neutralisation and pH adjustment with buffer.

8 PVC sensors with high parameter of cross-sensitivity were chosen for an array for detection of NO_3^-, SO_4^{2-} and chloride-selective electrode was applied for Cl^- determination (mol%):

1. Anion 1 PVC(2)+DOP(1)+TDA$_2$CO$_3$(0,01m)+HE(0,02m))
2. Anion 2 PVC(1)+DOP(1)+TDA$_2$CO$_3$(0,01m)+HE(0,01m)
3. Anion 3 PVC(1)+DOP(1)+TDA$_2$CO$_3$(0,01m)+HE(0,03m)
4. Anion 3(a) PVC(1)+DOP(1)+TDA$_2$NO$_3$(0,01m)+HE(0,03m)
5. “NO_3^-(1)” 1,5 TDA$_2$NO$_3$ - 65,5 DOP - 33PVC
6. “NO_3^-(2)” 2 TDA$_2$NO$_3$ - 65 DOP – 33PVC
7. “NO_3^-(3)” 4 TDA$_2$NO$_3$ - 63 DOP – 33PVC
8. “Cl^-“ 50AgCl – 50Ag$_2$S

The sensors of special configuration designed for flow-injection application (see experimental) were made on the basis of these cross-sensitive materials.

3.1.2. Sensors with solid inner contact: analytical characteristics and their comparison with sensors with liquid filling solution

The sensors with PVC membranes are usually made with liquid inner contact. This contact is widely used for the most of commercial PVC sensors as well. In this case a sensitive membrane is glued onto the sensor body and the inner volume is filled up by different solutions depending on what ion is to be determined. One of the essential components of this filling solution is also sodium chloride. This solution is in contact with inner reference electrode, which is silver/silver chloride and the presence of NaCl ensures reversibility of this interface. Sodium chloride and other components present in the filling solution are also responsible for the stable interfacial process on the inner solution/membrane phase boundary. Thus, if both interfaces inside a sensor are reversible and stable enough the response of whole device will be due to the changes occurring on the outer interface (membrane/analyte solution). Sensors with liquid inner contact normally display reasonable characteristic. However, we needed for FIMS relatively small and flat surface sensor membranes with long-term stable characteristics. It is very difficult to prepare such sensors with liquid inner contact.

Solid inner contact is much more prospective and convenient for various sensors applications. The review of the experimental data on the development of solid contact for various ion-selective electrodes is presented in [49].

The aim of a solid inner contact is to attach a metallic wire to a sensitive membrane. This cannot be done directly because of the different nature of conductivity in the membrane (mainly ionic) and in a metal (100% electronic). A contact material must provide a good and non-drifting electrical contact to both materials to ensure a long-term stable performance of a sensor. Development of such solid-state electrical contacts to PVC membranes is not a trivial task, since the gradient contact layer should display stable though controversial properties. Thus, to enable using multisensor arrays in a flow-injection set-up we had to develop special PVC sensors with no liquid inside.

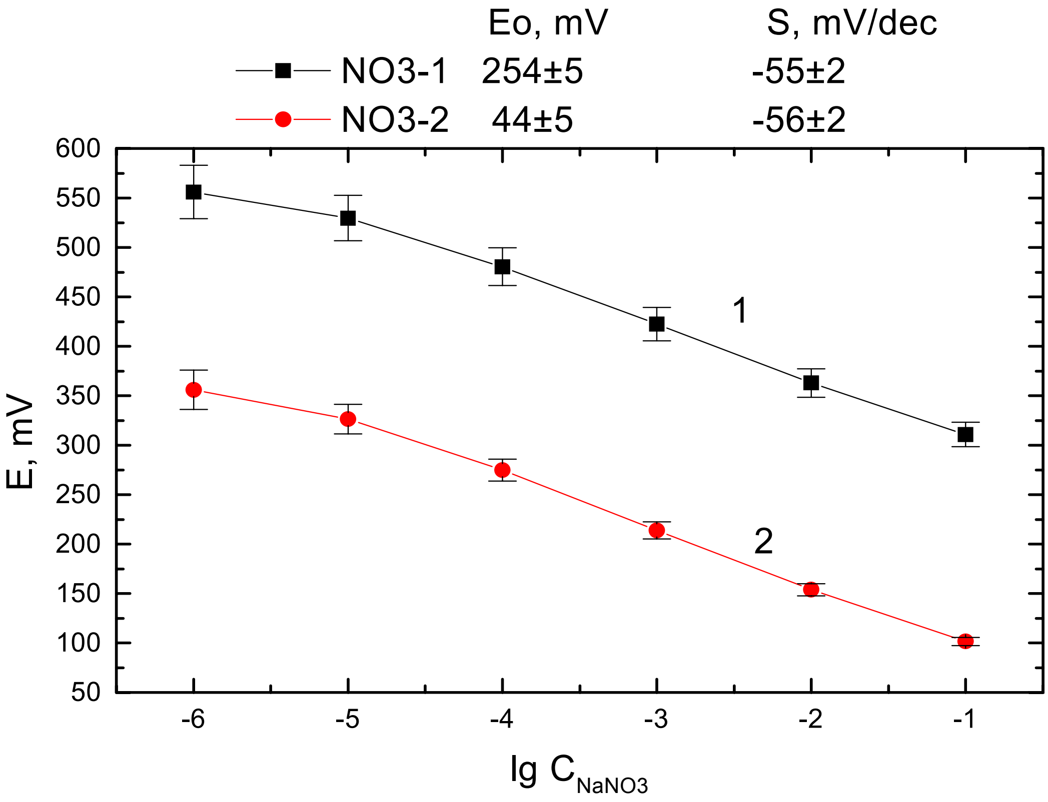


Fig. 10. Comparison of electrode response of NO_3^- PVC sensors with solid (1) and liquid (2) inner contact.

We carried out special research to prepare PVC sensors with solid inner contact. These sensors must have characteristic comparable to sensors with liquid inner contact to be properly applied in FIMS. Different contact compositions, consisting of special glue with incorporated materials with mixed ionic/electronic conductivity were investigated. Next pictures show characteristics of the sensors with solid inner contact prepared with one of these materials with dispersed silver chloride inside. Calibration plots of NO_3^- and other anion sensitive sensors with solid and liquid inner contact are shown in Fig. 10,12. Response slopes values of NO_3^- sensors with different contacts practically coincide. For SO_4^{2-} sensitive anion sensors with solid inner contact slope value is somewhat lower than for sensors with liquid inner filling but is still sufficient to use them as cross-sensitive sensors. An important characteristic of sensor stability is the value of standard potential E_0 and its time dependence (if any).

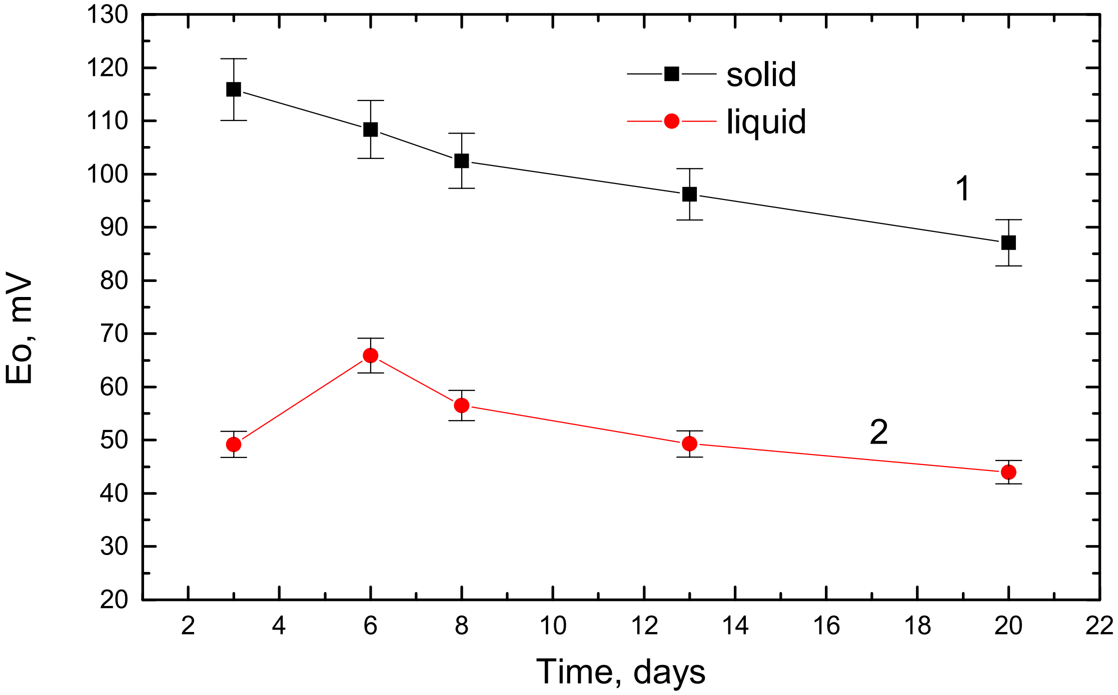


Figure 11. Change of E_0 in time for PVC sensors sensitive to NO_3^- ions with solid (1) and liquid (2) inner contact.

Possible change of equilibrium parameters in membrane phase and gradient layer of solid contact can cause the drift of standard potential. The experiments showed (Fig. 11,13), that the standard potential values of sensors with solid and liquid contact behave similarly. After preparation of membrane about 10-14 days are necessary to reach equilibrium between membrane itself and solid contact layer. Later on E_0 practically does not change. In case of SO_4^{2-} sensitive membranes with solid inner contact the standard potential becomes stable even faster, than that for appropriate liquid contact sensor.

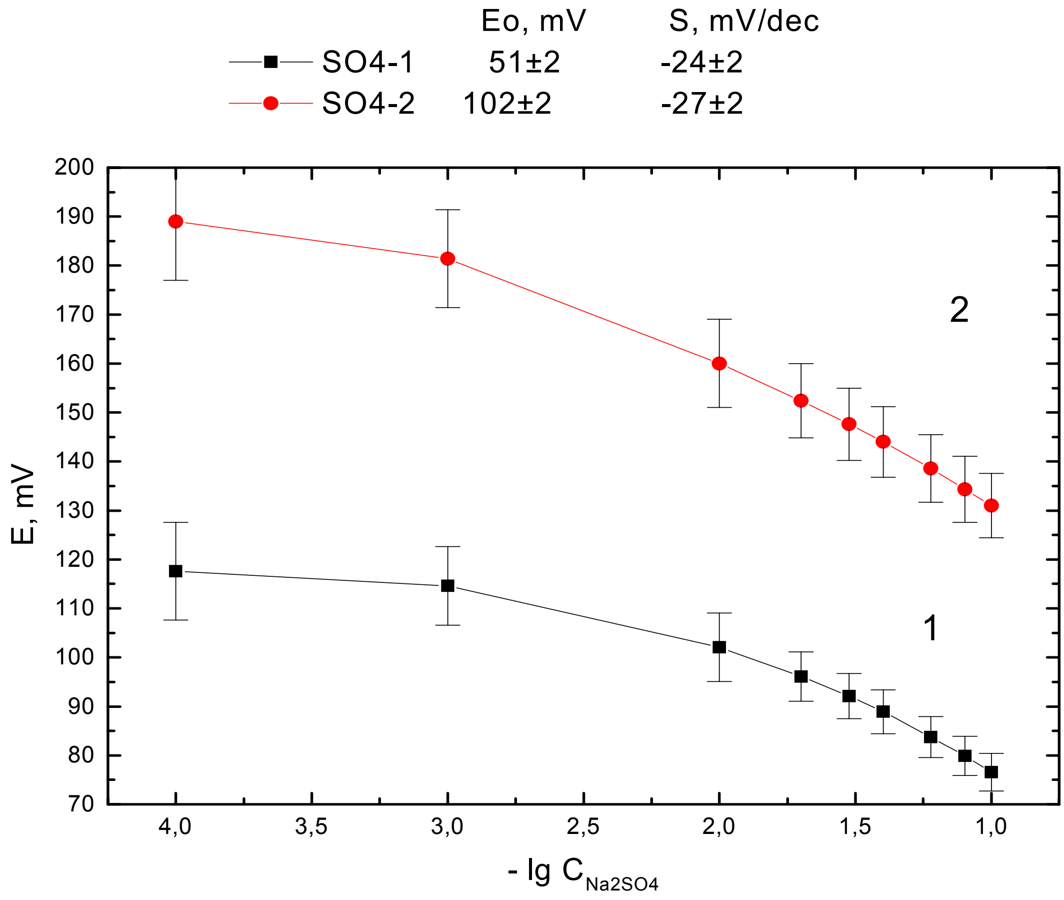


Figure 12. Comparison of electrode response to SO_4^{2-} for electrodes with solid (1) and liquid (2) inner contact.

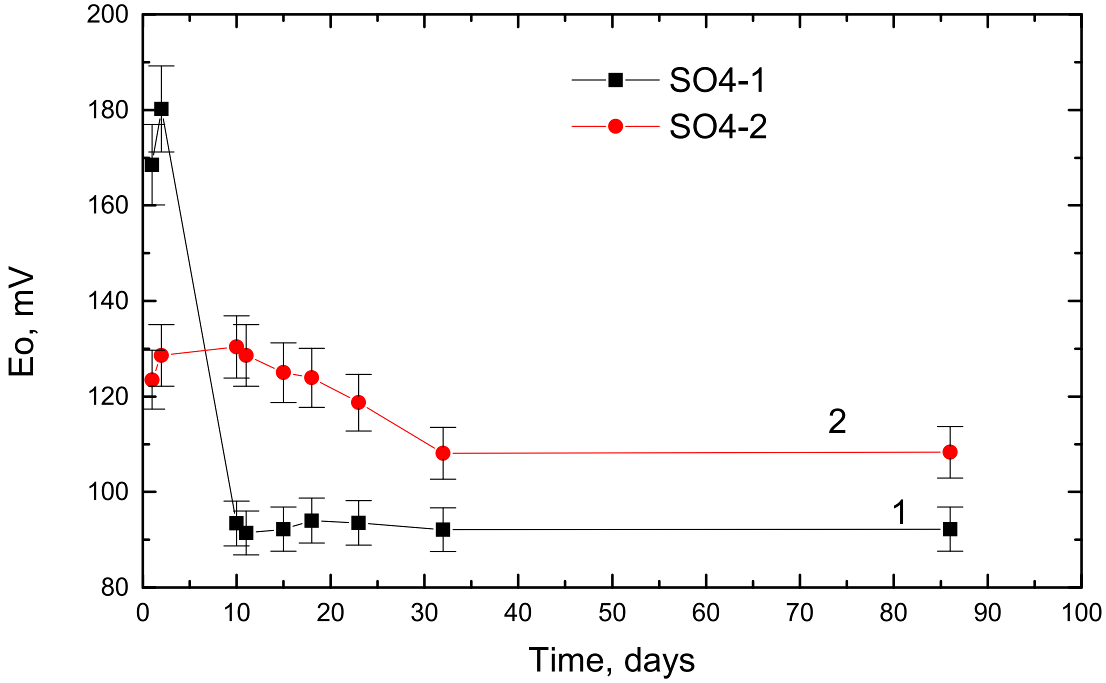


Figure 13. Change of E_0 in time for PVC sensors sensitive to SO_4^{2-} ions with solid (1) and liquid (2) inner contact.

Electrode characteristics of PVC sensors with solid and liquid inner contact are shown in the Table 4. The sensors with both types of contacts displayed comparable characteristics, which allow applying PVC sensors with solid inner contact in FIMS. Calibration data of sensors with different inner contact shown in Appendix1.

Table 4. Electrode characteristics of PVC sensors with solid and liquid internal contact

Type of sensor and contact	Detection limit, mg/dm^3	Slope mV/pX	ΔE_0 change in 2 weeks, mV
Anion 1 (liquid)	5	27 ± 2	5
Anion 1 (solid)	9,6	24 ± 2	10
Anion 2 (liquid)	40	23 ± 3	7
Anion 2 (solid)	55	22 ± 3	12
Anion 3 (liquid)	4	25 ± 2	27
Anion 3 (solid)	6	24 ± 3	24
NO_3^- (liquid)	0,6	58 ± 2	20
NO_3^- (solid)	0,6	56 ± 2	25

3.1.3. Choice of the optimum parameters of the flow-injection analysis

Optimisation of hardware parameters or FIA was performed after optimisation of sensor array composition. A series of experiments was carried out in which one of two FIA parameters were changed (flow rate, sample volume) while another one remained constant.

Analytical characteristics of membrane materials in flow mode can differ from those obtained in static conditions. The basic reason for this difference is that in flow-injection systems the measurement of sensor potential occurs under stationary conditions rather than near thermodynamic equilibrium. Therefore, magnitude of registered signal can depend significantly on parameters of FIA system. Usually, such parameters of the system as flow rate and sample volume are chosen with the aim to ensure sufficient time of contact of the sample with detector to achieve maximum peak height. On the other hand, smaller time is favourable for the so-called effect of “kinetic discrimination”, which can be used to increase sensor selectivity. In case of non-specific sensor array the criterion of the choice of optimal parameters was the contact time sufficient to ensure the response of all sensors to all analytes in multi component solution.

FIMS optimisation was performed in individual solutions of lead-, cadmium-, copper-ions for determination of cations and of sulphate, nitrate and chloride for determination of anions. For each sensor we found the optimum flow rate and sample volume on the basis of maximum magnitude and reproducibility of sensor signal.

Sample volume changed in the range from 100 up to 1500 μdm^3. For all sensors small sample volumes (less than 100 μdm^3) caused reproducibility deterioration. For the volumes more than 1500 μdm^3 the width of peaks and analysis time significantly increased. Therefore, sample volume of 500 μdm^3 was chosen for the further studies.

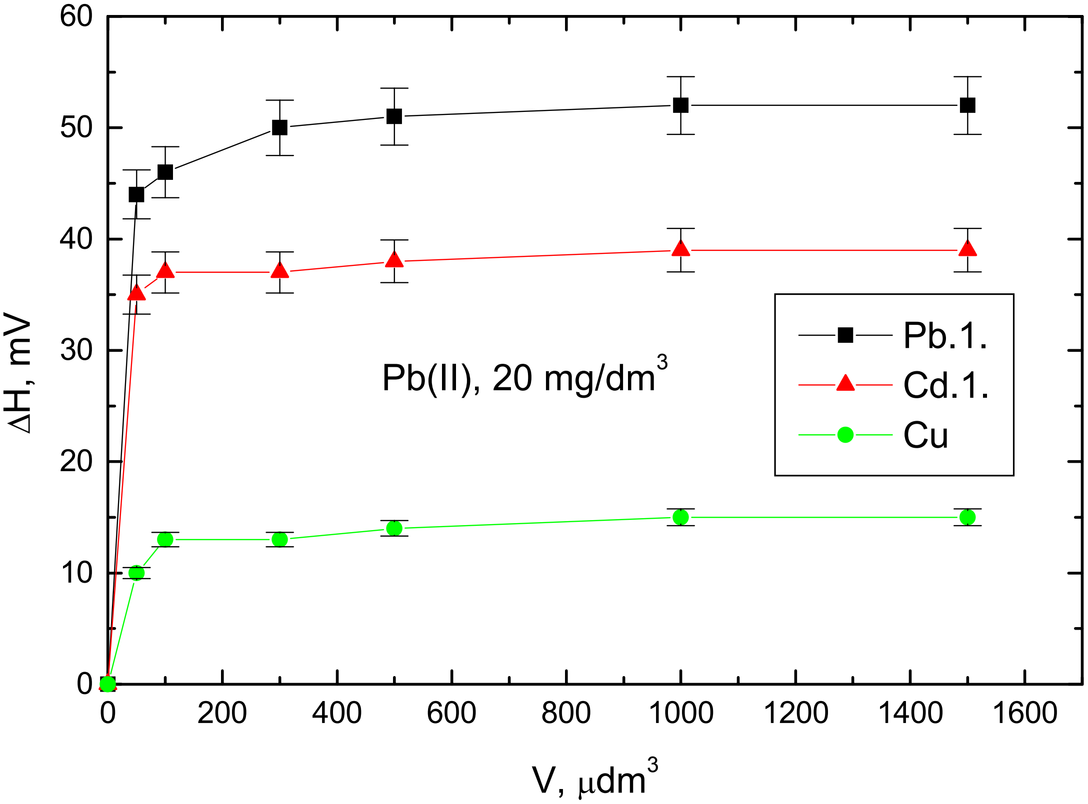


Fig.14. Dependence of peak height of Pb (1), Cd (1) and Cu -sensors on sample volume

As an example, the dependence of peak height on the sample volume for Cd (1) and Cu sensors at flow rate 300 μdm^3/min and for Pb (1) sensor at 20 mg/dm^3 are shown in a Fig.14. The change of sample volume from 100 up to 500 μdm^3 resulted in increase of the peak magnitude for Pb (1), Cd (1) and Cu sensors for 6 mV, 4 mV and 3 mV, respectively. Further increase of sample volume does not affect significantly the peak height.

The dependence of peak width on sample volume for these sensors is shown in Fig.15. When the sample volume increased the “relaxation” time necessary to return sensor potential to the baseline also increased, which resulted in longer analysis time and useless waste of reagents.

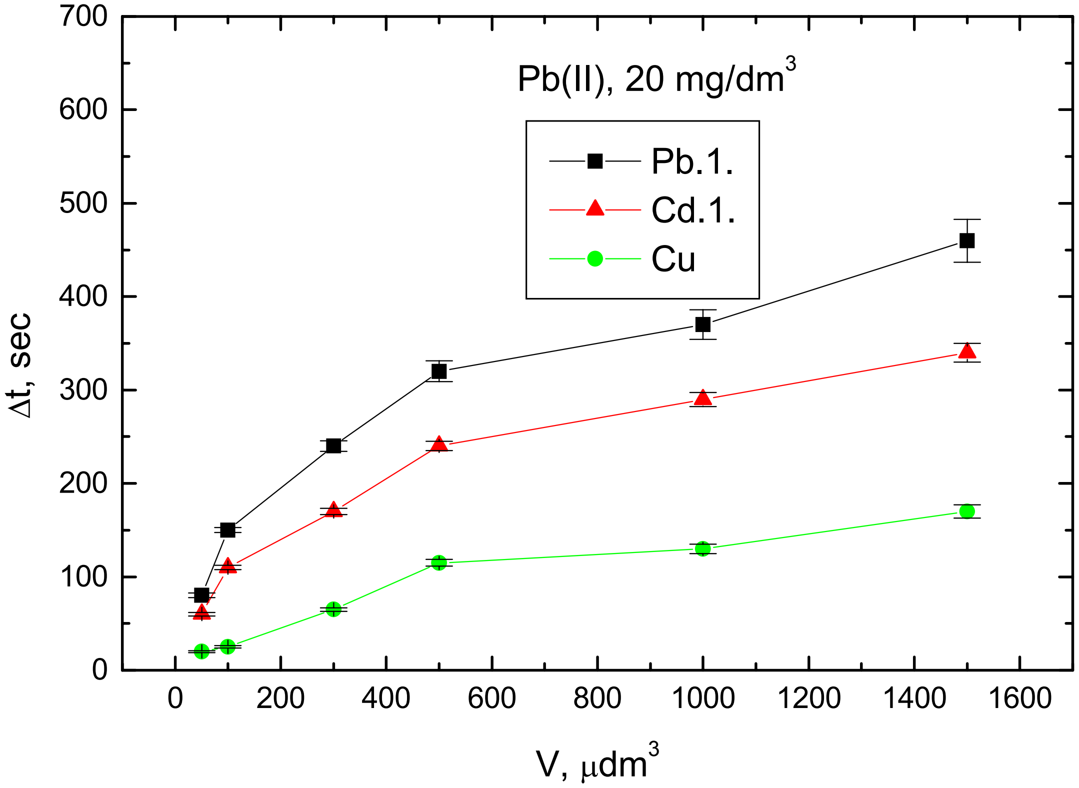


Fig.15. Dependence of relaxation time on sample volume for Pb (1), Cd (1) and Cu sensors

Dependence of peak height on flow rate was also studied. For all sensors some increase of peak magnitude with increase of flow rate was observed in the range of flow rates from 100 up to 1500 ml/min the. At lower flow rates longer relaxation time to reach the baseline was observed. Finally, the flow rate of 300 ml/min was chosen.

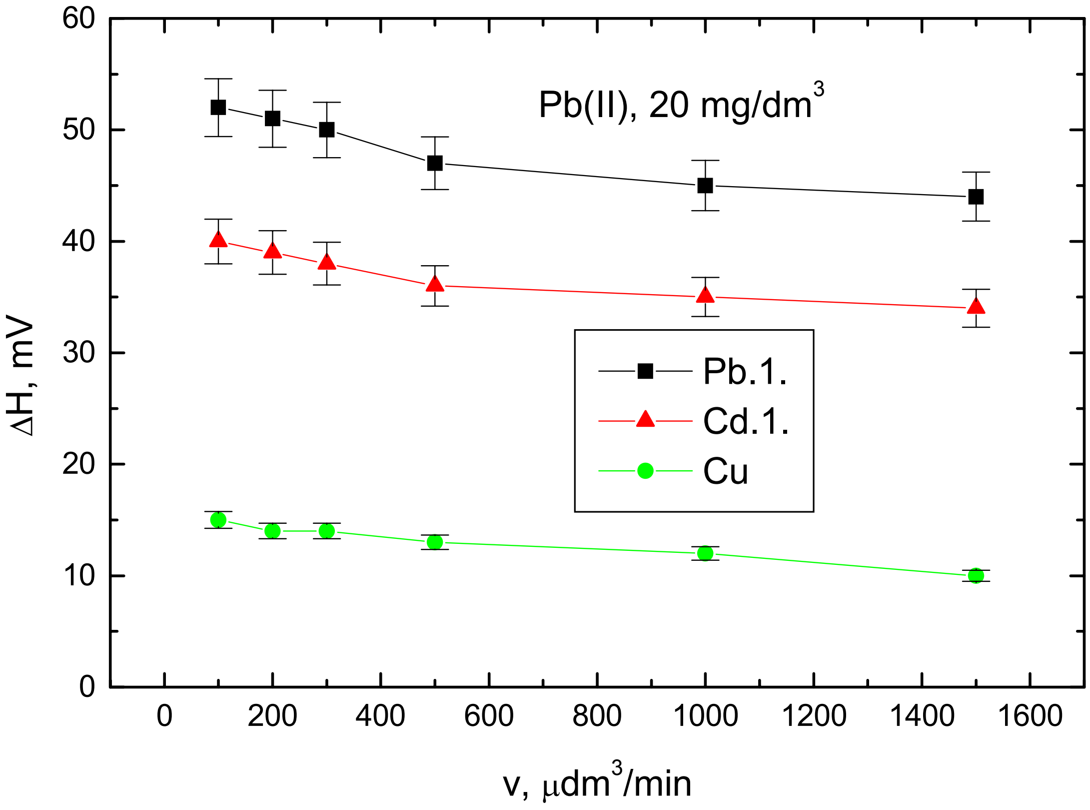


Fig.16. Dependence of peak height on flow rate for Pb (1), Cd (1) and Cu sensors.

Dependence of peak height on flow rate for Pb (1), Cd (1) and Cu sensors are shown in Fig.16 for constant sample volume of 500 μdm^3. The dependence of relaxation time on flow rate for Pb sensor is shown in Fig.17. The increase of flow rate over 300 μdm^3/min does not give rise to a significant reduction of relaxation time and, consequently, the rates higher than 500 μdm^3/min for FIMS are not justified.

For anion-sensitive sensors the increase of flow rate from 100 up to 1000 μdm^3/min resulted in reduction of analytical signal. At lower flow rates the relaxation time increased but less significantly compared to metal-sensitive sensors. For anion-sensitive sensors the flow rate of 300 μdm³/min was also chosen.

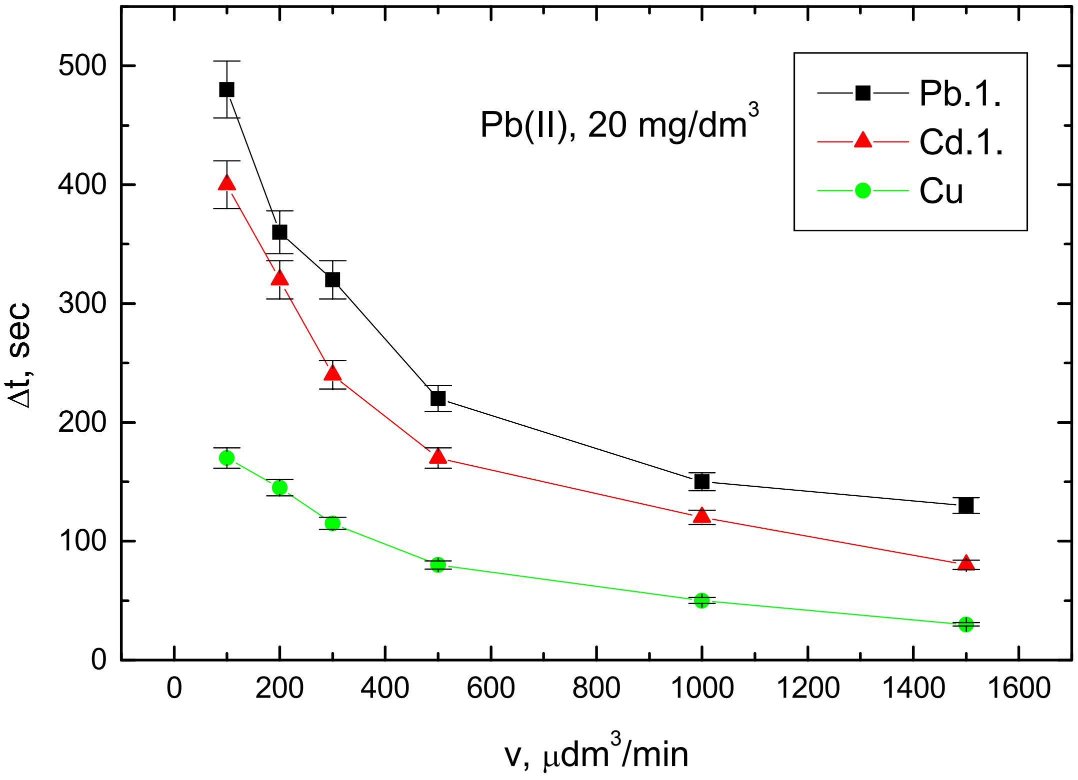


Fig.17. Dependence of relaxation time on flow rate for Pb (1), Cd (1) and Cu sensors.

Optimum parameters for sensors used in FIMS are shown in Table 5. Appendix 2 shows data for optimisation flow parameter for cation-sensitive sensors for Pb(II), Cd(II), Cu(II) –individual ions solution. Parameter values for all sensors are close, thus, it appeared possible to choose reasonable “unified” value of flow rate and of sample volume for multicomponent analysis task.

Table 5. Optimum parameters of flow rate and sample volume for sensors used in FIMS.

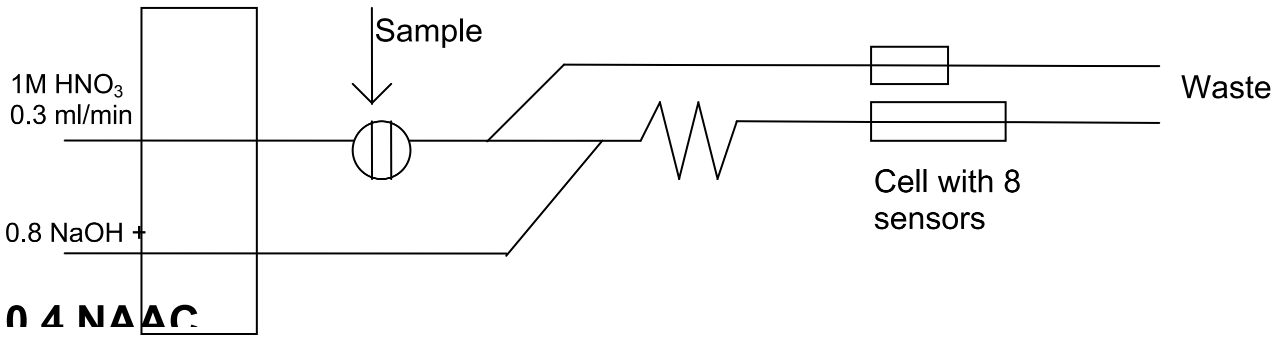
Type of sensor	Optimum flow rate of $\mu dm^3/min$	Optimum sample volume, μdm^3
Ag	300	300
Cu	300	300
Pb	500	500
Cd	700	500
Tl	700	500
Cr(VI)	300	100
Hg	300	100
Fe	300	100
Cl	300	500
Anion 1	300	500
Anion 2	300	500
NO_3^-	300	100

Therefore, optimised parameters for the sensors of array were chosen as follows: flow rate of the carrier 300 $\mu dm^3/min$ and sample volume 500 μdm^3. These parameters were used in FIMS for analysis of multicomponent solutions both for cations and anions. These parameters can differ essentially for other cells and other diameters of delivering tubes, however, ratio of parameters, as a rule, remain within the limits of one order of magnitude.

3.2. Development of flow-injection multisensor system for determination of heavy metal cations: Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr(VI)

The flow-injection system sketched in Fig.18 was designed for simultaneous determination of Cu^{2+}, Pb^{2+}, Cd^{2+} and Cr(VI) ions.

Figure 18. Scheme of FIMS for simultaneous determination of heavy metal ions



At the system start a stable baseline was obtained after a period from 20 min to 1 hour, after which the injections could have been done. Hereafter it was possible to stop the pump and the streams for a shorter time (within an hour) without loss of stable baseline when the pump was turned back on. Relaxation times were dependent on the load: higher sample concentrations gave longer relaxation times. The total width of the peaks was about 300 seconds giving practical sampling rates of 7 to 20 samples per hour, the flow rate being 300 μdm^3/min and sample volume 500 μdm^3.

Table 6. Calibration solutions of heavy metal cations

Components	Concentration range mg/dm^3	Number of solutions in calibration set
Pb(II), Cd(II)	0,02-200	15

Pb(II), Cu(II), Cd(II)	0,02-200	20
Pb(II), Cu(II), Zn(II)	0,02-200	20
Pb(II), Cu(II), Cd(II), Cr(VI)	0,02-200 0,02-40	25
Pb(II), Cu(II), Cd(II), Hg(II)	0,02-200 0,02-20	25

Calibration solutions were prepared in the concentration range shown in the Table 6. The full number of calibration solutions containing T components in N concentrations (within the given range) is equal to N^T. Therefore, in the analysis of solutions containing 3 and more components the total number of calibration solutions becomes very large assuming that we need at least several concentrations to be taken into account in calibration. There are special methods, which allow minimising number of solutions without severe loss of accuracy of the analysis. One of such methods is presented on 2.5 part of thesis. Appendix 6 shows optimisation table for calibration set for 3 ions (lead, copper and chromium).

The analysis of multicomponent solutions containing from 2 to 4 components was carried out.

Table 7. Result of simultaneous determination of Pb (II) and Cd (II) (n=5, p=0,95).

Component	Real, mg/dm^3	Found, mg/dm^3 $x_1 \pm \Delta x_1$	S_r standard deviation %
Pb(II)	0,020	0,020±0,007	28

	0,10	0,12±0,04	27
	0,20	0,21±0,05	19
	1	0,8±0,2	20
	2	2,4±0,5	17
Cd(II)	0,010	0,010±0,005	40
	0,05	0,05±0,02	32
	0,10	0,14±0,05	29
	0,5	0,6±0,2	27
	1,0	0,8±0,2	20

The results of simultaneous determination of lead and cadmium ions in mixed solutions are shown in Table 7. Appendix 3 shows data for determination lead and cadmium in mixed solution. With the help FIMS it is possible to perform simultaneous determination of these cations with reasonable precision. The detection limit of lead and cadmium practically is not decreasing in comparison with solutions of individual ions. Mutual interference of ions in mixed solutions caused some increase of error of measurement due to distortion of sensor response.

Appendix 4 shows potential (peak height) of 11 sensors and result simultaneous determination lead, cadmium and copper. Appendix 5 shows potential (peak height) of 11 sensors and result simultaneous determination lead, copper and chromium ion.

The results of measurements with sensor array can be processed with the help of various methods of multivariate analysis. In our expertise the most perspective methods are: multiple linear regression (MLR), partial least squares regression (PLS) and artificial neural networks (ANN). The data was processed by each of these methods to compare them. Appendix 7 shows comparison data processed different methods.

The results obtained by MLR contained a lot of uncertainty – the errors were up 50 % and even more. This result is correlated with experiment under static conditions carried out earlier and makes to conclude that MLR is hardly applicable for our data, likely due to the presence of non-linearity in them. Also the signals obtained from non-selective sensors can be partly correlated, which contradicts to the basics of MLR assuming independent variables.

On the other hand, the methods PLS and ANN have shown much better results, which were similar. The results of determination of heavy metal ion content in model solutions are given in the Tables 8 and 9. Table 8 deals with the results obtained with the help of PLS. The average errors of determination of Pb(II), Cd(II), Cu(II) and Cr(VI) ions were 8 %, 15 %, 18 % and 12 %, respectively. The results of the data processing with the help of ANN are shown in the Table 9. The average error for Pb(II), Cd(II), Cu(II) and Cr(VI) were 17 %, 22 %, 15 % and 22 %, respectively. The detection limit of Pb(II) was 0,2 mg/dm^3 and for other metals it was about 0,1 mg/dm^3. Thus, the results of calculations by PLS and ANN methods are comparable.

Table 8. Results of simultaneous determination of the heavy metal content with the help of FIMS (n=5, p=0.95), data processing being carried out by PLS

Component	Real content mg/dm^3	Found content mg/dm^3 $x_1 \pm \Delta x_1$	S_r standard deviation %
Pb(II)	3,3	3,5 ± 0,4	9
	6,7	6,7 ± 0,7	8
Cd(II)	1,2	1,3 ± 0,2	12

	2,6	2,6 ± 0,5	16
Cu(II)	0,41	0,48 ± 0,08	13
	1,00	1,05 ± 0,11	8
Cr(VI)	0,04	0,04 ± 0,01	20
	0,20	0,21 ± 0,03	12
	2,3	2,4 ± 0,2	8

PLS gives a possibility to find sensors, which are responsible for the greatest errors (or noise) in the results and also to find sensors, which give maximum useful information for calculation of valid calibration model and further optimisation of the sensor array. This is done by the analysis of sensor loadings and other options available in PLS. In the case of ANN the processing algorithm is a black box, which complicates understanding of how the system and sensors work. Therefore, we mainly used PLS for the data processing.

Table 9. Results of simultaneous determination of the heavy metal content with the help of FIMS (n=5, p=0.95), data processing being carried out by ANN

Component	Real content mg/dm^3	Found content mg/dm^3 $x_1 \pm \Delta x_1$	S_r standard deviation %
Pb(II)	3,3	3,9 ± 0,8	17
	6,0	6,2 ± 1,2	16
	41	50 ± 10	16
Cd(II)	1,2	1,2 ± 0,4	27
	2,9	3,0 ± 0,4	11

Cu(II)	0,5	0,4 ± 0,1	20
	1,0	1,1± 0,2	15
	2,0	1,9 ± 0,3	13
Cr(VI)	0,10	0,09 ± 0,03	27
	0,21	0,25 ± 0,05	16

In the analysis of multicomponent solutions containing lead, cadmium, copper and chromium ions the detection limit of each component is slightly higher than in the solutions of appropriate individual ions. This can be related to interference of multiple ions on the sensor response.

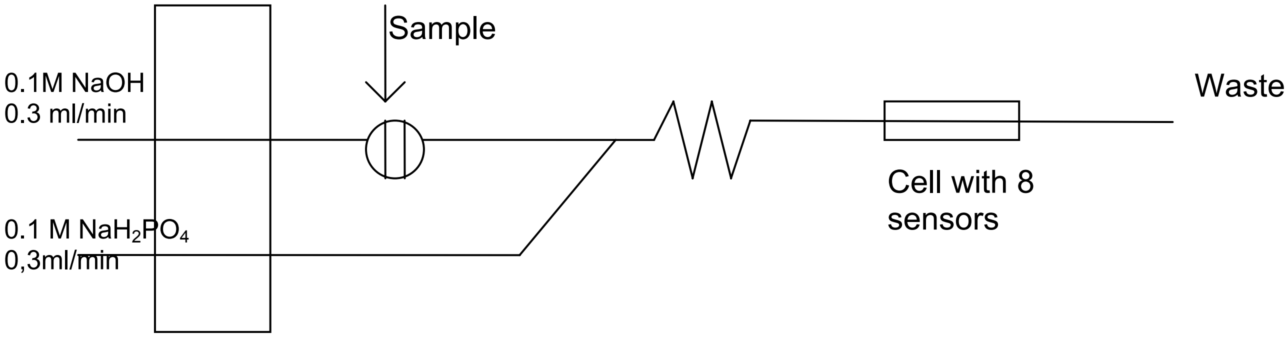
Determination of mercury ions in mixed solutions was also carried out. The presence of mercury ions in concentration higher than 0,2 mg/dm^3 in calibration solutions results in increase of errors of determination of other components. However, the level of mercury content in flue gas at real incinerators can give rise only to very low concentrations of mercury in solutions. This mercury content cannot prevent from precise determination of other components.

3.3 Development of flow-injection multisensor system for determination of inorganic anions: SO_4^{2-}, Cl^-, NO_3^-.

A flow cell comprising 8 sensors, solid-state and PVC-based, sensitive to inorganic anions such as NO_3^-, SO_4^{2-} and Cl^- was developed. Some of the sensors were mainly selective to NO_3^- ions (3 electrodes of different compositions) and chloride (1). The other 4 sensors were cross-sensitive PVC-based compositions mainly designed for sulphate determination. All these sensors (electrodes), as well as all previously described ones, were developed and prepared in the Laboratory of Chemical Sensors of St. Petersburg University. The sensor set for flow system was also based on the data obtained under static conditions. Scheme of flow-injection multisensor system for simultaneous determination of inorganic anions is shown in Fig.19.

To stabilise sensor performance it was important to elaborate a proper composition of background solution, which, on the one hand, has sufficient ionic strength (to minimise the errors of potential measurement), and on the other hand, contains the ions, which have minimum interference on analytes. Also, to eliminate pH influence on the sensor response it is strongly preferable to carry out the analysis in a buffer solution. We studied various background solutions (distilled water, sodium acetate, phosphate buffer) for anion determination.

Fig.19. Scheme of FIMS for determination of inorganic anions.



Finally, we worked out the appropriate background solution, which was 0,1 mol/dm^3 of sodium hydroxide neutralised with sodium dihydrophosphate. The width of peak was 100-200 sec that allowed to do up to 30 measurements per hour, the flow rate was 0.3 ml/ min and the sample volume was 500 μdm^3.

Table 10. Concentration range and number of calibration solutions for determination of inorganic anions.

Component	Concentration range mg/dm^3	Number of calibration solutions
SO_4^{2-}	9,6-9600	

NO_3^-	6,2-6200	20
Cl^-	0,35-3500	

Concentration range of calibration solutions for simultaneous determination of SO_4^{2-}, Cl^-, NO_3^- and the number of solutions is shown in Table 10. The number of solutions is reduced and their composition is optimised with the fractional design plan method. The results obtained after data processing by PLS are shown in Table 11. Appendix 8 shows data for determination nitrate, sulphate and chloride in mixed solution where as background solution was NaH_2PO_4.

Table 11. Results of determination of component concentrations in test solutions (n=5, p=0.95).

	Real content	Found content		Found content		Found content	
	mg/dm^3	$X \pm \Delta x$ mg/dm^3	S_r %	$x \pm \Delta x$ mg/dm^3	S_r %	$x \pm \Delta x$ mg/dm^3	S_r %
Backgr. Sol.		distilled water		0,1 M NaAc		0,1 M NaH_2PO_4	
SO_4^{2-}	9,6	27±17	51	-		-	
	96	155±60	31	-		140±50	29
	964	900±250	22	500±350	56	990±150	12
	9640	7700±2000	21	7000±2600	30	9100±1100	10
NO_3^-	6,2	9±5	45	-		6,5±1,3	16
	62	36±27	60	-		77±12	13
	621	910±400	35	570±160	23	670±90	11

	6210	8700±3100	29	6100±740	10	5750±530	7
Cl^-	3,5	4,0±0,6	12	3,7±0,6	13	3,8±0,5	11
	35	39±5	10	36±7	16	33±4	10
	347	320±40	11	380±40	8	340±30	7

Experiments were carried out with various composition of background electrolyte. Utilisation of dihydrophosphate, which helps to produce phosphate buffer gives the best results. In the distilled water sensor response was unstable and this increased errors of measurements. Sodium acetate as background electrolyte considerably influences some sensors of the array and this spoils detection limit for all components.

Background solution composition insignificantly influences detection limit of chloride ions. It is very likely that chloride is detected specifically by solid-state chloride ion-selective electrode, which is included in the array.

The Tables shows that it is possible to determine a set of anions using a sensor array in the flow-injection set-up. Average errors of determination are as follows: sulphate - about 15 %; nitrate -12 % and chloride – 10 %. The developed FIMS allows to determine chloride ions at the level of 0,4 mg/dm^3 in individual solutions. In the mixed solutions, when Cl^- is present simultaneously with other ions, the detection limit was 1,5 mg/dm^3.

Thus, a combination of flow-injection multisensor analysis with multivariate data processing (here by PLS) enables determination of anions in multicomponent solutions with reasonable accuracy.

3.4. Flue gas control

Table 12 deals with the data obtained by the standard analysis methods and official limits of some components in a flue gas from incinerators.

Table 12. Allowable concentration of some components in flue gas

	Incinerator Vestforbranding (Denmark) mg/m^3	ZSO (Russia) mg/m^3	Official limits, 2001 (EU and Russia) mg/m^3
Cd	<0,006*	n/a	0,05
Pb	<0,2*	n/a	0,5
Cu	<0,2*	n/a	0,5
HCl	2	0,5	10
SO_2	170	0,06	50
NO_x	330	traces**	200

*determined by standard technique (AAS or ICP MS) two times per year

**combustion temperature, according technology, does not exceed 870^0, thus nitrogen oxides are not formed in analytical concentrations.

Cadmium, lead, copper and other metals are not analysed in a real time mode at present time elsewhere. At ZSO, analysis of these components is not yet performed at all and consequently it is impossible to determine real emission of heavy metals to the atmosphere.

Concentration of analytes of interest in absorbing solution after bubbling of the gas is shown in the Table 13 along with detection limit for these components achieved with the help of FIMS. Actual content of analytes in the industrial samples is at least two times higher than the expected detection limit of the sensor arrays. Thus there is a principal opportunity to carry out the analysis with the help of FIMS almost on-line, after absorption of flue gas by an appropriate solution.

IUPAC method for detecting the limit of determination of a discrete selective sensor cannot be applied to the data processing from a sensor array of non-selective sensors because there is no theory realistically describing the sensor array response and behaviour of non-specific sensor. Therefore, instead of the deviation of the measured potential from the theoretically derived value one can use a measure of the deviation of the determined (predicted) concentration from the real concentration value. The predicted concentrations have been calculated for a sensor array using some multivariate calibration model. The deviation of the calculated concentration value from the real one, which corresponds to, e.g. the deviation of 9 mV from the theoretical slope of 29.6 mV/pX for doubly charged ions, makes 0.3 in terms of concentration logarithm. On the other hand, this assessment is based solely on concentration values and does employ any suppositions about the shape of the response, sensitivity and other parameters, which are not yet defined for the sensor arrays. Thus, the value of deviation of 0.3 in logarithmic scale from real concentration can be used as a measure of the detection limit dealing with the sensor arrays. Here and below all detection limit values for FIMS were calculated using this procedure.

Table 13. Concentration of components after bubbling through an absorbing solution and detection limits of FIMS

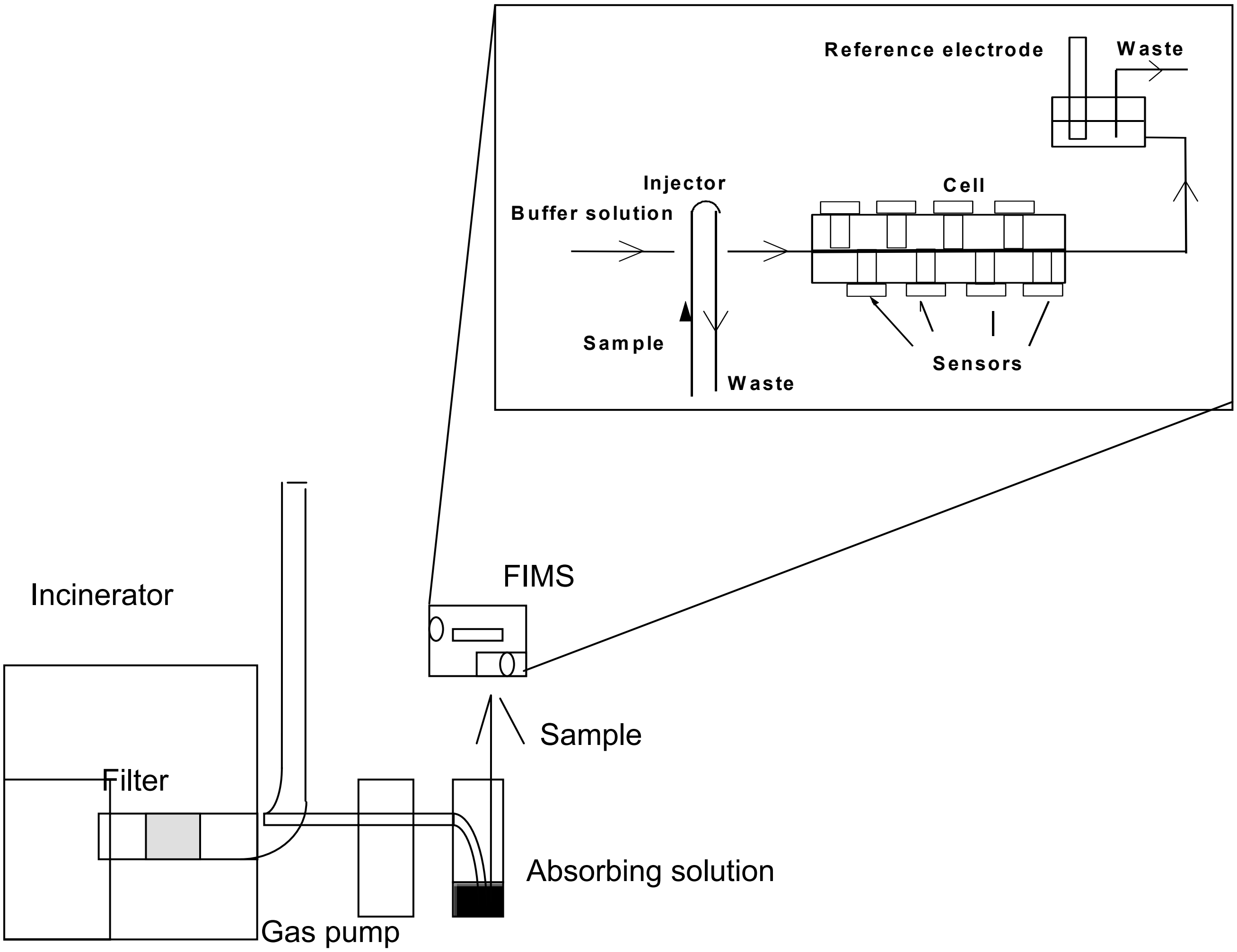
	Concentration of components after absorption for 1 hour with the rate 1 dm^3/hour mg/dm^3	Detection limits (FIMS) mg/dm^3
Cd	0,25	0,1
Pb	2,5	0,2
Cu	2,5	0,06

HCl	50	10
SO_2	250	50
NO_x	1000	6

The developed FIMS capable to determine both cations and anions can be applied to the analysis of flue gas from incinerators.

The scheme of FIMS designed for analysis at incinerators is shown in the Fig.20.

Figure 20. Scheme of analysis with the help flow - injection multisensor system at incinerators



The gas passed through an absorbing solution during the certain time (at bubbling rate of 1 m^3/hour for 1-3 hours). The time of absorption can be adjusted to reach the level of concentration of analytes in solution well above detection limits for chemical sensors (Table 12,13). The background solution passed through the cell constantly to ensure stable baseline and sensor performance. After an injection the sample passes through the cell and sensor potentials are measured and collected in the data file. The data are fitted to calibration model obtained as a result of multivariate calibration (e.g. by PLS) and, thus, concentrations of analytes in solution are determined. Known time, bubbling rate and also the absorption coefficients of components enable to calculate concentration of appropriate pollutant in the flue gas.

3.4.1. Determination of the content of heavy metals in real gas samples

The test of FIMS on experimental incinerator was carried out. It showed that the system works reproducibly under real conditions. The time of bubbling for collect heavy metals was about 1 hour and time of the analysis of obtained solution was 3-5 min. It was found that system application for determination of heavy metal content in the gas is actually possible. After measurements a part of the filter (according to a standard technique described on page 52), containing particles was dissolved in the acid in 24 hours. Resulting solution was analysed and sharp increase of sensor signals was observed, which means that the filter absorbs a lot of heavy metals. Modification of standard procedure of bubbling should allow measurement of total content of heavy metals in the gas and, hence, to derive also the efficiency of absorption of toxic components by the filter.

The data of independent method analysis (AAS) showed that typical concentrations of heavy metals in the smoke from the experimental incinerator are 0,001-0,5 mg/m^3. On the other hand, the time to collect heavy metal should be obviously smaller than 4 hours. At the flow rate of bubbling within the range 1-4 m^3/hours it is possible to obtain concentration levels of heavy metals in solution up to 1-10 mg/dm^3. The results of measurements of heavy metals in the concentration range expected for the flue gas from an incinerator are given in the Table 14.

Table 14. Results of simultaneous determination of heavy metal concentrations using FIMS (n=5, p=0.95).

N	Real mg/dm^3	Found FIMS $x \pm \Delta x$ mg/dm^3	S_r %	Found ICP MS $x \pm \Delta x$ mg/dm^3	S_r %
Cu					
	0,064	0,072±0,014	16	0,069±0,005	6
	0,42	0,45±0,08	13	0,380±0,015	3
Pb					
	0,208	0,20±0,05	20	0,200±0,01	4
	1,39	1,4 ± 0,2	12	1,31 ± 0,06	4
Cd					
	0,11	0,10±0,03	24	0,110±0,007	5
	0,75	0,82±0,15	15	0,742±0,010	1

It is necessary to mention that the set of background components (matrice) in multicomponent solution can significantly influence precision of quantitative determination of heavy metals in real samples. The most appropriate way to perform an adequate calibration of the system is to use the results of analysis of representative number of samples obtained by an independent standard analytical method, e.g. ICP MS (inductively coupled plasma mass-spectrometry) as the calibration data. On the other hand, the results of the analysis by an independent method (such as ICP MS) can produce information not only about analytes (heavy metals of interest) but also about other components, which are not analysed by FIMS, but can influence sensor response giving rise to additional errors. It is possible to prepare more adequate calibration solutions, which would allow take into account “matrice effect” on the basis of this information.

Two plants were selected to carry out the analysis of real samples using FIMS: Vestforbranding incinerator (Copenhagen) and ZSO incinerator (St. Petersburg).

The absorption at incinerator in Denmark was performed with the help of technique described on page 52. The experiments demonstrated that the efficiency of absorption with the method proposed in the present work is comparable with the standard technique (US-method EPA M.5) including partial filter dissolution.

Table 15. Comparison of analysis results of absorbing solutions obtained using different sampling methods but under fixed conditions, analysis being performed using ICP MS.

(rate - 4 m^3/hours, time - 2 hours, volume of a solution 400 ml).

	Cu, mg	Pb, mg	Cd, mg	Cr, mg
Standard method of absorption	1,6	4,1	0,12	2,1
Method proposed for FIMS	7,3	5,6	<0,2	2,3

The results of heavy metals determination in absorbing solutions using developed FIMS and standard analytical techniques are shown in the Table 15. The volume of absorbing solution (1 M HNO_3) was equal to 400 ml in Denmark and to 200 ml in Russia.

Table 16. Results of measurements by FIMS and by ICP MS (n=5, p=0.95).

	Found, FIMS $X \pm \Delta x$ mg/dm^3	S_r %	Found, ICP MS $X \pm \Delta x$ mg/dm^3	S_r %	Content in flue gas mg/ m^3
Cu					
1	<0,06		0,0003±0,0001	27	<0,01(6 10^{-5})
2	<0,06		0,0035±0,0005	13	<0,002(9 10^{-5})
3	<0,06		0,04		<0,003 (0,002)
Pb					
1	<0,2		0,0098±0,0005	4	<0,03 (0,002)
2	<0,2		0,0052 ±0,0005	8	<0,006 (0,0002)
3	<0,2		0,076		<0,01 (0,004)
Cd					
1	<0,1		<0,00001		<0,02 (2 10^{-6})
2	<0,1		0,0029±0,0005	14	<0,003 (6 10^{-5})

1, 2, - ZSO (St. Petersburg), gas bubbling rate - 0,03 m^3/hours, 1- absorption time 39 hours; 2 - 110 hours. 3 - incinerator Vestforbranding (Copenhagen), gas bubbling rate - 4 m^3/hours, absorption time - 2 hours.

The results of determination of heavy metal concentration in real samples resulted form gas absorption by 1 M nitric acid solution using FIMS and ICP MS are shown in Table 16.

The content of heavy metals in the solution after absorption of real flue gas is well below detection limit of FIMS as well as official limits. It is possible to conclude that the efficiency of cleaning of flue gases at both incinerators is high enough and metal content is within the required limits (Table 12). On the other hand, FIMS cannot produce quantitative results at such low concentration level. However, FIMS will produce quantitative results for higher content of metals, which are closer to (but still much lower) the official limits.

3.4.2. Determination of the content of HCl, nitrogen and sulphur oxides in the flue gas from the incinerator

Composition of absorbing solution for determination of hydrochloric acid and sulphur (SO_2 mainly) and nitrogen (NO_x) oxides was based on gas absorption technique described in [148, 149]. The absorbing solution of 0.1 M sodium hydroxide with addition of 1 % hydrogen peroxide was chosen. The idea of such a solution is to absorb acid and acidic oxides and transform them (oxidise, if necessary) into appropriate anions in solution such as Cl^-, SO_4^{2-} and NO_3^- and/or NO_2^-. The chosen solution quantitatively absorbs HCl and sulphur oxides. Absorption coefficient is about 0,3 for nitrogen oxides.

Four samples were taken from ZSO, the absorption time being 39, 24, 24 and 22,5 hours. The rate of gas flow was 0,03 м^3/hour. The results of anion determination by flow - injection multisensor system are shown in the table 17. The results of analysis of the same samples performed by independent method (ion chromatography) are also shown in the Table 17 for comparison.

Table 17. Results of simultaneous determination of inorganic anions by FIMS and by ion chromatography (n=5, p=0.95).

Anions, sample Number	Found by FIMS $x \pm \Delta x$ mg/dm^3	S_r %	Found by ion chromatography $x \pm \Delta x$ mg/dm^3	S_r %	Contents in flue gas mg/m^3
SO_4^{2-}					
1	3100±420	11	2800±100	3	96
2	1080±230	17	1350±40	2	38
3	98±15	13	105±4	3	3
4	230±50	16	192±6	3	5
NO_3^-					
1	31±7	18	26,4±0,7	3	0,3
2	29±6	17	20,3 ± 0,7	3	0,2
3	46±12	21	57±3	4	0,5
4	20±7	28	14,3±0,7	4	0,1
Cl^-					
1	15,8±1,5	8	*		0,5
2	202±15	7	*		5,6

3	225±30	10	*		6,2
4	6,7±0,9	11	*		0,2

* - the analysis was not carried out.

Results shown in the Table 17 demonstrate nice correspondence between anion content determined by ion chromatography and by flow-injection multisensor system. The error of anion determination by FIMS does not exceed 30 %.

Thus, it is possible to conclude that FIMS can be applied successfully for the analysis of solutions after absorbing of acidic oxides from the flue gas.

The developed FIMS is much more universal than it is demonstrated in the present study and can be used to analyse various industrial and laboratory samples where multicomponent express analysis of liquid is required.

4. CONCLUSIONS

1. A method of simultaneous determination of several components in solution with the help of flow-injection multisensor system (FIMS) is being developed and the opportunities of its analytical application are investigated. The efficiency of the method is achieved due to combination of flow-injection set-up and detection of analytes with the help of chemical sensor array. The sensor arrays comprised up to 11 potentiometric non-specific sensors with enhanced cross-sensitivity to heavy metal ions and inorganic anions. Data processing from the sensor array is performed using methods of multivariate analysis and pattern recognition.

2. A set of non-specific chemical sensors with solid-state (chalcogenide glasses) and PVC-based membranes for FIMS has been developed and applied. An original all-solid-state inner contact to PVC- based sensors for FIMS has been designed. Basic electrode characteristics of the sensors with solid contact were very similar to those with liquid one.

3. A technique of simultaneous determination of concentration of heavy metal ions in multicomponent solutions with the help FIMS has been developed. FIMS allows to determine the content of Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr(VI) ions in concentration range of 0,04 - 100 mg/dm^3 with an error within 15 %, the sample volume being 500 μdm^3.

4. A technique of simultaneous determination of content of inorganic anions in multicomponent solutions with the help of FIMS has been developed. FIMS allows determining concentration of SO_4^{2-}, Cl^-, NO_3^- in the range of 10-10000 mg/dm^3 with an error within 20 %, the sample volume being 500 μdm^3.

5. A mobile prototype of FIMS for control of flue gas from incinerators has been developed and feasibility tests were performed under industrial

conditions. The sample for FIMS was prepared by gas absorption in a special solution with subsequent analysis of composition of the solution. Is was demonstrated, that FIMS enables determination of heavy metals (Cu, Pb, Cd) in the range from 0,01 to 10 mg/m^3 and also detection of HCl, SO_2 and NO_x in a range from 0,1 to 500 mg/m^3. The expected error for real gas samples may be about 20% but this must be verified experimentally.

ACKNOWLEDGMENTS

This work was carried out in the framework of joint Danish-Russian project supported by grant №9600866 from Danish Research Councils, which financial input is kindly acknowledged.

The author wishes to thank the following companies:

dk-TEKNIK Energy and Environment, Soborg, Denmark and personally Dr. Klaus Hjuler for technical assistance and organisation of field measurements at Vestforbranding incinerator;

ZSO, St. Petersburg and personally Mr. Andrey Kupriyanov for technical assistance and organisation of field measurements at ZSO incinerator.

The author is grateful for assistance from and discussions with Boris Seleznev, Sergei Makarychev-Mikhailov and other colleagues from Laboratory of Chemical Sensors of St. Petersburg University.

Permanent assistance in experimental work and especially in the data processing from Dr. Alisa Rudnitskaya is particularly acknowledged.

REFERENCES

1. Hansen's Comprehensive Flow Injection Bibliography: http://www.flowinjection.com/search.html

2. The Flow Analysis Database http://www.fia.unf.edu/.

3. J. Ruzicka, E.H. Hansen, Flow injection analysis, 2nd edn., Wiley, New York, 1988.

4. J. Ruzicka, Microflow analysis.// In Proc. 8th International Conf. on Flow analysis., Warsaw, Poland, 2000, p.28.

5. E.H. Hansen, Flow injection analysis - looking back 25 years.// In Proc. 8th International Conf. on Flow analysis., Warsaw, Poland, 2000, p.58.

6. L.K. Shpigun Flow injection analysis//Russ. J. of Anal. Chem., 1990, 45(6), pp. 1045–1091.

7. Yu. A. Zolotov, L. K. Shpigun Flow-injection analysis in the USSR.// Microchem. Journal, 1992, V. 45, pp. 225-231.

8. L. Campanella, K. Pyrzynska and M. Trojanowicz: Chemical speciation by flow-injection analysis. A review.: English: Talanta, 43 (1996) 825-838.

9. N.W. Barnett, C.E. Lenehan, S.W. Lewis, Sequental injection analysis: an alternative approach to process analytical chemistry.// Trends in analytical chemistry, 1999, Vol. 18, No 5, pp. 346-353.

10. J. Ruzicka, A. Ivaska, Anal.Chem. 69(1997), 5024.

11. J. Ruzicka, E.H. Hansen, Flow injection analysis - Where are we heading? Trends in analytical chemistry, 1998, Vol. 17, No 2, pp. 69-73.

12. Yu.G. Vlasov, A.V. Legin, A.M. Rudnitskya, C. Di Natale, F. Davide, A. D' Amico, Russ. Jorn. of Anal. Chem., 1996, 69(6), pp. 958-964.

13. Yu.G. Vlasov, C. Di Natale, F. Davide, A. D' Amico,//Proc. of Int. Conf. ''Transducers'95-Eurosensors IX''. - Stockholm, Sweden, 1995. - Late News Contributions. - P. 36-37.

14. F.J. Saez de Viteri, D. Diamond, Determination and application of ISEs model parameters using flow injection and simplex optimization.//Analyst. - 1994. - V. 119. - N 5. - P. 749-758.

15. M. Otto, J.D.R. Thomas, Model studies on multiple channel analysis of free magnesium, calcium, sodium, and potassium at physiological concentration levels with ISEs.//Anal. Chem. - 1985. - V. 57. - N 13. - P. 2647-2651.

16. K. Beebe, D. Uerz, J. Sandier Sparingly selective ion-selective electrode array for multicomponent analysis.//Anal. Chem. - 1988. - V. 60. - N 1. - P. 66-71.

17. K. Beebe, B. Kovalski, Nonlinear calibration using projection persuit regression: application to an array of ISEs.//Anal. Chem. - 1988. - V. 60. - N 20. - P. 2273-2278.

18. M. Bos, A. Bos, W.E. Van der Linden, Processing of signals from an ion-selective electrod array by a neural network.//Anal.chim.acta. - 1990. - V. 233. - N 1. - P.31-39.

19. M. Hartnett, D. Diamondt, Ph.G. Barker Neural Network based recognition of flow injection patterns.//Analyst. - 1993. - V. 118. - N 4. - P. 347-354.

20. Yu.G. Vlasov, A.V. Legin, A.M. Rudnitskya, E.A. Bychkov, Cross-sensitivity of chalcogenide glass sensors in solutions of heavy metal ions.//Sensors and Actuators B 34. - N 1-3. - 1996. - P. 456-461.

21. A.V. Legin, E.A. Bychkov, B.L. Selesnev, Yu.G. Vlasov, Development and analytical evaluation of mutisensor system for water quality monitoring.// Sensors and Actuators B. - 1995. - V. 27. - N 1-3. - P. 377-379.

22. Yu.G. Vlasov, A.V. Legin, A.M. Rudnitskya, Cross-sensitivity evaluation of chemical sensors for electronic tongue: determination of heavy metal ions.//Sensors and Actuators B. - 1997. - V. 44. - N 1-3. - P. 532-537.
23. Yu.G. Vlasov, A.V. Legin, A.M. Rudnitskya, C. Di Natale, F. Davide, A. D' Amico, Russ. Jorn. of Anal. Chem.,1997, 52 (11), pp. 1214-1220.
24. W. Gopel, T.A. Jones, M. Kleitz, I. Lundstrom, T. Seiyama (eds.), Sensors: A Comprehensive Study, v.2/3, Chemical Sensors, VHC, Weinheim, 1990, p.191-237.
25. M.A. Sharaph, D.L. Illmen, B.R. Kowalski, Chemometrics, Leningrad: Chimiya, 1989, (in Russ.).
26. B.R. Kowalski //Computers in Chemical and Biochemical Research, 1974, v.2.
27. K.G. Joreskog, H. Wold, Systems under Indirect Obserbation Amsterdam: North Holland. - 1982. - 275p.
28. F. Lindgren, P. Geladi, S. Wold, A kernel algorithm for PLS // J. of Chemometrics. - 1993. - V.7. - P.45-49.
29. W. P. Linak, R.K. Srivastava, J.O. Wendt, Sorbent capture of nickel, lead, and cadmium in laboratory swirl flame incinerator,// Combustion and flame 100, 1995, pp. 241-250.
30. J.L. Casti, A. Karlqvist (eds.), Real Brans, Artificial Minds. Amsterdam: Noth-Holland. - 1987. - 226p.
31. R. Pfeifer, Z. Schreter, F. Fogelman-Soulie, L. Steels (eds.), Connectionism in Perspective. Amsterdam: Noth-Holland. - 1989. - 300p.
32. D.E. Rumelhart, G.E. Hinton, R.J. Williams Learning internal representations by error propagation // Parallel Distributed Processing: Exploration in Microstructure of Cognition / D.E. Rumelhart, J.I. McClelland (eds.) - Cambridge MA: MIT Press. - 1986. - V.1. - P.318-362.

33. D.E. Rumelhart, G.E. Hinton, R.J. Williams Learning representations by back-propagation error // Nature. - 1986. - V.323. - P.533-536.

34. D.C. Plout, Nowlan S.J., Hinton G.E. Experiments on Learning by Backpropagation. - Pittsburgh PA: Carnegie-Mellon Univ. - 1986. -329p.

35. G.L. Fruehauf, P.M. Sepe, M.S. Zaniboni, R.L. Rosa, M. Antoniazzi, Air quality impacts due two municipal waste incinerators, Tellus Ltd R. Mourato Coelho 1424, S. Paulo SP Brazil 05417, pp.1-6.

36. A. Carpi, Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere// Water, Air, and Soil Pollution 98: 1997, pp. 241–254.

37. J. Krissmann, M. A. Siddiqi, P. Peters-Gerth, A Study of the Thermodynamic Behavior of Mercury in a Wet Flue Gas Cleaning Process// Ind. Eng. Chem. Res., 1998, N37, pp. 3288-3294.

38. L. le Forestier, G. Libourel Characterization of Flue Gas Residues from Municipal Solid Waste Combustors // Environ. Sci. Technol. 1998, N32, pp. 2250-2256.

39. L. S. Morf, P.H. Brunner, The MSW incinerator as a monitoring tool for waste management,// Environ. Sci. Technol. 1998, N32, pp. 1825-1831.

40. T. Ishizuka, H. Tsuchiai, T. Murayama, T. Tanaka, H. Hattori, Preparation of Active Absorbent for Dry-Type Flue Gas Desulfurization from Calcium Oxide, Coal Fly Ash, and Gypsum// Ind. Eng. Chem. Res., 200, V. 39, pp. 1390-1396.

41. A. A. Lizzio, J. A. DeBarr, C. W. Kruse, Production of Activated Char from Illinois Coal for Flue Gas Cleanup,// Energy & Fuels 1997, N11, pp. 250-259

42. G. Centi and S. Perathoner, Role of the Size and Texture Properties of Copper-on-Alumina Pellets during the Simultaneous Removal of SO2 and N*Ox* from Flue Gas,// Ind. Eng. Chem. Res. 1997, N36, pp. 2945-2953

43. B. W.-L. Jang, J. J. Spivey, M. C. Kung, H. H. Kung, Low-Temperature N*Ox* Removal for Flue Gas Cleanup// Energy & Fuels 1997, N11,pp. 299-306.

44. Z.-M. Wang, Y.S. Lin, Sol-gel-derived alumina – supported copper oxide sorbent for flue gas desulfurization.// Ind. Eng. Chem. Res., 1998, V. 37, pp. 4675-4681.

45. A. Jacob, S. Stucki, P. Kuhn, Evaporation of heavy metals during the heat treatment of municipal solid waste incinerator fly ash,// Environ. Sci. Technol. 1995, N29, pp. 2429-2436

46. Vlasov Yu. G., Bychkov E. A., Legin A. V., Chalcogenide glass chemical sensors: research and analytical application. Talanta 41 (1994) 1059-1063.

47. www.statsoft.com

48.Camman K., Working with ion-selective electrodes, 1979, (Springer: Berlin).

49. B.P. Nikolski, E.A. Materova Solid contact in membrane ion-selective electrodes.// Ion-selective electrode Rev., 1985, Vol. 7. N1. P. 3-39.

Appendix 1

Calibration data for Anion2 and Anion3 sensors with different inner contact (l-liquid and s-solid) in sulphate ion solution:

Concentration SO_4^{2-} (mol/L)	anion2l	anion2s	anion3l	anion3s
10^{-5}	212	195	246	235
10^{-4}	210	194	236	226
10^{-3}	195	181	212	202
10^{-2}	172	159	187	179
10^{-1}	148	137	162	156

Appendix 2

The values of peak height (mV) for different sample volumes and flow rates for chalcogenide glass sensors for individual ion solution containing Pb(II) – 20 mg/L or Cd(II)- 20 mg/L or Cu(II) – 2 mg/L.

ΔH value for peak height in mV:

Sample volume 0,1 ml	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	5	12	46	37	34	0	0	6
Cd(II)	0	0	22	34	25	0	0	0
Cu(II)	0	58	46	51	65	0	0	0

Sample volume 0,5 ml	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	6	14	50	47	38	0	0	7
Cd(II)	0	3	26	40	30	0	0	0
Cu(II)	5	65	55	60	75	6	0	5

Sample volume 1,5 ml	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	7	14	52	47	40	0	0	7
Cd(II)	0	6	27	42	31	0	0	0
Cu(II)	6	67	56	63	77	8	0	7

Flow rate 0,1 ml/min	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	6	14	52	40	39	0	0	8
Cd(II)	0	4	28	42	33	0	0	0
Cu(II)	6	67	57	63	79	9	0	6

Flow rate 0,5 ml/min	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	6	14	47	37	32	0	0	6
Cd(II)	0	4	24	35	27	0	0	0
Cu(II)	5	61	50	57	68	7	0	5

Flow rate 1,5 ml/min	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	2	12	45	34	27	0	0	2
Cd(II)	0	0	21	32	22	0	0	0
Cu(II)	3	55	51	54	62	3	0	3

Δt value for peak width in sec:

Sample volume 0,1 ml	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	15	20	70	60	60	0	0	20
Cd(II)	0	0	40	50	40	0	0	0
Cu(II)	0	200	100	130	140	0	0	0

Sample volume 0,5 ml	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	25	100	300	240	200	0	0	35
Cd(II)	0	20	120	210	150	0	0	0
Cu(II)	23	270	400	450	550	25	0	40

Sample volume 1,5 ml	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	30	110	440	320	290	0	0	40
Cd(II)	0	35	210	300	230	0	0	0
Cu(II)	25	320	500	570	650	40	0	40

Flow rate 0,1 ml/min	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	24	170	480	400	380	0	0	45
Cd(II)	0	45	330	450	350	0	0	0
Cu(II)	30	350	750	850	1000	50	0	40

Flow rate 0,5 ml/min	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	25	95	220	190	150	0	0	40
Cd(II)	0	25	110	150	120	0	0	0
Cu(II)	25	290	370	430	550	40	0	30

Flow rate 1,5 ml/min	Ag	Cu	Pb	Cd	Tl	Cr(VI)	Hg	Fe
Pb(II)	15	24	130	77	60	0	0	10
Cd(II)	0	0	90	120	50	0	0	0
Cu(II)	15	240	320	330	370	15	0	10

Appendix 3

Potentials (mV) for the 8 sensors of the system employed for simultaneous determination of lead and cadmium in binary mixtures. Three replicas of each sample were run. The data processing carried out by PLS

Pb	Cd	Cu	Cd2	Tl	Fe	Ag	Pb2	Real Pb	Predicted Pb	Real Pb in mg/l	Predicted Pb in mg/l	Real Cd	Predicted Cd	Real Cd in mg/l	Predicted Cd in mg/l
1,0	0,0	0,0	1,4	0,0	0,0	0,0	0,0	-7,00	-6,69	0,02	0,04	-7,00	-6,42	0,01	0,0
0,0	0,0	0,0	0,0	0,0	0,0	0,6	0,0	-7,00	-6,71	0,02	0,04	-7,00	-6,46	0,01	0,0
0,0	0,0	0,0	0,0	0,0	0,0	1,1	0,0	-7,00	-6,73	0,02	0,04	-7,00	-6,46	0,01	0,0
10,5	12,1	0,0	11,1	14,0	0,0	0,0	7,0	-5,48	-5,82	0,69	0,32	-7,00	-6,04	0,01	0,1
11,1	12,0	0,0	10,8	13,2	0,0	0,6	7,0	-5,48	-5,75	0,69	0,37	-7,00	-6,08	0,01	0,1
11,0	10,6	0,0	9,6	13,9	0,0	0,0	7,0	-5,48	-5,62	0,69	0,50	-7,00	-6,27	0,01	0,1
29,0	29,9	0,0	28,1	26,6	0,0	0,0	27,6	-4,48	-4,53	7	6	-7,00	-6,00	0,01	0,1
29,1	29,7	1,0	28,4	27,0	0,0	0,0	27,5	-4,48	-4,53	7	6	-7,00	-6,01	0,01	0,1
29,4	30,3	2,5	28,9	27,3	0,0	0,0	27,8	-4,48	-4,53	7	6	-7,00	-6,00	0,01	0,1
46,1	48,1	9,8	47,1	39,2	10,0	9,0	45,7	-7,00	-4,45	0,02	7	-7,00	-5,38	0,01	0,5
45,1	47,8	10,2	46,8	39,0	10,5	8,5	45,1	-7,00	-4,55	0,02	6	-7,00	-5,33	0,01	0,5
46,0	48,2	9,5	46,5	39,1	9,5	7,5	45,5	-7,00	-4,35	0,02	9	-7,00	-5,43	0,01	0,4
54,5	50,3	15,1	49,6	47,0	11,1	10,5	51,4	-3,48	-3,62	69	50	-7,00	-6,00	0,01	0,1
54,6	50,8	14,9	49,8	46,9	11,5	10,6	51,3	-3,48	-3,68	69	44	-7,00	-5,94	0,01	0,1
55,0	49,8	15,6	48,7	47,8	10,6	10,7	52,2	-3,48	-3,42	69	79	-7,00	-6,21	0,01	0,1
71,7	67,8	21,0	65,7	60,2	21,6	15,8	69,4	-3,00	-3,21	209	130	-7,00	-5,64	0,01	0,3
71,5	68,8	21,3	65,3	59,6	22,2	15,5	69,0	-3,00	-3,31	209	101	-7,00	-5,55	0,01	0,3
71,9	67,0	20,9	64,9	59,8	22,7	15,6	68,6	-3,00	-3,26	209	116	-7,00	-5,68	0,01	0,2
93,2	87,1	27,3	82,1	76,3	32,4	18,0	90,0	-2,48	-2,22	690	1259	-7,00	-5,62	0,01	0,3
94,0	86,9	27,4	82,9	75,9	31,9	18,7	90,3	-2,48	-2,19	690	1337	-7,00	-5,62	0,01	0,3
93,9	86,5	27,9	81,5	76,3	32,0	18,5	91,1	-2,48	-2,05	690	1871	-7,00	-5,82	0,01	0,2
16,1	28,0	2,1	28,0	17,2	0,0	0,0	16,2	-7,00	-6,41	0,02	0,08	-4,48	-4,60	4	3
16,3	28,7	2,5	28,3	16,6	0,0	0,0	16,6	-7,00	-6,44	0,02	0,08	-4,48	-4,56	4	3
15,8	28,5	2,0	28,5	16,5	0,0	0,0	16,5	-7,00	-6,48	0,02	0,07	-4,48	-4,51	4	3
27,5	44,1	5,0	46,6	31,7	10,1	7,2	27,1	-7,00	-6,90	0,02	0,03	-3,48	-3,34	37	48
27,0	45,1	5,0	46,5	32,1	10,0	5,9	27,5	-7,00	-6,86	0,02	0,03	-3,48	-3,31	37	50
27,2	44,7	5,0	46,8	31,6	10,2	6,1	27,0	-7,00	-6,92	0,02	0,03	-3,48	-3,28	37	55
41,7	62,8	11,6	63,2	43,0	17,7	13,7	38,1	-7,00	-7,15	0,02	0,01	-2,48	-2,27	370	599
41,5	62,4	11,3	63,0	43,7	18,1	13,9	38,8	-7,00	-7,10	0,02	0,02	-2,48	-2,34	370	510
41,8	63,0	11,0	63,7	44,6	18,0	13,2	39,3	-7,00	-7,02	0,02	0,02	-2,48	-2,33	370	525
43,2	56,0	5,0	52,4	42,1	0,0	0,0	41,4	-4,48	-4,35	6,90	9	-4,48	-4,32	4	5
43,6	55,8	4,1	53,3	42,5	0,0	0,0	41,6	-4,48	-4,33	6,90	10	-4,48	-4,28	4	6
43,0	55,6	4,5	53,6	42,6	0,0	0,0	41,9	-4,48	-4,36	6,90	9	-4,48	-4,27	4	6
53,0	69,7	10,2	67,5	51,1	10,7	7,4	52,3	-4,48	-4,94	6,90	2	-3,48	-3,33	37	47
53,4	69,8	10,5	68,0	51,8	10,6	6,0	52,2	-4,48	-4,87	6,90	3	-3,48	-3,34	37	49
53,2	70,0	10,1	67,5	51,5	10,9	7,5	52,5	-4,48	-4,93	6,90	2	-3,48	-3,33	37	47
72,3	87,1	16,1	84,8	67,5	19,1	13,0	70,1	-4,48	-4,23	6,90	12	-2,48	-3,07	370	96
72,8	87,5	15,9	85,2	66,9	19,3	12,8	71,3	-4,48	-4,18	6,90	14	-2,48	-3,10	370	89
73,3	88,0	16,7	84,6	67,1	18,7	13,4	70,9	-4,48	-4,14	6,90	15	-2,48	-3,13	370	83
69,3	72,0	16,9	71,5	61,1	12,7	9,6	65,8	-3,48	-3,19	69	136	-4,48	-4,76	4	2
69,0	72,3	16,6	71,7	61,6	13,1	9,5	66,1	-3,48	-3,21	69	128	-4,48	-4,73	4	2
68,6	72,4	17,1	71,5	61,3	12,8	9,4	66,0	-3,48	-3,22	69	127	-4,48	-4,73	4	2
81,3	90,1	20,2	89,0	71,8	20,2	13,0	77,1	-3,48	-3,45	69	74	-3,48	-3,56	37	31
81,6	91,7	20,7	90,1	71,2	20,8	13,7	76,3	-3,48	-3,69	69	43	-3,48	-3,31	37	55
81,7	91,5	20,5	90,6	71,0	20,3	14,0	76,9	-3,48	-3,65	69	47	-3,48	-3,32	37	53
97,4	109,5	23,7	108,2	80,1	26,6	17,5	89,4	-3,48	-3,59	69	54	-2,48	-2,38	370	472
98,1	109,9	24,3	109,1	81,3	26,5	17,9	90,1	-3,48	-3,53	69	62	-2,48	-2,39	370	462
97,9	110,2	24,8	108,7	80,6	27,3	18,0	89,5	-3,48	-3,65	69	47	-2,48	-2,33	370	529

99,1	95,1	27,3	92,0	78,2	31,4	19,1	92,4	-2,48	-2,39	690	853	-4,48	-4,80	4	2
100,1	96,3	27,5	91,8	78,1	31,1	19,5	92,1	-2,48	-2,38	690	879	-4,48	-4,77	4	2
99,8	96,7	27,9	92,2	77,9	31,6	19,3	91,9	-2,48	-2,48	690	694	-4,48	-4,68	4	2
108,9	108,9	27,5	106,1	82,9	31,3	20,6	98,2	-2,48	-2,48	690	700	-3,48	-3,71	37	22
109,3	109,1	27,4	104,8	83,6	31,6	20,5	98,8	-2,48	-2,34	690	966	-3,48	-3,87	37	15
109,5	109,5	27,6	105,2	83,6	31,7	20,7	99,3	-2,48	-2,34	690	955	-3,48	-3,85	37	16
123,1	128,6	32,8	125,6	98,8	38,2	25,1	110,7	-2,48	-2,51	690	644	-2,48	-2,54	370	320
123,0	129,1	33,1	125,8	99,1	38,9	25,0	111,0	-2,48	-2,56	690	580	-2,48	-2,51	370	345
122,8	128,8	32,7	126,3	98,7	39,3	25,2	111,1	-2,48	-2,62	690	503	-2,48	-2,47	370	383

Average value of predicted concentrations and standard deviations for determination of Pb(II) and Cd(II) in mixed solution:

Realpb	Averagefoundpb	Deviation	%	realcd	averagefoundpb	Deviation	%
0,02	1,54	1,08	56	0,01	0,19	0,13	54
0,69	0,40	0,21	42	4	3	0,33	8
7	8	1	8	37	41	2,53	5
69	74	4	4	370	368	1,42	0
209	170	27	13				
690	851	114	11				

Appendix 4

Potential values (mV) of 11 sensors of the system and the result of simultaneous determination of lead, cadmium and copper:

	Pb	Cd	Cu	Cd2	Tl	Fe	Ag	Pb2	Fe	Cr	Hg
1	1,0	0,0	0,0	1,4	0,0	0,0	0,0	0,0	0,0	0,0	0,0
2	0,0	0,0	0,0	0,0	0,0	0,0	0,6	0,0	1,0	0,0	0,0
3	0,0	0,0	0,0	0,0	0,0	0,0	1,1	0,0	0,0	0,0	0,5
4	10,5	12,1	0,0	11,1	14,0	0,0	0,0	7,0	0,0	1,6	0,0
5	11,1	12,0	0,0	10,8	13,2	0,0	0,6	7,0	1,0	0,0	0,0
6	11,0	10,6	0,0	9,6	13,9	0,0	0,0	7,0	0,0	0,0	0,0
7	29,0	29,9	0,0	28,1	26,6	0,0	0,0	27,6	0,0	0,0	0,0
8	29,1	29,7	1,0	28,4	27,0	0,0	0,0	27,5	0,0	0,0	0,0
9	29,4	30,3	2,5	28,9	27,3	0,0	0,0	27,8	1,5	0,6	0,0
10	46,1	48,1	9,8	47,1	39,2	10,0	9,0	45,7	0,0	0,0	0,0
11	45,1	47,8	10,2	46,8	39,0	10,5	8,5	45,1	0,0	0,0	0,0
12	46,0	48,2	9,5	46,5	39,1	9,5	7,5	45,5	0,0	0,4	0,5
13	54,5	50,3	15,1	49,6	47,0	11,1	10,5	51,4	0,0	0,0	0,0
14	54,6	50,8	14,9	49,8	46,9	11,5	10,6	51,3	0,4	0,0	0,0
15	55,0	49,8	15,6	48,7	47,8	10,6	10,7	52,2	0,0	0,2	0,0
16	71,7	67,8	21,0	65,7	60,2	21,6	15,8	69,4	0,0	0,0	0,3
17	71,5	68,8	21,3	65,3	59,6	22,2	15,5	69,0	0,0	0,0	0,0
18	71,9	67,0	20,9	64,9	59,8	22,7	15,6	68,6	0,3	0,0	0,0
19	93,2	87,1	27,3	82,1	76,3	32,4	18,0	90,0	0,0	0,0	0,0
20	94,0	86,9	27,4	82,9	75,9	31,9	18,7	90,3	0,0	0,0	0,0
21	93,9	86,5	27,9	81,5	76,3	32,0	18,5	91,1	0,0	0,0	0,0
22	16,1	28,0	2,1	28,0	17,2	0,0	0,0	16,2	0,0	0,0	0,0
23	16,3	28,7	2,5	28,3	16,6	0,0	0,0	16,6	0,0	0,0	0,0
24	15,8	28,5	2,0	28,5	16,5	0,0	0,0	16,5	0,0	0,7	0,0
25	27,5	44,1	5,0	46,6	31,7	10,1	7,2	27,1	0,0	0,0	0,0
26	27,0	45,1	5,0	46,5	32,1	10,0	5,9	27,5	0,0	0,0	0,0
27	27,2	44,7	5,0	46,8	31,6	10,2	6,1	27,0	0,0	0,0	0,0
28	41,7	64,8	11,6	64,1	43,0	17,7	13,7	38,1	0,9	0,1	0,0
29	41,5	64,1	11,3	64,0	43,7	18,1	13,9	38,8	0,0	0,0	0,0
30	41,8	63,0	11,0	63,7	44,6	18,0	13,9	39,3	0,0	0,0	0,0
31	43,2	56,0	5,0	52,4	42,1	0,0	0,0	41,4	0,0	0,0	0,0
32	43,6	55,8	4,1	53,3	42,5	0,0	0,0	41,6	0,0	0,0	0,0
33	43,0	55,6	4,5	53,6	42,6	0,0	0,0	41,9	0,6	0,0	0,0
34	53,0	69,7	10,2	67,5	51,1	10,7	7,4	52,3	0,0	0,0	0,7
35	53,4	69,8	10,5	68,0	51,8	10,6	6,0	52,2	0,0	0,0	0,0
36	53,2	70,0	10,1	67,5	51,5	10,9	7,5	52,5	0,0	0,0	0,0
37	72,3	87,1	16,1	84,8	67,5	19,1	13,0	70,1	0,0	0,0	0,0
38	72,8	87,5	15,9	85,2	66,9	19,3	12,8	71,3	0,0	0,0	0,0
39	73,3	88,0	16,7	84,6	67,1	18,7	13,4	70,9	0,0	0,0	0,0
40	69,3	72,0	16,9	71,5	61,1	12,7	9,6	65,8	0,0	0,0	0,0
41	69,0	72,3	16,6	71,7	61,6	13,1	9,5	66,1	0,0	0,0	0,0
42	68,6	72,4	17,1	71,5	61,3	12,8	9,4	66,0	0,0	0,0	0,0
43	81,3	90,1	20,2	89,0	71,8	20,2	13,0	77,1	0,0	0,0	0,0
44	81,6	91,7	20,7	90,1	71,2	20,8	13,7	76,3	0,6	0,0	0,0
45	81,7	91,5	20,5	90,6	71,0	20,3	14,0	76,9	0,0	0,0	0,0
46	95,3	111,6	23,7	111,9	83,6	26,6	18,1	89,1	0,0	0,0	0,0
47	95,7	112,1	24,3	112,3	85,2	26,5	18,5	89,0	0,0	1,0	0,0
48	95,5	112,3	24,8	112,0	84,7	27,3	18,5	89,0	0,0	1,0	0,0
49	99,1	95,1	27,3	92,0	78,2	31,4	19,1	92,4	0,0	0,0	0,0
50	100,1	96,3	27,5	91,8	78,1	31,1	19,5	92,1	0,0	0,0	0,0
51	99,8	96,7	27,9	92,2	77,9	31,6	19,3	91,9	0,0	0,0	0,0
52	108,9	108,9	27,5	106,1	82,9	31,3	20,6	98,2	0,0	0,0	0,0

53	109,3	109,1	27,4	104,8	83,6	31,6	20,5	98,8	0,0	0,0	0,0
54	109,5	109,5	27,6	105,2	83,6	31,7	20,7	99,3	0,0	0,0	0,0
55	123,1	128,6	32,8	125,6	98,8	38,2	25,1	110,7	0,0	0,4	0,0
56	123,0	129,1	33,1	125,8	99,1	38,9	25,0	111,0	0,0	0,0	0,0
57	122,8	128,8	32,7	126,3	98,7	39,3	25,2	111,1	0,0	0,0	0,0
58	4,7	11,6	6,3	11,6	7,1	0,0	3,6	7,3	0,0	0,0	0,0
59	4,7	11,1	6,0	10,8	7,1	0,0	3,5	7,8	0,0	0,0	0,0
60	3,7	9,4	6,8	9,8	7,0	0,0	3,2	6,9	0,0	0,0	0,0
61	12,7	25,1	27,6	21,9	18,7	2,1	4,2	14,1	4,1	2,3	0,0
62	13,4	23,1	28,6	20,6	18,3	2,4	3,1	13,1	4,4	2,7	0,0
63	14,2	23,8	28,2	21,3	20,1	2,5	4,6	13,9	4,2	2,8	0,0
64	55,4	67,5	56,3	65,0	80,3	5,1	5,5	66,7	7,6	6,0	0,0
65	54,4	66,2	57,2	63,8	80,1	6,0	5,6	65,8	8,0	6,2	0,0
66	54,4	66,8	56,9	64,1	80,5	5,6	5,1	64,9	7,7	6,4	0,0
67	13,5	18,6	6,7	18,8	16,1	0,0	3,2	15,6	0,0	0,0	0,0
68	14,3	20,3	7,1	19,1	15,9	0,0	2,7	15,5	0,0	0,0	0,0
69	14,6	19,8	6,9	19,0	16,0	0,0	1,6	15,4	0,0	0,0	0,0
70	31,6	36,1	9,6	35,3	26,1	0,0	2,2	32,8	0,0	0,0	0,0
71	32,1	35,9	9,4	34,8	26,7	0,0	2,6	33,0	0,0	0,0	0,0
72	31,9	36,7	9,6	35,4	25,3	0,0	2,7	33,6	0,0	0,0	0,0
73	57,1	55,8	13,1	54,6	49,6	10,7	8,1	55,4	0,0	0,0	0,0
74	57,7	55,4	12,9	54,5	49,5	10,8	6,7	53,8	0,0	0,0	0,0
75	58,3	56,2	12,9	53,5	48,9	11,0	7,4	52,7	0,0	0,0	0,0
76	38,4	46,5	31,6	42,4	37,3	4,1	5,0	37,0	4,5	2,6	0,0
77	37,7	46,2	31,1	42,7	37,6	4,6	4,9	37,3	4,5	3,0	0,0
78	38,2	46,9	31,6	42,5	36,6	4,5	4,4	37,3	4,6	3,2	0,0
79	66,1	66,1	35,1	62,6	57,9	13,8	12,5	65,3	5,1	3,5	0,0
80	65,9	66,5	34,9	63,3	58,7	14,2	12,6	65,1	5,5	4,1	0,0
81	66,3	67,2	35,4	63,2	58,6	14,3	12,1	64,9	6,3	3,4	0,0
82	109,9	111,6	63,1	107,2	110,2	15,2	13,2	108,7	8,6	6,0	0,0
83	109,4	112,8	63,5	107,9	111,1	15,5	13,0	109,5	8,5	6,3	0,0
84	109,1	112,5	64,0	108,1	109,8	15,0	13,3	109,2	8,4	6,6	0,0
85	89,8	105,7	61,3	100,2	96,3	12,8	7,1	83,7	7,7	5,5	0,0
86	89,3	106,2	61,3	100,6	96,9	12,9	7,4	83,5	7,5	5,8	0,0
87	90,2	106,6	60,7	100,4	96,0	13,0	7,6	83,9	7,4	6,1	0,0
88	102,6	129,6	64,1	123,1	108,1	17,1	12,0	97,6	7,6	6,4	0,0
89	102,5	130,4	64,8	123,6	107,7	17,8	12,3	97,3	7,7	6,4	0,0
90	102,4	130,9	65,4	123,9	108,4	18,4	11,9	97,8	7,5	6,1	0,0
91	128,8	140,7	92,1	135,1	127,5	28,0	22,1	128,3	9,1	8,5	0,0
92	129,3	142,0	92,7	136,8	128,7	28,1	22,5	128,7	9,5	8,4	0,0
93	129,5	142,8	92,5	136,3	129,3	27,9	22,7	129,1	9,4	8,7	0,0
94	142,5	162,1	96,1	157,3	141,3	32,3	27,8	142,8	10,1	9,1	0,0
95	143,2	162,8	96,7	157,9	142,3	32,6	27,7	141,6	9,9	9,4	0,0
96	143,2	163,1	96,1	157,8	143,0	32,4	27,5	142,4	10,0	9,5	0,0
97	100,1	119,1	61,6	115,3	115,8	3,6	5,1	107,1	5,1	6,1	0,0
98	100,1	118,8	61,3	116,1	117,2	4,1	4,9	106,7	6,2	5,5	0,0
99	99,9	118,1	61,2	116,1	116,7	4,3	5,0	107,1	6,3	5,5	0,0
100	147,7	157,8	89,6	153,3	166,7	16,9	23,2	147,7	5,6	9,2	0,0
101	149,1	158,8	89,3	154,1	168,1	17,1	24,3	148,1	6,2	9,1	0,0
102	148,8	158,7	89,8	154,3	168,7	17,2	24,6	148,4	6,2	9,0	0,0
103	127,6	140,3	66,6	139,2	135,6	13,7	10,6	134,7	8,7	6,2	0,0
104	127,2	140,7	66,2	139,7	136,1	14,1	11,7	135,2	8,5	6,2	0,0
105	127,3	141,7	66,7	139,6	135,1	14,6	11,2	135,6	8,6	6,6	0,0
106	167,5	171,6	93,7	167,1	166,2	28,6	29,1	171,8	9,1	9,6	0,0
107	167,8	172,2	94,7	166,3	166,7	29,1	28,8	171,5	9,1	9,5	0,0
108	168,1	172,8	94,5	166,6	166,3	29,2	29,6	171,8	9,2	9,0	0,0
109	142,1	161,8	69,7	157,5	147,2	21,6	16,1	145,8	10,1	6,6	0,0
110	142,7	162,1	70,1	158,1	146,8	21,9	16,0	146,3	10,2	6,8	0,0

111	142,8	161,2	70,1	157,5	147,0	21,7	16,1	146,5	9,8	6,8	0,0
112	181,2	196,2	98,1	191,5	190,1	36,1	34,0	186,3	12,2	9,6	0,0
113	182,6	197,6	98,0	191,6	190,3	36,3	33,6	186,0	13,3	9,8	0,0
114	181,9	197,2	98,2	191,7	189,7	36,5	33,7	187,0	12,9	9,9	0,0
115	164,6	187,0	73,1	182,9	170,1	27,3	20,6	167,7	13,3	7,1	0,0
116	164,8	186,9	73,6	183,2	170,0	27,4	20,7	168,8	12,2	7,0	0,0
117	165,0	187,9	73,7	183,6	170,3	27,1	20,9	168,3	13,7	7,0	0,0
118	168,4	184,7	74,4	179,7	167,7	27,7	20,8	171,1	14,2	7,2	0,0
119	168,9	185,3	74,8	180,8	168,8	27,8	20,8	170,8	14,9	7,3	0,0
120	167,6	184,8	74,0	181,6	168,3	27,7	21,0	170,5	13,8	7,2	0,0
121	206,6	212,0	103,2	206,2	201,2	41,2	37,7	212,6	15,1	10,1	0,0
122	206,2	212,3	104,0	208,2	202,1	41,5	37,9	213,2	15,6	10,0	0,0
123	207,8	211,5	103,8	207,7	201,5	41,4	37,2	212,8	15,5	10,0	0,0
124	181,6	214,2	78,1	209,0	190,1	34,0	25,1	187,2	16,3	7,6	0,0
125	182,2	215,3	77,4	210,7	190,7	34,3	25,8	189,6	16,8	7,8	0,0
126	182,2	214,4	77,6	211,2	190,4	34,4	25,8	188,2	16,5	7,7	0,0
127	227,6	247,1	107,5	242,6	223,3	48,2	43,4	230,6	17,7	10,5	0,0
128	231,0	246,1	107,6	244,1	222,2	48,1	42,8	231,2	16,1	11,0	0,0
129	230,7	248,1	107,0	244,6	222,9	48,0	42,9	231,5	17,4	10,8	0,0

	Real Pb	Predicted Pb	Real Pb in mg/l	Predicted Pb in mg/l	Real Cd	Predicted Cd	Real Cd in mg/l	Predicted Cd in mg/l	Real Cu	Predicted Cu	Real Cu in mg/l	Predicted Cu in mg/l
1	-7,00	-6,30	0,02	0,1	-7,00	-7,55	0,01	0,00	-7,00	-6,86	0,006	0,009
2	-7,00	-6,31	0,02	0,1	-7,00	-7,68	0,01	0,00	-7,00	-6,84	0,006	0,009
3	-7,00	-6,32	0,02	0,1	-7,00	-7,60	0,01	0,00	-7,00	-6,85	0,006	0,009
4	-5,48	-5,67	0,69	0,4	-7,00	-7,19	0,01	0,01	-7,00	-6,81	0,006	0,010
5	-5,48	-5,60	0,69	0,5	-7,00	-7,31	0,01	0,01	-7,00	-6,83	0,006	0,010
6	-5,48	-5,54	0,69	0,6	-7,00	-7,34	0,01	0,01	-7,00	-6,81	0,006	0,010
7	-4,48	-4,15	7	15	-7,00	-7,13	0,01	0,01	-7,00	-6,85	0,006	0,009
8	-4,48	-4,18	7	14	-7,00	-7,12	0,01	0,01	-7,00	-6,85	0,006	0,009
9	-4,48	-4,19	7	14	-7,00	-7,22	0,01	0,01	-7,00	-6,84	0,006	0,009
10	-4,00	-4,21	21	13	-7,00	-6,69	0,01	0,02	-7,00	-6,86	0,006	0,009
11	-4,00	-4,28	21	11	-7,00	-6,68	0,01	0,02	-7,00	-6,85	0,006	0,009
12	-4,00	-4,19	21	14	-7,00	-6,72	0,01	0,02	-7,00	-6,86	0,006	0,009
13	-3,48	-3,56	69	57	-7,00	-6,84	0,01	0,02	-7,00	-6,71	0,006	0,012
14	-3,48	-3,59	69	54	-7,00	-6,82	0,01	0,02	-7,00	-6,73	0,006	0,012
15	-3,48	-3,49	69	68	-7,00	-6,97	0,01	0,01	-7,00	-6,68	0,006	0,013
16	-3,00	-3,11	209	162	-7,00	-6,73	0,01	0,02	-7,00	-6,67	0,006	0,014
17	-3,00	-3,09	209	170	-7,00	-6,63	0,01	0,03	-7,00	-6,69	0,006	0,013
18	-3,00	-3,12	209	159	-7,00	-6,73	0,01	0,02	-7,00	-6,69	0,006	0,013
19	-2,48	-2,41	690	815	-7,00	-4,29	0,01	6	-7,00	-6,77	0,006	0,011
20	-2,48	-2,37	690	887	-7,00	-4,19	0,01	7	-7,00	-6,78	0,006	0,011
21	-2,48	-2,28	690	1102	-7,00	-4,39	0,01	5	-7,00	-6,74	0,006	0,012
22	-7,00	-6,27	0,02	0,1	-4,48	-4,72	4	2	-7,00	-6,97	0,006	0,007
23	-7,00	-6,25	0,02	0,1	-4,48	-4,71	4	2	-7,00	-6,97	0,006	0,007
24	-7,00	-6,28	0,02	0,1	-4,48	-4,71	4	2	-7,00	-6,99	0,006	0,007
25	-7,00	-6,62	0,02	0,1	-3,48	-3,22	37	68	-7,00	-7,10	0,006	0,005
26	-7,00	-6,58	0,02	0,1	-3,48	-3,28	37	58	-7,00	-7,10	0,006	0,005
27	-7,00	-6,62	0,02	0,1	-3,48	-3,21	37	69	-7,00	-7,10	0,006	0,005
28	-7,00	-7,03	0,02	0,02	-2,48	-2,55	370	313	-7,00	-7,07	0,006	0,006
29	-7,00	-6,98	0,02	0,02	-2,48	-2,59	370	290	-7,00	-7,07	0,006	0,005
30	-7,00	-6,88	0,02	0,03	-2,48	-2,71	370	216	-7,00	-7,06	0,006	0,006
31	-4,48	-4,20	6,90	13	-4,48	-4,87	4	2	-7,00	-6,93	0,006	0,008
32	-4,48	-4,20	6,90	13	-4,48	-4,92	4	1	-7,00	-6,95	0,006	0,007
33	-4,48	-4,26	7	12	-4,48	-4,90	4	1	-7,00	-6,94	0,006	0,007
34	-4,48	-4,66	7	5	-3,48	-3,77	37	19	-7,00	-7,01	0,006	0,006
35	-4,48	-4,55	7	6	-3,48	-3,91	37	14	-7,00	-6,99	0,006	0,007

36	-4,48	-4,65	7	5	-3,48	-3,85	37	16	-7,00	-6,99	0,006	0,007
37	-4,48	-4,19	7	13	-2,48	-3,12	370	84	-7,00	-7,00	0,006	0,006
38	-4,48	-4,09	7	17	-2,48	-3,07	370	96	-7,00	-7,03	0,006	0,006
39	-4,48	-4,14	7	15	-2,48	-3,21	370	69	-7,00	-6,98	0,006	0,007
40	-3,48	-3,40	69	83	-4,48	-4,94	4	1	-7,00	-6,81	0,006	0,010
41	-3,48	-3,37	69	90	-4,48	-5,02	4	1	-7,00	-6,82	0,006	0,010
42	-3,48	-3,43	69	77	-4,48	-4,95	4	1	-7,00	-6,80	0,006	0,010
43	-3,48	-3,64	69	48	-3,48	-3,68	37	24	-7,00	-6,92	0,006	0,008
44	-3,48	-3,72	69	40	-3,48	-3,62	37	27	-7,00	-6,93	0,006	0,007
45	-3,48	-3,74	69	38	-3,48	-3,50	37	36	-7,00	-6,94	0,006	0,007
46	-3,48	-4,41	69	8	-2,48	-2,45	370	394	-7,00	-6,95	0,006	0,007
47	-3,48	-4,45	69	7	-2,48	-2,41	370	434	-7,00	-6,91	0,006	0,008
48	-3,48	-4,48	69	7	-2,48	-2,49	370	366	-7,00	-6,91	0,006	0,008
49	-2,48	-2,55	690	593	-4,48	-3,39	4	46	-7,00	-6,88	0,006	0,008
50	-2,48	-2,55	690	585	-4,48	-3,45	4	40	-7,00	-6,88	0,006	0,008
51	-2,48	-2,66	690	454	-4,48	-3,43	4	41	-7,00	-6,87	0,006	0,009
52	-2,48	-2,55	690	596	-3,48	-3,50	37	35	-7,00	-6,96	0,006	0,007
53	-2,48	-2,52	690	636	-3,48	-3,58	37	29	-7,00	-6,93	0,006	0,008
54	-2,48	-2,43	690	775	-3,48	-3,62	37	27	-7,00	-6,94	0,006	0,007
55	-2,48	-2,75	690	373	-2,48	-2,11	370	875	-7,00	-6,94	0,006	0,007
56	-2,48	-2,81	690	323	-2,48	-2,11	370	879	-7,00	-6,95	0,006	0,007
57	-2,48	-2,81	690	322	-2,48	-2,10	370	884	-7,00	-6,97	0,006	0,007
58	-7,00	-6,67	0,02	0,0	-7,00	-7,08	0,01	0,01	-6,48	-6,72	0,021	0,012
59	-7,00	-6,60	0,02	0,1	-7,00	-7,20	0,01	0,01	-6,48	-6,71	0,021	0,012
60	-7,00	-6,65	0,02	0,05	-7,00	-7,25	0,01	0,01	-6,48	-6,68	0,021	0,013
61	-7,00	-8,08	0,02	0,00	-7,00	-6,52	0,01	0,03	-5,48	-5,61	0,211	0,157
62	-7,00	-8,05	0,02	0,00	-7,00	-6,63	0,01	0,03	-5,48	-5,58	0,211	0,168
63	-7,00	-8,02	0,02	0,00	-7,00	-6,61	0,01	0,03	-5,48	-5,54	0,211	0,185
64	-7,00	-7,01	0,02	0,02	-7,00	-7,22	0,01	0,01	-4,48	-4,20	2,1	4
65	-7,00	-7,03	0,02	0,02	-7,00	-7,28	0,01	0,01	-4,48	-4,15	2,1	4
66	-7,00	-7,11	0,02	0,02	-7,00	-7,28	0,01	0,01	-4,48	-4,15	2,1	5
67	-5,48	-5,83	0,69	0,3	-7,00	-7,14	0,01	0,01	-6,48	-6,69	0,021	0,013
68	-5,48	-5,87	0,69	0,3	-7,00	-7,03	0,01	0,01	-6,48	-6,69	0,021	0,013
69	-5,48	-5,79	0,69	0,3	-7,00	-7,12	0,01	0,01	-6,48	-6,70	0,021	0,013
70	-4,48	-4,51	6,90	6	-7,00	-6,86	0,01	0,02	-6,48	-6,74	0,021	0,012
71	-4,48	-4,43	6,90	8	-7,00	-6,96	0,01	0,01	-6,48	-6,73	0,021	0,012
72	-4,48	-4,50	6,90	7	-7,00	-6,87	0,01	0,02	-6,48	-6,75	0,021	0,011
73	-3,48	-3,40	68,97	82	-7,00	-6,72	0,01	0,02	-6,48	-6,79	0,021	0,010
74	-3,48	-3,42	68,97	80	-7,00	-6,62	0,01	0,03	-6,48	-6,79	0,021	0,010
75	-3,48	-3,47	68,97	72	-7,00	-6,52	0,01	0,03	-6,48	-6,79	0,021	0,010
76	-4,48	-6,06	6,90	0,2	-7,00	-6,41	0,01	0,04	-5,48	-5,51	0,21	0,20
77	-4,48	-6,03	6,90	0,2	-7,00	-6,46	0,01	0,04	-5,48	-5,49	0,21	0,21
78	-4,48	-6,03	6,90	0,2	-7,00	-6,44	0,01	0,04	-5,48	-5,51	0,21	0,20
79	-3,48	-4,58	68,97	6	-7,00	-6,69	0,01	0,02	-5,48	-5,54	0,21	0,18
80	-3,48	-4,64	68,97	5	-7,00	-6,68	0,01	0,02	-5,48	-5,64	0,21	0,15
81	-3,48	-4,65	68,97	5	-7,00	-6,68	0,01	0,02	-5,48	-5,59	0,21	0,16
82	-3,48	-3,96	68,97	23	-7,00	-6,28	0,01	0,06	-4,48	-4,42	2,1	2,4
83	-3,48	-4,01	68,97	20	-7,00	-6,26	0,01	0,06	-4,48	-4,41	2,1	2,5
84	-3,48	-4,02	68,97	20	-7,00	-6,22	0,01	0,07	-4,48	-4,41	2,1	2,5
85	-7,00	-7,05	0,02	0,02	-3,48	-3,45	37	40	-4,48	-4,47	2,1	2,2
86	-7,00	-7,02	0,02	0,02	-3,48	-3,49	37	36	-4,48	-4,49	2,1	2,1
87	-7,00	-6,99	0,02	0,02	-3,48	-3,39	37	45	-4,48	-4,53	2,1	1,9
88	-7,00	-7,31	0,02	0,01	-2,48	-2,31	370	551	-4,48	-4,70	2,1	1,3
89	-7,00	-7,45	0,02	0,01	-2,48	-2,22	370	680	-4,48	-4,70	2,1	1,3
90	-7,00	-7,49	0,02	0,01	-2,48	-2,21	370	691	-4,48	-4,68	2,1	1,4
91	-7,00	-6,56	0,02	0,06	-3,48	-3,89	37	14	-3,48	-3,48	21	21
92	-7,00	-6,63	0,02	0,05	-3,48	-3,81	37	17	-3,48	-3,46	21	22
93	-7,00	-6,57	0,02	0,06	-3,48	-3,88	37	15	-3,48	-3,46	21	22

94	-7,00	-6,76	0,02	0,04	-2,48	-2,49	370	362	-3,48	-3,53	21	19
95	-7,00	-6,78	0,02	0,03	-2,48	-2,39	370	462	-3,48	-3,52	21	19
96	-7,00	-6,73	0,02	0,04	-2,48	-2,48	370	372	-3,48	-3,52	21	19
97	-4,48	-4,74	7	4	-4,48	-4,40	4	5	-4,48	-4,33	2,1	3,0
98	-4,48	-4,79	7	3	-4,48	-4,44	4	4	-4,48	-4,33	2,1	3,0
99	-4,48	-4,82	7	3	-4,48	-4,51	4	3	-4,48	-4,30	2,1	3,2
100	-4,48	-4,19	7	14	-4,48	-4,17	4	8	-3,48	-3,21	21	40
101	-4,48	-4,15	7	15	-4,48	-4,15	4	8	-3,48	-3,22	21	39
102	-4,48	-4,19	7	13	-4,48	-4,18	4	7	-3,48	-3,19	21	41
103	-3,48	-3,51	69	64	-4,48	-4,70	4	2	-4,48	-4,41	2,1	2,5
104	-3,48	-3,53	69	62	-4,48	-4,59	4	3	-4,48	-4,43	2,1	2,4
105	-3,48	-3,60	69	52	-4,48	-4,60	4	3	-4,48	-4,43	2,1	2,4
106	-3,48	-3,03	69	197	-4,48	-4,81	4	2	-3,48	-3,46	21	22
107	-3,48	-3,06	69	180	-4,48	-4,80	4	2	-3,48	-3,43	21	24
108	-3,48	-3,01	69	203	-4,48	-4,89	4	1	-3,48	-3,45	21	23
109	-3,48	-3,86	69	29	-3,48	-3,20	37	71	-4,48	-4,55	2,1	1,8
110	-3,48	-3,83	69	31	-3,48	-3,20	37	71	-4,48	-4,54	2,1	1,8
111	-3,48	-3,82	69	32	-3,48	-3,26	37	61	-4,48	-4,52	2,1	1,9
112	-3,48	-3,46	69	73	-3,48	-3,50	37	36	-3,48	-3,45	21	23
113	-3,48	-3,46	69	73	-3,48	-3,47	37	38	-3,48	-3,46	21	22
114	-3,48	-3,44	69	76	-3,48	-3,55	37	31	-3,48	-3,46	21	22
115	-3,48	-3,48	69	69	-2,48	-2,29	370	574	-4,48	-4,58	2,1	1,7
116	-3,48	-3,45	69	74	-2,48	-2,44	370	411	-4,48	-4,57	2,1	1,7
117	-3,48	-3,50	69	66	-2,48	-2,29	370	581	-4,48	-4,57	2,1	1,7
118	-2,48	-2,62	690	497	-3,48	-3,34	37	51	-4,48	-4,53	2,1	1,9
119	-2,48	-2,68	690	435	-3,48	-3,30	37	56	-4,48	-4,51	2,1	2,0
120	-2,48	-2,74	690	381	-3,48	-3,15	37	79	-4,48	-4,55	2,1	1,8
121	-2,48	-2,09	690	1711	-3,48	-3,83	37	17	-3,48	-3,51	21	20
122	-2,48	-2,10	690	1645	-3,48	-3,90	37	14	-3,48	-3,46	21	22
123	-2,48	-1,98	690	2194	-3,48	-3,96	37	12	-3,48	-3,46	21	22
124	-2,48	-3,60	690	52	-2,48	-2,31	370	551	-4,48	-4,59	2,1	1,6
125	-2,48	-3,53	690	62	-2,48	-2,45	370	395	-4,48	-4,64	2,1	1,5
126	-2,48	-3,56	690	58	-2,48	-2,29	370	581	-4,48	-4,63	2,1	1,5
127	-2,48	-2,80	690	335	-2,48	-2,77	370	191	-3,48	-3,65	21	14
128	-2,48	-2,60	690	529	-2,48	-2,70	370	223	-3,48	-3,70	21	13
129	-2,48	-2,50	690	665	-2,48	-2,81	370	175	-3,48	-3,69	21	13

Average values and standard deviation of concentration determination of Pb(II), Cd(II) and Cu(II) in mixed solution:

Real Pb	Found Pb	Deviation	%	Real Cd	Found Cd	Deviation	%	Real Cu	Found Cu	Deviation	%
0,02	1,08	0,75	56	0,01	0,38	0,26	55	0,006	0,008	0,001	13
0,69	0,52	0,12	18	4	12	6	39	0,02	0,02	0,01	34
7	25	13	41	37	34	2	5	0,21	0,17	0,07	29
69	60	6	8	370	433	45	8	2	2	0,06	2
209	165	62	28					21	23	1,35	5
690	668	16	2								

Appendix 5.

The values of potentials of 11 sensors of the system and the result of simultaneous determination of lead, copper and chromium in mixed solutions

	Pb	Cd	Cu	Cd2	Tl	Fe	Ag	Pb2	Fe	Cr	Hg	Pbconc	Cuconc	Crconc	Predicted Pb	predicted Cu	Predicted Cr
1	0	0	0	0	0	0	12	0	2	12	2	-7,00	-7,00	-6,48	-6,93	-7,01	-6,46
2	0	0	12	19	0	9	30	0	11	39	8	-7,00	-7,00	-5,48	-7,06	-6,93	-5,62
3	8	0	30	43	12	44	114	7	38	87	24	-7,00	-7,00	-4,48	-6,88	-6,90	-4,44
4	11	12	9	19	14	0	12	40	3	13	2	-5,48	-7,00	-6,48	-5,30	-7,19	-6,46
5	28	30	21	52	27	0	11	68	4	14	3	-4,48	-7,00	-6,48	-4,36	-7,02	-6,38
6	55	52	41	72	48	12	11	100	5	15	3	-3,48	-7,00	-6,48	-3,52	-6,87	-6,40
7	56	52	50	87	46	18	39	100	14	46	11	-3,48	-7,00	-5,48	-3,37	-7,06	-5,42
8	28	33	34	52	35	16	31	67	13	38	8	-4,48	-7,00	-5,48	-4,69	-6,99	-5,68
9	63	57	71	116	92	44	118	107	40	82	24	-3,48	-7,00	-4,48	-3,72	-5,97	-4,53
10	36	36	51	96	39	58	115	74	40	89	22	-4,48	-7,00	-4,48	-4,51	-7,03	-4,39
11	25	24	54	60	25	19	31	34	12	42	9	-7,00	-5,48	-5,48	-7,14	-5,66	-5,57
12	47	67	80	89	88	25	33	64	8	43	10	-7,00	-4,48	-5,48	-7,17	-4,41	-5,47
13	55	69	98	113	95	65	124	71	40	90	24	-7,00	-4,48	-4,48	-7,01	-4,45	-4,40
14	35	36	86	116	45	49	133	82	41	92	25	-5,48	-5,48	-4,48	-5,49	-5,43	-4,45
15	53	54	76	112	65	12	37	101	14	44	11	-4,48	-5,48	-5,48	-4,59	-5,37	-5,45
16	61	59	93	137	69	50	135	108	41	92	25	-4,48	-5,48	-4,48	-4,43	-5,45	-4,42
17	49	59	87	118	84	15	40	105	13	43	11	-5,48	-4,48	-5,48	-5,22	-4,55	-5,48
18	74	80	90	121	98	11	14	130	5	11	3	-4,48	-4,48	-6,48	-4,43	-4,44	-6,48
19	75	82	101	141	99	16	40	131	13	45	11	-4,48	-4,48	-5,48	-4,28	-4,52	-5,42
20	83	83	119	165	103	69	137	138	42	92	25	-4,48	-4,48	-4,48	-4,27	-4,65	-4,45
21	79	68	85	116	67	13	13	133	4	14	4	-3,48	-5,48	-6,48	-3,67	-5,37	-6,48
22	80	71	95	132	68	21	41	134	13	45	12	-3,48	-5,48	-5,48	-3,55	-5,50	-5,53
23	88	73	113	157	80	76	142	141	43	92	25	-3,48	-5,48	-4,48	-3,63	-5,44	-4,59
24	102	108	121	161	116	35	44	164	16	45	13	-3,48	-4,48	-5,48	-3,50	-4,50	-5,51
25	110	111	139	185	121	79	145	171	44	92	26	-3,48	-4,48	-4,48	-3,42	-4,51	-4,56

Appendix 6.

The results of simultaneous determination of Pb, Cu, and Cr(VI) in a reduced set of mixed solution. The reduced set of solutions was obtained by the optimisation using fractional design.

	Pb	Cd	Cu	Cd2	Tl	Fe	Ag	Pb2	Fe	Cr	Hg	Pbconc	Cuconc	Crconc	Predicted Pb	predicted Cu	Predicted Cr
1	11	12	9	19	14	0	12	40	3	13	2	-5,48	-7,00	-6,48	-5,47	-7,19	-6,51
2	35	36	86	116	45	49	133	82	41	92	25	-5,48	-5,48	-4,48	-5,50	-5,43	-4,49
3	49	59	87	118	84	15	40	105	13	43	11	-5,48	-4,48	-5,48	-5,38	-4,55	-5,52
4	36	36	51	96	39	58	115	74	40	89	22	-4,48	-7,00	-4,48	-4,50	-7,03	-4,43
5	53	54	76	112	65	12	37	101	14	45	11	-4,48	-5,48	-5,48	-4,56	-5,40	-5,47
6	74	80	90	121	98	11	14	130	5	11	3	-4,48	-4,48	-6,48	-4,56	-4,44	-6,42
7	56	52	50	87	46	18	39	100	14	46	11	-3,48	-7,00	-5,48	-3,45	-7,06	-5,51
8	79	68	85	116	67	13	13	133	4	14	4	-3,48	-5,48	-6,48	-3,46	-5,37	-6,49
9	110	111	139	185	121	79	145	171	44	92	26	-3,48	-4,48	-4,48	-3,46	-4,51	-4,51

Appendix 7.

A comparison of the results of simultaneous determination of lead, cadmium, copper and chromium by FIMS. The data from the same set was processed by different methods, here MLR, PLS and ANN (BPNN).

Potential values of 11 sensors of the systems

	Pb	Cd	Cu	Cd2	Tl	Fe	Ag	Pb2	Fe	Cr	Hg
1	101,5	120,2	61,3	117,4	118,2	5,7	16,6	108,3	6,0	13,2	2
2	149,9	159,6	89,5	155,2	169,0	18,9	35,6	149,8	8,0	13,6	2,1
3	129,3	142,6	66,5	140,5	136,9	15,3	22,4	136,2	12,3	12,5	3,1
4	168,9	174,0	94,3	168,2	167,7	30,2	40,3	173,6	10,3	12,4	2,5
5	144,1	163,7	69,9	159,1	148,0	23,7	27,6	147,7	11,0	12,6	1,5
6	183,0	198,9	98,1	192,8	191,1	37,7	45,6	188,4	13,5	13,5	1,9
7	166,3	189,0	73,4	184,3	171,1	29,2	32,2	170,0	13,5	12,4	2,6
8	169,5	186,8	74,4	182,3	170,2	28,9	32,0	172,3	16,5	12,8	2,6
9	208,3	213,3	103,6	208,4	203,4	42,5	48,8	213,9	16,5	12,2	1,6
10	183,6	215,9	77,7	212,3	192,1	35,9	37,2	189,8	17,0	13,5	2,1
11	231,2	248,8	107,3	245,3	224,4	49,9	54,3	232,3	18,2	14,1	2,6
12	101,3	120,6	68,9	147,1	117,8	11,9	35,3	108,3	18,5	39	8,5
13	150,1	159,5	97,1	185,1	169,2	25,4	54,3	149,5	18,0	38,5	9,4
14	128,6	142,6	74,1	170,9	137,1	22,4	41,1	136,4	19,3	39,4	9,2
15	169,7	173,9	101,8	198,4	167,6	37,8	59,3	173,0	19,5	40,1	8,7
16	143,7	163,0	77,5	188,7	148,6	30,3	46,2	148,0	20,0	40,6	8,5
17	183,1	198,1	105,6	223,4	191,5	44,5	64,4	187,7	21,6	41,5	8,6
18	166,0	189,0	81,0	214,8	171,4	35,2	51,3	169,6	20,6	42	8,8
19	169,9	186,7	81,9	212,4	170,1	35,7	51,4	172,6	24,3	41,6	9,3
20	208,2	212,9	111,2	239,2	203,5	49,9	68,2	214,6	24,9	40,7	9,5
21	183,8	215,7	85,3	241,4	191,5	42,8	56,5	189,3	27,3	42,3	8,2
22	231,3	248,4	114,9	274,9	224,1	56,7	74,0	232,1	29,6	44,9	8,4
23	113,8	120,2	80,3	179,5	123,3	42,2	115,7	113,4	40,1	87,6	24,3
24	162,5	159,8	108,5	218,1	174,8	55,4	134,1	154,5	41,2	87,9	21,3
25	140,7	142,6	85,4	203,8	142,3	52,6	121,8	141,5	43,6	88,6	25
26	181,4	173,3	113,2	230,7	172,6	66,6	139,4	178,5	44,5	90,5	26,5
27	156,1	163,1	88,9	221,8	153,8	59,5	126,3	153,1	45,6	89,2	28
28	195,5	198,5	117,0	255,6	196,3	74,1	144,2	192,9	47,2	87,5	26,3
29	179,1	188,6	92,4	247,3	176,3	65,0	130,8	174,5	48,2	89,6	24,3
30	182,0	186,2	93,3	244,6	174,5	65,5	131,0	177,1	49,3	90,6	25,9
31	220,8	213,8	122,6	271,1	208,7	79,1	148,5	219,4	49,1	90,1	28,6
32	195,7	216,2	96,6	274,6	197,3	72,6	136,1	194,3	51,1	92,1	24,3
33	243,8	248,3	126,2	307,3	229,4	86,1	153,7	237,5	51,5	93,5	28,3

Real values of Pb, Cd, Cu, Cr content and predicted values by different data processing methods (mg/l).

	Pb real	predicted Pb MLR	Predicted Pb PLS	Pb Output ANN	Cd real	predicted MLP Cd	Predicted Cd PLS	Cd Output ANN	Cu real	predicted MLP Cu	Predicted Cu PLS	Cu Output ANN	Cr real	predicted MLP Cr	Predicted Cr PLS	Cr Output ANN
1	6,9	6,0	6,5	7,3	3,7	3,0	3,7	3,8	2,11	2,2	2,0	2,1	0,02	0,02	0,02	0,02
2	6,9	7,3	7,5	7,0	3,7	4,4	3,6	3,8	21	20	22	21	0,02	0,02	0,02	0,02
3	69	109	75	83	3,7	4,2	4,0	7,4	2,11	1,9	2,2	2,1	0,02	0,02	0,02	0,02
4	69	49	57	80	3,7	6,8	3,7	5,2	21	20	18	21	0,02	0,02	0,02	0,02
5	69	50	65	75	37	38	38	31	2,11	2,3	2,0	2,1	0,02	0,02	0,02	0,02
6	69	115	65	79	37	25	33	32	21	21	19	21	0,02	0,02	0,02	0,02
7	69	214	70	99	370	118	301	290	2,11	2,0	2,1	2,1	0,02	0,02	0,02	0,02
8	690	415	580	544	37	57	41	56	2,11	2,1	2,3	2,1	0,02	0,02	0,02	0,02
9	690	902	680	721	37	14	34	33	21	24	26	21	0,02	0,02	0,01	0,02
10	690	284	590	570	370	1050	420	634	2,11	2,0	2,0	2,2	0,02	0,02	0,02	0,02
11	690	396	694	730	370	749	390	290	21	21	18	21	0,02	0,02	0,02	0,02
12	6,9	16,7	8,9	8,5	3,7	0,9	3,3	3,2	2,11	2,3	1,9	2,1	0,17	0,15	0,19	0,17
13	6,9	5,7	7,5	7,8	3,7	4,6	3,5	3,1	21	21	23	21	0,17	0,16	0,17	0,17
14	69	56	66	74	3,7	8,1	4,2	4,5	2,11	2,0	2,4	2,1	0,17	0,19	0,16	0,17
15	69	47	59	80	3,7	7,5	4,6	2,7	21	20	19	21	0,17	0,16	0,15	0,17
16	69	60	62	87	37	25	36	31	2,11	2,3	2,1	2,1	0,17	0,17	0,16	0,17
17	69	72	56	74	37	25	35	35	21	21	20	21	0,17	0,19	0,18	0,17
18	69	161	80	84	370	124	344	321	2,11	2,1	2,3	2,1	0,17	0,16	0,16	0,17
19	690	338	590	810	37	70	43	45	2,11	2,2	2,5	2,1	0,17	0,16	0,16	0,17
20	690	809	680	815	37	20	35	31	21	22	27	21	0,17	0,18	0,16	0,17
21	690	473	674	720	370	593	390	324	2,11	2,1	2,0	2,1	0,17	0,16	0,17	0,17
22	690	1546	901	950	370	204	347	331	21	21	18	21	0,17	0,20	0,19	0,17
23	6,9	5,6	6,5	7,9	3,7	2,9	3,2	2,9	2,11	2,3	2,0	2,2	1,72	1,61	1,81	1,71
24	6,9	3,7	7,0	6,1	3,7	6,1	3,8	3,8	21	22	23	21	1,72	1,69	1,79	1,72
25	69	53	64	60	3,7	8,9	4,4	4,8	2,11	1,9	2,3	2,1	1,72	1,99	1,70	1,71
26	69	71	65	59	3,7	5,0	4,2	4,6	21	19	18	21	1,72	1,68	1,73	1,72
27	69	71	69	59	37	28	32	41	2,11	2,2	2,0	2,1	1,72	1,80	1,71	1,72
28	69	76	61	59	37	32	34	43	21	21	19	21	1,72	1,63	1,65	1,72
29	69	287	70	72	370	79	290	278	2,11	2,0	2,1	2,1	1,72	1,68	1,61	1,71
30	690	398	480	441	37	60	45	50	2,11	2,1	2,4	2,1	1,72	1,73	1,55	1,71
31	690	733	747	640	37	20	34	43	21	24	26	21	1,72	1,53	1,51	1,70
32	690	443	621	577	370	752	410	324	2,11	2,1	2,0	2,3	1,72	1,72	1,72	1,70
33	690	607	692	679	370	344	358	341	21	211	19	20	1,72	1,96	1,69	1,65

Appendix 8.

Sensor potential values and the results of simultaneous determination of nitrate, sulphate and chloride in mixed solution by FIMS

Anion 1	Anion 2	Anion 3	Anion 3(a)	“NO3-(1)”	“NO3-(2)”	“NO3-(3)”	“Cl-“	real NO3	foundNO3	realso4	foundSO4	realCl	foundCl
8	6	5	6	0	0	0	0	0	0	9,6	4	0	0
22	22	17	19	14	6	7	2	0	0	96	53	0	0
36	36	29	32	24	9	10	5	0	0	960	1228	0	0
50	50	41	46	34	18	18	4	0	0	9600	13781	0	0
50	50	41	46	34	18	18	6	0	0	96000	13313	0	0
36	12	20	18	24	28	25	3	6,2	3	0	0	0	0
81	32	56	52	67	74	68	2	62	58	0	0	0	0
122	52	92	88	106	116	108	4	620	463	0	0	0	0
162	72	128	120	149	162	149	0	6200	5110	0	0	0	0
53	18	32	30	29	28	25	19	6,2	5	9,6	5	4	3
85	41	54	53	50	41	39	62	6,2	6	96	133	35	25
117	62	80	80	76	55	55	112	6,2	3	960	2846	350	424
113	69	78	79	70	52	50	64	6,2	4	9600	34062	35	34
116	45	78	73	82	81	76	68	62	116	9,6	4	35	31
148	68	104	101	109	99	95	115	62	73	96	56	350	248
144	75	102	99	102	91	86	69	62	84	960	1423	35	42
140	82	104	103	101	92	86	22	62	76	9600	10478	4	3
174	72	128	123	138	134	128	113	620	763	9,6	4	350	459
170	81	126	123	132	129	122	68	620	829	96	72	35	41
167	88	128	126	130	125	118	23	620	636	960	1118	4	5
199	109	150	149	151	141	133	71	620	657	9600	18125	35	57
193	94	152	145	164	168	155	25	6200	6767	96	24	4	2
225	115	174	167	184	178	166	73	6200	6200	960	858	35	38
257	136	200	195	211	198	186	118	6200	4802	9600	9168	350	279