

Neural network data analysis for intracavity laser spectroscopy

Petr V. Nazarov^a, Vladimir V. Apanasovich^a, Katsiaryna U. Lutkovskaya^a,
Vladimir M. Lutkovski^a, Pulat Y. Misakov^b

^aBelarusian State University*,

4 F. Skaryna Ave., Minsk 220050, Belarus

^bInstitute of Molecular and Atomic Physics NASB**,

70 F. Skaryna Ave., Minsk 220072, Belarus

ABSTRACT

The method of data analysis in intracavity laser spectroscopy is considered. The artificial neural network was used as an analyzing tool for the determination of elements concentration in trace amounts samples using absorption spectra. The special neural network training algorithm based on simulation of experimental spectra was developed to solve the problem of non-sufficient experimental data set. The application of this method allows achieve the better sensitivity than conventional analytical methods and proved itself more robust. The proposed method was tested on spectra of Cs water solutions.

Keywords: neural network, intracavity laser spectroscopy, atomic absorption, data processing.

1. INTRODUCTION

Laser techniques are widely used for determination of trace amounts of elements, especially toxic and biologically significant, in environmental samples and human tissues. The intracavity laser spectroscopy method used in this work is one of the most sensitive analytical techniques.

It was shown that advanced data processing based on digital filtering and regressive analysis improves the detection limits¹. The mean-square error for the trace concentrations of cesium in water solutions was decreased to the value less than 10%.

Unfortunately, practically available conventional analytical devices and linear data processing have reached their limits. The relationship between evaluated parameters and the experimental input parameters is nonlinear and very complex. It does not allow to eliminate all errors in experimental data. This is the reason to develop new approaches for data processing in the high-resolution spectroscopy.

Adaptive nonlinear algorithms based on artificial neural networks (ANNs) are regarded in this contest as a very attractive tool. ANN is a data processing system consisting of a large number of simple highly interconnected processing elements. It utilizes the weight matrices to perform the mathematical transformation of the input vector to the output vector. Special learning procedures are used to adjust the weight matrix for required relationship between input and output of ANN. It is quite different from the traditional computing system. ANNs have some remarkable properties such as flexibility, capability of learning and generalization. Special software tools for emulation of ANNs in conventional computers are available nowadays and this approach is becoming more and more popular².

The brief review of ANN implementation in data processing algorithms is presented in the next section. The intracavity laser spectrometer used as the experimental setup is described in the third section.

Experimental data and preprocessing technique are reviewed in the section four.

* Tel/fax: +375 17 2789345. E-mail: lutkovski@bsu.by

** Tel.: +375 17 2841618. E-mail: misakov@imaph.bas-net.by

The neural network procedure for data processing is presented in the fifth section. Finally the received measurement errors are estimated and conclusions are made in the last sections of the work.

2. NEURAL NETWORKS AS A DATA PROCESSING TOOL

A solution of inverse problems is one of the most important attributes of spectroscopy. It was shown that ANNs allow solving both direct and inverse problems using standard experimental data involved in the calibration procedure. The unique opportunities of ANN were used for solving the following inverse problems³:

- precise determination of water temperature from Raman spectra,
- determination of small fluorescent contributions for components of an organic compounds mixture in water from their fluorescence spectra,
- determination of molecular parameters of organic compounds from fluorescence spectra,
- time-resolved kinetic spectroscopy performed with long excitation pulse and a detector with low temporal resolution.

There are examples of applications of ANN for signal processing of transient atomic absorption signal⁴, classification and recognition of spectra⁵⁻⁹, evaluation of extremely low concentrations of analyzed substances in soil⁷ and water samples¹⁰⁻¹³.

Neural networks based on radial basis functions (RBF) were applied to the classification of visible and ultraviolet spectra and they were implemented in the auto-diagnosis process of a flow injection analytical system. The classification error was 13%, which was a significant reduction compared with the 20% when using counterpropagation neural networks (CPNN) as the classification technique. The importance of this reduction lies in the fact that the number of analytical errors which have a considerable effect on the system is reduced to half. The spectra did not have to be preprocessed to distinguish between the five classes and this means less extra work and a reduction in computation time. The training procedure is also simpler in the case of using RBF because there are fewer parameters to optimize. With CPNN the number of epochs, the number of neurons, the type of transfer function and the initialization of the weights have to be optimized but when using RBF only two parameters have to be optimized: the width of the radial functions and the number of neurons in the hidden layer⁶. Thus neural networks based on RBF proved to be a useful tool in the classification of ultraviolet and visible spectra.

The same methodology with the backpropagation ANN was used for encoding and pattern recognition of infrared spectra⁷.

ANN were also used for determination of ruthenium in flow-injection analysis systems¹⁴ and as catalyst for simultaneous determination V(IV) and Fe(II) through the single catalytic kinetic run¹⁵ due to high speed data processing. Counterpropagation, backpropagation^{7,10} or RBF¹¹⁻¹³ neural networks may be used for achieving better accuracy depending on problem. Thus flexibility and universality of ANNs are the important advantages of the discussed approach.

3. EXPERIMENTAL SETUP

The intracavity laser spectrometer was used in the experiment. It consists of the four basic modules: dye laser, electrothermal atomizer with graphite furnace for liquid samples, high-resolution spectrograph and data processing system as it is shown schematically in the Fig.1.

The tunable dye laser is used as the primary light source. Being flash-lamp pumped it radiates a smooth broad-band spectrum in the range 440-700 nm. The spectrum width depends on a dye type and usually is 10-15 nm. A Fabri-Perot interferometer in laser cavity was used in some cases for dye laser spectrum stabilization near an absorption line. With an interferometer the maximal width of a laser spectrum decreases to 1.0-1.5 nm. Laser pulse duration can easily be changed between 1 and 10 μ s by variation of power supply parameters. For the measurement of dye laser pulse duration a silicon photodiode is used.

A graphite furnace, electrothermal atomizer was used in the intracavity laser spectrometer for atomization of cesium samples. The atomizer was located in the laser cavity between dye cell and output mirror. It has special wedge windows for preventing interferometric structure in dye laser spectrum. Spherical cavity mirrors were used for the same purpose as well as for collimating of dye laser radiation inside a cavity through a graphite furnace. Moreover wedge cavity mirrors were employed, but in this case it is desirable to adjust the inner diameters of the furnace and the dye cell. The graphite tube was 28 mm long with a 6 mm inner diameter and 8 mm outer diameter. The atomizer has 20 - 3070 C heating temperature interval and 64 heating steps with the step duration 1 - 799 s.

Stock and standard solutions were prepared by using de-ionized triply distilled water in accordance with a conventional sample preparation procedure¹⁶.

Atomic absorption signals were measured at the cesium wavelength of $\lambda = 455.531$ nm. The use of a 5 μ s dye laser makes it possible to provide an effective length of absorbing layer of about 100 m for geometrical length of a graphite furnace of 28 mm.

Dye laser spectra with absorption lines were recorded with the help of a 0.001 nm resolution echelle spectrograph with an optical multichannel analyzer. The charge coupled device (CCD) array was used for detection of optical radiation. The grating (300 lines/mm) operating in high orders of the spectrum (6 -25) with double dispersion was used as a dispersion element. The focal length of the objective was 1377 mm, the relative aperture was 1:21. Processing of obtained data as well as controlling of spectrometer modules was performed by the personal computer (PC).

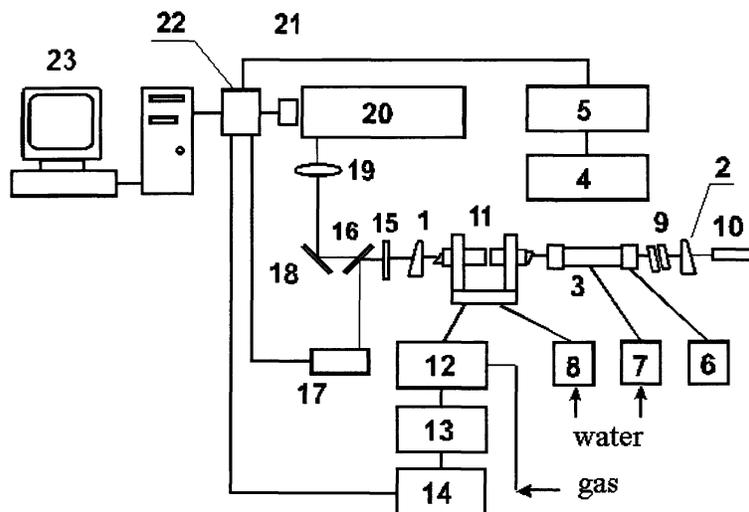


Figure 1: Intracavity laser spectrometer: 1 – output cavity mirror, 2 – back cavity mirror, 3 – dye laser, 4 – laser power supply, 5 – laser control unit, 6 – dye pump, 7 – laser water pump, 8 – atomizer water pump, 9 – Fabry-Perot interferometer, 10 – He-Ne laser, 11 – atomizer, 12 – atomizer gas supply, 13 – atomizer power supply, 14 – atomizer control unit, 15 – attenuator, 16 – beam splitter, 17 – photodiode, 18 – mirror, 19 – cylindrical lens, 20 – high-resolution spectrograph, 21 – CCD-camera, 22 – optical multichannel analyzer, 23 – PC.

4. EXPERIMENTAL DATA AND ITS PREPARATION

4.1. Absorption spectra

The developed method of spectra analysis was tested on absorption spectra of cesium in water solutions. The Cs I resonant line at $\lambda = 455.531$ nm corresponding to the transition $6s\ ^2S_{1/2} - 7p\ ^2P_{3/2}^0$ was used as analytical one. The typical raw absorption spectrum of the Cs 455.531 nm line is presented in the Fig. 2.

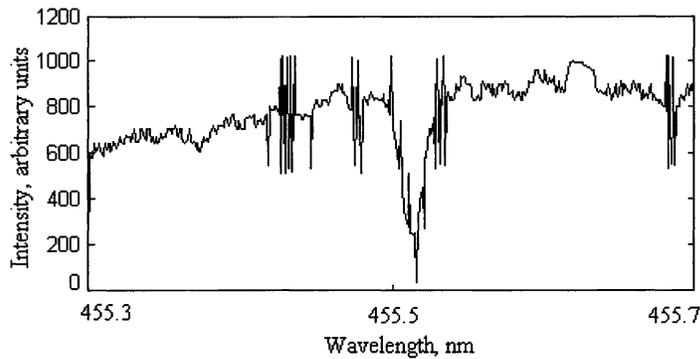


Figure 2: Raw absorption spectrum of Cs.

The most commonly used function of element concentration definition in the intracavity laser spectroscopy is relative depth of dip $\Delta I/I_0$ (Fig. 3). In some works equivalent breadth of absorption $\Delta S/I_0$ was considered as a spectra parameter. Physical meaning of that parameter could be seen from the Fig. 3. These parameters are used in classical approaches to analyze absorption spectra. Such approaches were realized and the rate mean square errors (RMSE) of those methods come to approximately 10%.

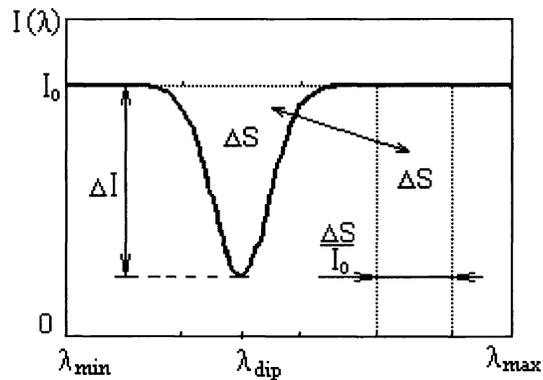


Figure 3: Parameters of absorption spectra.

The main factors which make processing of spectrums difficult are:

1. Non-stable time and spectral shape of lasing pulse. This results in the change of the base line and its non-linearity.
2. The presence of interference components in a spectrum. A base line has irreproducible structure, which is similar to a low-frequency noise. This interference special structure appears in the cavity of the laser and exerts multiplicative influence upon an absorption dip.
3. A multiplicative high-frequency noise of a CCD detector.
4. A noise appearing in detection system during a laser pulse. High power electrical discharge in flash lamps supply initiated errors in analog-digital converter.

4.2. Preprocessing of experimental spectra

The application of preprocessing procedures, aimed to diminish the influence of disturbing factors, is the first step in any any processing procedure of real-world signals.

Before analysis a spectrum should be cleared from glitches (sharp over fall noise) because it does not carry any information. To achieve this purpose a spectrum was looked for consecutive samples with highly different values (like δ -peaks). If such a sample was found, its value was changed to the mean of the nearest samples.

The filtration of spectrums was realized in the following way. The Fourier transform of a spectrum was calculated. Its real and imaginary parts were multiplied by a window of the special shape (several functions were tried, and the best results were obtained with the help of Gaussian window). After that the inverse Fourier transform was applied. A result of such filtration is shown in the Fig. 4

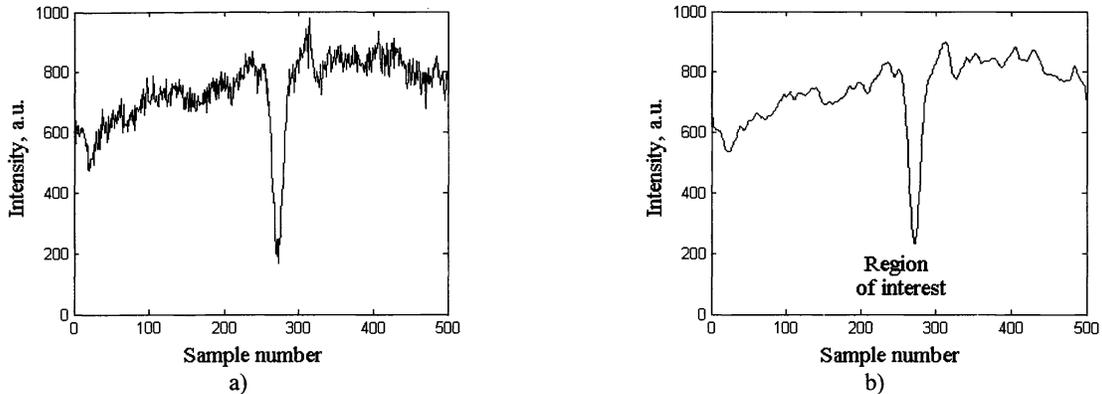


Figure 4: High frequency noise cancellation by Fourier filtration: a – initial spectrum, b – filtered spectrum

5. NEURAL NETWORK PROCESSING OF ABSORPTION SPECTRA

5.1. Application of ANN

The main idea in application of ANN for analysis of absorption spectra is the following. The central and most informative part of the preprocessed (see Fig. 4b) and normalized spectrum was used as inputs of neural network. The information is processed and the normalized assumed concentration of element was obtained from an output.

The 3-layer feed-forward neural network (so called multilayer perceptron) was used for analysis of absorption spectra (Fig. 5). ANN was trained by gradient descent with momentum and adaptive learning rate backpropagation error method.

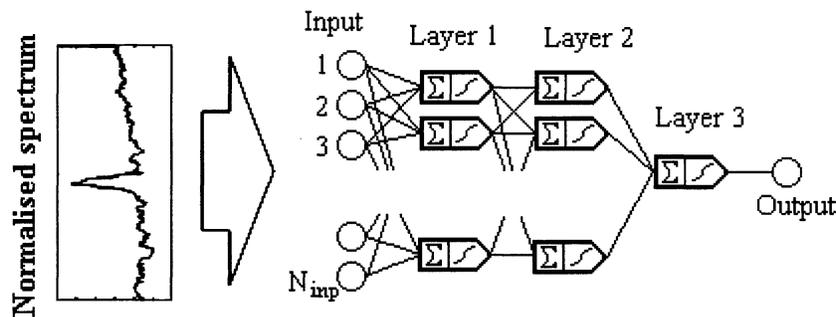


Figure 5: Three-layered feed-forward neural network.

There are several problems of such application of ANN. These problems and proposed solutions are listed below in sections 5.2 and 5.3.

5.2. Selection of optimal neuron number in hidden layers

The problem of optimal neuron number selection is still unsolved in the theory of multilayer networks. That is why we use the following empirical scheme to obtain an estimation of optimal number of neurons. Let us denote the target function F as a mean error of operation of ANN on a test set. This F can be considered as a function of neuron number in hidden layers. Now the problem of finding optimal neuron number turns to the problem of two-parametrical minimization of function F . In the current work this minimization was carried out by two standard procedures: scanning

of parameter space to obtaining initial estimation and then sharpening of solution by the method of local variations. It should be mentioned that each value of F was calculated as a mean of 10 (for estimation) or 20 (for accurate solution) experiment.

The search of the optimal structure of a neural network was carried out. The network with 17 neurons in layer 1 and 4 neurons in layer 2 showed the best results.

5.3. Avoiding of the lack of experimental training pairs

ANN usually needs quite large representative training set to work in a proper way. Unfortunately it is very difficult to obtain enough training pairs from an experiment because of high time costs and and material charges. To avoid this computer simulation of additional training pairs was used as follows. The spectra from primary training set are analyzed and approximated by deterministic and stochastic functions as it is shown in the Fig. 6.

Artificial spectra were created to form a new training set for ANN. This simulated training set was used for initial training of a neural network. It is obvious that the performance of ANN trained in such a way is quite rough. To make it more exact ANN is trained once more on experimental training set. This algorithm is shown in fig 7. The robustness of the algorithm to the overtraining problem was solved by checking the ANN efficiency on the control training set, as it was proposed in ³.

The proposed method of neural network spectra analysis was tested on spectra of Cs 25 μ g/l water solutions. As a result of application of neural network RMSE of concentration definition was reduced from 9.1% (regression approach) to 8.4 %. Moreover, the time of neural processing is much smaller, then by using of conventional methods of analysis. However, it should be mentioned, that the neural network should be retrained if a new element is to be analyzed, or if a new dye is used.

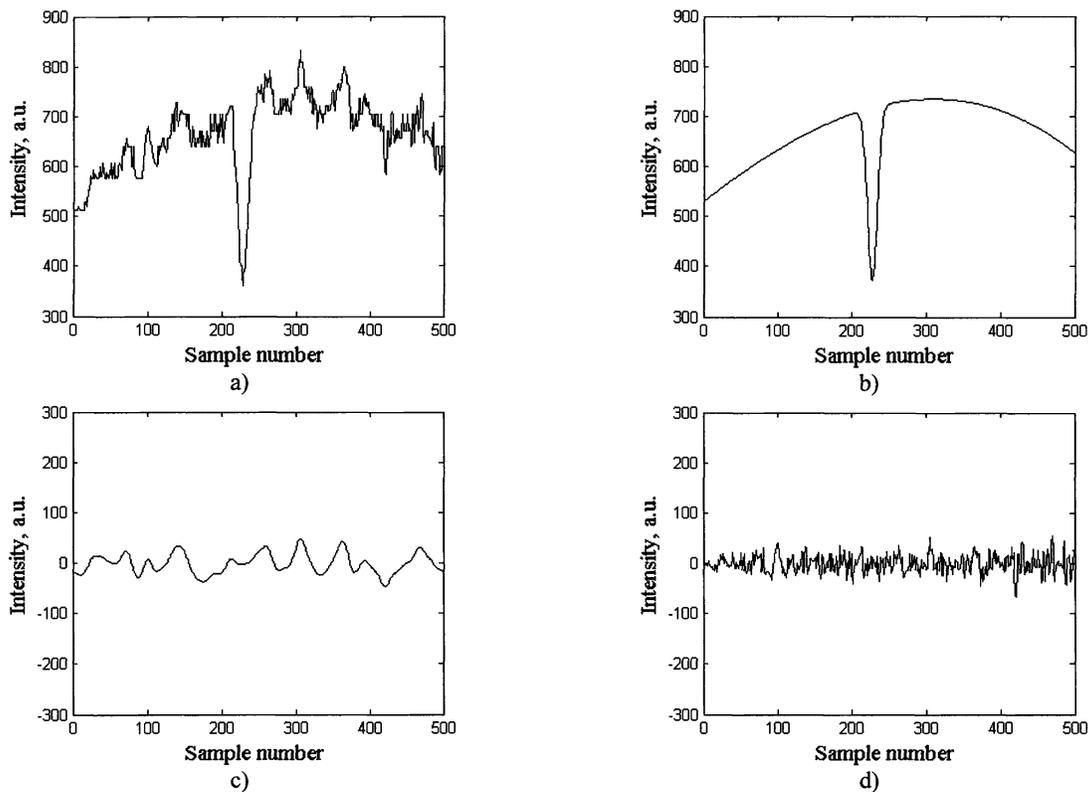


Figure 6: Separation of initial spectra to compounds for simulation a – initial spectrum, b, c, d – its components.

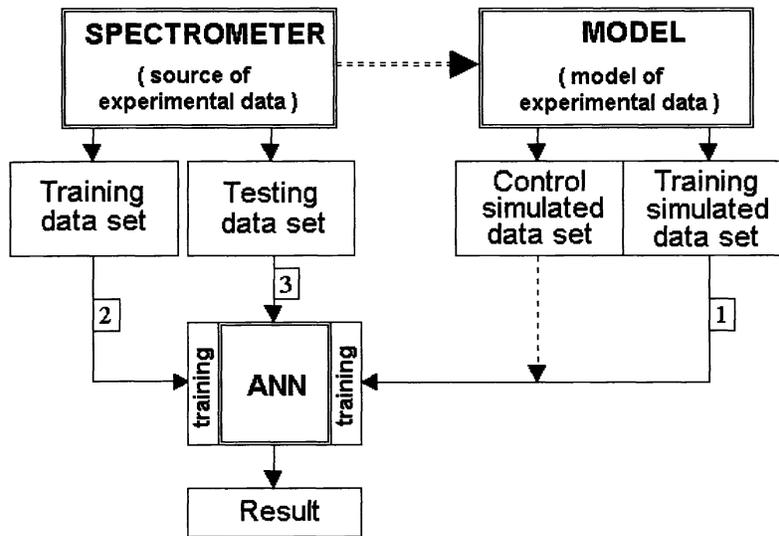


Figure 7: The algorithm of ANN training in the case of lack of experimental data.

6. ESTIMATION OF THE MEASUREMENT ERRORS

To accomplish the statistical analysis first of all it is necessary to find out a sort of distribution of measurement errors. After that, statistical characteristics of results are determined.

The distribution of recognized concentration (Fig. 8) was built using histograms and polygons of distributions for definition the sort of errors.

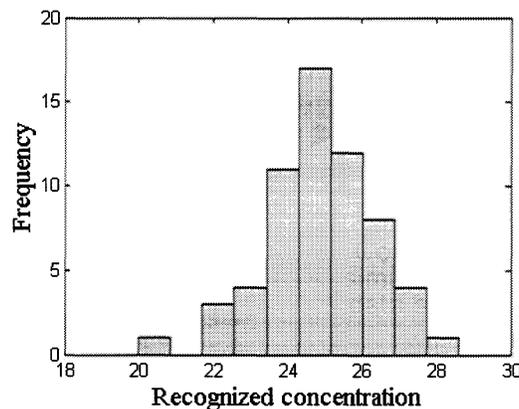


Figure 8: The histogram of recognized concentrations of Cs.

The data from 61 spectra were obtained on Cs solutions with the constant concentration of 25 $\mu\text{g/l}$. Beforehand two suppositions were made. The first is that function of errors distribution is smooth and that measured value itself is continuous. Moreover the claim of symmetry of the errors distribution could be made. This is concerned with the relative smallness of errors. Even if the transfer function of our measuring equipment is essentially non-linear, the changing of its steepness on the small length, corresponding to the errors value, cannot lead to noticeable skewness of the distribution.

The following estimations of the measurement errors had been received.

Table 1. Statistical parameters of measurements distributions for ANN method.

| Parameters | | Concentration |
|----------------------|--|-----------------|
| Distribution center | $X_C \pm \Delta_{0.9} (X_C)$ | 24.9 ± 0.53 |
| Standard deviation | $\sigma \pm \Delta_{0.9} (\sigma)$ | 2.05 ± 0.27 |
| Kurtosis | $\varepsilon \pm \Delta_{0.9} (\varepsilon)$ | 2.76 ± 0.75 |
| Antikurtosis | $\kappa \pm \Delta_{0.9} (\kappa)$ | 0.60 ± 0.09 |
| Entropic coefficient | $k \pm \Delta_{0.9} (k)$ | 2.02 ± 0.10 |

On the assumption of available estimations of k and κ , with the help of topographic classification of mathematical models of distribution, it is possible to assert that our distribution belongs either to exponential distributions or to triangle ones.

7. DISCUSSION

From the review presented in the second part of this work it may be concluded that for last few years artificial neural networks were applied as analytical tool in chemistry and close areas. The motivation for it was the intention to achieve better features of the available analytical system. There are examples of successful application of this flexible and powerful tool in atomic and molecular spectroscopy^{3,7} as well as in electron microscopy¹⁷ and mass-spectrometry¹⁸.

This study as far as we know is the first attempt to use ANN for analysis of absorption spectra obtained from a high resolution spectrometer. As a rule a very limited volume of experimental data is the main restriction for ANNs implementation in high resolution spectroscopy.

Due to a novel approach the feed-forward ANN was successfully applied for absorption spectra processing and concentration extraction. The multilayer perceptron with 17 neurons in the first layer and 4 neurons in the second layer proved to be a quite suitable tool for this application. The simulated spectra were used for initial training of the ANN. Finally the neural network was trained with real experimental data. In the frame of the discussed approach the main problem in practical ANN application was avoided.

The approach discussed above is not limited by the area of high resolution spectroscopy and may be applied for different architectures of ANNs. We suppose that neural networks based on radial basis functions¹³ may be widely used for the solving of similar problems along with multilayer perceptrons.

8. CONCLUSIONS

The problems of data processing in high resolution laser spectroscopy were discussed. The structure of intracavity laser spectrometer was described. The absorption line of explored atoms was selected by tuning of the flash lamp pumped dye laser.

The application of ANN results in decreasing of measurements error. The obtained relative standard deviation for definition of small concentrations of cesium in water solutions is decreased with respect to standard processing methods and equals to 8.4 %. The processing using ANN is robust and more accurate then the conventional methods. Furthermore it is less time consuming in comparison with regressive analysis and other conventional procedures.

ACKNOWLEDGEMENTS

The experiments in the frame of this work were performed in the Laboratory of Laser Diagnostics of Plasma, Institute of Molecular and Atomic Physics, National Academy of Sciences, Belarus. The financial support of the Belarusian State University project 540/18 is also gratefully acknowledged.

REFERENCES

1. V.S. Burakov, V.V. Apanasovich, A.V. Isaevich, V.M. Lutkovski, P.Y. Misakov, P.V. Nazarov, "Data processing and estimation of measurements errors in intracavity laser spectroscopy", *Abstracts of 17 th International Conference on Coherent and Nonlinear Optics (ICONO'2001)*, FS29, 2001.
2. C.M. Bishop, *Neural Networks for Pattern Recognition*, 482, Oxford University Press, 1995.
3. I.V.Gedova (Boychuk), I.V.Churina, S.A.Dolenko, T.A.Dolenko, V.V. Fadeev, I.G.Persiantsev, "New opportunities in solution of inverse problems in laser spectroscopy due to application of artificial neural networks", *Abstracts of 17 th International Conference on Coherent and Nonlinear Optics (ICONO 2001)*, SK6, 2001.
4. U. Kale, E. Voigtman, "Signal processing of transient atomic absorption signal", *Spectrochimica Acta Part B*, **50**, 1531-1541, 1995.
5. Z. Ramadan, Xin-Hua Song, P. K. Hopke, M. J. Johnson, K. M. Scow, "Variable selection in classification of environmental soil samples for partial least square and neural network models", *Analytica Chimica Acta*, **446**, 233-244, 2001.
6. A.Pulido, I. Ruisanchez, F.X. Rius, "Radial basis functions applied to the classification of UV-visible spectra" *Analytica Chimica Acta*, **388**, 273-281, 1999.
7. H. Schulz, M. Derric, D. Stulik, "Simple encoding of infrared spectra for pattern recognition. Part 2. Neural network approach using back-propagation and associative Hopfield memory", *Analytica Chimica Acta* , **316** , 145-159, 1995.
8. B.Walczak Neural networks with robust backpropagation learning algorithm, *Analytica Chimica Acta*. 1996, **322**, pp. 21-29.
9. A.Eghbaldar, T.P. Forrest, D. C. Bass, "Development of neural networks for identification of structural features from mass spectral data", *Analytica Chimica Acta*, **359**, 283-301, 1998.
10. B.Walczak, D.L. Massart, "The radial basis functions – partial least squares approach as a flexible non-linear regression technique", *Analytica Chimica Acta*, **331**, 177-185, 1996.
11. B.Walczak, D.L. Massart, "Application of radial basis functions – partial least squares to non-linear pattern recognition problems: diagnostics of process faults", *Analytica Chimica Acta*, **331**, 187-193, 1996.
12. I.Ruisanchez, J. Lozano, M.S. Larrechi, F.X. Ruis, J. Zupan, "On-line automated analytical signal diagnosis in sequential injection analysis system using artificial neural networks", *Analytica Chimica Acta*, **348**, 113-127, 1997.
13. V.V. Apanasovich, A.Y. Balakhontsev, V.M. Lutkovski, P.Ya. Misakov, P.V. Nazarov, "Application of Neural Networks in Analysis of Atomic Emission Spectra", *Proceedings of the Second International Conference on Neural Networks and Artificial Intelligence ICNNAI-2001*, Minsk, 177-180, 2001.
14. H. Wang, Y. Zhou, Y. Zao, Q.Li, X.Chen, Z.Hu, "Optimization of on-line microwave flow-injection analysis system by neural network for the determination of ruthenium", *Analytica Chimica Acta* , **429** , 207-213, 2001.
15. A.Safavi, G.Absalan, S.Maesum. "Simultaneous determination V(IV) and Fe(II) as catalyst using neural networks through the single catalytic kinetic run", *Analytica Chimica Acta* , **432**, 229-233, 2001.
16. *Philips Scientific Atomic Absorption Data Book*, Fifth Edition, Black Bear Press Limited, Cambridge, 1988.
17. Dietrich Wienke, Ying Xie, Philip K. Hopke, "Classification of airborne particles by analytical scanning electron microscopy imaging and a modified Kohonen neural network", *Analytica Chimica Acta* , **310**,1-14, 1995.
18. A.Eghbaldar, T.P. Forrest, D. Cabrol-Bass "Development of neural networks for identification of structural features from mass spectral data", *Analytica Chimica Acta*, **359**, 283-301, 1998.