

Data processing and estimation of measurements errors in intracavity laser spectroscopy

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ABSTRACT

Methods of absorption spectra processing in intracavity laser spectroscopy (ICLS) are investigated for the case of very low quantities of cesium in water solutions. Common procedures in such cases require fitting or filtering of the laser generation broadband spectrum, search for the investigated atomic or molecular absorption lines, calculating the examined substance concentration in quantitative analysis or its state determination in quality analysis. In this study various methods of absorption spectra processing in the case of atomic cesium line $\lambda = 455.531$ nm in the intracavity laser spectrometer are examined. Methods based on digital filtering and approximation were tested. The artificial neural network algorithm was tried as a tool to reduce the apparatus error. For the trace concentration definition the mean-square error was decreased to a value less than 9%.

Key words: intracavity laser spectroscopy, atomic absorption, data processing.

1. INTRODUCTION

The developing of laser techniques for determining trace amounts of elements, especially toxic and biologically significant, in environmental samples and human tissues is very important today, because conventional analytical methods have almost reached their practical limits. In this work the most sensitive absorption spectrometric technique – intracavity laser spectroscopy (ICLS) method [1-3] is developed and experimental equipment is described for detection limit lowering of cesium in water solutions.

2. EXPERIMENTAL SECTION

Measurements were carried out using the intracavity laser spectrometer, that is shown schematically in the fig.1 and consists of the four basic modules: dye laser, electrothermal atomizer with graphite furnace for liquid samples, high-resolution spectrograph and data processing system.

A tunable flash lamp pumped dye laser as the primary light source radiates a smooth broad-band spectrum in the range 440 – 700 nm. The maximal 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 laser spectrum decreases to 1.0 – 1.5 nm. A laser pulse duration can easily be changed between 1 and 10 μ s by variation of power supply parameters. For measurement of dye laser pulse duration a photodiode is used.

An electrothermal atomizer with graphite furnace 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 a special wedge windows for preventing interferometric structure in dye laser spectrum. A 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. Also a 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 step duration 1 – 799 s.

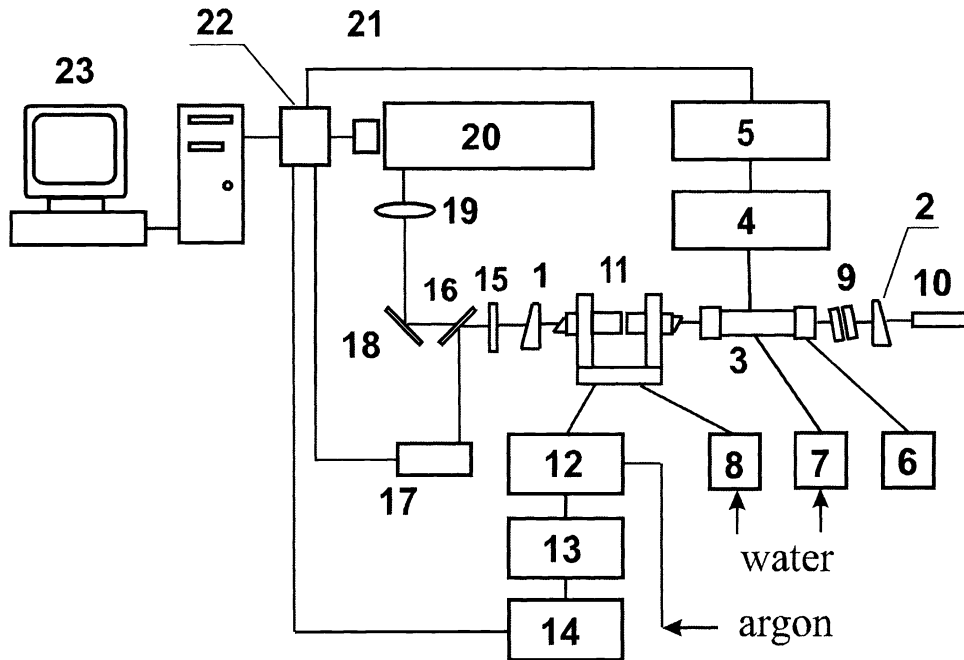


Fig. 1. Schematic representation of the intracavity laser spectrometer: 1 - output cavity mirror, 2 - back cavity mirror, 3 - dye laser, 4 - laser power supply, 5 - laser control unit, 6 - dye pump, 7 - laser water pump, 8 - atomizer water pump, 9 - Fabry-Perot interferometer, 10 - He-Ne laser, 11 - electrothermal 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-array, 22 - optical multichannel analyser, 23 - computer.

A stock and standard solutions were prepared by using de-ionized triply distilled water in accordance with conventional sample preparation procedure [4].

Atomic absorption signals were measured at the cesium wavelength of $\lambda = 455.531$ nm. The use of a $5 \mu\text{s}$ 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 analyser on a base of a CCD-array. As a dispersion element a grating (300 lines/mm) operating in high orders of the spectrum (6 -15) with double dispersion is used. The focal length of the objective is 1377 mm, the relative aperture is 1:21. Processing of obtained data as well as controlling of spectrometer modules were performed by a personal computer.

3. PROCESSING OF ABSORPTION SPECTRA

3.1. General conditions

The selection of optimal processing methods for absorption spectra in ICL-spectrometer was carried out for the analysis of cesium in water solutions. The Cs I resonant line at $\lambda = 455.531$ nm corresponding to transition $6s^2S_{1/2} - 7p^2P_{3/2}^0$ was used as analytical.

The typical absorption spectrum of the Cs 455.531 nm line is presented in the fig. 2.

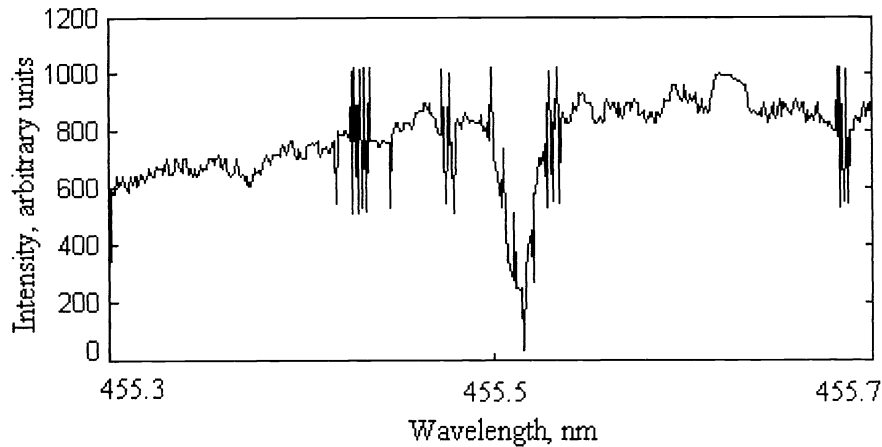


Fig.2. Typical unprocessed absorption spectrum.

Spectra parameters. The most common measure function of element concentration definition in intracavity laser spectroscopy is relative depth of dip $\Delta I/I_0$ (fig.3). Besides, 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.

The main factors which make difficult a processing of spectrums are:

1. Non-stable time and spectral shape of laser pulse. This results in a changing of the base line and its non-linearity.
2. The presence of interference components in a spectrum. The base line has irreproducible structure, which is similar to low-frequency noise. This interference spectrum occur in a cavity of laser and exert multiplicative influence upon an absorption dip.
3. Noises of the CCD detector result in appearance of a multiplicative high-frequency noise.
4. Noise pickup, which appear in detection system during a laser pulse. This errors are concerned with fails in analog-digital converter, given by high power electrical discharge.

Preprocessing. Several methods of analysis of absorption spectra are described below. But first of all, methods of spectra preprocessing should be discussed. Those methods are: cancellation of noise pickup and digital filtration of spectra.

Before the analyses a spectrum should be cleared from noise. To achieve this purpose a spectrum was looked for sharp overfall in samples values (that mean for δ -peaks). If such sample was found, its value was changed to the mean of nearest samples.

The filtration of spectrums was realized in the following way. A 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 received with the help of Gaussian window). After that the inverse Fourier transform was applied.

3.2. Method 1 – without deep processing

Approximation of the laser pulse. To find out the value of I_0 in the area of a dip a spectrum was approximated by polynomial function of 3 degree. This approximation also gave a base line. The approximation was carried out by the Hooke-Jeeves method.

Parameters calculation. The global minimum was searched in the specified range. An interval between this minimum and the base line was equal to ΔI , and an area between a base line and spectrum was equal to ΔS .

The method was applied for analysis of Cs spectra. Values of parameters and relative mean-root-square error (RMSE) of concentration definition for calibrating solutions are presented below.

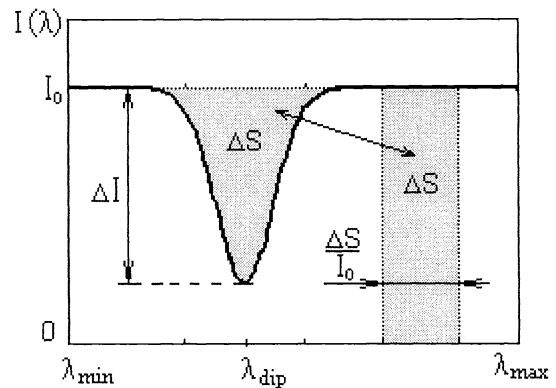


Fig.3.Parameters of absorption spectra.

Table 1. Values and RMSE of concentration definition for calibrating solutions received by method 1.

Parameters	Values of parameters and RMSE			
	5 µg/l	10 µg/l	25 µg/l	50 µg/l
$\Delta I/I_0$	0.33 ($\pm 37\%$)	0.44 ($\pm 21\%$)	0.55 ($\pm 15\%$)	0.81 ($\pm 6\%$)
$\Delta S/I_0$	4.9 ($\pm 40\%$)	10.1 ($\pm 30\%$)	14.3 ($\pm 17\%$)	29.5 ($\pm 10\%$)

3.3. Method 2 – approximation of spectra

The approximation of the laser pulse. To find out the value of I_0 in the area of dip a spectrum was approximated by polynomial function of 3 degree. This approximation also gave a base line. The approximation was carried out by the Hooke-Jeeves method.

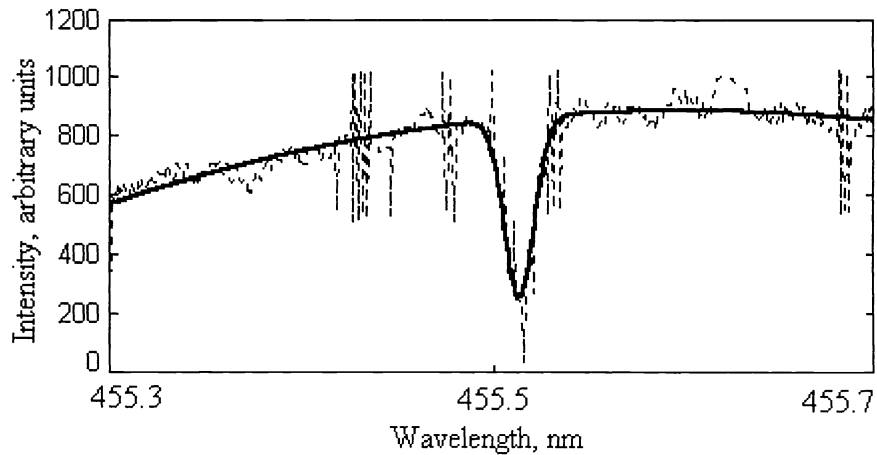


Fig.5. Approximated spectrum

The approximation of an absorption dip. Approximate location of a dip was found out using correlation functions between certain etalon (Gaussian was used) function and data, received by subtraction of spectrum from its base line. The offset of the maximum of correlation function from zero indicated the approximate location of the dip. If the estimation of the dip location and the rough value of the dip width are known, it is possible to approximate the spectrum with the following function

$$f(\lambda) = \sum_{i=0}^3 a_i \lambda^i - \Delta I \cdot \exp \left[- \left(\frac{\lambda - \lambda_{np}}{\Delta \lambda} \right)^2 \right], \quad (1)$$

where a_i – polynomial coefficients, ΔI – the dip size, λ_d – location of the dip, $\Delta \lambda$ – coefficient of the width of the absorption line. During approximation the following parameters are changed: a_i , ΔI , λ_d , $\Delta \lambda$. The acuteness of the problem of multi-parameter optimization is removed by knowledge of those parameters estimations. It should be mentioned, that absorption dip is supposed to have one local minimum. This condition is implemented for most of elements. An example of an approximated spectrum is shown in the fig.5.

The described method was applied for analysis of Cs spectra. Values of parameters and relative mean-root-square error (RMSE) of concentration definition for calibrating solutions are presented below (fig.6). The RMSE of concentration definition for 25µg/l Cs solution on 61 measurements was equal to 10%.

Table 2. Values and RMSE of concentration definition for calibrating solutions.

Parameters	Values of parameters and RMSE			
	5 µg/l	10 µg/l	25 µg/l	50 µg/l
$\Delta I/I_0$	0.38 ($\pm 37\%$)	0.48 ($\pm 18\%$)	0.68 ($\pm 9\%$)	0.83 ($\pm 6\%$)
$\Delta S/I_0$	7.4 ($\pm 39\%$)	11.6 ($\pm 20\%$)	19.6 ($\pm 11\%$)	33.1 ($\pm 8\%$)

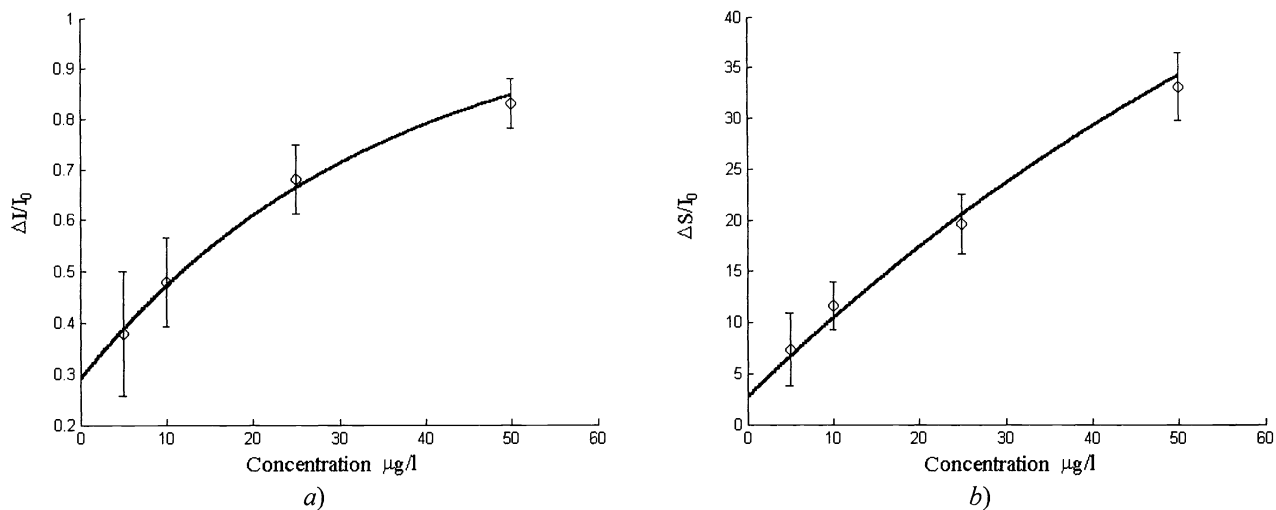


Fig.6. Calibration diagram for $\Delta I/I_0$ (a) and $\Delta S/I_0$ (b).

The method is quite stable to dip drifts and noises, but it requires quite high computer power. For example the time of processing of one spectrum by PC with PII566 CPU is about 5 seconds.

3.4. Method 3 – application of a neural network for analysis of spectra

The 3-layer feed-forward neural network was used for analysis of absorption spectra (fig 7). This architecture is known as the multilayer perceptron. A section of filtered and normalized spectrum with a dip was input neural network data, and normalized value of concentration was output data.

Neural network was trained by gradient descent with momentum and adaptive learning rate backpropagation error method in two stages. In the beginning neural network was trained on a set of simulated absorption spectra (about 500) with differently expressed dips. This allows to impart the network an adequate response on input data. The network had been trained for about 10000 epochs. After that it had been trained on real calibration spectra for 1000 epochs. Numbers of epoch was chosen quite approximately.

The search of 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. The most fitting activation function was a logistic one

$$f(x) = \frac{1}{1 + e^{-x}} \quad (2)$$

The method was tested on spectra of Cs 25 $\mu\text{g/l}$ water solutions. As a result of application of neural network RMSE of concentration definition was reduced to 8.4 %. Moreover, the time of neural processing is much smaller, then in the method 2. 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. In addition, the network should be retrained every time the spectroscope is switched on, if its work is non-stable.

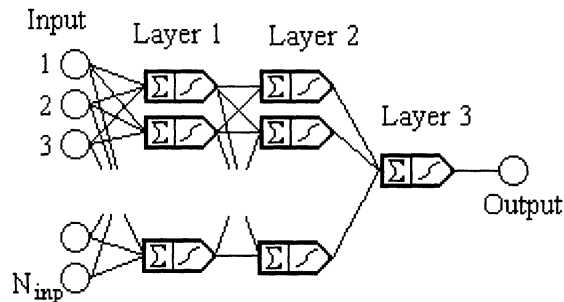


Fig 7. Three-layered feed-forward neural network

4. Processing of the measurements

To perform a 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.

Building of histograms and polygons of distributions by principles described in [5], were carried out to define the sort of errors distribution for relative intensity ($\Delta I/I_0$). The data (61 spectra) were received on Cs solutions with the constant concentration of 25 $\mu\text{g/l}$. Beforehand two supposition 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 3. Statistical parameters of measurements distributions for methods 2,3.

Parameters		Method 2. Relative intensity	Method 3. Concentration
Distribution center	$X_C \pm \Delta_{0.9}(X_C)$	68.4 ± 1.5	24.9 ± 0.53
Standard deviation	$\sigma \pm \Delta_{0.9}(\sigma)$	6.50 ± 0.87	2.05 ± 0.27
Kurtosis	$\varepsilon \pm \Delta_{0.9}(\varepsilon)$	2.60 ± 0.74	2.76 ± 0.75
Antikurtosis	$\kappa \pm \Delta_{0.9}(\kappa)$	0.62 ± 0.09	0.60 ± 0.09
Entropic coefficient	$k \pm \Delta_{0.9}(k)$	2.02 ± 0.10	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 distributions belong either to exponential distributions or to triangle one.

CONCLUSIONS

In this study analysis of trace concentrations of cesium (from 5 up to 50 $\mu\text{g/l}$) in water solutions by a method of intracavity laser spectroscopy is carried out on the basis of the flash lamp pump dye laser. For the samples atomization the electrothermal atomizer with a graphite cell was used. Producing and the recording of the spectrum was carried out with the high-resolution spectrograph equipped with CCD-array.

It was shown that it is possible to reduce errors of measurements due to selection of an optimum processing techniques of spectrums of the broadband dye laser with the characteristic absorption lines of explored atoms. It resulted in lowering a detection limit. The relative standard deviation obtained in this work at definition of trace concentrations of cesium in water solutions is equal to quantity smaller 9 %.

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