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The possibility of recognizing complex spectral characteristics of optical breakdown using neural networks

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A method for analyzing the signals of laser induced breakdown spectroscopy using artificial neural networks is proposed. The possibility of using artificial neural networks to recognize complex spectral characteristics in problems of laser induced breakdown spectroscopy of marine areas in situ is shown by the example of estimating the contribution of dissolved organic and inorganic carbon in a carbon landfill.

Keywords: Optical breakdown, laser spark spectroscopy, spectral lines, optoacoustic effects, ultrasound, principal component method, neural networks.

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Laser-inspired spectroscopy, or laser-induced breakdown spectroscopy (LIBS), is a type of atomic emission spectroscopy associated with the generation of plasma by focusing a laser pulse on the surface of a condensed medium or gas, the scattered radiation of which is recorded using a high-sensitive spectrometer [1]. Laser-inspired spectroscopy has shown great potential in qualitative and quantitative analysis, it also has many advantages associated with rapid chemical analysis [1–7]. The LIS method has evolved rapidly over the past few decades. Chemical elements can be detected in different aggregate states of samples, i.e. whether the sample is solid [1–3], liquid [4,5,7,8] or gaseous [6]. However, it should be noted that LIS for liquids is less developed than for solids. First of all it is connected with labor-intensive processing of breakdown spectra taking into account numerous factors of radiation transport through liquid. Earlier in the works [9,10] it was shown that the use of ultrasound to create a zone of compression and stretching of the liquid during single-pulse laser-induced breakdown leads to an increase in the intensity of the lines. This is some modification of the standard LIS, labelled here as ultrasonic LIS. Atomic spectra of chemical elements of breakdown inside the liquid due to powerful self-absorption and other accompanying mechanisms are, as a rule, strongly broadened, and the intensity of the registered line in such a case greatly complicates the possibility of quantitative analysis. In [10,11], a method of reducing the dependence of the increasing undesirable effect of explosive boiling and surface instability of aqueous solutions on the increase of energy, associated with the separation of plasma fronts, was proposed, which partially removes this problem.

However, it should be noted that the operational processing of numerous spectra obtained from optical breakdown measurements involves detailed analysis and is in a significant number of cases a labor-intensive procedure. The rapid development of current trends involving the use of neural networks and machine learning algorithms may come to the rescue and allow more accurate classification, regression, clustering and other sample operations to be performed to obtain spectrum information and investigate the substance [12,13].

In the present work, to further improve the sensitivity of the LIS method, a breakdown signal analysis using artificial neural networks (ANN) was proposed and used to estimate the contribution of dissolved organic and inorganic carbon in the carbonaceous polygon.

The method involves processing the data in several sequential steps. In the first step, the data is put into a particular form after the pre-processing described below, i.e., the raw data is not directly used without processing. In the second step, background subtraction, averaging and normalization are common approaches in LIS signal processing. These combinations of approaches help to reduce signal intensity variations and LIS error caused by variations in laser power, time variations, focal distance differences, and sample surface condition. However, simple signal processing does not give the spectra a shape suitable for use as input to artificial neural networks. Slightly different signal processing approaches have been applied to adapt the signals to the requirements of using ANNs.

The first approach states that for successful ANN training, the largest possible accumulation of data should be used to avoid over-fitting. In practice, the accumulation of a large sample of data was carried out using a flow-through spark spectrometer, which was successfully used in two expeditions in the Sea of Japan and the Tatar Strait during the voyage of the R/V No 81 „Professor Gagarinsky" in August 2022 and in the Atlantic Ocean during the voyage of the R/V No 52 „Akademik Boris Petrov" in October-December 2022.

The second approach was to apply normalization by the total intensity of the whole spectrum. When the background is subtracted, a strong continuum spectrum is observed at an early stage of plasma formation due to the high plasma

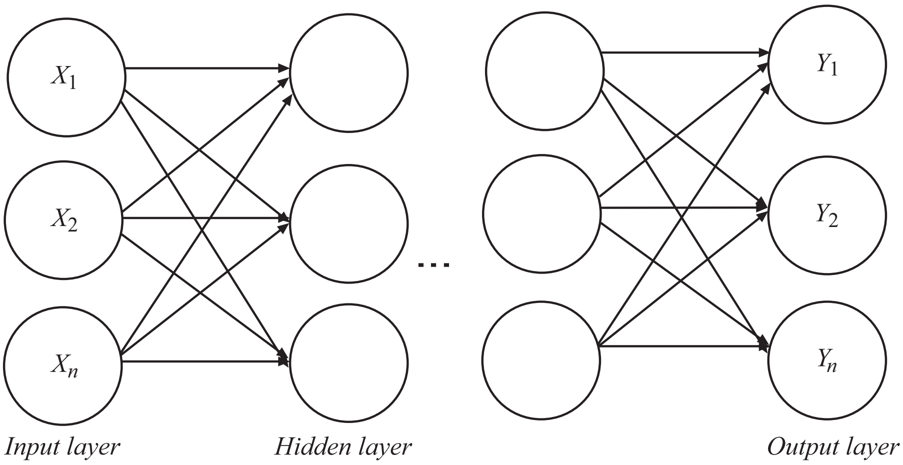

Figure 1. Artificial neural network used in the present work.

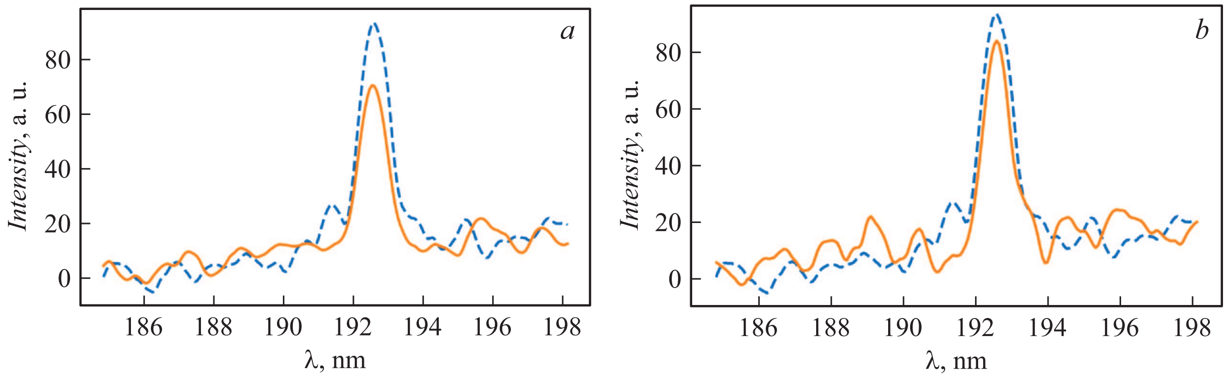

Figure 2. Use of ANN to increase the sensitivity of the LIS method in recording the intensity of the CI carbon atomic line at a wavelength of 193 nm.

density in the liquid. For baseline correction, each spectrum was divided into several sections depending on the observed spectral range.

A third approach, successfully demonstrated by a number of authors [6–10], is to use the logarithmic distribution of peak intensities after the previous step. Note, that nonlinear effects due to self-absorption of spectral lines still introduce powerful distortions, and methods for correcting self-absorption of LIS spectra are very important for quantitative and qualitative evaluations when using laser-IR spectroscopy.

The artificial neural network model demonstrated in this paper is an ANN comprising a multilayer perceptron of three types of layers: an input layer, several hidden layers, and an output layer (Fig. 1). Note, that the number of neurons in the input layer is equal to the size of the input signal, and the number of neurons in the output layer is equal to the number of samples for identification. The number of layers and neurons for each hidden layer was tuned to match the characteristics of the database of recorded items.

The model was implemented in Python using TensorFlowTM [14], and the weights and biases of this model were optimized using the back propagation algorithm. The following are examples of ANNs using this model.

In Fig. 2, the dashed line shows single registrations of the CI carbon atomic line intensity at a wavelength of 193 nm obtained *in situ* on two expeditions in the Sea of Japan and the Tatar Strait during the voyage No 81 of the R/V „Professor Gagarinsky“ in August 2022 and in the Atlantic Ocean during the voyage of the R/V No 52 „Akademik Boris Petrov“ in October-December 2022.

In Fig. 2, *a* the solid line shows the result of averaging over 30 realizations (30 laser shots) obtained at the same geographic coordinate. Fig. 2, *b* shows the result of signal processing by the artificial neural network. As can be seen in Fig. 2, *a*, data accumulation using a flow spectrometer increases the efficiency of carbon detection, but the additional use of ANN, shown in Fig. 2, *b*, increases the sensitivity of the LIS method.

Fig. 3, *a* and *b* show similar results of using ANN to increase the sensitivity of the LIS method in recording the intensity of the CI carbon atomic line at a wavelength of 248 nm in the above expeditions.

Thus, the successful application of ANN has been demonstrated on a real example of carbon analysis of the marine environment, which allowed to partially compensate

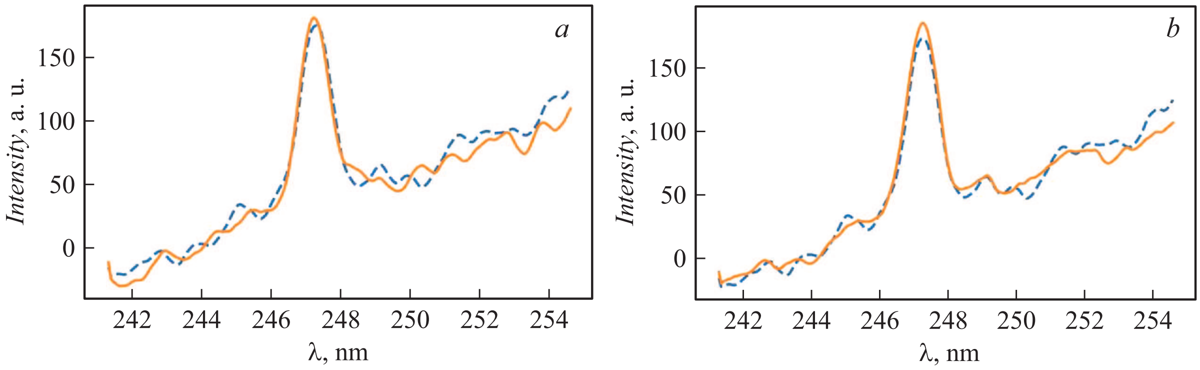

Figure 3. Use of ANN to increase the sensitivity of the LIS method in recording the intensity of the CI carbon atomic line at a wavelength of 248 nm.

for matrix effects and self-absorption in the analysis of spark spectra and to increase the sensitivity of the LIS method. The proposed method of using ANN for recognition of complex spectral characteristics in LIS tasks in real time allows to make an assessment of the environmental friendliness of marine areas in monitoring and research *in situ*.

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Conflict of interest

The author declares that he has no conflict of interest.

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