

Solution of Inverse Problems in Laser Spectroscopy of Water Media with the Help of Neural Networks

S.A. Dolenko¹, I.V. Boychuk², B. Carse³, I.V. Churina²,
T.A. Dolenko², V.V. Fadeev², I.G. Persiantsev¹

¹Nuclear Physics Institute, Moscow State University, Vorobjovy Gory, Moscow, 119899, Russia

²Physical Department, Moscow State University, Vorobjovy Gory, Moscow, 119899, Russia

³University of the West of England, Bristol, United Kingdom

dolenko@radio-msu.net

Abstract

Two methodological approaches to inverse problems solution with the help of neural networks are considered: "experiment-based" and "model-based". Their merits, drawbacks, and characteristics of their use are discussed. Successful application of neural networks for solution of three inverse problems in laser spectroscopy of water media is reported: (1) simultaneous determination of sea water temperature and salinity from Raman spectra, (2) determination of contributions for components of an organic compounds mixture in water from their fluorescence spectra, and (3) determination of molecular parameters of organic compounds from fluorescence saturation curves.

Inverse Problems and Their Correctness

One of the areas of successful application of neural networks (NN) in the last years was the solution of various inverse problems in science and technology.

The general statement of an inverse problem is the following. Consider the studied object of an arbitrary nature, whose behavior is determined by the vector of input parameters $\mathbf{X} = \{x_1, x_2, \dots, x_n\}$. Let the value of \mathbf{X} be unknown and the behavior of the object be expressed as a vector of observed values $\mathbf{Y} = \{y_1, y_2, \dots, y_m\}$. Therefore, the studied object implements an unknown function $\mathbf{Y} = \mathbf{F}(\mathbf{X})$. As a rule, $m \gg n$, i.e. the system can in fact be described by much less parameters than observed. To do this, it is necessary to study how to restore \mathbf{X} values from \mathbf{Y} values. Such problem is a problem of modeling the inverse function $\mathbf{X} = \mathbf{F}^{-1}(\mathbf{Y})$ and it is called an inverse problem.

Such a problem may not be always solved unambiguously because of possible non-uniqueness and instability of the solutions.

An inverse problem is called *correct by Hadamar*, if:

- (1) $\forall \mathbf{Y} \exists ! \mathbf{X}: \mathbf{Y} = \mathbf{F}(\mathbf{X})$ (the solution is unique);
- (2) $\forall \delta \exists \varepsilon: (\Delta \mathbf{Y} < \delta) \Leftrightarrow (\Delta \mathbf{X} < \varepsilon)$ (the solution is stable)

in the whole domain of definition of \mathbf{X} .

An inverse problem is called *correct by Tikhonov* (Tikhonov, Dmitriev, and Glasko 1983) (in the case when correctness by Hadamar is breached), if it is possible to extract such more narrow set of solutions $\{\mathbf{X}'\}$ from the space $\{\mathbf{X}\}$, that:

(1) it is known *a priori* that $\exists \mathbf{X} \in \{\mathbf{X}'\}$ (the solution exists);

(2) $\forall \mathbf{Y} \exists ! \mathbf{X} \in \{\mathbf{X}'\}: \mathbf{Y} = \mathbf{F}(\mathbf{X})$ (the solution is unique);

(3) $\forall \delta \exists \varepsilon: (\Delta \mathbf{Y} < \delta) \Leftrightarrow (\Delta \mathbf{X} < \varepsilon)$, if $(\mathbf{X} + \Delta \mathbf{X}) \in \{\mathbf{X}'\}$ (the solution is stable).

It should be noted that even when the problem is theoretically correct, it can be practically incorrect because of presence of noise in experimental data (that may lead to instability of the solution) and because of discreteness of the set of experimental points (that may break the uniqueness of the solution – the observed values may be described by several different functions $\mathbf{Y} = \mathbf{F}_1(\mathbf{X})$, $\mathbf{Y} = \mathbf{F}_2(\mathbf{X})$ etc.).

Due to the well-known properties of NN (ability to generalize the available information if the data are contradictory, and thus to rise the effective signal to noise ratio noticeably), it is possible to use them to oppose the emergence of practical incorrectness during solution of inverse problems.

Two Methodological Approaches to the Solution of Inverse Problems with the Help of Neural Networks

Practical solution of inverse problems with the help of NN is possible based on two principally different methodological approaches.

1. "Experiment-based" approach.

An experimental data array $S_k = (X, Y)_k$, $k=1...N$ is given. The work with NN is carried out in two stages:

(a) Division of the whole data array into the training, test and examination sets.

(b) Training of the NN on these data sets to estimate the values of the inverse function $X=F^{-1}(Y)$.

2. "Model-based" approach.

Existence of a sufficiently adequate model of the direct function $Y=F(X)$ is assumed. Such a model may be an analytical formula or an algorithm of computational solution of the direct problem. The work with NN is carried out in three stages:

(a) Setting the range of X and the grid of values for each of the problem parameters x_1, x_2, \dots, x_n .

(b) Generation of the necessary amount of representative data for all the data sets (training, test, examination ones) by solving the direct problem using the available model of the direct function $Y=F(X)$.

(c) Training of the NN on these data sets to estimate the values of the inverse function $X=F^{-1}(Y)$.

Comparative analysis of these two methodological approaches is given in Table 1. Note that if an adequate model is available, the "model-based" approach looks more preferable.

Table 1.

Feature	"Experiment-based"	"Model-based"
Representativity of the data sets	As a rule, insufficient	Adequate
Presence of noise in the data	Always present	May be introduced artificially during data generation or during NN training
Noise level in the data	Determined by the experiment	Set during modeling or during training
Conduction of experiments	Necessary	Advisable to test the results
Availability of an analytical or computational model of the direct problem solution	Not necessary	Necessary
Adequacy of the solution to the real object	High	As adequate as the model used

This report considers from this point of view the statement of several inverse problems in laser spectroscopy of water media. Some results of solution of these problems are presented.

Problem 1: Simultaneous Determination of Temperature and Salinity of the Sea Water from Raman Spectra

The analyzed data are Raman spectra of liquid water under laser excitation. The inverse problem consists in simultaneous determination of temperature and salinity of water from 500 values of the Raman spectrum intensity in different channels.

Unfortunately, direct spectra modeling is practically impossible in this problem because of high complexity of the object. The only approach possible in this situation is the "experiment-based" approach. The situation is additionally hampered by the small number of experimental spectra and by the complications with their registration.

Up to now, the problem has been solved in a simplified variant (Dolenko et al. 2000) – for fresh water with determination of its temperature only. The representativity of the data sets was provided by manual division of the total number of spectra into the training set (43 spectra in the temperature range from 19.7°C to 91.4°C), the test set (10 spectra in the same range), and the examination set (6 spectra in the same range). In Fig.1, characteristic outlook of the valence band of water Raman spectra at different temperatures is presented.

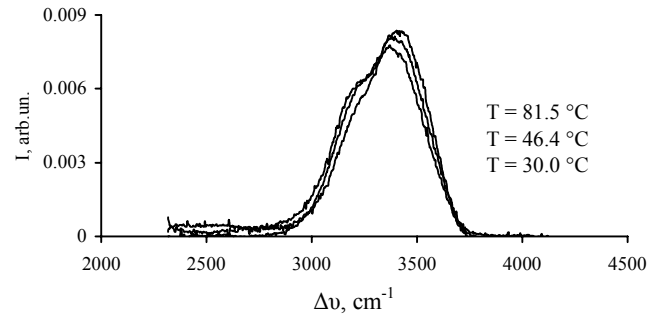


Fig.1. Characteristic outlook of the valence band of water Raman spectra.

Only the values from the most informative central region of the spectra (250 channels) were used as the observed values for network training. No curve smoothing was performed. The best results among all the tested NN architectures has been demonstrated by the General Regression NN (GRNN) (Specht 1991).

It was obtained that the relative mean squared error of temperature determination (on the examination set) was 0.4%, and the mean absolute error did not exceed 0.3 °C. The obtained precision of temperature determination from water Raman spectra exceeds the precision of temperature determination obtained by other methods (Leonard, Caputo, and Fridman 1981).

At the next stage, it is planned to solve the two-parameter problem of simultaneous determination of water

temperature and salinity from Raman spectra valence band in laboratory conditions, and then to test this method in nature conditions. From the other side, it is supposed to perform indirect modeling of spectra by preliminary analysis of temperature dependence of intensity in each channel, with subsequent use of the found dependence and of several reference experimental spectra to simulate model spectra in the whole temperature range. From the point of view of optimizing the NN work it seems reasonable to perform data preprocessing by compression with the help of auto-associative memory.

Problem 2: Determination of Contributions for Components of an Organic Compounds Mixture in Water from Their Fluorescence Spectra

The analyzed data are the fluorescence spectra of nature water and of model samples under laser excitation. The inverse problem consists in the determination of partial fluorescent contributions of admixtures (in particular, oil pollution (OP) against the background of aquatic humic substance (AHS)) from 500 values of the fluorescence spectrum intensity in different channels.

The "model-based" approach to this problem is hampered for the following two reasons. First, the studied object is very complex, therefore the direct modeling of real spectra is not possible. Second, non-linear interaction of the admixtures (fluorescence quenching) introduces distortions at the attempts of modeling the spectrum of the mixture as a superposition of the components' spectra.

Indirect modeling can be implemented in this case by numeric simulation of mixtures' spectra as superposition of experimental spectra of the components. Such a numeric experiment has been performed as the first step to

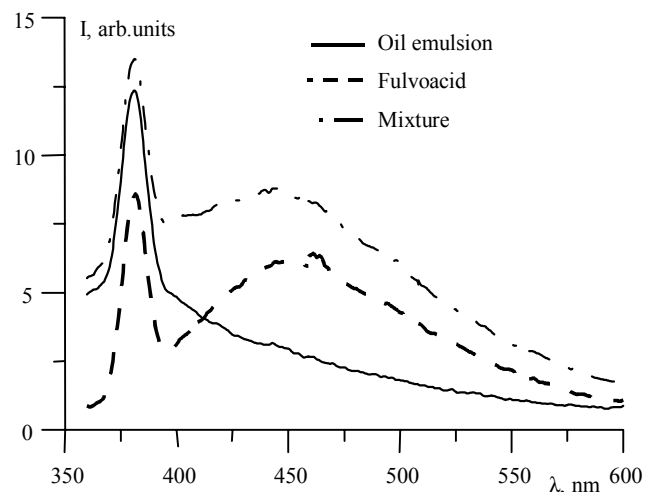


Fig.2. Experimental fluorescence spectra of model samples of fulvoacid solution and oil emulsion in water, and of their mixture.

finding out the possibilities of determination of small fluorescent contributions by direct analysis of the spectra. Fluorescence spectra of model samples of fulvoacid (FA) solution in water and of oil emulsion in water, have been used (Fig.2). The water Raman band that is convenient for use as an internal benchmark to calibrate the fluorescence band (Klyshko and Fadeev 1978) is also present in the spectra. In this case, it is convenient to work with the fluorescent parameter $\Phi_0 = N_{f0}/N_{RS}$, where N_{f0} is the number of fluorescence photons (when fluorescent saturation is not present), and N_{RS} is the number of Raman photons.

The problem was solved under the assumption of no interaction between the components. The spectra of the mixture were modeled as a linear superposition of the initial (reference) experimental spectra of the components with variable weight coefficients. It was convenient to choose partial values of the fluorescent parameter Φ_0 as such coefficients.

Using this "linear" model, the training set (2209 patterns), the test set (361 pattern), and the examination set (64 patterns) were generated within the following ranges of the parameters: Φ_{0FA} : 0.01..20, Φ_{0OP} : 0.01-20. These model spectra were used to train different NN architectures.

When the NN was applied to model (simulated) spectra, the best results were obtained by the five-layer perceptron and by the polynomial network (Group Method of Data Handling (Madala and Ivakhnenko 1994)). These networks were able to determine the OP contribution down to the value of the fluorescent parameter $\Phi_{0OP} = 0.02$ against the background of the FA fluorescence with the parameter value up to $\Phi_{0FA} = 20.0$. In this case, the error in determination of the Φ_{0OP} parameter did not exceed 10%. When the values of the Φ_{0OP} parameter increase, the error goes down, so the value of the error averaged over the whole range of the parameters Φ_{0OP} and Φ_{0FA} was less than 2% (as for Φ_{0OP} , as for Φ_{0FA}).

Then all the obtained NN were applied to the examination set whose spectra were degraded by adding noise with amplitude of up to 10%. The minimal detectable level of Φ_{0OP} was 1.7 against the background of $\Phi_{0FA} = 20.0$, with the Φ_{0OP} determination error not exceeding 5%. The best results here were shown by the GRNN and by the five-layer perceptron that was trained with up to 20% noise added to the training set spectra during training.

At the next stage, the network trained as above on the spectra simulated using the linear model, was applied not to simulated spectra, but to experimental fluorescence spectra. The error increased up to 25-30%, the minimal detectable value of the fluorescent contribution Φ_{0OP} increased for more than an order of magnitude. This means that the fluorescence spectrum of a real mixture does not fully correspond to the model for which the network was trained. There can be several reasons for that: large experimental measurement errors, breakdown of the linearity due to interaction between components, influence of organic compounds on the water Raman band etc.

The majority of these factors are accounted for by themselves if the "experiment-based" approach is used. In this

case, the detection error for Φ_{00P} was lower than that in the preceding case, but it did not reach the extremely low values obtained on model spectra when no noise was present. This meant that the "experiment-based" approach actually removed the errors connected with the difference between the real spectra presented to the network, and the model ones. However, significant reduction of the volume of data used to train the network in comparison with training on simulated spectra, did not allow to achieve good precision of determination of the desired parameters.

At the next stage, it is planned to perform experiments of higher quality, to improve the results of the "experiment-based" approach. Transfer from the linear superposition of the components' spectra to a more adequate model of simulating the spectra of a mixture, taking into account the interaction of the components, is also planned. Besides that, for this problem also it seems reasonable to perform data preprocessing by compression with the help of auto-associative memory.

Problem 3: Determination of Molecular Parameters of Organic Compounds from Fluorescence Saturation Curves

This is a representative example of a problem that manifests the advantages of the "model-based" approach to the highest degree. This happens due to the fact that there is a sufficiently adequate model elaborated for the studied object. The analyzed data are the fluorescence saturation curves of organic compounds (dyes) under laser excitation. The inverse problem consists in the determination of molecular parameters of the object (absorption cross section of exciting radiation, lifetime of the excited level, quantum output into triplet state as a result of intercombinational conversion, rate constant of singlet-singlet annihilation etc.) from the shape of the fluorescence saturation curves, i.e. the dependences of the number of fluorescence photons on photon flow density of the exciting radiation.

The results of solving this problem has been described in detail in several publications (Fadeev et al. 1997; Fadeev et al. 1999; Dolenko et al. 1999) and they will not be presented here. However, it should be noted that due to successful application of the "model-based" approach, it was possible to achieve results that are up to date unreachable by any other methods that do not use NN.

Conclusion

Two different methodological approaches to solution of inverse problems with the help of neural networks have been considered. The "model-based" approach gives better results when an adequate model of the studied object is available, due to the possibility to make the data sets used for training as large and representative as needed. At the same time, the "experiment-based" approach is able to take into account a large number of various factors affecting the ob-

ject that are very difficult to include in a model. Great capabilities of neural networks at the solution of inverse problems have been confirmed on three different problems from the domain of laser spectroscopy of water media.

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