INFLUENCE OF GROUP DETERMINATION OF PARAMETERS ON THE QUALITY OF NEURAL NETWORK SOLUTION OF AN INVERSE PROBLEM IN RAMAN SPECTROSCOPY OF MULTY-COMPONENT SOLUTIONS OF INORGANIC SALTS

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Modern chemical methods of determination of concentrations of substances dissolved in water along with good accuracy also possess a number of disadvantages: they require laboratory equipment and availability of special reagents. Besides that, each test requires substantial time. Therefore, elaboration of express non-contact methods for determination of concentrations of substances dissolved in water is an important task for the needs of environmental monitoring of coastal waters.

In the studies (1,2,3,4) it has been suggested to use Raman spectroscopy as a method that meets the requirements of being express and non-contact. The shape of the Raman spectrum of a solution is highly sensitive to changes in ionic composition and concentrations of its constituent ions. However, at the moment there is no adequate mathematical model capable of describing these changes with due precision. Therefore, the inverse problem (IP) of determination of the concentration of ions by the shape of Raman spectra was solved with artificial neural networks (ANN), which can learn by example, requiring no *a priori* information on the form of the required dependence.

The problem considered in this study* was the use of ANN-processed Raman spectra to determine concentrations of 10 ions (Cl^-, F^-, HCO_3^-, K^+, Li^+, Mg^{2+}, Na^+, NH_4^+, NO_3^-,SO_4^{2-}) contained in multi-component solutions of 10 salts ($MgSO_4$, $MgNO_3$, LiCl, $LiNO_3$, NH_4F, $(NH_4)_2SO_4$, KF, $KHCO_3$, $NaHCO_3$, NaCl). The studied solutions contained from 1 to 10 salts in the concentration range 0 - 1.5 M with a step of 0.15 - 0.25 M. Raman spectra were excited with an argon ion laser at 488 nm wavelength. Each spectrum was recorded in 1824 channels in the Raman shift range 565…4000 cm^{-1}. The whole data array contained 4445 spectra.

Thus, the present study considered a multi-parameter IP of determination of 10 parameters by 1824 input features. In ANN solution of multi-parameter IP, the following approaches are possible:

1. *Autonomous determination* – solution of the IP individually for each determined parameter, by constructing a separate single-output ANN. Such an approach is the most universal one, and it is applied most often.
2. *Simultaneous determination* of all parameters by constructing a single common ANN. While the precision of the solution provided by this method rapidly degrades with increasing number of the simultaneously determined parameters, sometimes it can improve the quality of problem solution in comparison with autonomous determination.
3. An intermediate approach – joining parameters into groups with simultaneous determination within each group (*group determination*). The method of grouping is dictated by the physical meaning of the determined parameters and known relationships between them.

In the preceding studies, at the example of the IP of magnetotellurics (5) it was shown that in some cases the group determination of parameters allows improving the quality of the IP solution in re-

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spect to autonomous determination. The purpose of this study is to show the applicability of the group determination method of parameters as a way to improve the quality of solution for the IP of determining the ion concentrations in multicomponent inorganic salts solutions.

The following ways of parameter grouping were considered: simple ions, complex ions, cations, anions. The results were compared with those for autonomous and simultaneous determination.

The IP was solved with a perceptron with three hidden layers containing 64, 32, 16 neurons, respectively. Logistic activation function was used for the hidden layers, and linear for the output layer. For each case, 5 networks with various weight initializations were trained. The statistics of the results of applying the 5 networks were averaged.

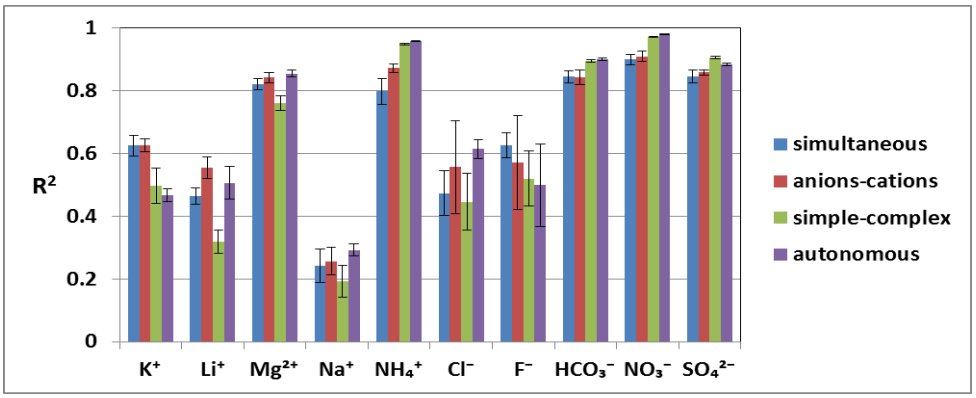

Figure 1: The value of the coefficient of multiple determination R^2 for each ion, for various methods of parameter determination.

Figure 1 displays the values of R^2 coefficient for each ion, for various methods of parameter determination. It can be seen that complex ions (HCO_3^-, NH_4^+, NO_3^-, SO_4^{2-}) are preferable to be determined autonomously, or to be grouped with other complex ions. Simple cations (K^+, Li^+, Mg^{2+}, Na^+) should be grouped with other cations. For simple anions (Cl^-, F^-) the situation is ambiguous.

Thus, this study demonstrates applicability of the approach connected with group determination of parameters in ANN solution of the considered multi-parameter IP. The direction of further studies is search for optimal ways of grouping and interpretation of the results from physical point of view.

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