

## MONITORING OF WASTE AND FORMATION WATERS USING RAMAN SPECTROSCOPY AND ARTIFICIAL NEURAL NETWORK

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Currently development of methods of express remote diagnostics of complex multi-component liquid systems, primarily aquatic media, becomes very urgent. Problems of monitoring of technical and waste waters; diagnostics and control of water reservoirs used for irrigation of agricultural land; determination of salt composition of seas, rivers and formation waters reach the crucial level of importance. It is known that chemical composition and physical properties of formation waters are very important for the development of oil and gas deposits, because a course of many processes in the reservoir depends on them.

Formation waters of oil fields are saturated by various chemical elements, mainly by ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Si}^{4+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ . In the formation waters of oil and gas deposits the mineralization varies within a wide range: from 1 g/l (soft water) to 400 g/l and more (strong brine). A composition of waste and industrial waters is also characterized by a large amount of dissolved inorganic salts, the concentration of which varies widely reaching tens of g/l in some cases. Salinity and chemical composition of the waters directly influence on their basic physical properties. Therefore, one needs to develop the reliable methods of express determination of type and concentration of dissolved ions in the water. Widespread chemical methods of solution of this problem include sampling and sample processing in the laboratory. It takes a lot of time, so the productivity of these methods is small.

Raman spectroscopy (RS) does not have these drawbacks: the Raman spectra can be obtained quickly, without preparation of samples, in the mode of remote sensing. The principal opportunity to determine the type and concentration of dissolved ions by Raman spectra is caused, firstly, by the presence of own Raman peaks of complex ions and, secondly, by the influence of ions on the vibrational bands of water (mainly on the most intensive valence band).

However, it is quite difficult to extract the information about the influence of one concrete ion in the presence of the other ions from Raman spectra. Therefore, the method of artificial neural networks (ANN) was used in order to solve such multivariable inverse problem. ANN is the class of mathematical algorithms widely used for solving optimization problems, pattern recognition, forecasting, etc. ANN are widely used in spectroscopy because of such properties as robustness to noise, ability to work with incomplete or controversial data, etc.

In this study, the problem of determination the type and concentration of each ion in multicomponent solutions of salts  $\text{MgSO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{LiCl}$ ,  $\text{LiNO}_3$ ,  $\text{NH}_4\text{F}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{KHCO}_3$ ,  $\text{KF}$ ,  $\text{NaHCO}_3$ ,  $\text{NaCl}$  with total concentration 0-1.5 M was solved.

In Fig. 1 one can see the spectra of solutions of several inorganic salts. In the low frequency region of the spectrum there are Raman peaks of complex anions, the wide band near  $3400\text{ cm}^{-1}$  is water Raman valence band.

For solution of the problem ANN with different architectures were used. The best results were obtained using a multilayer perceptron with 3 hidden layers. It was found that the proposed approach gives the possibility to determine the concentration of ions with an accuracy of 1-4 g/l (i.e. 0.02 - 0.08 M). It makes it quite suitable for use in monitoring of formation and waste waters.

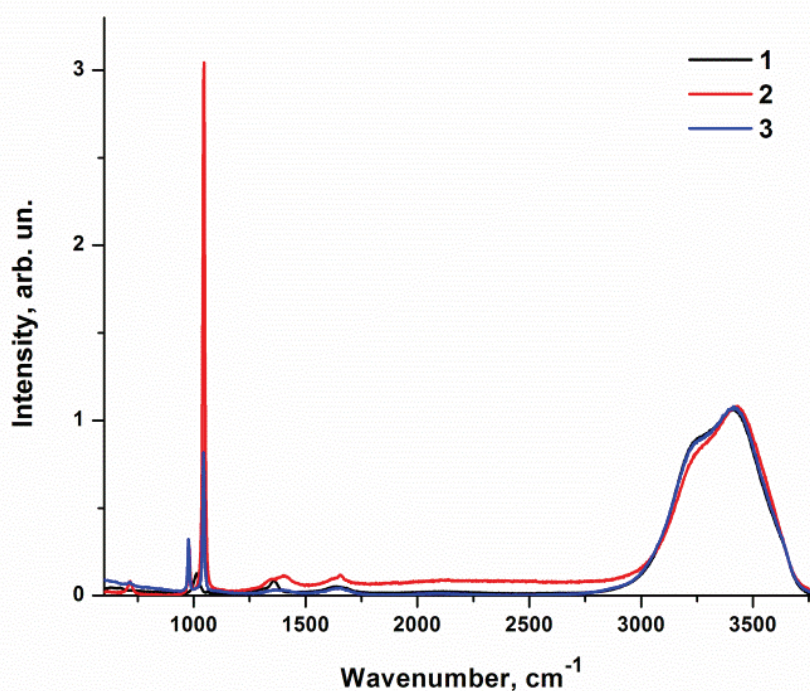


Figure 1 Raman spectra of solutions of inorganic salts. 1-  $\text{KHCO}_3$  (1M, i.e. 100 g/l); 2-  $\text{MgSO}_4$  (0.25M, i.e. 30 g/l),  $\text{Mg}(\text{NO}_3)_2$  (1.25M, i.e. 185 g/l); 3-  $\text{Mg}(\text{NO}_3)_2$  (0.25M, i.e. 37 g/l),  $\text{LiNO}_3$  (0.25M, i.e. 17 g/l),  $\text{NH}_4\text{F}$  (0.3M, i.e. 11 g/l),  $(\text{NH}_4)_2\text{SO}_4$  (0.25M, i.e. 33 g/l),  $\text{KHCO}_3$  (0.25M, i.e. 25 g/l).

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