

DIAGNOSTICS OF WATER MEDIA WITH THE HELP OF RAMAN SPECTROSCOPY

Tatiana Dolenko

Physics Department; M.V.Lomonosov Moscow State University, Moscow, Russia;
[tdolenko\(at\)mail.ru](mailto:tdolenko(at)mail.ru)

At present, the following problems of diagnostics of water media are extremely relevant: diagnostics and control of waters used for irrigation of agricultural land; control of composition of mineral waters; determination of the salt composition of sea, river and reservoir waters, estimation of the content of organic pollutants in natural waters. In this study, the results of solving the problem of recognition of the each component present in the dissolved state in aqueous media, and determination of its concentration, are presented.

There are contact and noncontact methods of solving these problems. Ion concentrations are measured by chemical methods (for example, by using ion-selective electrodes). Chemical methods provide the highest accuracy of the determination of ion concentrations – from units down to a few hundredths of $\mu\text{g/l}$ [1]. However, these methods are individual for each ion, and they do not take into account presence of other ions. Besides that, their implementation takes a long time. Using chemical methods it is impossible to measure ion concentration at a certain point at a certain depth. Therefore, contact methods do not fully satisfy the requirements of oceanology and ecology.

It is obvious that for successful solution of the above-mentioned problems it is necessary to develop remote sensing methods. Such methods should be 1) express, i.e., they should provide information in real time; 2) noncontact, i.e., they should allow one to obtain information without "intrusion" into the investigated medium; 3) sensitive to each component of a complex mixture, i.e., they should have high selectivity in relation to each component of a complex mixture in presence of many other components. The last point means the necessity of elaboration of completely new scientific methods, able to recognize the presence/absence of each component in the medium and to determine the concentration of each component in multicomponent mixture simultaneously.

The lecture is devoted to elaboration of a remote diagnostic method of water media on the basis of Raman spectroscopy with the use of artificial neural networks (ANN).

It is known that dissolved salts significantly affect the shape and position of the Raman bands of water [2,3]. With increasing salt concentration, the intensity of the high-frequency region of water Raman valence band increases, that of the low-frequency one decreases, the band shifts to higher frequencies (Fig.1). Moreover, quantitative changes of shape and position of the Raman bands are different for each type of ions. In addition, if the salts in their composition contain complex ions (e.g., NH_4^+ , NO_3^- , PO_3^{2-} , SO_4^{2-}), the Raman spectrum includes proper Raman lines of the molecular groups of these ions (Fig.1b). With change in ion concentration, the intensity of the proper Raman bands of molecular groups of the complex ions changes. This sensitivity of the Raman spectrum of water solutions to the type and concentration of each ion present in the solution provides the basis for the development of express remote method for determination of the types and concentrations of salts present in natural waters by Raman spectra.

However, the biggest difficulty lies in the fact that the changes of the shape and position of water spectral bands, caused by the presence of various salts, are similar. Therefore, separating the effect of a specific ion in a multicomponent solution is extremely difficult. Such multi-parameter inverse problems of Raman spectroscopy can be successfully solved using artificial neural networks (ANN).

The workers of the Laboratory of laser spectroscopy of solutions of supramolecular compounds from the Physical Department of Lomonosov MSU together with the workers of the Laboratory of adaptive methods of data processing from Skobeltsyn Institute of Nuclear Physics (MSU) have elaborated the methods for solving inverse problems to determine the type and concentration of

dissolved salts in two-, three - and five-component water solutions of salts [4-5] using laser Raman spectroscopy with application of ANN.

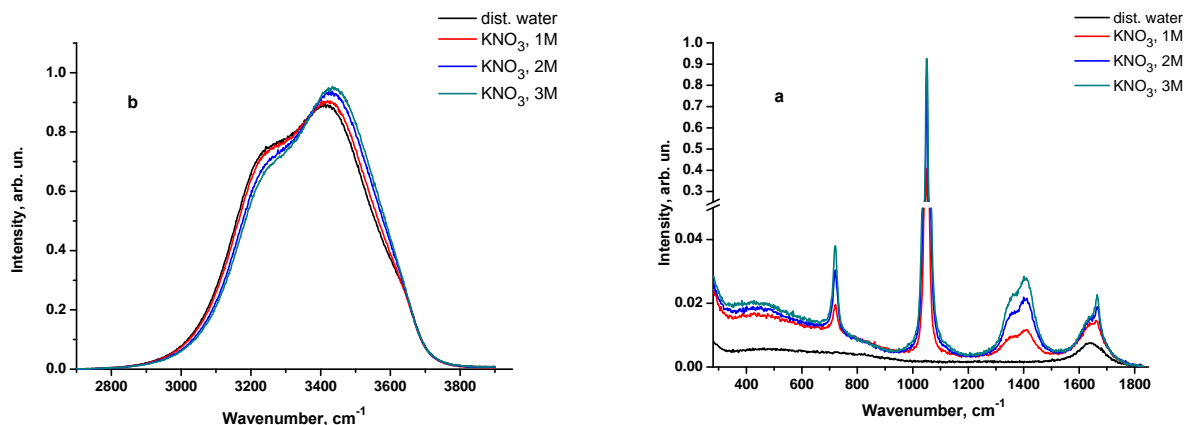


Figure 1: High-frequency (a) and low-frequency (b) areas of Raman spectra of KNO_3 water solutions with different concentrations.

At present, the method of diagnostic of water solution with 10 different ions present in it is being elaborated. Such a problem – determination of the concentration of each of the 10 ions present in it by the Raman spectra of the solution with use of ANN – is important for waste water monitoring and for quality control of mineral waters.

The selection of the type and concentration of salts was based on the information about the ions most common in the mineral and technology water media and about their content there. As the objects of the study, solutions of the following salts were selected: $MgSO_4$, $Mg(NO_3)_2$, $LiCl$, $LiNO_3$, NH_4F , $(NH_4)_2SO_4$, $KHCO_3$, KF , $NaHCO_3$, $NaCl$.

We obtained the set consisting of 5147 experimental Raman spectra of water solutions containing from 0 up to 10 ions in various combinations and with various concentrations changing in the range from 0 up to 1.5 M with increments in concentrations of 0.15-0.25 M (Fig.2).

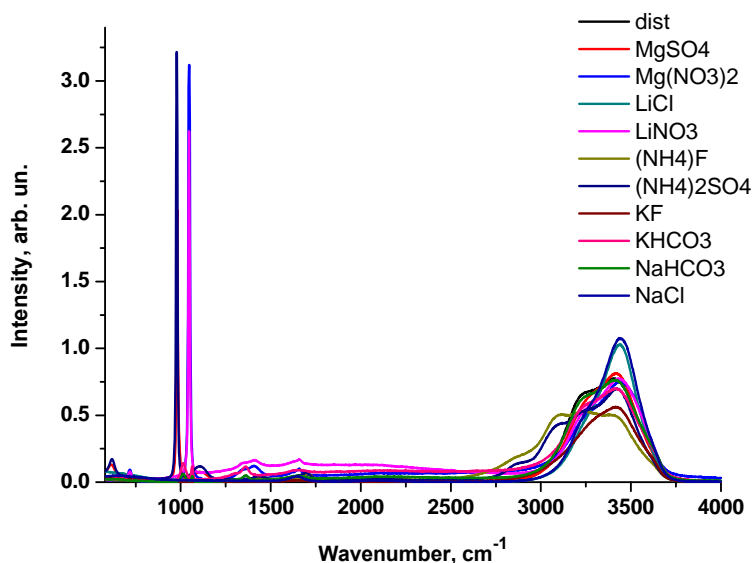


Figure 2: Raman spectra of water solutions of all salts with maximum concentration/maximum solubility of salts.

As the result of ANN application, the obtained average error of determination of the concentration of each ion in presence of the other ones was about 0.016 M (0.368 g/L).

Testing of neural network methods of ions diagnostics in multi-component solutions was performed using real mineral waters. About 160 samples of mineral waters from various manufacturers and from different parts of the globe were collected. The Raman spectra of these mineral waters were recorded; some spectra were obtained with excitation of Raman signal directly through the glass of the bottle without opening it.

The concentration values of each ion obtained using ANN were compared with the values indicated on the bottle label, and also measured using an ion meter with ion-selective electrodes. Some results of application of ANN to the real mineral waters are presented in Fig.3. It turned out that using ANN it was possible to determine the concentration of ions by Raman spectra of the mineral waters with mean absolute error from 0.003 M to 0.06 M (from 0.069 g/L to 1.38 g/L). In Fig.3, the data are presented for five ions which are often present in mineral waters.

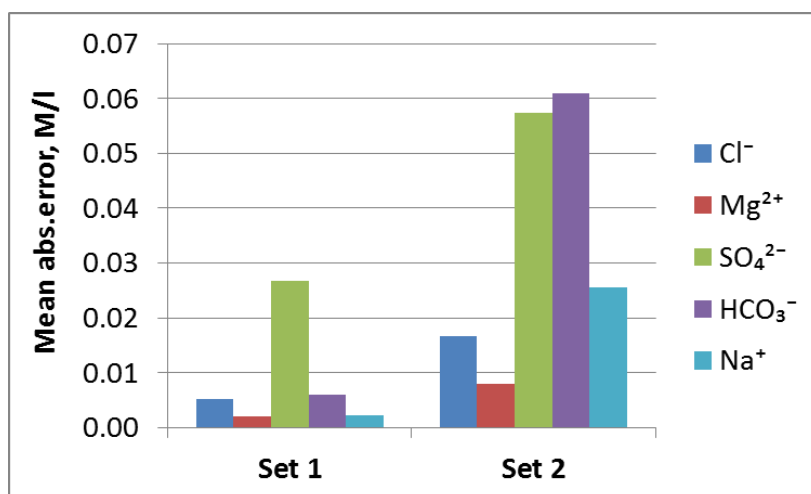


Figure 3: The results of application of ANN to different data sets.

The results showed that relative errors of ion determination in the waters belonging to the category "drinking" with significantly lower salinity, are significantly higher than those for the waters belonging to the category "medicinal". This means that at this stage the elaborated method should be applied for diagnostics of waters with high mineralization.

Possible practical applications of the described complex method (Raman spectroscopy + ANN data processing) include diagnostics of nature waters, mineral waters among them, and also industrial and waste waters.

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