New Opportunities in the Determination of Inorganic Compounds in Water by the Method of Laser Raman Spectroscopy

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Abstract—The characteristic peculiarities of the valence band shape of Raman scattering by water molecules in the solutions of KBr, KCl, KI, NaCl, and NaI electrolytes have been revealed. These peculiarities allowed us to perform noncontact recognition of salt type and determination of salt concentration in water solutions by means of artificial neural networks. We suppose that the classification algorithms applied in this study, which use artificial neural networks, may also be useful for other problems in Raman spectroscopy, in fluorimetry, and in application of these methods in ecology. Use of laser radiation for exciting Raman and fluorescence bands provides high spectral resolution that registers even weak bands. This may turn out to be key for the implementation of the approach developed here in the identification of a wide class of objects in aqueous and other liquid media.

INTRODUCTION

It is well known that interaction of molecules of liquid water with inorganic and organic compounds manifests itself in changes of the vibrational characteristics of bound water molecules [1–5]. These changes can be determined by the method of Raman spectroscopy. Several bands are present in the Raman scattering spectrum of water, but it is very attractive to use the most intensive valence band for the solution of inverse problems of Raman spectroscopy, for example, to solve the problem of the determination of ion concentration in water under the conditions when the type of the electrolyte is known and when a preliminary concentration calibration of some parameter characterizing the Raman band shape has been made for this type. Both from a theoretical and a practical point of view, it would be interesting and important to find specific peculiarities in the changes of water Raman band characteristics under the influence of each individual salt. After that, the problem of noncontact identification of such admixtures in water and of the determination of their partial concentrations in mixtures could be met. There are principal preconditions to solving such task successfully, because it is known that the interaction of different ions with water molecules is different [6]. In particular, this is manifested in the difference of their characteristics of ion hydration, which can be positive or negative. In [4, 5], it was found that the characteristics of the concentration dependence of water Raman band shape are connected with ion hydration numbers.

This paper is devoted to the development of a method of laser diagnostics of water media (including natural media) and to the determination of admixture concentrations in them. The application of artificial neural networks (ANN) for more precise analysis of water Raman valence bands in solutions provided an opportunity for the recognition of the type of the dissolved salts and increased the sensitivity of the method of determination of the admixture concentration.

EXPERIMENTAL

Our research objects were water solutions of alkaline-haloid salts with cations (Na^+, K^+, NH_4^+) and anions (F^-, Cl^-, Br^-, I^-) in the whole concentration ranges of their dissolubility. The Raman scattering (RS) signal was excited by the radiation of an argon laser with a wavelength $\lambda = 488$ nm. The power of the laser radiation was about 200 mW, and the polarization was vertical. Diffused under the angle 90°, Raman radiation was collected on the input slit of the polychromator of an optical multichannel analyzer OMA-1 (Princeton Applied Research Corporation) equipped with a grating with 550 lines per mm, which can ensure parallel detection of a spectrum range 70 nm wide with a resolution of 0.14 nm/channel (slit width 25 μm).

Raman scattering spectra of water in the solutions were recorded at room temperature. Some of the obtained data are presented in Fig. 1.

Experimental data obtained by different authors [1–3] and our data [4, 5] showed that, with increasing concentration of salts dissolved in water, the intensity of the high-frequency region of the RS valence band increases, and that of the low-frequency region decreases; the band shifts to higher frequencies, and the band width decreases (Fig. 1). An exception is the behavior of water RS spectra of the solutions of ammonium and fluorine salts (Fig. 1). From Fig. 1, one can see that, with increasing concentration of the NH_4F

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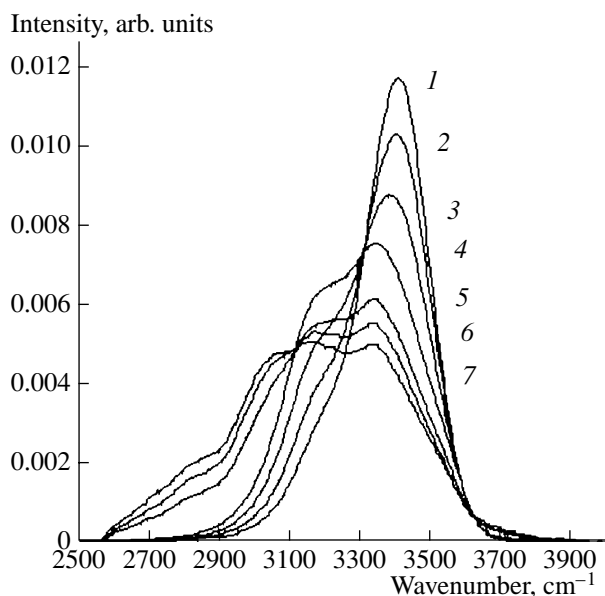
Fig. 1. Water Raman scattering valence bands in electrolyte solutions under different salt concentrations: (*1*) NaI, 6 m; (*2*) NaI, 4 m; (*3*) NaI, 2 m; (*4*) distillate; (*5*) NH$_4$F, 7 m; (*6*) NH$_4$F, 12 m; (*7*) NH$_4$F, 15 m.

Intensity, arb. units
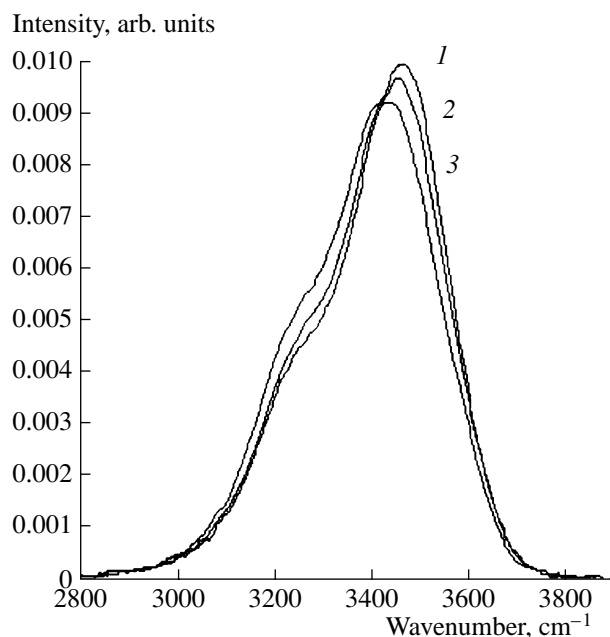
Fig. 2. Water Raman scattering valence bands in potassium salt solutions (the solution concentration is 3.2 m): (*1*) KI, (*2*) KBr, (*3*) KCl.

solution, the position of the spectrum maximum does not change, the intensity of the high-frequency shoulder decreases, the intensity of the low-frequency shoulder increases, and the half-width of the band practically does not change. Besides, an additional band appears in the low-frequency area. Anomalies in the behavior of water Raman spectra of solutions of ammonium and fluorine salts are explained by the individual properties of these ions.

In Fig. 2, one can observe the behavior of the water Raman spectra in the solutions with the same concentration of the salts with different anions and the same cation K$^+$. A comparative analysis of the obtained data confirms the fact that the intensity of water Raman spectra in the solutions depends not only on the concentration of the dissolved ions but also on their kind. Our investigations showed that the influence of anions on the water Raman band appeared to be much stronger than that of cations. One can note that the influence of anions on the spectrum increases in the following sequence: Cl$^-$ < Br$^-$ < I$^-$ (Fig. 2). This series matches the theory of ion hydration. A similar sequence for cations is difficult to obtain exactly due to their insignificant influence on water Raman spectra.

## DETERMINATION OF CONCENTRATION OF A KNOWN SALT

In [5], it was shown that the changes in the shape of a water Raman band could be used to determine the concentration of a known salt (also the concentration, or salinity, of a known salt mixture, like sea salt). In this case, the error in the concentration measurement is 0.1–0.2 m (molality) if the solution temperature is known and stabilized with 0.1°C precision. A two-parameter inverse problem can also be solved: both the temperature of the water solution and the concentration of a known dissolved salt can be determined [4], but, in this case, the error in the determination of the parameters is higher.

As was mentioned above (Figs. 1, 2), salts dissolved in water change the shape of the RS valence band considerably. The method of determination of the concentration of salts dissolved in water (including water salinity) is based on this fact. As the quantitative characterization of changes in the water RS valence band shape (3000–3800 cm^{-1}) under the influence of different dissolved salts, the parameter χ_{32} is used (it is equal to the ratio of intensities of high-frequency and low-frequency regions of the water RS valence band: $\chi_{32} = I(\nu_3)/I(\nu_2)$; Fig. 3, [4]).

The frequencies ν_3 and ν_2 are chosen to correspond to critical points of the first derivative of the pure water RS valence band and then fixed (Fig. 3). The dependence of the parameter χ_{32} on the concentration (C) of various salts is shown in Fig. 4.

In the whole range of concentration changes, the dependence $\chi_{32}(C)$ can be approximated with good accuracy by a straight line [4–6] (we used the regression method). From the obtained linear equations $\chi_{32} = AC + B$ (A and B are coefficients that are determined for every salt experimentally), it is possible to determine unknown concentrations.
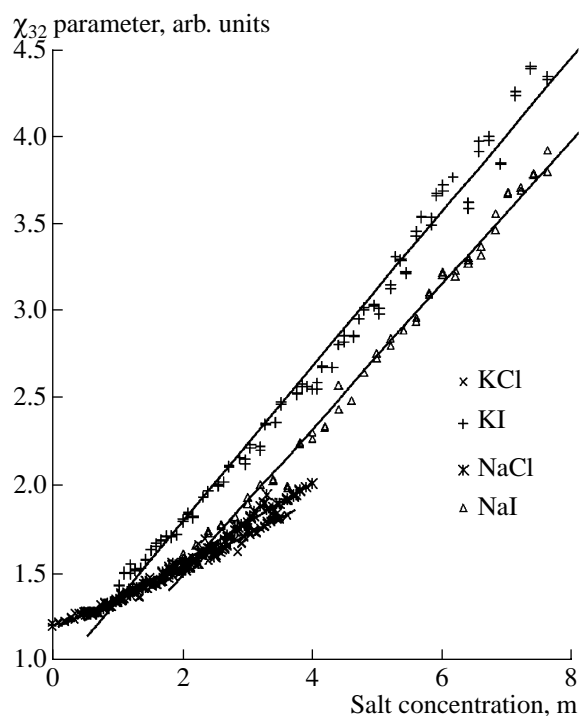
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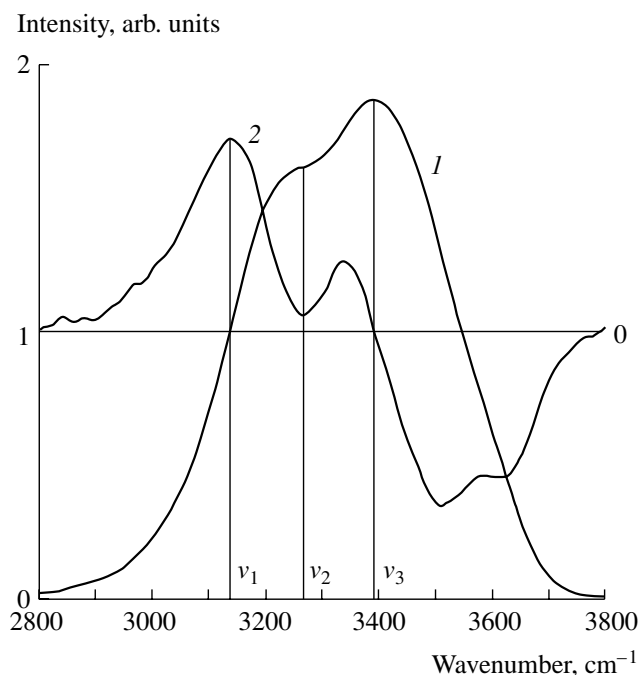
Fig. 3. Illustration of the calculation of the parameters χ_{32}:
(*1*) Raman band, (*2*) derivative.

χ_{32} parameter, arb. units

Fig. 4. Dependence of the parameter χ_{32} on concentration of salts dissolved in water.

We have obtained experimentally the calibration dependences $\chi_{32}(C)$ for the salts of potassium and sodium in the whole range of their dissolubility at room temperature (Fig. 4). Then, with the help of these calibration dependences, the concentrations of these salts were determined for 20 water RS spectra of solutions of every salt. The mean-square errors of salt concentration determination were calculated for RS spectra of solutions. The results are shown in Table 1.

IDENTIFICATION OF SALTS AND DETERMINATION OF THEIR CONCENTRATION

As was mentioned above, the influence of the salts is manifested in particular in the change of three easily determined features of the band: the χ_{32} parameter, the position of the valence band maximum ν_{max}, and the bandwidth at half-maximum (FWHM) $\Delta\nu$. The thorough analysis of the spectra presented in Fig. 1 shows that there are no concentrations of the electrolytes at which the combination of these parameters (χ_{32}, ν_{max}, $\Delta\nu$) is the same for different electrolytes. Therefore, this combination can be used to identify electrolytes. For example, at the same molal concentration ($C = 3$ m) of NaI and KI salts, the values of the χ_{32} parameter differ by 0.3; the positions of the band maximum ν_{max}, by 13 cm^{-1}; the FWHM $\Delta\nu$, by 10 cm^{-1}. It is obvious that moving to a multifrequency analysis increases the dimensionality of the identification feature, i.e., enables

one to use a larger number of parameters for identification. Therefore, there are principal preconditions for the identification of salt type by the spectral image of the Raman band. The only question concerns the probability (the reliability) of salt identification under real conditions. The results of the investigations that gave an answer to this question are presented below.

We have used artificial neural networks (ANN) [8] to approach the combined problem of determination of the kind of salt dissolved in water and the subsequent determination of the salt concentration. In this part of the study, we have used the same experimental spectra as in the part devoted to the χ_{32} method. Prior to further processing, each spectrum was set to zero pedestal and normalized to unit area. At both stages of this part of the study, the intensities of the most informative central area of each spectrum (220 channels) were then fed to the inputs of a neural network.

Table 1. Errors in the determination of salt concentration °C (molality) by the χ_{32} method

Salt	Mean absolute error of concentration, m
NaI	0.13
NaCl	0.1
KCl	0.1
KBr	0.1
KI	0.12

Table 2. The results of solving the recognition problem

Real class	Recognized as class					Total	True, %
	NaI	NaCl	KCl	KBr	KI		
NaI	9	0	0	0	0	9	100.00
NaCl	1	4	0	0	0	5	80.00
KCl	0	0	12	0	1	13	92.31
KBr	0	0	10	4	0	14	28.57
KI	0	0	0	0	16	16	100.00
Number of assigned spectra	10	4	22	4	17	57	80.18

The first part of the task was to determine which one of the five salts (NaI, NaCl, KCl, KBr, KI) was present in the sample for each spectrum, i.e., to solve the classification problem. In each sample, only one salt was dissolved. The classification network had five outputs, one for each kind of salt. During training, the desired output value for the network was unity for the output corresponding to the salt present in the sample and zero for the other four outputs. When the network was applied, the pattern (spectrum) was assigned to the class whose corresponding output had a maximum value among all five outputs.

For correct work with the ANN, all of the experimental spectra were divided into three sets of data (training, test, and examination sets). The first set was used to train the network; the second one was used to test the network during training to avoid overtraining. The examination set was not used during training at all, and it could be used to estimate the real performance of the obtained set on out-of-sample data. The architecture used was a conventional three-layer perceptron [8].

The results of solving the salt classification task are presented in Table 2 for the examination set. The total number of examination set spectra of each salt presented to the network upon completion of the training is displayed in the column "Total" of Table 2. The lower line of Table 2 displays the number of examination set spectra assigned to each salt. The cells in the central part of the table show the distribution of the recognized spectra (network answers) over the salts. The last col-

umn of the table displays the fraction of the correct answers of the network for each salt and for the whole examination set (the lowest cell).

Two interesting facts are evident from Table 2. First, four classes (NaI, KI, NaCl, and KCl) are recognized very well (with nearly 100% rate); the fifth class (KBr) is often erroneously assigned to KCl. This matches the known fact that the influence of I^- anions on water Raman spectrum is much stronger than that of Cl^- and Br^-. Second, the recognition rates obtained for all three datasets (training, test, and examination sets) are very close, which is evidence of the fact that the datasets are all equally representative and that the results may be considered reliable.

After the kind of salt is determined, the second part of the task is the determination of the salt concentration. We have solved this problem by neural networks, too. In this case, there were five networks, one for each salt, and the single output of each network was trained to determine the salt concentration. We have also compared the performance of neural networks (five-layer perceptrons) with that of the group method of data handling (GMDH) algorithm [9]—a special algorithm of modeling that builds a complex polynomial formula as a model of the studied dependence, which is, in our case, the dependence of the salt concentration on the intensities in different channels of the spectrum. Comparative results (on the examination set) are presented in Table 3. We can see that, for this task, the neural network performs better than GMDH.

Comparing Table 3 to Table 1, one can also see that the five-layer perceptron outperforms the χ_{32} method, providing more accurate determination of concentration for all the salts.

We have also used artificial neural networks to approach the combined problem of the determination of ions dissolved in water. This task was solved in the same way as the recognition of the kind of salt. In each sample, only one salt was dissolved. The classification network had five outputs, one for each kind of ion (Na^+, K^+, Cl^-, Br^-, I^-). During training, the desired output value for the network was unity for the two outputs (the cation and the anion) corresponding to the salt present

Table 3. Mean absolute error of the determination of salt concentration by ANN and GMDH for different salts (error on the examination set)

Salt	Mean absolute error, m (five-layer perceptron)	Mean absolute error, m (GMDH)
NaI	0.08	0.19
NaCl	0.07	0.22
KCl	0.09	0.10
KBr	0.06	0.06
KI	0.06	0.14

Table 4. The results of solving the recognition problem

Real ion	Recognized as ion					Total	True, %
	Na^+	K^+	Cl^-	Br^-	I^-		
Na^+	14	0	–	–	–	14	100.00
K^+	0	44	–	–	–	44	100.00
Cl^-	–	–	8	10	1	19	42.11
Br^-	–	–	7	7	0	14	50.00
I^-	–	–	0	0	25	25	100.00
Number of assigned spectra	14	44	15	17	26	116	84.48

in the sample and zero for the three remaining outputs. When the network was applied, the pattern (spectrum) was assigned to two classes: one whose corresponding output had a maximum value among the two outputs responsible for cations, and one whose corresponding output had a maximum value among the three outputs responsible for anions. The architecture used was a three-layer perceptron. The results of solving the ion classification task are presented in Table 4 for the examination set.

From Table 4, one can see that the ions Cl^- and Br^- become mixed with each other, which matches the results of Table 2.

The results of solving such a recognition problem will be used to determine the kind of ions and their concentrations in solutions of mixtures of different salts.

CONCLUSIONS

We propose a method for salt classification (determination of which salt is present) in water solution and for determination of its concentration using artificial neural networks. We suppose that these classification algorithms using artificial neural networks may be also useful for other problems in Raman spectroscopy and in fluorimetry, and in application of these methods in ecology. The use of laser radiation for exciting Raman and fluorescence bands allows one to provide high spectral resolution that registers even weak bands. This may turn out to be key to the implementation of the approach developed here for identification of a wide class of objects in aqueous and other liquid media.

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REFERENCES

1. P. Terpstra, D. Combes, and A. Zwick, J. Chem. Phys. **92**, 65 (1989).
2. F. Rull and J. A. De Saja, J. Raman Spectrosc. **17**, 167 (1986).
3. F. Rull, Pure Appl. Chem. **74**, 1859 (2002).
4. T. A. Dolenko, I. V. Churina, V. V. Fadeev, and S. M. Glushkov, J. Raman Spectroscopy **31**, 863 (2000).
5. T. A. Gogolinskaya, S. V. Patsaeva, and V. V. Fadeev, Dokl. Akad. Nauk **290** (5), 1099 (1986) [Sov. Phys. Dokl. **31** (5), 820 (1986)].
6. V. V. Pal'chevskii, *Aqueous Solutions of Electrolytes* (Leningr. Univ., Leningrad, 1984) [in Russian].
7. K. Furic, I. Ciglenecki, and B. Cosovic, J. Molecular Structure **6**, 225 (2000).
8. M. H. Hassoun, *Fundamentals of Artificial Neural Networks* (MIT Press, Cambridge, 1995).
9. H. Madala, and A. Ivakhnenko, *Inductive Learning Algorithms for Complex Systems Modeling* (CRC Press, Boca Raton, 1994).

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