NEW APPROACHES TO DETERMINATION OF TEMPERATURE AND SALINITY OF SEAWATER BY LASER RAMAN SPECTROSCOPY

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ABSTRACT

Laser Raman spectroscopy can be an effective method for simultaneous determination of temperature and salinity of nature waters. In this paper, a new way of processing spectra is suggested. Artificial neural networks are applied to solve the two-parameter inverse problem of determining temperature and salinity using the shape of the valence band of liquid water Raman scattering. Two approaches are used: training the neural network on experimental data and on model data. The errors of simultaneous determination of temperature and salinity are calculated; the ways of reducing these errors are specified.

Keywords: Raman scattering, seawater temperature and salinity, neural networks, inverse problems

INTRODUCTION

Temperature and salinity of seawater are widely used parameters in oceanography. The simplest contact methods of measuring these parameters (with electronic thermometers and conductivity-based salinometers), do not satisfy the requirements of oceanography to the full extent. Express monitoring of temperature and salinity in large water areas, i.e. their simultaneous remote determination, is an important problem, and the method of laser Raman spectroscopy is one of the possibilities to solve this problem. In particular, this method allows the determination of the absolute thermodynamic temperature, which cannot be determined by measuring the sea surface temperature (SST) with radiometers on the basis of its emissivity in the thermal infrared. However, results obtained with the laser Raman method so far (1) had a precision of ΔT=0.7°C and ΔS=1, which did not satisfy the requirements in oceanography. Some time ago, new opportunities concerned with the development of new algorithmic approaches to the solution of inverse problems have emerged (2,3). Methods for temperature and salinity determination were developed as *T* and *S* are indicators of the ecological state of water areas.

For the first time, the method of determination of water temperature by the changes of the shape of water Raman valence band was suggested by the authors of (4,5). Leonard described such changes by the temperature dependence of the parameter, which is equal to the ratio of intensities of high frequency and low frequency regions of the Raman valence band. Using the linear section of this dependence, Leonard (4,5) developed and tested a method of measuring the temperature of water with an accuracy of 0.5°C at laboratory conditions and 2°C in field conditions.

One of two approaches to temperature measurement is used nearly in all publications on this subject. In one case, the above-mentioned ratio of intensities of high frequency and low frequency regions of the valence band is used as the thermo-sensitive parameter (4,5,6). In the other variant, the valence Raman band of water is decomposed into several component curves of a specific shape (usually Gauss or Voigt), and the ratio of the two most intense components (high frequency and low frequency) is used as the thermo-sensitive parameter (7). The authors of (8) use the linear section of the temperature dependence of the ratio of differential spectrum intensity to the intensity of the initial Raman spectrum.

In (6,8) it is suggested to use the linear section of the dependence of the same parameters on salinity (concentration of dissolved salts) to measure the salinity of seawater.

Unfortunately, no measurements of temperature and salinity were performed in (6). In (8), no estimation of the precision of the results was made. In (7), the achieved precision of temperature measurement was 1K.

METHODS

Experimental investigations of the dependence of the water Raman scattering curve on temperature and on salt concentration (seawater salinity) showed that changes of temperature and salt concentration result in a wide variation of the shape of the Raman scattering valence band, reported by many authors (1,9,10,11,12,13,14,15,16,17). As an example, Figures 1 and 2 present typical dependences recorded by the authors of this paper; experimental set-up and spectra processing for these measurements were described elsewhere (1,13,14). Such changes are reliably detectable by modern measurement methods.

The Three-wave number method

Previous studies showed (1,13,14) that temperature T and salinity S can be determined simultaneously using the shape of the water Raman band. In principle, a possibility of simultaneous account for the influence of T and S on the Raman band is concerned with its complex nature: it is possible to expect a substantial difference in the influence of temperature and admixtures on different components of the spectrum.

We described the changes of the shape of the Raman valence band with temperature and salinity quantitatively with parameters $\chi_{31}(T,S)$ and $\chi_{32}(T,S)$ (Figure 3).

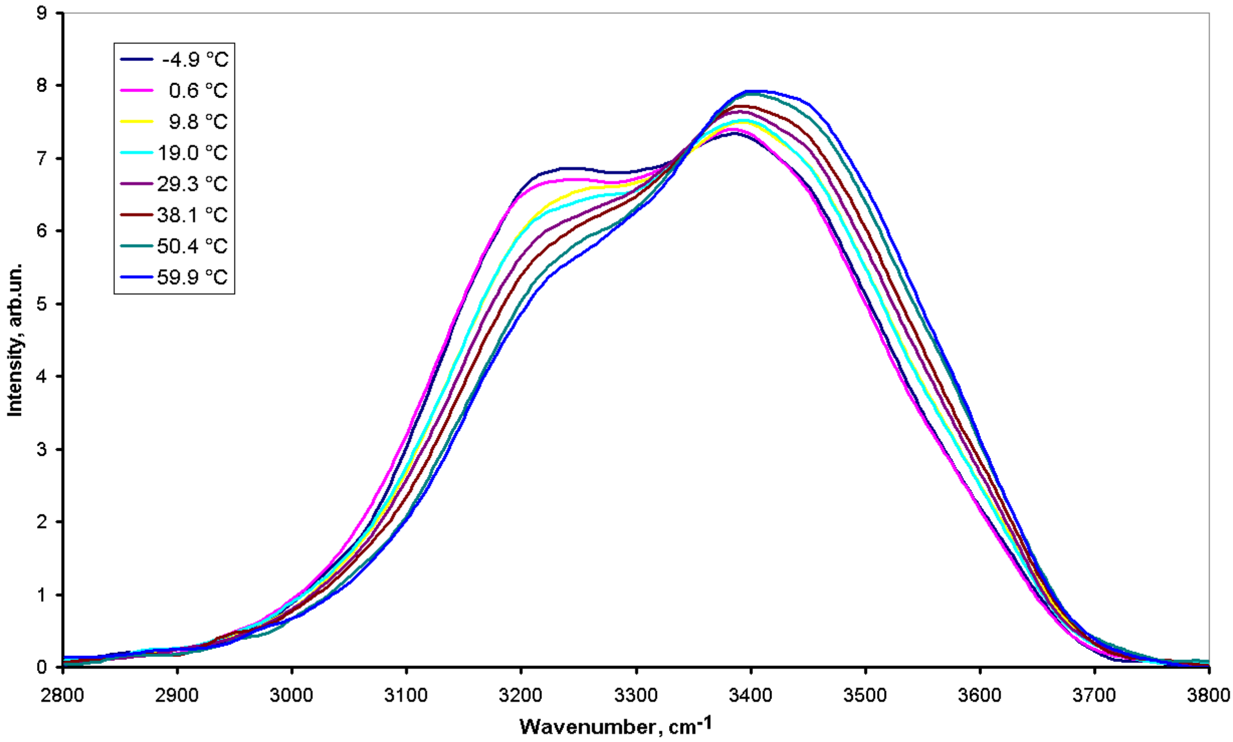

Figure 1: Dependence of the shape of the Raman valence band of liquid water on temperature T; the spectrum taken at –4.9 °C is from supercooled water.

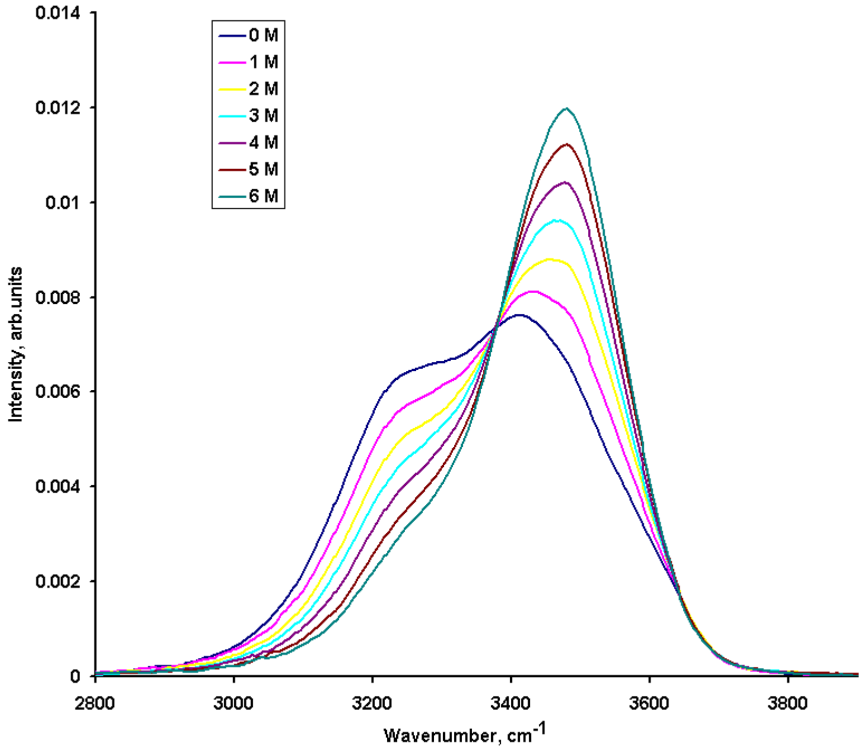

Figure 2: Dependence of the Raman valence band of liquid water in NaCl solutions on salt concentration (spectra taken at room temperature). Typical seawater salinity 35 corresponds to NaCl concentration 0.47 M.

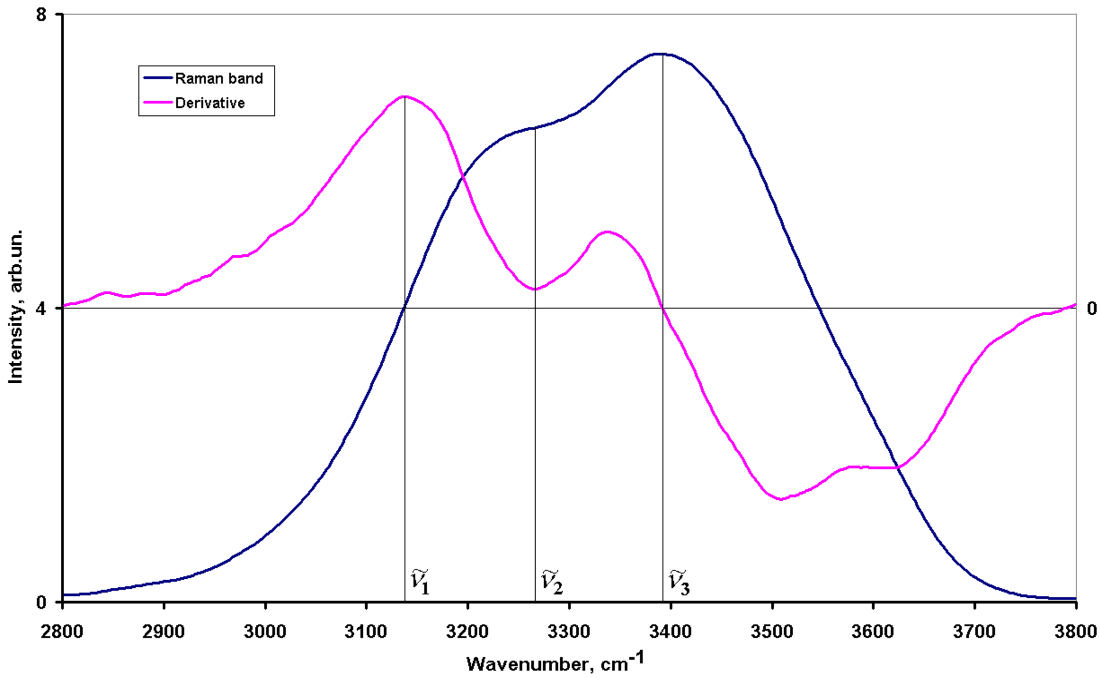

Figure 3: Illustration of the calculation of the parameters χ_{ij}.

One of the first stages of the Raman spectra processing was the Fourier smoothing with Gauss-shaped filtering function (14). The obtained spectra were normalized to the unit area. Afterwards, the shape of the water Raman band was described by the following parameters:

$$\chi_{ij} = \frac{J(\tilde{\nu}_i)}{J(\tilde{\nu}_j)}$$

where $\tilde{\nu}_i$, $\tilde{\nu}_j$ are some characteristic points of the spectrum (Figure 3). These points were selected based on singularities of the derivative band; the frequencies were: $\tilde{\nu}_1 = 3136\,\text{cm}^{-1}$, $\tilde{\nu}_2 = 3264\,\text{cm}^{-1}$, $\tilde{\nu}_3 = 3392\,\text{cm}^{-1}$. $J(\tilde{\nu}_i)$ and $J(\tilde{\nu}_j)$ are the Raman intensities in these points, *i*, *j* = {1,2,3}.

Expanding the two-parameter function $\chi_{ij}(T,S)$ in a Taylor series in the neighbourhood of some point (T_o,S_o) yields the following equations:

$$\Delta\chi_{32} = \chi_{32} - \chi_{32}\big|_{T_o,S_o} = \frac{\partial\chi_{32}}{\partial T}\bigg|_{T_o,S_o} \Delta T + \frac{\partial\chi_{32}}{\partial S}\bigg|_{T_o,S_o} \Delta S + \ldots.$$

$$\Delta\chi_{31} = \chi_{31} - \chi_{31}\big|_{T_o,S_o} = \frac{\partial\chi_{31}}{\partial T}\bigg|_{T_o,S_o} \Delta T + \frac{\partial\chi_{31}}{\partial S}\bigg|_{T_o,S_o} \Delta S + \ldots.$$

Taking several terms and solving the system with respect to $\Delta T = T - T_o$ and $\Delta S = S - S_o$, one can determine *T* and *S* of the water.

The coefficients necessary to solve the system were obtained from experimental dependences $\chi_{ij}(T)$ and $\chi_{ij}(S)$ in the temperature range of 20-80°C and salinity range of 5-35 ("normal" seawater diluted with purified water), Figure 4.

This method of simultaneous determination of temperature and salinity has a precision of 0.7°C and 1.0, respectively (1,13,14), at laboratory conditions. (Here and in the following, the precision denotes the absolute error). It was tested in field conditions in the 43rd cruise of the research vessel *Akademik Kurchatov* off the coast of Namibia. The processing of the remote data of natural seawater with the "three-wave number method" resulted in temperatures and salinities that differed from *in situ* measured *T* and *S* on average by 1.1°C and 1.4, respectively (14), in the whole measurement ranges (*T*: 16 to 24.3°C; S: 32 to 36).

Such errors in simultaneous determination of water characteristics do not satisfy the requirements of oceanography, thus the suggested method needed further development.

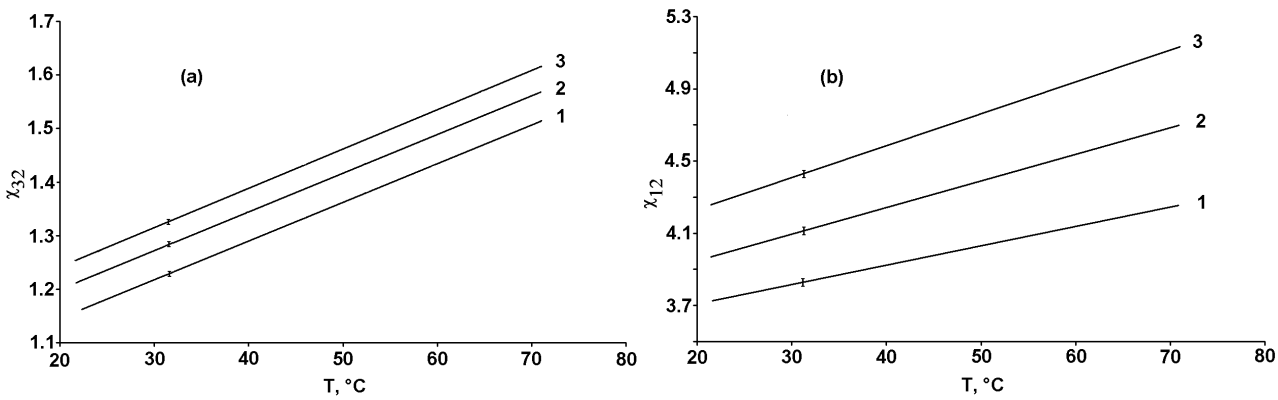

Figure 4: Temperature dependences of the parameters χ_{32} (a) and χ_{31} (b) for distilled water (curve 1, salinity S=0), for "normal" seawater (curve 3, S=35), and for their mixture in proportion 1:1 (curve 2, S=17.5).

The ANN method

The method of the artificial neural networks (ANN) (18) is one of the widely used methods of solution of the inverse problems. Artificial neural networks are a powerful tool for solving different problems of pattern recognition, classification and prediction, when parallel testing of multiple hypotheses and high computational speed are required.

This technique was also successfully applied in the solution of the inverse problems in the non-linear fluorimetry of complex organic compounds (19).

Our studies on application of ANN in Raman spectroscopy of water began by solving the simplest one-parametric problem, i.e. the determination of water temperature. Expanding the program was intended, investigating inverse problems with two and three parameters.

At the first stage, general regression neural networks (20) were used to estimate the precision of the temperature determination from water Raman spectra. This ANN architecture was most suitable for our application, because it can give good results trained even on a small number of patterns (20). From experimental spectra of the Raman valence band obtained before, three data sets for ANN training were formed: the training set (99 spectra in the temperature range from 20 to 80^{o}C), the test set (36 spectra in the same range), and the examination set (17 spectra in the same range). Only the most informative central part of the spectra was used. No smoothing of the curves was performed, since neural networks are stable to noise, and they reveal useful information against a noisy background, which is one of their advantages.

The calculations were made with the software package NeuroShell 2 (Ward Systems Group, Inc.). The obtained results are presented in Figure 5 as a scatter plot, where the *x* axis stands for the true temperature, and the *y* axis stands for the values determined by the neural network. The relative mean squared error of temperature determination (on the examination set) was about 0.4%, and the mean absolute error did not exceed 0.3°C.

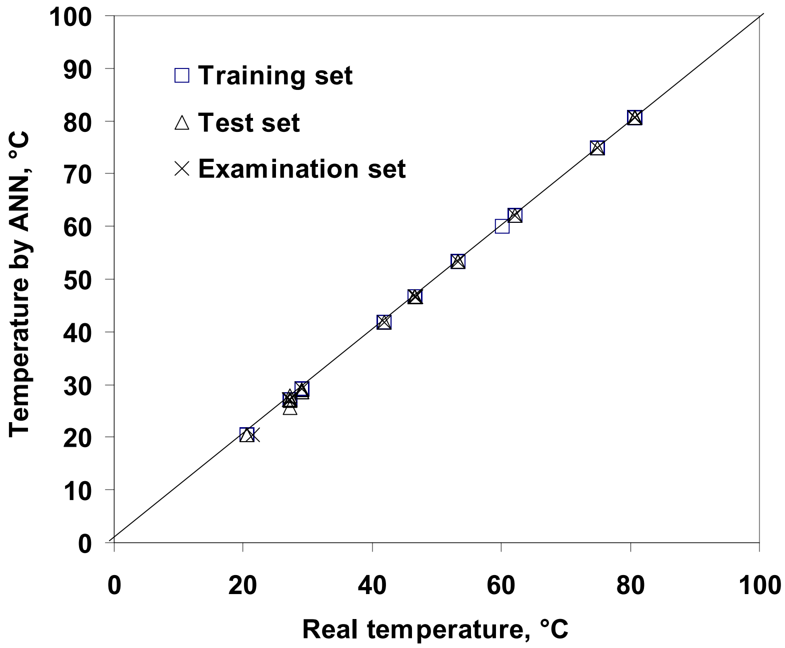

Figure 5: Scatter plot illustrating the determination of water temperature from Raman spectra with the help of ANN.

Thus, the precision of the temperature determination obtained from water Raman spectra with the help of artificial neural networks is higher than the precision of the temperature determination obtained by other methods (14).

The results should be treated as preliminary ones, since these calculations used the available experimental data that did not provide uniform filling of the whole desired temperature range.

To solve the inverse two-parametrical problem of determining temperature and salinity, several series of Raman spectra of "normal" seawater were measured. Raman spectra were recorded from water samples in the temperature range from 4 to 47°C at four salinity values (0, 10, 17, 36), corresponding to natural water in inner reservoirs and in the ocean. An Argon laser LG-106-M1 (λ_{exc}=488 nm) was used as the light source with 250 mW output power; the laser beam polarization was vertical. The Raman signal radiation scattered at a right angle was collected by a system of two lenses at the input slit of the polychromator of an OMA 1 optical multi-channel analyser (Princeton Applied Research Corp.). A grating with 550 lines per mm (low blaze) was used, providing 0.1 nm spectral resolution. The dispersion of the polychromator was 0.14 nm/channel.

To provide the necessary sample temperature during measurements, a cell system with temperature stabilization and adjustment of sample temperature was used. This device allowed an accuracy of temperature stabilization to be better than ±0.1°C during the time of recording. The range of the temperatures that could be stabilized was -60°C...+100°C. The sample volume was about 25 cm^3. Figure 6 shows representative Raman spectra.

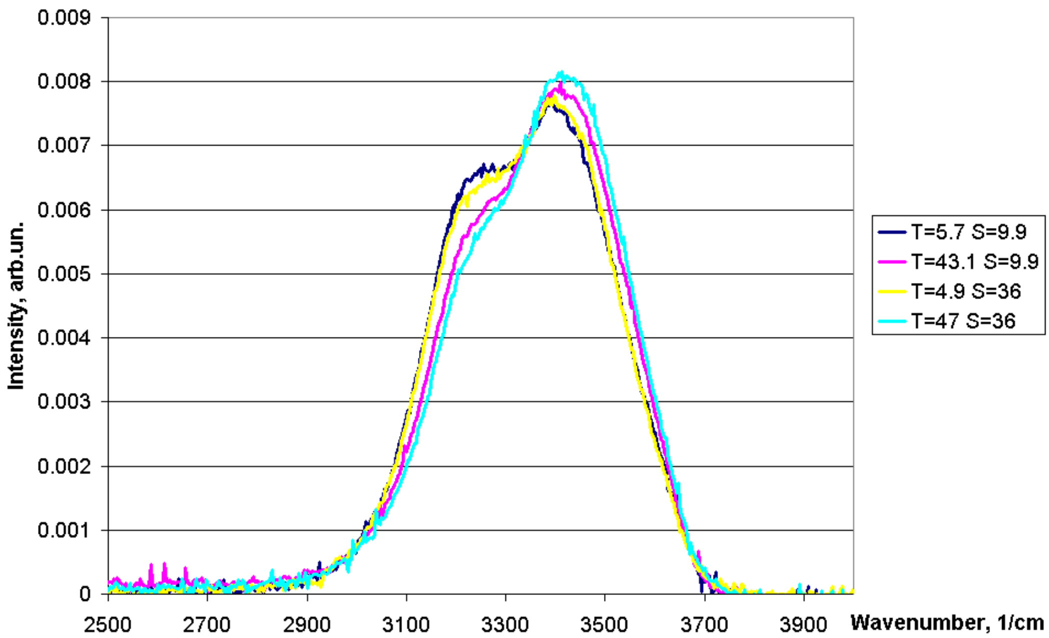

Figure 6: Experimental Raman spectra of liquid water at different temperatures and salinities.

RESULTS

Two approaches were used: 1) direct solution of the inverse problem using experimental water Raman spectra to train the ANN; 2) creation of an optimal analytical model for the dependence of the spectrum on temperature and salinity (using Group Method of Data Handling, GMDH (21)) with successive training of ANN on model spectra obtained based on this model.

In the first case, the neural networks were trained on experimental spectra. The best precision of temperature and salinity determination from water Raman spectra was demonstrated by the 5-layer perceptron. All available water Raman valence band spectra were used to compose three data sets which are necessary to train the network: the training set (117 spectra in the temperature range from 4 to 47°C and in the salinity range from 0 to 36), the test set (36 spectra in the same ranges), and the examination set (13 spectra in the same ranges). The spectra were normalized to unit area. To train and apply neural networks, the most informative central part of the spectra (200 channels) was used. No smoothing was performed.

It turned out that the mean absolute error of temperature determination did not exceed 0.5°C; the mean absolute error of salinity determination) did not exceed 0.7 (both on the examination set). It should be noted that the precision of the temperature determination from water Raman spectra, obtained by the ANN technique, is better than that obtained by other methods (14).

The second approach to water temperature and salinity determination from its Raman valence band was based on training of the ANN on model (simulated) spectra (model-based approach). Such a model was developed using the Group Method of Data Handling (GMDH) (21). The whole array of experimental spectra (166 water Raman spectra at different temperatures and salinities in the target ranges) was used to build a polynomial model of the dependence of intensity in each channel of the most interesting central part of water Raman spectra on temperature and salinity with the help of GMDH. The polynomial obtained with GMDH is optimal for the following reasons: it has a small error on the training set, and it provides a good generalization ability and to be adequate on independent data. For each channel, the model coefficients and its relative mean squared error were recorded.

The complexity of the models developed as described above in different channels varied mostly from a linear model $Y=A+B\cdot t$ to a full cubic model $Y=A+B\cdot t+C\cdot t^2+D\cdot t^3$. Only in the most complicated region of the so-called isobestic point the model turned out to be a full fourth order polynomial. GMDH has never created more complex models. For the given number and quality of experimental spectra, this fact may serve as an evidence that the temperature dependences of intensity in most studied channels of the spectra are adequately described by models which are not more complex than a cubic parabola.

To determine temperature and salinity within the model-based approach to ANN, the necessary sets of spectra were calculated using the described GMDH model. As a result, the obtained precision of temperature determinations from model curves and the one of salinity determinations were about 1.1°C and 1.5, correspondingly. This means that the number and quality of the initial experimental spectra for creating the model were insufficient to build a model good enough to provide the necessary precision. Further research in this direction should be aimed at elaboration of a more precise model.

CONCLUSION

The application of ANN to solve the inverse problem of simultaneous determination of temperature and salinity by the shape of the water valence Raman band has increased the precision of determination, but to a very small extent. Nevertheless, this result can be appreciated with optimism, taking into account that the set of experimental data used to train the network was far from optimal and that the search for *T* and *S* was performed in large ranges for both variables. For real situations, when the ranges for *T* and *S* known *a priori* are significantly smaller than those used in this paper, the training process may be significantly optimised, resulting in an increased precision of the determination of the target parameters.

The results obtained by the second approach (network training on model data) should also be considered as the initial stage. The development and the improvement of this approach are important not only for the solution of the inverse problem, but also for the investigation of the structure of valence band of liquid water.

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