

REMOTE DETERMINATION OF TEMPERATURE AND SALINITY IN PRESENCE OF DISSOLVED ORGANIC MATTER IN NATURAL WATERS USING LASER SPECTROSCOPY

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ABSTRACT

During the last years, the problem of remote determination of parameters of natural waters became very important. This is due to the fact that salinity and temperature are the key parameters determining ocean circulation, and transfer of energy and mass in conterminous layers of the ocean. The authors of this study have previously suggested and implemented a method of simultaneous determination of temperature and salinity of seawater using laser Raman spectroscopy. In this paper, the results of the next step of this work are presented: the determination of temperature and salinity of natural water using Raman spectra in presence of fluorescence of dissolved organic matter as dispersant pedestal under the Raman valence band. This inverse problem of laser spectroscopy was successfully solved using Raman and fluorescence spectra of aqueous media and using artificial neural networks.

INTRODUCTION

The necessity of global monitoring of salinity (S) and temperature (T) arises from the tendency observed during last years of decreasing of icecaps in polar latitudes because of global warming. Melting of ice leads to desalination of the surface layer of the ocean. It can give an impulse to reconstruct the oceanic current system and be the reason of considerable climate changes not only in polar areas but on a planetary scale.

It is obvious that for ecological monitoring of natural waters and for determination of such key parameters as temperature and salinity, one needs express non-contact methods of diagnostics, which can be implemented in real time. Such properties are inherent in the non-contact radiometric method of determination of either salinity or temperature of the surface of sea waters (1,2), which is most widespread in oceanology. Measurement of seawater salinity with the help of radiometers, based on the dependence of the absorbing capacity of water surface on concentration of salts, allows the determination of S with an error not better than one practical salinity unit (psu). The error of determination of sea surface temperatures with the radiometric method, e.g. the Advanced Very High Resolution Radiometer (AVHRR) (3), is 1°C . Errors in measuring T and S are mainly due to the complexity of extracting relatively small changes of thermal radiation caused by variations of salinity or temperature, against much greater signals caused by surface roughness. Besides that, the absorbing capacity of the water surface may change significantly under the influence of wind, cloudiness, and due to the presence of oil films. Methods of laser vibrational and fluorescence spectroscopy are free of these shortcomings and can provide information about water parameters at any point in the water column. The most convenient procedure here is sounding from board of a ship and obtaining the signal using a waveguide cable.

For the first time the dependence of water Raman spectrum on temperature and dissolved salts was shown in works of Walrafen (4,5,6). Soon after, the method of measuring water temperature using the water Raman valence band was elaborated (7,8,9). Authors described temperature changes by a parameter, which is derived from the ratio of intensities of high and low frequency regions of the Raman valence band. An accuracy of 0.5°C *in vitro* and 2°C in field conditions was achieved.

An advantage of using vibrational spectroscopy (in particular, Raman spectroscopy) for diagnostics of aqueous media is its high sensitivity of quantitative characteristics of spectral bands to the type and concentration of substances dissolved in water (10,11), and to water temperature (12). Experimental data obtained by different authors (10,12) and our data (11) showed that with increasing temperature and salinity the intensity of the high-frequency region of Raman spectra valence band increases, and that of the low-frequency region decreases; the band shifts to higher frequencies and the bandwidth decreases (Figures 1 and 2 from (13)).

A specific method to determine water temperature decomposes the water valence Raman band into several component curves of Gauss or Voigt shape, and the linear section of the temperature dependence of the ratio of the two most intense components (high frequency and low frequency ones) is used as the thermo-sensitive parameter (14). In (14), the achieved error of temperature measurement was 1°C.

In (15,16) it is suggested to use the linear section of the dependence of the same parameters on salinity (in (16), on concentration of dissolved salts) to measure the salinity of seawater. Unfortunately, no simultaneous measurements of temperature and salinity were performed in (15). In (16), no estimation of the error of the results was made.

Previous studies of the authors of this paper showed that temperature T and salinity S can be determined simultaneously using the shape of the water Raman band (13,17). The three-wavenumber method of simultaneous determination of temperature and salinity had an error of 0.7°C and 1.0 psu, respectively, *in vitro*, and 1.1°C and 1.4 psu in field conditions (hereinafter, the error is estimated by the mean absolute error). The application of artificial neural networks (ANN) to solve the inverse problem of simultaneous determination of temperature and salinity by the shape of the water valence Raman band has decreased the error of T and S determination *in vitro* (13) but to a very small extent, i.e., down to 0.5°C and 0.7 psu.

In this paper, the results of the next step of this work are presented, i.e., the determination of temperature and salinity of natural water using Raman spectra. New approaches make it possible to solve the inverse problem of T and S determination at a higher level in the following sense:

- taking into account the influence of dissolved organic matter (DOM) fluorescence as noise (as dispersant pedestal under Raman valence band) or as the third parameter; this procedure allows to use the method also in coastal waters;
- simultaneous use of low- and high-frequency regions of water Raman spectra (from 500 up to 4000 cm^{-1}) provides additional identifiers for T and S determination because: 1) low-frequency Raman bands depend on T and S , too, and 2) anions such as NO_3^- , SO_4^{2-} , PO_4^{3-} and HCO_3^- have their own Raman bands near 1000 cm^{-1} ; and this spectral information is useful for a more accurate determination of S .

Artificial neural networks (ANN) were used as modern methods to solve multi-parametrical inverse problems and pattern recognition problems.

METHODS

A solution of the given inverse problem with ANN assumes obtaining a representative database of experimental spectra with different values of the sought-for parameters temperature, salinity, and concentration of dissolved organic matter. To prepare the solutions, bi-distilled water, sea salt, and river humus were used. Solutions having salinities between 0 and 45 psu in step of 5 psu and in a DOM range from 0 to 350 mg/l were prepared. The temperature of the solutions was changed between 0 and 35°C in 5°C steps. The specified parameter ranges were selected according to natural temperature and salinity variabilities of seawater. The chosen DOM range is wide enough to use this method not only for diagnostics of waters in the open ocean but also in coastal zones and in the regions of river mouths.

Raman spectra of the solutions were recorded in the wavenumber range from 800 to 4000 cm^{-1} with a Raman spectrometer (Figure 1). Excitation of Raman scattering in water was done with an argon laser with 488 nm wavelength and an optical power of approx 500 mW. To suppress scat-

tered radiation at non-shifted frequency, an interference edge filter (Semrock) was used, which made it possible to approach the excitation laser line down to 100 cm^{-1} . Spectra registration was done with a CCD camera in a parallel detection mode (Jobin Yvon, Synapse1024-128 BIUV-SYN). Prior to registration, the scattered radiation passed a double monochromator (Acton 2500i, grating 900 lines/mm, focal length 500 mm). The spectral resolution of the Raman spectrometer was 2 cm^{-1} .

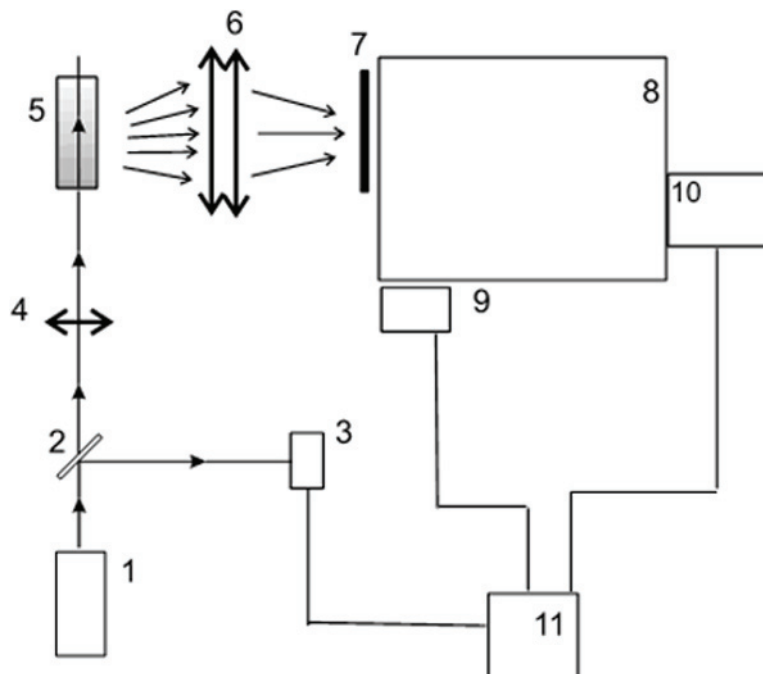


Figure 1: Scheme of the experimental setup. 1: argon laser (488 nm), 2: beam splitter, 3: laser power meter, 4: focusing lens, 5: thermo stabilised cuvette, 6: system of lenses, 7: edge-filter, 8: monochromator, 9: photomultiplier, 10: CCD camera, 11: computer.

During the experiment the sample temperatures were set, controlled and measured with a special thermostatic system, which provided control and measurement of water temperatures within 0.1°C . Spectra were normalised to the power of laser radiation and to the spectrum accumulation time.

In Figure 2 panoramic Raman spectra of solutions are shown in a wide spectral range of $800 - 3800\text{ cm}^{-1}$ and a wide range of temperature, salinity and DOM concentration. Registration was performed with a photomultiplier tube (PMT) (a CCD is sensitive in a narrow spectral range only). That is why the quality of these spectra is not so high (for example, in comparison with Figures .3 and 4). Hereafter these spectra were not used for training ANN.

As already stated above, at this stage of the study, measurements of the valence band were supplemented by an additional set of identification features: the low-frequency region of water Raman spectra from 800 up to 1800 cm^{-1} (Figure 2), which depends on T , S and DOM as well and can have its own Raman bands from anions as NO_3^- , SO_4^{2-} , PO_4^{3-} , HCO_3^- . Besides that, the method was elaborated taking into account dissolved organic matter (DOM) fluorescence as noise (as dispersant pedestal under Raman valence band) or as a third parameter

All spectra used with the ANN were measured at the same experimental conditions: the camera exposure time was 5 s for valence bands and 10 s for low-frequency bands (averaging of 10 spectra).

In this study, the inverse problem of determining T and S of seawater by Raman spectra in presence of DOM fluorescence was solved with ANN within the "experiment-based" approach (18). That is, the data used for ANN training are obtained experimentally. This approach does not require a model to be available, and it makes it possible to take non-linear properties of the object into account.

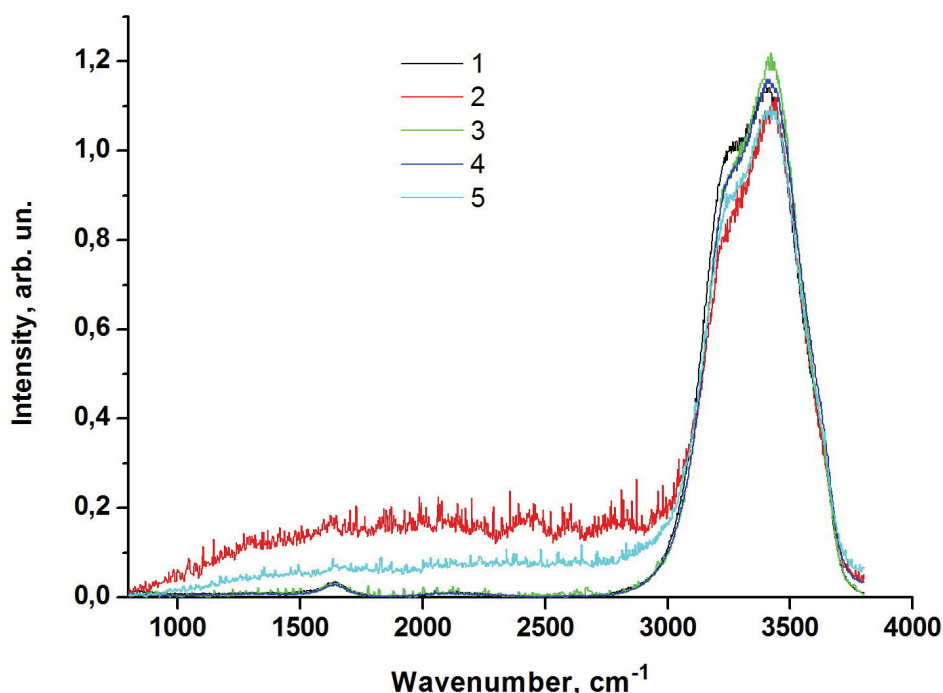


Figure 2: Raman spectra of aqueous solutions with the following set of values of T , S , and DOM parameters in $^{\circ}C$, psu and mg/l . 1: 25-0-0; 2: 25-45-350; 3: 50-0-0; 4: 25-45-0; 5: 25-45-175.

The design of the ANN consists in the choice of the net architecture (topology) and training parameters (19). The most widely used architecture is a multilayer perceptron, a net consisting of at least three layers: input, output, and one or more hidden, each neuron in the layer being bonded to all neurons of the next layer. These nets are trained by means of a back propagation algorithm. In contrast to the simple neuron (one layer perceptron) the topology allows to solve complex problems. Another type of ANN is general regression (GRNN) (20). These nets remember train examples exactly and produce results relying on weighted train examples which are close to submitting an example in some sense.

We tested a number of ANN architectures and picked out the best nets:

- three-layer perceptron having 16 neurons in the hidden layer;
- five-layer perceptron having 16-8-4 neurons in the hidden layers;
- GRNN: the smoothing parameter is chosen using a test set.

RESULTS

Two bands of a Raman spectrum were recorded in the frequency regions $800\dots1800\text{ cm}^{-1}$ (low-frequency band) and $2200\dots4000\text{ cm}^{-1}$ (valence band) (Figures 3 and 4, respectively). The low-frequency band (Figure 3) includes a Raman band of the sulphate anion SO_4^{2-} in the region of 1100 cm^{-1} , a water Raman bending band in the region of 1630 cm^{-1} , and DOM fluorescence. All these bands depend on T , S and DOM concentration. Therefore in this study this low-frequency band is used as an additional set of identification features for ANN-based pattern recognition for Raman spectra of natural waters.

In Figure 4, the dependence of water Raman bands on T and S is presented. The presence of DOM is manifested in its changing fluorescence, i.e., a change of pedestal under the valence band at wavenumbers of 2200 cm^{-1} and higher.

For ANN use, the whole obtained array of data (482 spectra) was randomly divided into training, test and examination sets at a 70:20:10 ratio.

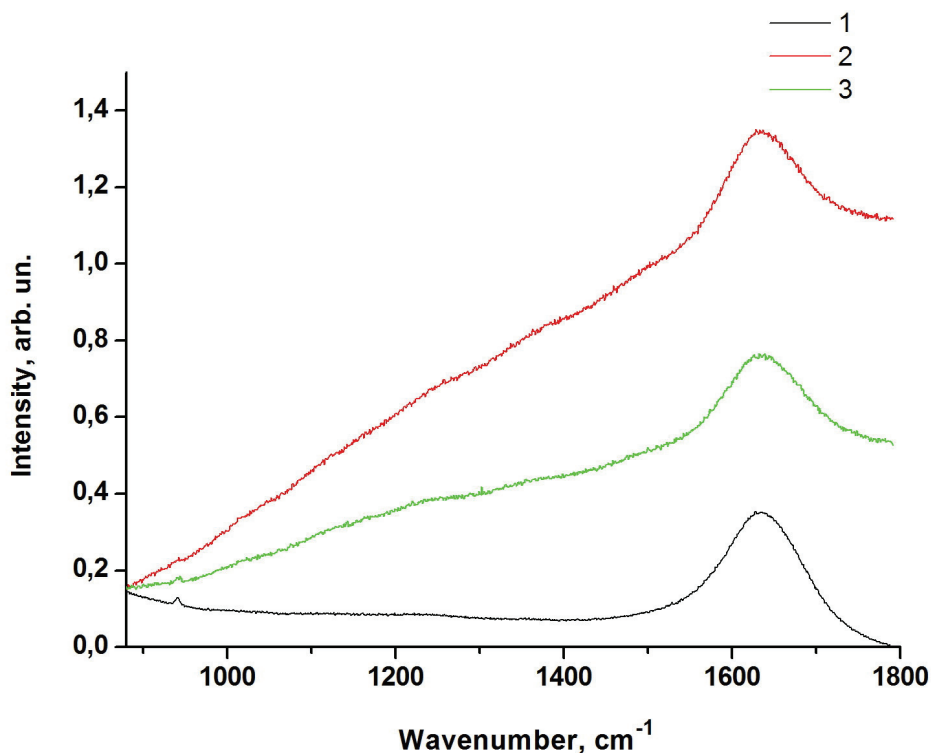


Figure 3: Low-frequency Raman bands of aqueous solutions with the following set of values of parameters in °C, psu and mg/l. 1: 15-40-0; 2: 25-15-175; 3: 21-15-58.3.

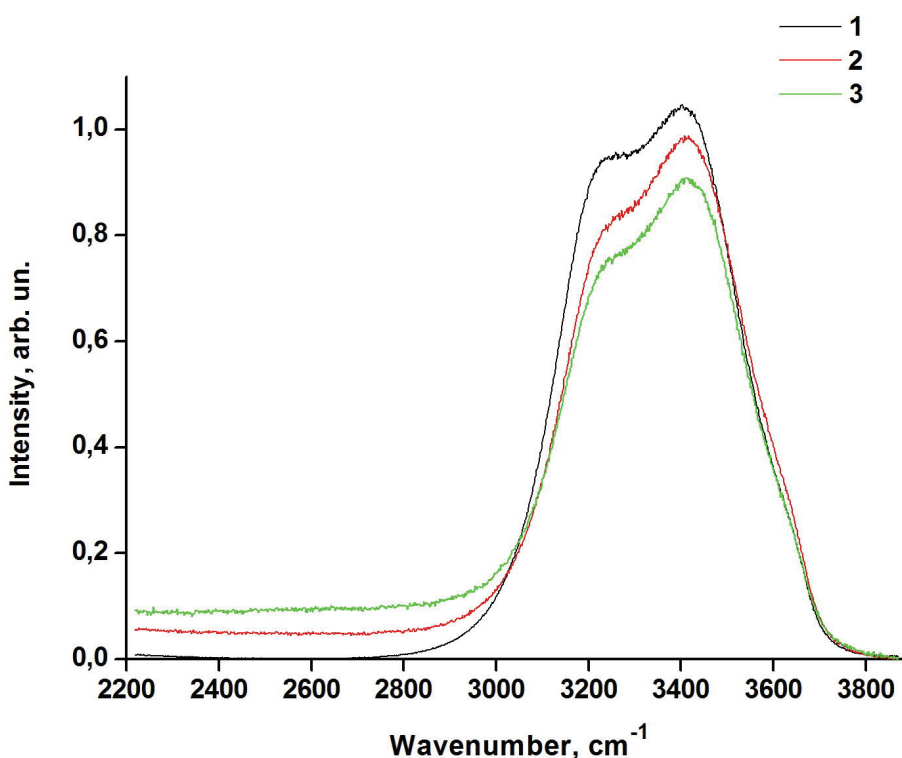


Figure 4: Raman valence bands of aqua solutions with the following set of values of parameters in °C, psu and mg/l. 1: 0-25-0; 2: 25-15-175; 3: 15-45-350.

Table 1 presents the results of the inverse problem solution using different ANN architectures for two cases: using the Raman valence band only, and using the low- and high-frequency Raman bands to determine T and S in the presence of DOM.

Table 1: Comparative results of use of different ANN architectures for determination of seawater temperature and salinity by water Raman spectra, in presence of DOM fluorescence, DOM range 0÷350 mg/l.

Method of solution of the inverse problem, ANN architecture	Absolute errors of determination of temperature, °C (range 0÷35 °C)			Absolute errors of determination of salinity, psu (range 0÷45 psu)		
	Mean	Min	Max	Mean	Min	Max
Using high-frequency (valence) Raman spectra bands						
Three-layer perceptron	1.4	0.4	2.4	1.6	0.5	2.7
Five-layer perceptron	1.2	0.2	2.0	1.5	0.4	2.4
GRNN (General Regression NN)	1.1	0.2	2.8	1.6	0.5	2.9
Using low- and high-frequency Raman spectra bands						
Three-layer perceptron	1.1	0.3	2.0	1.2	0.5	2.5
Five-layer perceptron	0.8	0.1	1.7	1.1	0.3	1.8
GRNN (General Regression NN)	0.9	0.3	1.8	1.2	0.4	2.0

As can be seen, the method of T and S determination using low- and high-frequency regions of water Raman spectra and ANN (five-layer perceptron) allows the determination of T and S with mean absolute errors of 0.8°C and 1.1 psu, respectively. Using both regions of the Raman spectrum provides a lower error of T and S determination even in a wide DOM concentration range.

CONCLUSIONS

In this paper it is demonstrated that the method using low- and high-frequency regions of water Raman spectra simultaneously and ANN (five-layer perceptron) allows the determination of T and S with an accuracy of 0.8°C and 1.1 psu, respectively, in presence of fluorescence of dissolved organic matter (DOM) as dispersant pedestal under Raman bands.

This study is the first stage of elaborating the method of remote determination of T and S of seawater through solving a two-parameter problem using the “experiment-based” approach. In future, it is planned to apply the “quasi-model” approach to the available experimental data. Within this approach, the dependence of the Raman spectra intensity in each point on the sought-for parameters is described by a polynomial “quasi-model”. Then this “quasi-model” is used to increase the representativeness of the data sets by modelling the necessary amount of Raman spectra.

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