DETERMINATION OF SALT COMPOSITION IN WATER BY RAMAN SCATTERING SPECTROSCOPY*

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One of the important tasks in study of aqueous media of coastal zones is determination of water parameters, primarily, water temperature and salinity. A more specific and a much more complex problem is determination of the list of components present in the dissolved state in aqueous media, and of the concentration of each of the components.

Usually, this problem is solved either by chemical methods, or by using ion-selective electrodes. In the last case, determination of pH of the solution, or of concentration of any salt, is based on the measurement of the conductivity of the studied solution using the specific selective electrode for each studied ion. Both these methods can provide high measurement precision, but they require direct chemical contact with the studied solution, and are relatively slow. An alternative family of methods are the methods of spectroscopy, which do not require direct contact of the measuring device with the studied medium. Thus, the measurement can be conducted through a closed transparent vessel (bottle), or during off-board measurement of nature waters from a ship. Also, fast extraction of information from the spectra enables online use of spectroscopy methods.

The lecture is devoted to the discussion of Raman spectroscopy as an instrument for remote express determination of salt composition of aqueous solutions, and it consists of three main parts. First, Raman scattering is briefly described, and its properties are discussed. As any other spectroscopic method, Raman spectroscopy uses the dependence of the shape of spectra on the studied properties of the medium, in this case – on the concentrations of ions present in the medium. Complex ions consisting of several atoms have their own Raman lines, the intensities of which are proportional to their concentrations. Simple single-atom ions affect the shape of the Raman band of water; the quantitative characteristics of the change are also proportional to the ion concentration, and are different for different types of ions. The sensitivity of the spectra to ion concentrations is quite high. All this provides necessary conditions for use of Raman spectroscopy for determination of concentrations of ions in water solutions.

In the second part of the presentation, experimental technique of Raman spectroscopy of liquids is discussed: sources of excitation, scattering schemes, means of spectra registration. The most popular type of Raman spectrometer for liquid media, including continuous wave laser source, an optical system, and a broadband CCD camera registration, is described.

The third part of the lecture is devoted to spectra processing. While the described properties of the Raman spectra allow one to determine the concentration of a salt in a single-component solution by Raman intensities in one or several channels of spectrum, the situation is much more complicated for the case when multiple salts/ions are present in the studied medium/solution. Due to non-linear interaction between different ions, and also with water molecules, the dependence of the shape of Raman spectrum on the concentrations of the components in multi-component solutions is much more complex. To extract the necessary information from the spectrum, one needs to analyse the intensities in multiple channels. What is worse, for the described reasons, at present there is still no analytical or computational model capable of modelling the shape of the Raman spectrum as a function of concentrations of ions. So probably the only way out is use of computational methods capable of training by examples, such as artificial neural networks (ANN).

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An ANN trained on a sufficiently large array of experimental spectra with known concentrations of ions (determined by alternative methods) turns out to be capable of simultaneously determining presence and concentrations of multiple ions with a reasonably small error – within 5% of the maximum concentration of an ion over the solutions, on the spectra of which the ANN was trained. Additional data processing methods that can be used together with ANN to improve the precision of the method in the whole are briefly discussed.

The presentation is illustrated by the results obtained by the lecturer and her colleagues for multi-component solutions containing 5 salts composed of 10 different ions (a special statement of the problem for determination of concentrations of salts), and for multi-component solutions containing 10 salts composed of 10 various ions (in the modes of salt determination and ion determination).

Possible practical applications of the described complex method (Raman spectroscopy + ANN data processing) include diagnostics of nature waters, including mineral waters, and also industrial and waste waters. In each case, the ANN should be trained on an array of spectra including the target ions in the required concentration ranges.