DOI: http://doi.org/10.21698/simi.2024.ab17

DETERMINATION OF THE CONTENT OF HUMIC SUBSTANCES IN THE NATURAL WATERS OF THE REPUBLIC OF MOLDOVA

Diana Shepel, Maria Rusu, Tudor Lupascu

Institute of Chemistry of the Moldova State University, 3 Academiei, MD-2028, Chisinau, dianashepel@gmail.com, Republic of Moldova

Keywords*: humic substances, methylene blue, spectrophotometric determination*

Introduction

Humic substances (HS) are organic mixtures of complex composition formed in soils as a result of the chemical and biological decomposition of plants and animals. In the structure of HS, aromatic blocks are connected by aliphatic bridges. Due to carboxyl, hydroxyl, carbonyl groups, and aromatic fragments, HS could be involved in ionic, donor-acceptor, and electrostatic interactions with various organic and inorganic substances. The quality of water used in the food industry depends on the content of HS. Therefore, monitoring their content in natural waters is important. Water-soluble HS may enter into natural waters when wastewater is discharged into water bodies. Existing spectrophotometric methods for the determination of HS, are based on the optical density measurement of an extract from the dry residue of water using toluidine blue. These methods have several significant shortcomings, such as the complexity and length of HS isolation and the absence of HS characteristic absorption maximum. The maximum limit of determination of HS with toluidine blue is less than 40 mg/L. The result of HS determination in water is influenced by various cations, polysaccharides, carbonates, and silicates. Instead of toluidine blue, we proposed the use of the basic dye methylene blue (MB) for the analysis of HS.

Materials and methods

The determination of HS was carried out according to the method described in Patent MD 4305 B1 2014.09.30. The spectrophotometric method of determination was based on the interaction of HS with MB. HS was extracted with methanol from the dry natural water residue. The dry residue of the methanolic extract was dissolved in distilled water; an aqueous solution of MB was poured into the dry residue solution of the methanolic extract of HS. The initial solution of MB and the solution with the associated "humic substances - methylene blue" (HS-MB) were subjected to photometric analysis after 20 minutes at a wavelength of 609-611 nm. The content of HS was determined by the difference ΔA of light absorption between the MB solutions and the MB associated with HS at 609-611 nm. Spectra in the region of 190-1100 nm were recorded on a Lambda 25 spectrophotometer (PerkinElmer, USA, 2005); the thickness of the absorbing layer was 1 mm. The content of HS was determined in water samples from sources in the areas of Calarashi, Sarata Noua, Hinceshti, Costeshti, and the Dniester River water of the Tiraspol region. The error in the HS determination content did not exceed 5%. IR spectra were recorded on an FTIR Spectrometer Spectrum 100 instrument (PerkinElmer, USA, 2005) in the range of 4000-650 cm^{-1} using an ATR attachment.

Results and conclusions

Rapid and efficient extraction of HS with methanol was proposed. Inorganic salts, polysaccharides, and polypeptides that interfere with determination did not pass into the methanol extract. It was found that MB had interacted with HS according to the same principle as toluidine blue. Quantitative determination was based on measuring the difference in light absorption between the original MB solution and the MB solution with the addition of HS; as a result, a decrease in the light absorption of the 609 nm band of MB was observed with increasing HS content in water.

The effect on the interaction with MB of organic substances extracted with chloroform from the dry residue of Hincesti natural water was studied. Organic substances dissolved in natural water were heterogeneous. In addition to HS, they also contained a group of compounds that did not interact with MB. Non-humic substances extractable with chloroform were esters of polymeric fatty acids formed as a result of the decomposition of organisms that did not contain lignin.

Non-humic organic substances dissolved in natural waters practically did not affect the result of HS determination with MB. SiO_2 silicates, as mineral components of the dry residue of the investigated water, interacted with MB, forming a precipitate, which influenced the result of the analysis.

When analyzing natural waters, components that interfere with the determination of HS were separated during extraction with methanol. In this case, neither $CaCO_3$ nor SiO_2 passed into the solution, which was confirmed by IR spectroscopy. In the IR spectrum of the dry residue of water from Hinceshti after extraction of HS, intense bands were observed: $\nu_{as}(CO_3^{2-})$ = 1437 cm^{-1}, $\nu_s(CO_3^{2-})$ = 865 cm^{-1} and $\nu(SiO_2)$ = 1111 cm^{-1}. These bands were absent in the spectrum of the dry residue of the methanol extract.

The proposed method allowed the increase of the sensitivity of the analysis by 50 times compared to the method which involved toluidine blue. According to the elaborated method, 0.267 mg/L of HS was determined in natural well water in the Hinceshti region, 0.209 mg/L in the Costeshti region, 2.330 mg/L in the Sarata Noua region, 4.170 mg/L in the Calarashi region, 0.376 mg/L in the Dniester River of the Tiraspol region. As can be seen from the results, the content of HS varied between the sampling points and could affect the quality of natural water.

Acknowledgment

The investigations were carried out within the project of the Moldovan State Program 2024-2027 with the title "Advanced research in computational and ecological chemistry, identification of technological procedures for treatment, formation of water quality and quantity", code 010603.