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Manganese determination in coastal water

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Abstract. The present work describes the application of spectrophotometric method for the determination of manganese (Mn) used in water samples collected from the coastal zone of the Black Sea. We studied a colorimetric method for the determination of manganese using UV-VIS molecular absorption spectrophotometry. We measure absorbance of the 450 nm charge transfer band of permanganate. In all analysed samples we found that the levels of manganese did not exceed the pollution threshold.

1. Introduction

Manganese (Mn), an important micronutrient, is an indispensability for the appropriate function of a few enzymes in plant, plays a vital role in photosynthesis by aiding in chlorophyll synthesis and produces oxygen needed for normal marine life [1]. Manganese accelerates germination and crop maturity while increasing the availability of calcium and phosphorus in marine plants [2].

Is an essential micro-nutrient for most marine organisms for the function of the brain, normal bone growth, in nervous system: it maintains the electrical potential in nerves [3].
Sea food as a whole food has a wide variety of nutrients elements that are absorbed easily in the digestive system and is one of the best dietary sources of food, therefore, it is essential to know the nutritional value of water, in order to quantify its health benefits [3].

The values of the manganese in water must be compared with the values of the element in marine plant samples, in fish samples, due to the relationship of all in marine system. The concentrations of the micronutrient could be analysed due to the fact that accumulation of these elements from the aqueous environment by fish, depends upon the availability and persistence in water, plant, fish diet, during all stages of the life cycle.

Thermodynamically, in most oxygenated marine waters, at an approximate pH of 8 the stable form of manganese is manganese oxide MnO_2 insoluble. Under reducing conditions it may be present as the free Mn^{2+} ion, as soluble inorganic complexes or, more likely, as insoluble oxides and carbonates. Dissolved Mn costal water profiles reveal that the surface waters contain high levels of soluble Mn^{+2}. A portion of the soluble Mn is from direct dissolution of dust which contains Mn^{+2}. Slow oxidation to the Mn^{+3} or Mn^{+4} allows Mn to stay dissolved on the order of days. The oxidation of Mn^{+2} is rapid under opportune conditions, especially when increased by the catalytic action of micro-organisms to reach equilibrium in natural ecosystems. However, Mn still should oxidize over time and precipitate out of the surface water [4].

The reactivity and solubility of manganese in living systems is strongly dependent on redox conditions. Most manganese salts, with the exception of phosphates and carbonates, are soluble in water [5,6].

Manganese is considered to be the 12th most abundant element in the biosphere. It is widely distributed in water, soil, sediment and biological matrix. Manganese has cumulative properties [7]. The major sources of this micro-nutrient for the Black Sea are rivers and atmospheric deposition [8,9].

Concentrations of manganese in open seawater range from 0.05 to 0.3 mg/L, 0.05 mg/L in drinking water, 1 mg/L in waste water discharged into the natural receptors in accordance to SR 8662-1:1997, SR 8662-2:1997 and SR ISO 6333:1996. In Europe, the Directive 2006/60 EC is an important guideline for the regulation of water areas [10].

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis.

2. Spectrophotometric analyses and pH measurement

Absorption spectra and absorbance measurements were determinate by a JASCO V_630, UV–VIS spectrophotometer using 1 cm quartz cells (1.0 mL).

pH measurements of the water samples tested in this study were made by a pH-meter Consort C932.

3. Reagents

Water samples were collected in 12 clean glass bottles samples and were collected from the coastal zone of the Black Sea in July, August and September 2016. All the collected samples were conserved and analysed according to standards methods [11-13].

All the mentioned samples were filtered through a 0.45 µm membrane filters to remove the suspended and floated particles. The parameters pH and temperature were determined at the time of sampling.

4. Results and discussion

pH is a measure of the acidic or basic (alkaline) nature of a solution. The pH was varied between 7.6 and 8.6.

The results are presented in figures 1 and 2 and show that the levels presented were in conformity within the allowed limits.

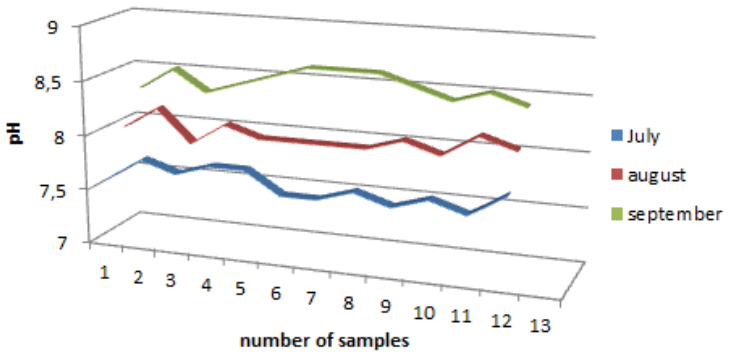

Figure 1. Variation of pH

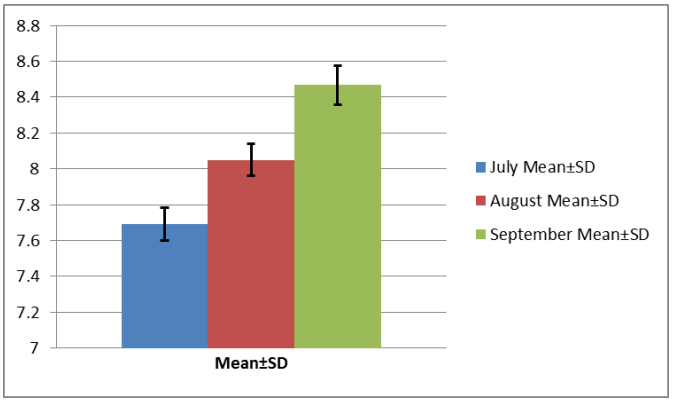

Figure 2. Mean of pH ± standard deviation

The absorbance of the prepared solutions was determined at 450 nm. Calibration curve was constructed with twelve points, as shown in Figure 3.

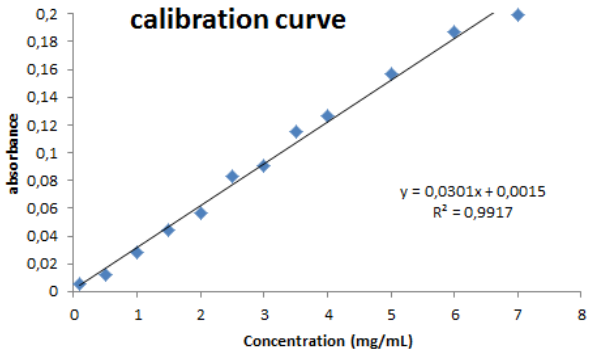

Figure 3. Calibration curve for manganese

Regression analysis of the Beer plots showed good correlation in the concentration ranges of 0.10–7.00 mg/mL for Mn^{+2}. Twelve points calibration curve were obtained. The response was found to be linear in the investigated concentration range and the statistical data are presented in Table 1.

Table 1. Calculated parameters of the linear regression analysis

Statistic parameter	Values
Concentration range (mg/mL)	0.1-7.00
Regression equation	y= 0.0301 x + 0.0015
Slope of the regression line	0.0301
Intersection to the origin	+0.0015
Regression coefficient r	0.9958
Determination coefficient r^2	0.9916
Standard deviation SD	0.0660
Residual standard deviation	9271.11

The data obtained are presented in Figure 4 and show that the values were within the permissible limits.

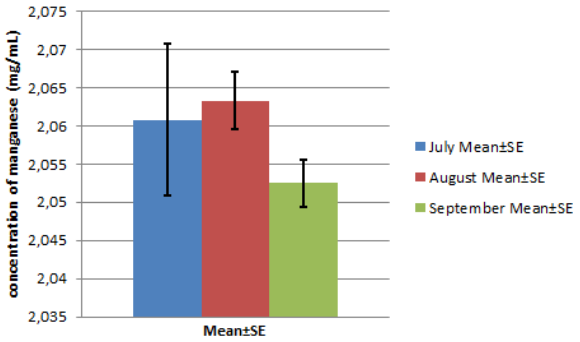

Figure 4. Determination of manganese in water samples spikes with 2 mg/mL working solution

Conclusions

In this work, we studied a colorimetric method for manganese, measure absorbance of the 450 nm charge transfer band of permanganate. In all analysed samples we found that the levels of manganese are in conformity concentration. No significant difference was observed in the amount of manganese between the different samples of water in terms of concentration. We also analysed the pH of the samples and the results indicated that the levels presented were in conformity within the allowed limits.

Is important to study all the physic-chemical parameters that contribute to the quality of marine water such as pH and concentration of manganese and all factors involved and relevant to surface water and industrial process.

It should be emphasized that the results obtained during the present study is that it is an initiating phase for the qualitative and evaluation of physical – chemical parameters which can influence the quality of marine water from the Black Sea coast. The water is an important factor for the ecological equilibrium, and its pollution is a current issue with consequences more or less severe to the living environment.

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