Study of the features of determination of heavy metals in bottom sediments

IOP Conf. Series: Earth and Environmental Science **1348** (2024) 012014 doi:10.1088/1755-1315/1348/1/012014

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Abstract. In the work with the application of the atomic absorption method, the peculiarities of the influence of sample preparation on the degree of extraction of heavy metals in samples of bottom sediments were analyzed. Acid, acid-microwave sample preparation and their variations were used in the study. It was found that the greatest influence of the type of sample preparation on the degree of extraction is observed for iron and manganese. For zinc, the smallest dependence of the type of sample preparation on the completeness of its extraction from bottom sediments was noted. There is an ambiguous influence of the type of sample preparation on the degree of extraction for cobalt, copper and nickel, which may be related to the peculiarities of the chemical composition of the bottom sediments.

1. Introduction

The significant impact of anthropogenic load today leads to serious environmental pollution [1]. One of the vulnerable components is the water environment. The need of cities for drinking water quality, the need to provide the production cycles of enterprises and the agricultural-and-industrial complex with a sufficient amount of water force researchers to carefully monitor the quantity and quality of available water resources [2, 3]. At the same time, the intensification of agriculture with the use of various chemical additives [4], plant protection products, fertilizers and pesticides significantly worsens the condition of soil and nearby water bodies [5-7]. One of the factors that is difficult to control, but which affects the environment, is emergency situations [8]. Various negative impacts are caused by fires, industrial accidents, epidemics, etc [9-13]. The unprovoked aggression of Russia in 2022 led to large-scale hostilities on the territory of Ukraine and enormous pollution of its territory [14, 15]. In addition to the direct physical danger due to the presence of explosive objects in the environment [16], there is

also a long-term effect of the chemical component of these munitions with heavy metals and organic pollutants entering water bodies, air and soil [17, 18].

In the future pollutants may accumulate in living organisms [19] and cause toxic effects [20]. These can be both heavy metals and, for example, fluorine- and chlorine-organic compounds [21].

The migration of hazardous compounds includes not only their entry into the aquatic environment, but also their accumulation in bottom sediments [22, 23]. Considering the heterogeneous composition of this component of the environment, an important stage of its qualitative research is the correct preparation of the sample for research [24].

However, the use of various solvents such as hydrogen chloride, hydrogen fluoride, nitric acid or their combinations [25-27], alkaline medium [28], application of the microwave decomposition procedure [29-31], comparison of different sample preparation methods [32, 33] indicate the ongoing search for optimal approaches of the sample preparation of bottom sediments.

The purpose of this work is to study the specifics of determining a number of heavy metals in bottom sediments of a natural water body.

2. Methods

Reagents. State standard samples (Physical Institute named after A.V. Bogatsky, Ukraine) were used to prepare working solutions of metals (Fe, Mn, Cu, Co, Ni, Zn). The solutions were prepared in bidistilled water. Other used reagents were qualified not lower than “chemically pure”.

Equipment. The Milestone ETHOS EASY system was used for microwave preparation of the samples, the content of metals in the samples was determined on an Agilent Technologies 240FS AA atomic absorption spectrometer (acetylene-air flame). The samples were weighed on electronic analytical scales with an accuracy of 0.0001 g and electronic techno-chemical scales with an accuracy of 0.001 g.

Experiment methods. Bottom sediment samples were freed from foreign impurities and dried. A sample weighing 200 g was taken by the “quarting method”, crushed and sieved through a sieve with a hole diameter of 1 mm, then reduced to a representative sample, ground in a mortar to a powdery state, and transferred to bags, which were then stored in a desiccator [34, 35].

The samples were prepared in three ways by heating acid decomposition (HNO_3), by heating acid decomposition with microwave treatment of nitric acid and a mixture of nitric, and hydrofluoric acids.

In the case of acid decomposition of the samples, the weight of the bottom sediments, taken with an accuracy of ± 0,001 g, was transferred to a heat-resistant glass, 10 ml of HNO_3 (diluted 1:1) was added, covered with a watch glass and boiled for 10 minutes. Next, 5 ml of concentrated HNO_3 was added, heated for 30 min, and after reducing the volume to 5 ml, the mixture was cooled. Then, 2 ml of water, H_2O_2 (w = 30 %) were added until the end of gas bubbles, boiled until the volume was reduced to 5 ml. After that, 10 ml of concentrated hydrochloric acid were added and boiled for another 15 minutes. The contents of the beakers were cooled and transferred to volumetric flasks with a capacity of 100 ml, filtering through a “blue ribbon” filter [36].

For acid decomposition of samples (HNO_3) with microwave treatment, the weight of the sample, taken on an analytical balance with an accuracy of 0.0001 g, was transferred to an autoclave glass, treated with 10 ml of HNO_3 (conc.) and heated to a temperature of 180 °C for 10 min, then kept at this temperature for 10 min. With the simultaneous placement of 3 samples, the power of microwave radiation was 800 W. At the end of the program, the contents of the glasses were quantitatively transferred through a “blue tape” filter into volumetric flasks with a capacity of 25 ml [37].

For acid decomposition of samples using a mixture of acids and microwave treatment, a sample weight taken with an accuracy of 0.0001 g was transferred to an autoclave glass, treated with 9 ml of HNO_3 (conc) and 3 ml of hydrofluoric acid. Then the mode was used, as in the previous version. After the end of the program, the samples were extracted and cooled, 10 ml of H_3BO_3 (w = 3%) were added and again placed in the microwave system in the heating mode to 170°C for 45 min. Then the contents were quantitatively transferred into volumetric flasks with a capacity of 25 ml [38].

Each study was conducted 3 times (n = 3), the obtained results were processed using standard statistical approaches. The relative root mean square deviation for all studied results did not exceed 3.6 %.

With each method of sample preparation, a “blank sample” was prepared, which passed all the stages of sample processing, but did not contain the weight of the bottom sediment sample.

Grading solutions of metals were prepared by diluting the standard metal solution. 0.1 ml of concentrated nitric acid and an aliquot of the standard solution were added to volumetric flasks with a capacity of 50 ml.

The analytical signal was measured at the following wavelengths: Fe: 372.0 nm; Mn: 279.5 nm; Zn: 213.9 nm; Cu: 324.8 nm; Co: 240.7 nm; Ni: 232.0 nm.

3. Results and discussion

The paper investigated the features of determining the content of heavy metals in bottom sediments of the Danube River (Ukraine). For analysis, 6 samples of bottom sediments, taken from different sections of the river, were prepared. Given that the content of heavy metals in bottom sediments is not regulated by the legislation of Ukraine [39], it is important to conduct a comparative analysis of the influence of different methods of sample preparation for analysis on the final result of the determination of heavy metals.

The results of the determination of the content of heavy metals (*C*, mg/kg) in bottom sediment samples (1-6) are presented, respectively, in figures 1-6.

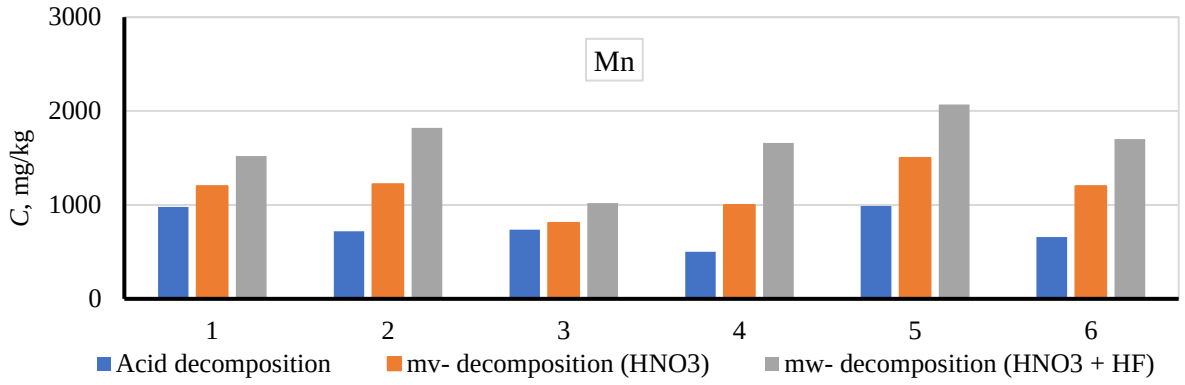

Figure 1. Results of determination of manganese in bottom sediment samples using different methods of sample preparation.

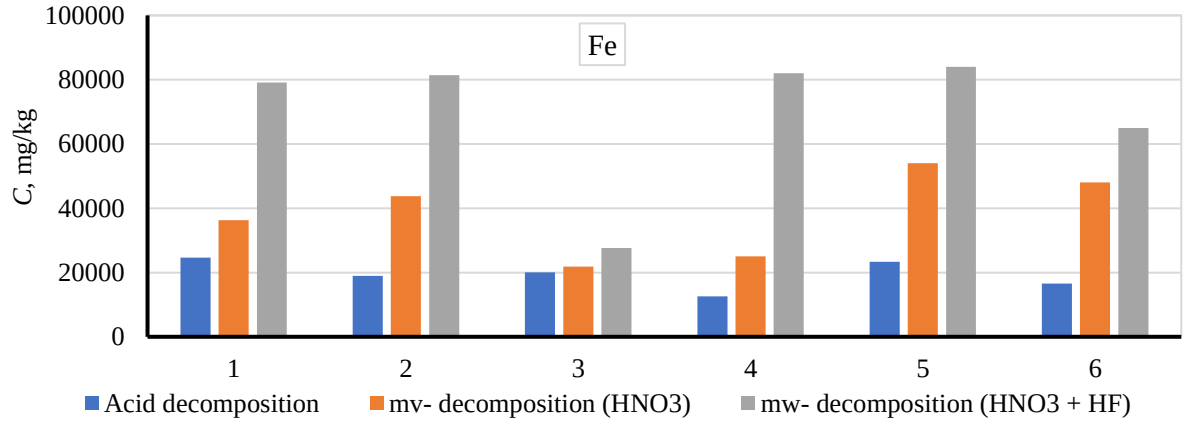

Figure 2. Results of determination of iron in bottom sediment samples using different methods of sample preparation.

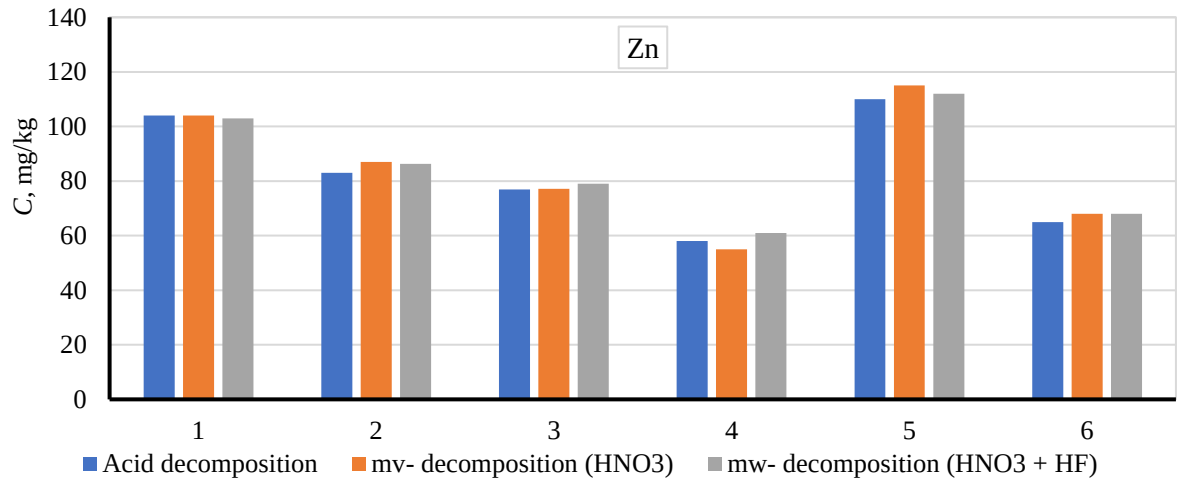

Figure 3. Results of determination of zinc in bottom sediment samples using different methods of sample preparation.

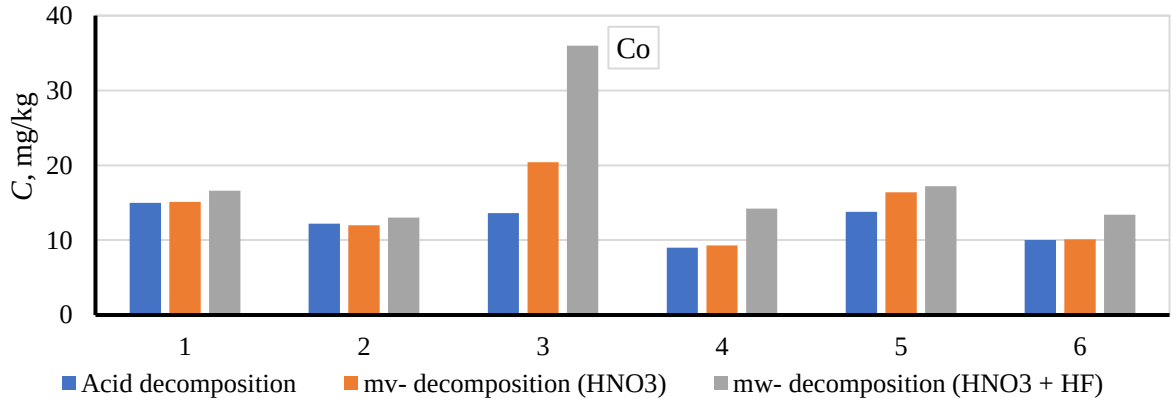

Figure 4. Results of determination of cobalt in samples of bottom sediments using different methods of sample preparation.

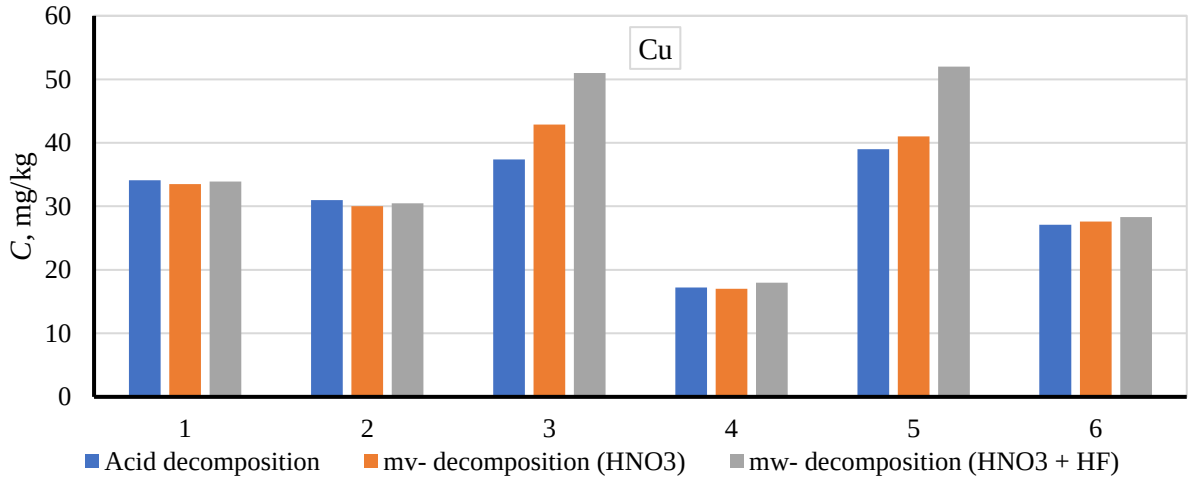

Figure 5. Results of determination of copper in bottom sediment samples using different methods of sample preparation.

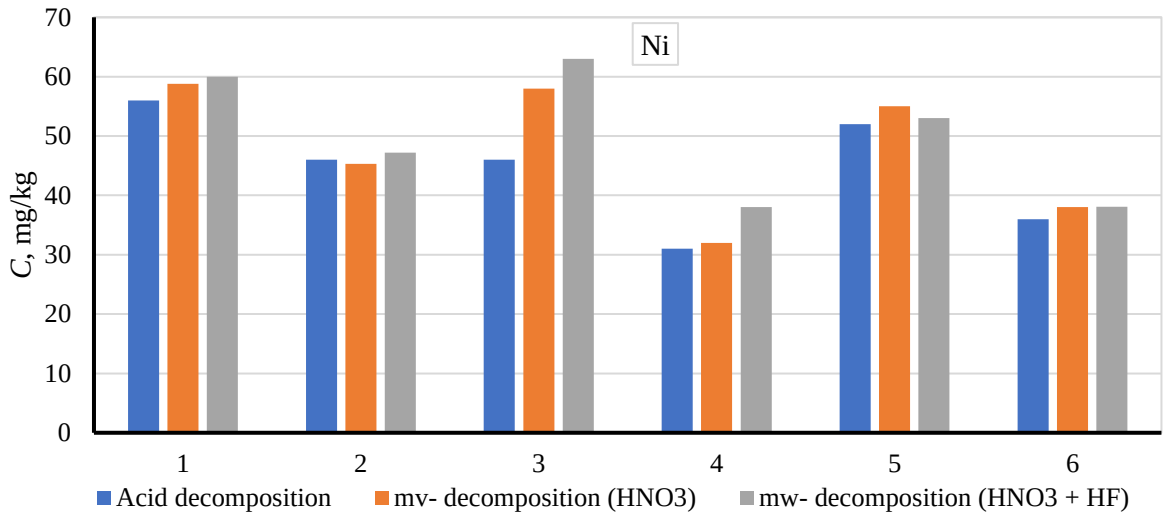

Figure 6. Results of determination of nickel in samples of bottom sediments using different methods of sample preparation.

The addition method was used to check the correctness of the obtained results. Cu, Ni, Zn were introduced into sample 5 at the stage of weighing and three methods of sample preparation were carried out. The results are presented in table 1. As can be seen from the obtained data, there is no systematic error in the analysis results.

As can be seen from the data obtained, the biggest differences between the content of the specified metal and the type of sample preparation are observed for iron and manganese. As the intensity of sample preparation increases, the completeness of extraction of these components increases. Also, the concentration values of these components are the highest and reach about 80.000 mg/kg and 2.000 mg/kg, respectively, for iron and manganese in the case of simultaneous application of nitric and hydrochloric acid and microwave radiation.

Table 1. The results of determining the content of metals (Cu, Ni, Zn) in sample 5 by the additive method, n = 3.

Type of decomposition	Metal	Sample without additive (mg/kg)	Supplement (mg/kg)	Sample + additive, expected (mg/kg)	Sample + additive, found (mg/kg)
acid decomposition	Cu	39 ± 2	30	69	68 ± 3
	Ni	52 ± 3	42	94	92 ± 7
	Zn	110 ± 5	86	196	198 ± 3
microwave decomposition (HNO_3)	Cu	41 ± 2	25	66	68 ± 3
	Ni	55 ± 3	35	90	91 ± 6
	Zn	115 ± 6	70	185	182 ± 6
microwave decomposition (HNO_3 + HF)	Cu	52 ± 3	24	76	76 ± 5
	Ni	53 ± 4	33	86	84 ± 4
	Zn	112 ± 5	68	180	182 ± 5

For copper, cobalt, and nickel, the situation is ambiguous, and, most likely, uneven fluctuations in their content in different samples may be related to the peculiarity of the chemical composition of these samples and the interfering influence of other compounds available in the sample [40]. It can be noted that the type of sample preparation has the least influence on the determination of zinc content.

4. Conclusions

Thus, the paper investigates the peculiarities of the effect of different methods of sample preparation on the extraction of heavy metals in samples of bottom sediments. It is noted that pH variations, microwave decomposition and their combination are used for sample preparation.

The number of samples of bottom sediments were analyzed using different methods of sample preparation for atomic adsorption content determination Mn, Fe, Ni, Zn, Co, Cu. It is shown that for iron and manganese, the greatest influence of the type of sample preparation on the determined metal content is observed. The increase in the intensity of sample preparation directly correlates with their extraction.

The completeness of zinc extraction is the least dependent on the type of sample preparation of the studied bottom sediments. For cobalt, copper, and nickel, an ambiguous influence of the type of sample preparation on their degree of extraction was noted, which is probably related to the peculiarities of the chemical composition of the bottom sediments. A further detailed study of the bottom sediments regarding the interfering effects of other components on the extraction of these metals is necessary.

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