Assessment of the metal content in seawater and sediments (Coastal Area of the Black Sea)

Research article

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Abstract

The aim of this study was to develop a method for simultaneous determination of Cd, Cr, Cu, Fe, Mn, Ni and Zn from saline matrices (seawater and sediments) using the ICP-EOS technique. The developed method has quantification limits between 3.6÷11.7 $\mu g \cdot L^{-1}$, precision expressed in RSD < 6%, recovery tests in the range of 90÷115%. The evaluation of 38 seawater samples taken from the Black Sea area indicated that some metals were below the limit of determination of the applied method (Cd, Mn and Ni), others were below the maximum value allowed by the Order 161/2006 (Cr, Fe). Copper exceeded the maximum allowed limit only in 2 analyzed samples and Zn exceeded the maximum allowed concentration according to the current legislation in 50% of the analyzed samples. For the sediment samples, a certified reference material sediment-type with low metal and organic matter content purchased from LGC was used in the validation process.

Keywords: ICP-EOS, metals, method, seawater, sediments

1. INTRODUCTION

Heavy metals are included in the category of harmful pollutants due to the toxic effects they produce in the human organism.

On a global level, heavy metal pollution of the aquatic environment has been brought to the center of attention by a series of serious incidents, with implications on the human population, due to poisoning with mercury, cadmium and other metals. The case of mercury pollution of the waters of Minamata Bay, Japan, due to the discharge of industrial wastewater is well known. Thus, in 1956, about 2,000 cases of alkyl mercury poisoning caused by the consumption of contaminated fish and molluscs were reported among the local population [1]. This kind of serious incidents stimulated, starting with the 60s and 70s, the studies dedicated to marine pollution. In addition to natural sources (rock erosion, volcanic emissions), heavy metals are released into the environment in large quantities following activities associated with mining, the metallurgical industry, manufacturing products, burning fossil fuels or incinerating waste.

In the last four decades, the Black Sea has undergone important changes induced by human activities. The ecosystem of the Black Sea, just like that of other European seas (the Baltic Sea, the Mediterranean Sea) underwent dramatic changes in all its subsystems, immediately after 1970, as a result of industrialization and intensive agriculture, marked by the phenomenon of eutrophication (overfertilization of marine waters with compounds of nitrogen and phosphorus derived mostly from agriculture, domestic and industrial sources). Waste from cities, farms and factories is poured into the Black Sea, most of it coming from the big rivers that flow into the sea (Danube, Nipru, Nistru). Heavy metal pollution in the marine environment is a topic of great interest for the Black Sea due to the fact that heavy metals are part of the category of persistent pollutants in the environment.

1.1. Toxicity

The spread of metals in water, sediments and the atmosphere results from their presence in the earth's crust. Metals play an essential

role in many biochemical processes in the body, but their presence in the environment in high concentrations becomes toxic. Due to human activity, metal concentrations are higher than in natural conditions, representing a threat to organisms, metals being harmful even in moderate concentrations [2]. The toxic potential of metals depends on their bioavailability and physical-chemical properties [3]. The general sources of pollution of the marine environment are represented by cities and coastal industries, wastewater and industrial residues, household waste and rainwater, naval transport, waste discharge into the sea, shipwrecks, atmospheric deposition. Terrestrial sources that generate heavy metals are mainly represented by wastewater treatment plants, mining, agriculture. Once they reach the aquatic environment, they can follow several paths: dissolved in water, stored in sediments, volatilized in the atmosphere or can be taken up by aquatic organisms.

Toxic metals such as lead, cadmium or mercury seriously affect the environment and human health. Other metals (eg, iron, aluminum, zinc) are essential for many marine organisms [4].

Cadmium (Cd) is a non-essential metal for organisms. It has been shown that this metal is extremely toxic to wildlife and is teratogenic and carcinogenic to humans [5]. Cadmium is one of the most harmful contaminants in seafood and is accumulated in very high concentrations by marine organisms. In general, clams have a high content of cadmium due to the efficient assimilation of this metal and the very low elimination rate [6].

Copper (Cu) is an element present in all aquatic environments, being an essential element for all organisms, but it can be toxic in high concentrations. The accumulation of copper in marine organisms has been known for many years. It was found that oysters contain higher concentrations of copper compared to other bivalve species [7].

Although iron (Fe) is one of the most abundant elements in the earth's crust (5%), its concentration in seawater is extremely low (0.1-10 nmol L^{-1}) [8]. Fe is biogenic and plays an important role in photosynthesis because it exists in the active sites of molecules that are responsible for oxygen transport and mitochondrial electron transfer, making it an essential trace element for the growth of phytoplankton in marine ecosystems [9].

Chromium (Cr) is found in several valence forms with different physicochemical and toxicological properties. While trivalent chromium is found naturally in the environment, hexavalent chromium results mainly from various industrial activities and can be a danger to both humans and the environment. Trivalent chromium (Cr^{3+}) is an essential nutrient with limited oral and dermal bioavailability and limited acute and chronic toxicity. Hexavalent Cr (Cr^{6+}) is very toxic, the International Agency for Research on Cancer (IARC), the Environmental Protection Agency (EPA) and the World Health Organization (WHO) proving that exposure of animals to chromium in this oxidation state can cause cancer. Hexavalent chromium is strongly absorbed and is classified as a respiratory carcinogen [10].

Prolonged exposure to high concentrations of manganese (Mn) affects the lungs, increasing the risk of pneumonia or bronchitis. Occupational exposure to manganese has been associated with neurological disorders mimicking Parkinson's disease.

Nickel (Ni) is the most common cause of contact dermatitis, including in children. Exposure to large amounts of nickel has been associated with lung and nasal cancers. Soluble forms of nickel such as nickel chloride or nitrate increase the risk of cancer and intensify the carcinogenic action of less soluble forms such as nickel oxide or hydroxide [11].

Zinc (Zn) is present in all organisms and is an essential trace element for metabolic processes. There are some marine invertebrates that tend to accumulate Zn at a very high concentration in the body [12].

1.2. Environmental legislation

The quality of sea water (coastal) is regulated by the Order of the Ministry of the Environment and Water Management no. 161/2006 (Table 1) for the approval of the Normative regarding the classification of surface water quality in order to establish the ecological status of water bodies.

Tabel 1. Order 161/2006 for the approval of the normative regarding the qualification of surface water quality in order to establish the ecological status of water bodies

Metal	Measurement unit	The maximum limit allowed according to Order 161/2006
Cd	$\mu g \cdot L^{-1}$	5
Cr	$\mu g \cdot L^{-1}$	100
Cu	$\mu g \cdot L^{-1}$	30
Fe	$\mu g \cdot L^{-1}$	100
Mn	$\mu g \cdot L^{-1}$	-
Ni	$\mu g \cdot L^{-1}$	100
Zn	$\mu g \cdot L^{-1}$	50

1.3. Techniques for the determination of metals from seawater samples and marine sediments

Monitoring the presence of trace metals in water matrices and marine sediments is of major importance because they interact with the majority of marine fauna, especially in estuaries - unique ecosystems with complex and dynamic processes of ecological and environmental importance and due to the effect that metals have on human development.

There are few analytical methods that allow the determination of metals in seawater at very low concentrations, namely: anodic stripping voltammetry and inductively coupled plasma mass spectrometry (ICP-MS) coupled with DGT (thin film diffusion gradient) [13].

The determination of metals in seawater at very low concentrations can also be achieved by ICP-EOS (optical emission spectrometry with inductively coupled plasma) using an extraction phase (Triton X-114) and a chelating agent (TTA) [14].

2. MATERIALS AND METHODS

2.1. Development and optimization of the method for the determination of metals in seawater through ICP-EOS

Due to the high content of salts, seawater presents a complex matrix, difficult to analyze. Coupling a humidifier to the ICP-EOS and choosing an optimal pretreatment method will allow the quantification of some metals in low concentrations. The tests necessary to validate the concentration of metals in the seawater matrix were performed. In the specialized literature, no studies were found regarding the description of the method of determining metals from saline matrices using the ICP-EOS technique.

The method of simultaneous determination of metals (Cd, Cr, Cu, Fe, Mn, Ni and Zn) was carried out by the technique of atomic emission spectrometry with inductively coupled plasma using the ICP-EOS Avio 500 Perkin Elmer equipment to which a humidifier was connected, its purpose being to moisten the argon and allow the plasma to remain lit under the conditions of using seawater samples with a high salt content.

The experimental tests were carried out and a multi-element curve in the concentration range of $100 \div 500$ $\mu g \cdot L^{-1}$ was obtained, by integrating the peak area of the obtained signals. All the specific wavelengths of each element were tested (Table 2), selecting only those for which the performance parameters presented the best values for an ICP-EOS determination method.

Tabel 2. Wavelengths specific to each element

Metal	Wavelength, nm	Metal	Wavelength, nm
Cd	228.802	Fe	259.939
Cd	214.440	Fe	239.562
Cd	226.502	Mn	257.610
Cr	267.716	Mn	259.372
Cr	205.560	Mn	293.305
Cr	283.563	Ni	231.604
Cr	284.325	Ni	221.648
Cu	327.393	Zn	206.200
Cu	324.752	Zn	213.857
Fe	238.204		

2.2. Working procedure for method validation

Standard stock solution: 100 mg·L^{-1} Certified Reference Material, Quality Control Standard, 21 Pure Elements (Cd, Cr, Cu, Fe, Mn, Ni and Zn) in 5% HNO$_3$, CPA CHEM.

Working standard solutions: 100 µg·L^{-1}; 200 µg·L^{-1}; 300 µg·L^{-1}; 400 µg·L^{-1}; 500 µg·L^{-1} (0.1 mL; 0.2 mL; 0.3 mL; 0.4 mL; 0.5 mL of the standard stock solution brought to a 100 mL volumetric flask). The standards were brought to the mark with the sea water matrix (prepared according to ASTM D 1141-2003- Practical guide for the preparation of the sea water matrix) to which 1% HNO$_3$ was added.

2.3. Validation of the method

The experimental tests applied in the validation of the method for the determination of metals in seawater consisted in determining the limit of detection (LOD), the limit of quantification (LOQ), repeatability (RSD$_r$), intermediate precision RSD$_{Ri}$), accuracy, recovery and linearity tests.

For the determination of metals in seawater, the following parameters presented in Table 3 were validated:

Tabel 3. Tests performed for determination of the method's performance parameters

LOD and LOQ	Repetability	Intermediate accuracy	Test for the homogenity of the variance	Recovery	The accuracy of the equipment
- 5 independent standard solutions prepared at the lowest determined concentration (10 µg·L^{-1} Cd, Cr, Cu, Fe, Mn, Ni, Zn)	- 10 independent standard solutions of 300 µg·L^{-1} of Cd, Cr, Cu, Fe, Mn, Ni, Zn prepared in saline water matrix	- 12 independent standard solutions of 300 µg·L^{-1} Cd, Cr, Cu, Fe, Mn, Ni, Zn prepared in saline water matrix (4 solutions were read in 3 different days)	- 10 independent standard solutions of 100 µg·L^{-1}, respectively 10 independent solutions of 500 µg·L^{-1}	- 4 independent seawater solutions (real seawater samples) made at 2 different concentrations	- 1 independent standard solution of 300 µg·L^{-1} from which 10 readings were made

The operational parameters for the optic emission spectrometer with inductively coupled plasma are shown in Table 4.

Table 4. Working conditions of the ICP-EOS spectrometer

ICP-EOS Spectrometer parameters	
Plasma gas rate (argon)	15 L·min^{-1}
Auxiliary gas rate	0.2 L·min^{-1}
Nebuliser gas rate	0.75 L·min^{-1}
Sample uptake rate (peristaltic pump)	1.9 mL·min^{-1}
Power RF	1400 W
Number of replicates	4
Delay	60 s
Aria integration	10 points
λ (nm)	228,812
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Heater temperature	140°C
Cooler temperature	3°C

For each analyzed metal, several wavelengths were tested. After carrying out all the experimental tests, the wavelengths where the signal was weak and the precision and recovery were low were eliminated from the determination method. In choosing the optimal wavelength for the determination of metals in seawater, the interferences present at certain wavelengths were also taken into account. The results obtained after the validation of the method are presented in Table 5.

Tabel 5. Performance parameter values for the determination of metals in seawater

Metal Λ, nm	LOD µg·L^{-1}	LOQ µg·L^{-1}	RSDr* %	RSD$_{Ri}$** %	Recovery %	Liniarity
Cd 228.802	2.00	6.67	2.68	3.46	90.6÷105	R=0.9996
						PG1/10=0.01<5.35
Cr 267.716	1.5	5.1	3.40	4.05	104 ÷108	R=0.9997
						PG1/10=0.07<5.35
Cu 327.393	1.98	6.6	2.66	4.62	108 ÷ 109	R=0.9997
						PG1/10=0.05<5.35
Fe 239.562	3.5	11.7	4.3	5.24	105 ÷ 109	R=0.9996
						PG1/10=0.13<5.35
Mn 257.610	1.1	3.6	3.13	3.93	102 ÷ 105	R=0.9997
						PG1/10=0.03<5.35
Ni 231.604	2.66	8.9	3.67	4.80	108 ÷ 112	R=0.9994
						PG1/10=0.12<5.35
Zn 206.200	1.8	6.0	3.36	4.56	108 ÷ 115	R=0.9993
						PG1/10=0.1<5.35

*Repeatability; **Intermediate accuracy

The developed method presented quantification limits between 3.6÷11.7 µg·L⁻¹, the method was precise (RSD<6), the recovery tests having values between 90÷115% for all 7 analyzed metals.

Figure 1 shows the regression curves for the studied metals (Cd, Cr, Cu, Fe, Mn, Ni and Zn) only for the wavelengths at which the best results were obtained.
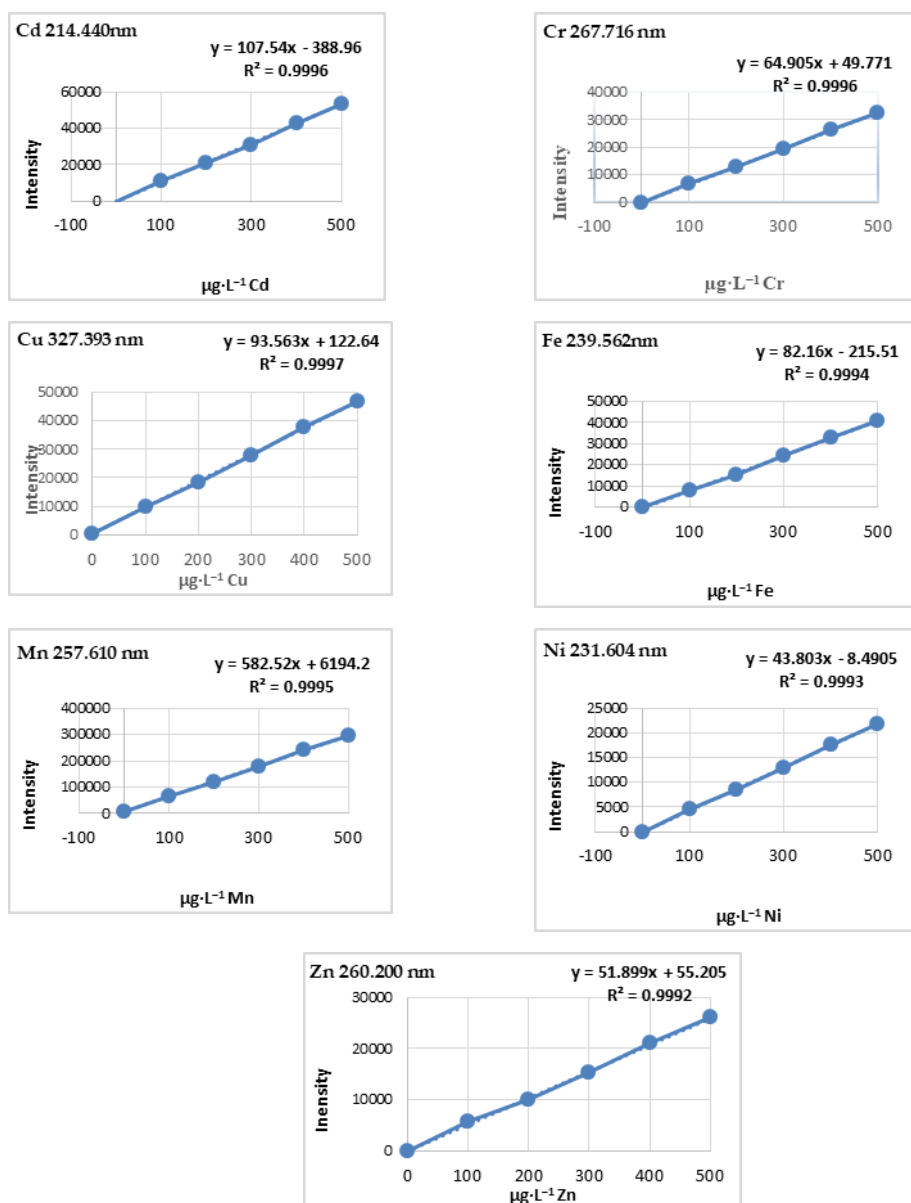
Figure 1. Linear regression curves for Cd, Cr, Cu, Fe, Mn, Ni, Zn determination

3. RESULTS AND DISCUSSION

3.1. *Evaluation of the presence of metals in seawater samples*

38 water samples were taken from the coastal area of the Black Sea, approximately 1m from the beach. The coordinates of the sampling points are presented in Table 6.

Tabel 6. Coordinates of sampling points for marine water samples

Crt. Nr.	Location	Sample code	Latitude	Longitude
1	Vama Veche	S1	43.748	28.578
2	Vama Veche	S2	43.750	28.577
3	Vama Veche	S3	43.755	28.575
4	2 Mai	S4	43.784	28.580
5	2 Mai	S5	43.786	28.580
6	2 Mai	S6	43.789	28.581
7	Mangalia	S7	43.818	28.589
8	Mangalia	S8	43.811	28.587
9	Mangalia	S9	43.813	28.587
10	Mangalia	S10	43.814	28.588
11	Mangalia	S11	43.815	28.588
12	Saturn	S12	43.835	28.591
13	Saturn	S13	43.833	28.591
14	Saturn	S14	43.831	28.591
15	Venus	S15	43.879	28.607
16	Jupiter	S16	43.878	28.607
17	Jupiter	S17	43.877	28.607
18	Neptun	S18	43.888	28.611
19	Neptun	S19	43.887	28.611
20	Neptun	S20	43.951	28.639
21	Eforie Sud	S21	43.951	28.639
22	Eforie Sud	S22	43.950	28.638
23	Eforie Sud	S23	44.024	28.657
24	Eforie Nord	S25	44.049	28.644
25	Eforie Nord	S26	44.048	28.644
26	Eforie Nord	S27	44.047	28.645
27	Costinesti	S28	44.070	28.641
28	Costinesti	S29	44.068	28.641
29	Costinesti	S30	44.066	28.642
30	Navodari	S31	44.299	28.627
31	Navodari	S32	44.303	28.628
32	Navodari	S33	44.305	28.629
33	Navodari	S34	44.307	28.631
34	Navodari	S35	44.309	28.631
35	Navodari	S36	44.311	28.632
36	Navodari	S37	44.314	28.633
37	Navodari	S38	44.315	28.634
38	Navodari	S39	44.317	28.635

The samples were taken in the summer, from the surface (30 cm) of the Black Sea, in 2 L plastic containers fixed with nitric acid and stored in a refrigerator before being transported to the laboratory. The samples were taken from 12 beaches: Vama Veche, 2 Mai, Mangalia, Saturn, Venus, Jupiter, Neptun, Eforie Sud, Eforie Nord, Costinesti, Navodari.
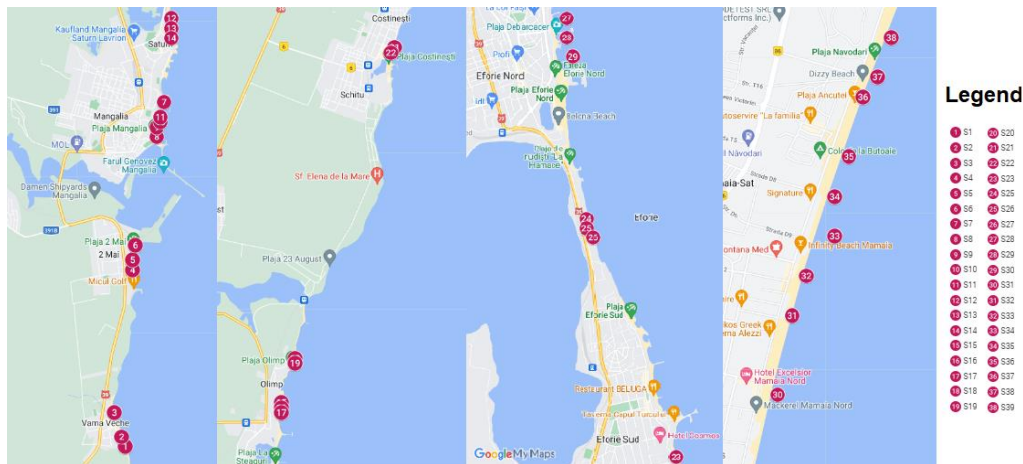

Figure 2. Mapping of sampling points for seawater samples

The water samples were mineralized in an open system, 10 mL of the sample was taken and 2 mL of nitric acid were added. The samples were brought to a final volume of 25 mL with ultrapure water. The samples were analyzed in duplicate, the presented results being the arithmetic average of the two determinations.

Following the analysis of sea water samples taken from the Black Sea coastal area, it was observed that, in all samples, cadmium, manganese and nickel had concentrations below the quantification limit of the method.
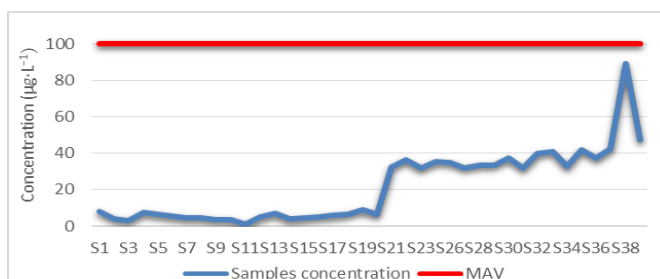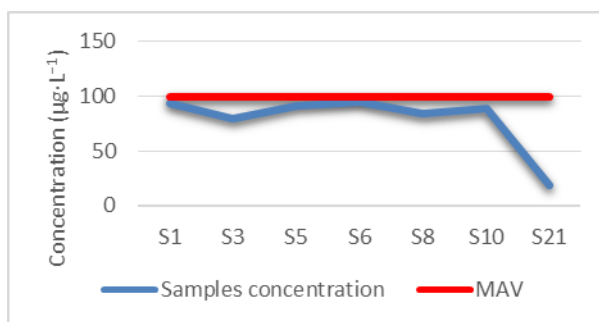

Figure 3. Chromium concentration in seawater samples

The concentration of chromium (Figure 3) in seawater samples (S1-S20) taken from the localities of Vama Veche, 2 Mai and Mangalia, Saturn, Venus, Jupiter, Neptune have had values between $3 \div 9$ µg·L^{-1}, being approximately 10 times lower compared to the chromium concentration found in samples S21-S39 (taken from Eforie, Costinesti, Navodari, Constanta and Mamaia). The chemical quality of the sea water is influenced by the quality of the waste water discharged from the treatment plants, but also by the composition of the water from the Danube that flows into the sea. It should be noted that none of the analyzed samples exceeded the maximum allowed concentration (100 µg·L^{-1}) for chromium according to Order 161/2006 (Tabel 1).
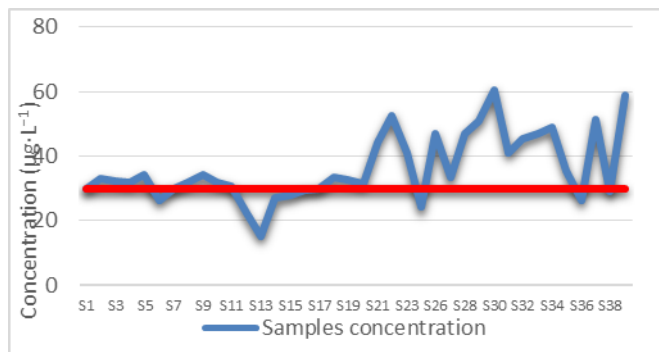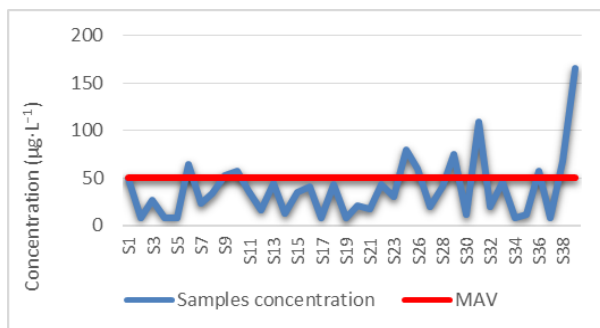

Figure 4. Copper concentration in seawater samples

Copper (Figure 4) was found in all analyzed water samples, the highest concentrations of copper being in Costinesti (S30) and Navodari (S39) where the allowed concentration (of 30 µg·L^{-1}) mentioned in Order 161/2006 is exceeded. Increased concentrations of copper may be due to household and industrial waste water discharged from treatment plants.

Figure 5. Iron concentration in seawater samples

Iron was found in the waters sampled from Vama Veche (S1 and S3), 2 Mai (S5 and S6), Mangalia (S8 and S9) and Eforie Sud (S21), but without exceeding the maximum limits allowed by Order 161/2006 (Figure 5).

Figure 6. Zinc concentration in seawater samples

Zinc (Figure 6) was ~~is~~ present, as well as Cu and Cr in high concentrations in Navodari, where the maximum value recorded in sample S39 was 116 $\mu g \cdot L^{-1}$. Zinc exceeded the maximum value allowed by the current legislation (50 $\mu g \cdot L^{-1}$) in 50% of the analyzed samples.

Increased concentrations of zinc in marine waters were also reported in other studies where values between 64÷500 $\mu g \cdot L^{-1}$ were found [15].

In the period 2006-2011, concentrations of Cu between 0.01÷93.51 $\mu g \cdot L^{-1}$, Cd 0.01÷18.32 $\mu g \cdot L^{-1}$; Ni 0.01÷ 30.59 $\mu g \cdot L^{-1}$ and Cr 0.01÷ 59.74 $\mu g \cdot L^{-1}$ were reported in the coastal area of the Black Sea [16]. Another study of heavy metal pollution of the water on the Romanian coast of the Black Sea carried out in 2017 reported the following metal concentrations: Cd – 14.34÷ 18.7 $\mu g \cdot L^{-1}$; Zn – 32.58÷ 48.88 $\mu g \cdot L^{-1}$[17].

 In an other study, metal concentrations in coastal water were 0.23÷ 0.80 mg·L⁻¹ Ni, 0.08÷ 1.45 mg·L⁻¹ Zn, 0.15÷ 0.25 mg·L⁻¹ Cd, 0.88÷ 1.77 mg·L⁻¹ and 0.88÷ 10.29 mg·L⁻¹ Cu [18].

3.2. *Evaluation of the presence of metals in marine sediment samples*

The sediment samples were taken from the coastal area of the Black Sea (2 Mai, Mangalia, Saturn, Venus, Jupiter, Neptun, Eforie Nord, Eforie Sud, Costinesti). The sampling points and the code of the sediment samples are presented in Table 7.

Tabel 7. Sampling points for sediment samples

Crt. Nr.	Location	Sample code
1	Vama Veche	Sd1
2	2 Mai	Sd2
3	Mangalia	Sd3
4	Saturn	Sd4
5	Olimp	Sd5
6	Venus	Sd6
7	Jupiter	Sd7
8	Neptun	Sd8
9	Eforie Nord	Sd9
10	Eforie Sud	Sd10
11	Costinesti	Sd11
12	Navodari	Sd12

For the total metal content determination, the sediment was air-dried and then sieved through a sieve smaller than 63 μm. To determine the total metal content, approximately 2g of sediment was weighed in Berzelius glasses, a mixture of 7 mL HNO_3 and 21 mL HCl (ultrapure reagents) was added and the final mixture was left to mineralize in an open system for 3 hours until the remaining liquid has cleared. The mixture was filtered, washed with distilled water, and the obtained filtrate was collected in a 50 mL volumetric flask (SR ISO 11466/99 – Soil quality. Extraction of trace elements soluble in aqua regia).

The results obtained for the determination of metals in sediments were compared with Order 161/2006 - Chemical quality elements and standards for sediments - fraction <63 μm (Table 8).

**Tabel 8.** Elements and chemical quality standards for sediments - fraction < 63 μm

Crt. Nr.	Indicator	MU	Quality standard
1	Copper (Cu^{2+})	mg·kg⁻¹	40
2	Cadmium (Cd^{2+})	mg·kg⁻¹	0.8
3	Chromium ($Cr^{3+}+Cr^{6+}$)	mg·kg⁻¹	100
4	Nickel (Ni^{2+})	mg·kg⁻¹	35
5	Lead (Pb^{2+})	mg·kg⁻¹	85
6	Zinc (Zn^{2+})	mg·kg⁻¹	150

After interpreting the results, it was found that in the analyzed sediments, cadmium had values below the quantification limit of the method.
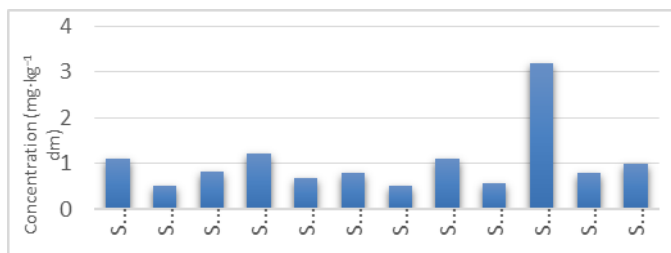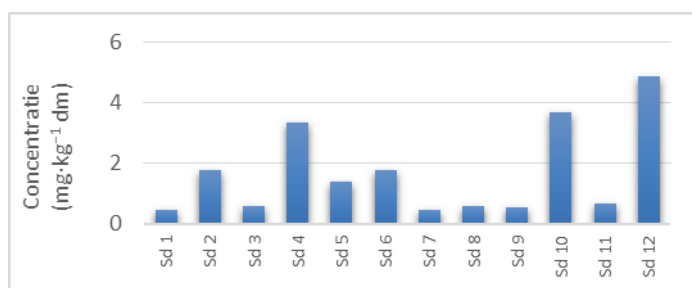

Figure 7. Copper concentration in sediment samples

The concentration of copper (Figure 7) in the sediments had values between 0.5÷ 3.18 mg·kg⁻¹ dm. The highest value was recorded in Eforie Sud (Sd10). All copper concentrations were located below the maximum limit allowed according to the legislation in force.
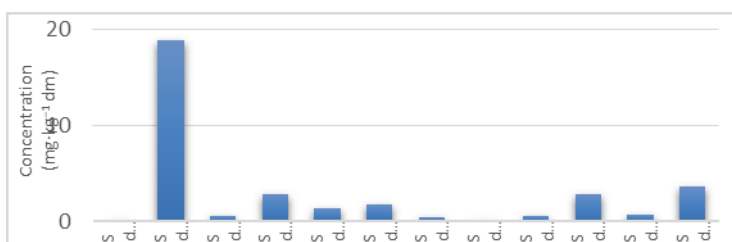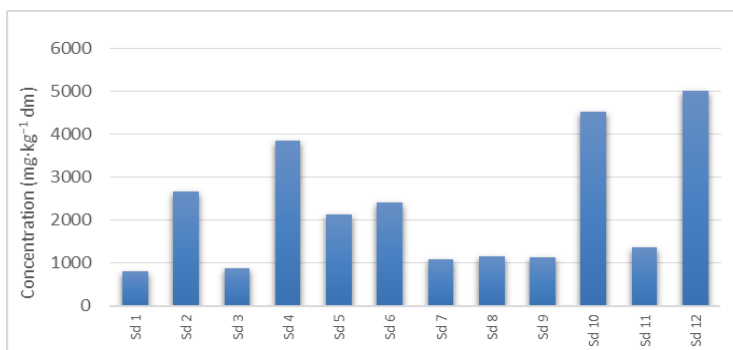

Figure 8. Chromium concentration in sediment samples

Chromium (Figure 8) had very low values between 0.07÷ 3.67 mg·kg⁻¹ dm with one exception, sample Sd 2 taken from the 2 Mai location. The recorded concentrations were below the maximum limit allowed according to the current legislation.
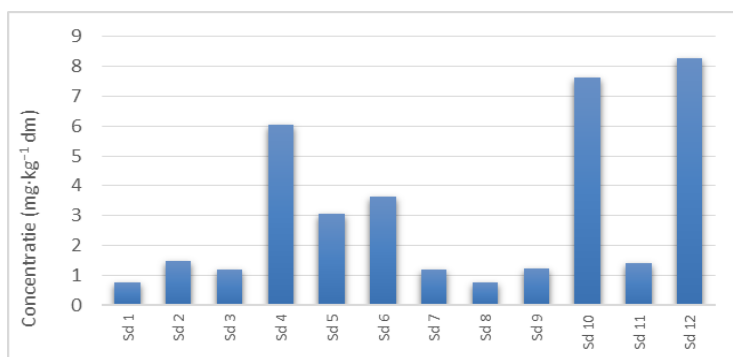

Figure 9. Nickel concentration in sediment samples

In the analyzed sediment samples (Figure 9), nickel was below 35 mg·kg⁻¹ dm (the maximum value allowed in Order 161/2006), the highest values being recorded in Sd10 (Eforie Sud) and Sd12 (Navodari).

Figure 10. Iron concentration in sediment samples

Figure 10 shows the concentration of iron for the analyzed sediments. The values recorded for this element were between 795 (Sd 1-Vama Veche) and 4992 mg·kg⁻¹ dm in the sample Sd 12 taken from Navodari.

Figure 11. Zinc concentration in sediment samples

Zinc (Figure 11) had values below the maximum limit allowed by Order 161/2006 (150 mg·kg⁻¹ dm), the highest value being taken from the Navodari station (sample Sd 12).

The method for metals determination in sediments was verified by an interlaboratory comparison scheme LGC -AQUACHECK 609 - Round 609. The results obtained are presented in Table 9.

Tabel 9. Results obtained for the certified sediment sample

Metal	Certified value (mg·kg⁻¹)	Obtained value (mg·kg⁻¹)	Recovery performance (%)	Recovery performance* (%)
Cd	0.11±0.0112	0.12 ±0.114	109	105.9
Cr	5.5±0.37	6.3±0.8	114	93
Cu	7.08±0.289	7.74±0.93	109	106.5
Mn	42±1.5	41±3	97.6	102.3
Ni	1.43±0.198	1.49±0.20	104	99.9
Pb	6.9±0.28	7.3±0.7	106	107.7
Zn	16.2±0.52	16.4±1.6	101	103.1

* Recovery performance according to the standard of digestion of soluble elements in aqua regia (SR EN ISO 54321/2021).

The results obtained in the interlaboratory comparison scheme for the determination of metals from sediment samples had recovery yields between 97.6% ÷ 114% and are very close to the values of recovery yields recommended according to the new standard for the digestion of elements soluble in aqua regia - SR EN ISO 54321 published in March 2021.

CONCLUSION

A new method was developed for the simultaneous metal determination in saline matrices (seawater and sediment) using ICP-EOS coupled with a humidifier necessary to moisten the argon and allow the plasma to remain lit under the conditions of using seawater samples with a high content of salts.

Following the results obtained from the experimental tests, it was demonstrated that the developed method presented quantification limits between 5÷11.7 µg·L⁻¹ for Cd, Cr, Cu, Fe, Mn, Ni and Zn and can be used to determine these metals from samples of coastal waters. The method is precise (RSD <6) and the recoveries had a very high yield (84÷115%).

In the water samples taken from the Black Sea coast, Cd, Mn and Ni recorded values below the quantification limit of the method. Chromium and iron had values below the maximum limits allowed according to Order 161/2006 in all seawater samples analyzed. Copper exceeded the maximum allowed limits in 2 of the 38 analyzed samples and zinc exceeded the

maximum allowed concentration according to the legislation in force in 50% of the analyzed samples.

No cadmium was found in the analyzed sediment samples, as in the case of seawater. Lead had values lower than the quantification limit of the method in all analyzed sediment samples. For nickel, iron and zinc, the highest values were recorded in the sample taken from Navodari. Chromium had the highest concentration in the sample taken from Navodari and for copper a maximum value was recorded in the sample taken from Eforie Sud.

For the sediment samples, the recovery yields obtained following the analysis of a sediment with a certified value were calculated. The values were in the range of 97.6% ÷ 114% and are very close to the recovery yields recommended according to the new standard for the digestion of soluble elements in aqua regia - SR EN ISO 54321 published in March 2021.

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