

HEAVY METALS IN SEDIMENTS FROM BOKA KOTORSKA BAY

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ABSTRACT

In this work, several toxic heavy metals (Cd, Pb, Cr, Cu, Fe, Mn, Ni, Co, Hg and As) were determined in marine sediments from different sampling points from Boka Kotorska Bay. The dried sample was digested with mixture of HNO₃ + HClO₄ + HF (4+1+6). The contents of Cd, Pb, Cr, Cu, Ni, Co and Fe have been determined by using AAS method, for determined of Hg the technique of cold mercury and for determination of As the hydride technique has been used. The analytical results were compared with the published data and with the results of determination of heavy metals in MESS 3 references materials.

Key words: heavy metals, marine sediments, atomic absorption spectrometry.

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REZIME

U ovom radu određen je sadržaj nekih teških metala (Cd, Pb, Cr, Cu, Fe, Mn, Ni, Co, Hg i As) u morskom sedimentu na različitim pozicijama u Bokokotorskom zalivu. Suvi uzorci razarani su smešom HNO₃ + HClO₄ + HF (4+1+6). Sadržaj Cd, Pb, Cr, Cu, Ni, Co i Fe određen je AAS metodom, za određivanje Hg tehnika hladne živine pare i za određivanje As korišćena je hidridna tehnika. Rezultati određivanja upoređeni su sa literaturnim podacima i sa rezultatima koncentracije teških metala u referentnom materijalu MESS 3

Ključne riječi: teški metali, morski sedimenti, atomski absorpcioni spektrometar

INTRODUCTION

Heavy metals are highly persistent and can be toxic to life even in trace amount. To know their distribution in sediment, water and biological materials

is of great importance in environmental pollution studies as a means of evaluating the stresses imposed on the environment by anthropogenic activity.

The availability of elements to organism depends on their physicochemical state, which in turn depends on the overall biogeochemical cycle. An important step of this cycle is the accumulation and/or release of elements by the sediments.

Because of their environment, these sediment are somewhat different in their makeup from inorganic silicons rocks, the essential difference is their higher organic matter content. The correlation between organic matter and trace metal content of sediments is now well known for several elements. Therefore, in the preparation of sediment samples, the important step of destruction of organic matter must be very rigorous.

Boyden (1975) and Talbot *et al.* (1976) decomposed sediments sample with $\text{HNO}_3\text{-HClO}_4$ and Sanches *et al.* (1994) the soil sample were digested with aqua regia-HF acid. All of these techniques are very effective in dissolving siliceous material but they do not destroy the large quantities of organic matter present in some silt and clay sediments. Therefore it was necessary to develop a much stronger oxidizing mixture, which would give complete recovery of as many metals as possible after the destruction of the organic matter. The acid mixture employed must satisfy a few important conditions. It should dissolve the silica matrix of the sediment, it should destroy the organic matter and it should put all the metals into solution, no interfering ions should be introduced. A mixture of nitric, perchloric and hydrofluoric acids satisfies these conditions, Agemian and Chau (1975).

In this work several toxic metals (Cd, Pb, Cr, Cu, Fe, Mn, Ni, Co, Hg and As) were determined in marine sediments from different sampling points from Boka Kotorska Bay (Kotor, Plagenti, IBM, Orahovac, Risan, Morinj, Verige, Sv. Nedelja, Tivat, Kukuljina, Solila, Bijela, Herceg Novi and Mamula).

MATERIALS AND METHODS

Atomic absorption spektrometer equipped with a deuterium-arc background corrector and Perkin Elmer MHS-10 hydride generator were used. Standard hollow cathode lamps were used for all elements except arsenic, for which a Electrodes Discharge (EDLs) lamp was used. The argon head pressure was 250 kPa.

Reagents: High-purity certified reagents were used for all analyse(»Merck«): Nitric acid 65%, Nitric acid 1,5%, Perchloric acid 60%, Hydrochloric acid 37%, Hydrochoric acid 1,5%, sulfuric acid 1,5%, Sodium-

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borohydrid 3% in 1% NaOH, Sodium-hydroxide, Boric acid, Marine sediment MESS-3, National Research Council Canada.

Stock standard solutions of metals:

Arsenic (1000 mg/L): Dissolve 1,320g of arsenious oxide As_2O_3 in 25 ml of 20% (w/t) KOH solution. Neutralize with 20% (v/v) H_2SO_4 to a phenolphthalein endpoint. Dilute to 1L with 1% (v/v) H_2SO_4 .

Cadmium (1000 mg/L): Dissolve 1,000g of cadmium metal in a minimum volume of (1/1) HCl. Dilute to 1 L with 1% (v/v) HCl.

Cobalt (1000 mg/L): Dissolve 1,000g of cobalt metal in minimum volume of (1+1) HCl. Dilute to 1 L with 1% HCl.

Chromium (1000 mg/L): Dissolve 3,735g of potassium chromate, K_2CrO_4 in deionized water and dilute to 1 L with deionized water.

Copper (1000 mg/L): Dissolve 1,000g copper metal in minimum volume of (1+1) HNO_3 . Dilute to 1 L with 1% (v+v) HNO_3 .

Iron (1000 mg/L): Dissolve 1,000g of iron wire in 50 ml of (1+1) HNO_3 . Dilute to 1 L with deionized water.

Mercury (1000 mg/L): Dissolve 1.080g of mercury (II) oxide, HgO , in a minimum volume of (1+1) HCl. Dilute to 1 L deionized water.

Manganese (1000 mg/L): Dissolve 1.000g of manganese metal in a minimum volume of (1+1) HNO_3 . Dilute to 1 L with 1% (v/v) HCl.

Nickel (1000 mg/L): Dissolve 1.000g of nickel metal in a minimum volume of (1+1) HNO_3 .

Lead (1000 mg/L): Dissolve 1.598g of lead nitrate, $Pb(NO_3)_2$, in 1%(v/v) HNO_3 and dilute to 1 L with (v/v) HNO_3 .

Zink (500 mg/L): Dissolve 0,500g of zink metal in a minimum volume of (1+1) HCl and dilute to 1 L with 1%(v/v) HCl.

Sample preparation. Dry sample (about 0.3g) is dissolved with $HNO_3 + HClO_4 + HF$ (4+1+6). After the remains were cooled, the were quantitatively transferred from Teflon dishes into polypropylene bottles with 2g of boric acid in 30 mL of deionised water, in order to completely dissolve the built metal fluorides. The solution was then transferred to measurement dishes of about 100 mol, 6 mol of HCl was added and water was added until it reached the lion. Then this solution was kept in plastic bottles and analysed by using FAST and Bg correction.

To determine Hg the samples of marine sediments were decomposed by the mixture (2+1) of 18 M $H_2SO_4 - 12$ M HNO_3 at the temperature of 50-60 °C by addition of $KMnO_4$. The surplus of permanganate and formed MnO_2 were eliminated by hydrazine-sulfate. After the centrifugation, the conent of Hg was determined by using cold mercury vapour technique.

To determine arsenic, the samples of marine sediments were decomposed by the mixture of (2+1) concentrated $HNO_3 - 7$ M H_2SO_4 . After

the decomposing of organic material the solution was vapourized until sulphuric acid was completely decomposed. Certain aliquotes were measured from this solution and arsenic was determined after the reduction As (V) in As (III) with KJ by using hydride AAS.

RESULTS AND DISCUSSION

When choosing methods for determination of macro and microelements in the sediment, special care should be taken of precise the methods is, the minimal concentration needed for detection, the concentration range, the total analysis time, cost of instrument, as analytic interferences (annoyances) and their removal.

In order to detect heavy metals in marine sediments, following methods are usually used:

- Neutron activation analysis
- Mass spectrometry
- Atomic absorption and emission spectrometry (FAAS, FAES, ETAAS, HAAS)
- Inductively coupled plasma (ICP-EES)
- Atomic fluorescent spectrometry (AFS)
- Stripping voltametry

The lowest detectable levels ($\mu\text{g/L}$) for water solution of certain element and various analytical methods are given in Table 1.

Table 1. Instrumental limits of the detection for some metals

Element	FAAS	FAES	ET-AAS	HAAS	ICP-AES	ICP-MS	AFS
Al	30	10	0.04	-	30	0.2	0.6
Si	60	5000	0.4	-	3	-	-
Fe	3	50	0.02	-	1	7	30
S	-	-	-	-	50	-	-
Ca	1	0.1	0.05	-	0.08	50	0.08
K	2	3	0.02	-	50	-	-
Ti	50	200	1	-	0.5	-	2
Na	0.2	0.1	0.05	-	4	-	0.1
P	50000	-	30	-	30	-	-
Mg	0.1	5	0.04	-	0.08	-	0.2
Ba	8	1	0.1	-	0.1	0.05	8
Sr	2	0.1	0.02	-	0.05	0.03	0.3
B	700	30000	20	-	2	0.8	-
Mn	1	5	0.01	-	0.4	0.06	0.4
Zn	0.8	50000	0.01	-	1	0.3	-
V	40	10	0.2	-	2	0.1	30
Cr	2	5	0.01	-	2	0.4	1
Cu	1	10	0.02	-	0.9	0.1	1

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Li	0.5	0.003	0.05	-	0.9	-	0.5
Pb	10	200	0.05	-	20	0.3	-
Rb	2	0.3	0.05	-	300	0.03	-
Co	6	50	0.01	-	2	0.03	200
Cs	8	8	0.05	-	0	0.03	-
Mo	30	100	0.04	-	5	0.1	12
Ni	4	30	0.1	-	4	0.2	2
Sb	30	-	0.2	0.1	60	0.1	50
Sn	100	300	0.2	0.5	40	0.1	-
Se	70	-	0.2	0.02	60	2	-
Be	1	40000	0.01	-	0.06	0.2	-
Cd	0.5	2000	0.003	-	1	0.2	8
Th	-	-	-	-	30	0.1	-
U	10000	-	100	-	10	0.1	-
Hg	200	-	1	0.008	20	-	-
As	100	50000	0.2	0.02	20	0.2	-
Bi	20	-	0.1	0.02	20	-	3
Ag	0.9	-	0.005	-	3	1	4
Ce	-	-	-	-	10	0.04	-

Neutron activation analysis (detection limit pg/L) can detect very small but is a very expensive method (in order to get neutrons it is necessary to have a nuclear reactor). Mass spectrometry can also detect small amounts (below 1 µg/L). The sample used for analysis may be in solid, liquid or gaseous state and it is enough to have a sample of 0.01-0.5 mg. ICPMS is a multi-element technique and it is not necessary to make a solution of the sample. However, this method is also very expensive so it is used only to determine those elements in marine sediments that cannot be detected with other, less expensive methods.

We have decided to use AAS method (absorption, emission, technique cold mercury vapours and hydride AAS) in order to determine content of marine sediments.

In order to prepare the sample for analysis (Cd, Pb, Cr, Cu, Mn, Ni, Co, Ni), various techniques may be used:

- Mixture of HNO₃-HClO₄ (4:1)
- 10 mL 7 M HNO₃ + 3 mL conc. HClO₄
- 3 M HCl (5)
- HF-aqua regia
- HNO₃ + HClO₄ + HF (4+1+6) + H₃BO₃

The technique used to prepare the sample depends on which parameter should be determined in the sample. We have set the goal to determine all parameters with a single method for sediment analysis (except for easily evaporating Hg and As). Therefore, for determination of Cd, Cu, Pb, Cr, Mn, Fe, Ni, Co and Zn, dissolution of sediments we used the mixture of HNO₃, HClO₄ and HF.

In order to be sure that the chosen method can be used to analyse sediments, we have pre-tested it on the referent material MESS 3 which determined the content of elements by AAS method (Flame emission, absorption, hydride technique). The results of analysis on certain elements in referent material are given in Table 2.

Table 2. Found and certified some the fraction of referent materials - MESS 3

Element	Reference value ($\mu\text{g/g}$)	found value ($\mu\text{g/g}$)
Co	14.4 \pm 2	13.83
Mn	324 \pm 12	316.91
Cu	33.9 \pm 16	34.3
Fe	4.34 \pm 0.11	4.3
Zn	159 \pm 8	151.31
P	0.12	0.13
As	21.2 \pm 1	20.9

The results of the determination (the average values of three measurements) of heavy metals in marine sediments are shown in Table 3. Data for these elements are given in the same table.

Table 3. Content of some heavy metals in sediments from Boka Kotorska Bay ($\mu\text{g/g}$)

	Mn	Cu	Co	FE	Cr	Ni	Pb	Cd	Ag	Zn	Hg	As
Kotor-c.b.	1045.9	54.3	5.3	41626	288.4	127.6	59.3	2.7	0	132.4	0.20	6.7
Plagenti	560.3	128.2	2.4	26179	214.5	104.2	68.4	0.4	0	532.4	0.17	2.3
IBM	685.8	28.4	1.8	25815	177.3	80.8	16.7	0	0	91.2	0.25	1.9
Orahovac	848.9	46.8	5.5	38249	235.8	99.6	0	0	0	130.7	0.16	3.3
Risan	412.9	40.5	7.1	34105	242.9	96.0	47.4	3.0	0	98.8	0.13	3.5
Morinj	491.7	50.9	11.6	40361	240.1	107.9	55.1	2.3	0	124.3	0.17	4.5
Verige	1400.7	32.9	0	21537	130.3	57.7	56.4	1.9	0	70.8	0.19	5.0
S. Nedelja	437.1	26.1	1.2	20564	112.8	42.1	27.7	2.9	0	53.7	0.20	5.4
Tivat	836.3	64.8	9.5	47117	329.3	152.8	3.7	0.4	0	142.5	0.24	5.0
Kukuljina	810.9	22.6	0	29792	169.6	52.0	55.5	3.4	0	60.6	0.18	1.7
Solila	432.9	44.8	11.1	46362	327.2	156.8	53.0	1.6	0	119.4	0.12	3.1
Bijela	475.5	57.2	4.8	28336	156.9	62.4	45.0	1.7	0	95.9	0.19	4.4
H. Novi	545.6	50.9	11.2	42520	308.3	146.4	1.5	0.4	0	112.8	0.21	4.0
Mamula	389.3	55.9	0	12447	99.9	55.8	59.9	1.5	0	43.4	0.06	4.8

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Table 4. Trace elements content of sediments from Kaštela Bay ($\mu\text{g/g}$)

Mn	Cu	Co	Fe	Pb	Cd	Zn	Hg	As
315.0 – 480.0	6.5 – 550.0	0.6 – 10.0	1.0 – 2.4	11.8 – 1275.0	0.1 – 2.1	33.0 – 1300.0	0.01- 4.4	11.5 – 28.0

The content of manganese in the sample marine sediments was 389.3-1045.9 $\mu\text{g/g}$ in dry sample, copper 26.1-128.2 $\mu\text{g/g}$, cobalt 0-11.2 $\mu\text{g/g}$, iron 12477-47117 $\mu\text{g/g}$, chromium 112.8-327-2 $\mu\text{g/g}$, nickel 55.8-156.8 $\mu\text{g/g}$, lead 0-68.4 $\mu\text{g/g}$, cadmium 0-3.4 $\mu\text{g/g}$, zinc 43.4-532.4 $\mu\text{g/g}$, mercury 0.06-0.25 $\mu\text{g/g}$ and arsenic 1.7-6.7 $\mu\text{g/g}$.

Our researches show that concentration of manganese is largest at Verige an in Kotor and copper at Plagenti, while in other localities it is more or less uniform. The maximal recorded value for cobalt was from Morinj. Minimal and maximal values of chromium and nickel were recorded in identical localities: maximal at Tivat, Solila, Herceg-Novi and Kotor, and minimal at Sv. Nedelja. Values for lead and cadmium at Orahovac, Tivat and Herceg-Novi are either minimal or these elements are missing. Zinc was recorded at Plagenti in four-time larges amount than in any other locality. The values of mercury and arsenic are much lower than the literature data. All values for Hg are relatively uniform, between 0.1 and 2.5 $\mu\text{g/g}$. Arsenic was analysed for the first time and highest concentration is in Kotor, being almost five time lower than in the sediment from Kaštela Bay.

CONCLUSIONS

In order to detect heavy metals in marine sediments, AAS method should be used (heat hydride technique, technique of cold mercury vapours).

In order to dissolve the material, the solution of HNO_3 , HClO_4 , HF , (with addition of H_2O_2 and H_3BO_3) should be used. This way, Si (as SiF_4) is eliminated from the solution, and when boric acid was added, the hard-to-dissolve metal fluorides were also dissolved.

The results show that the contents of Pb, Cd, Cu, Hg, As, Cu and Zn in the investigated samples of marine sediments are above the corresponding MPQ-values (for soil).

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