

MACRO AND MICRO ELEMENTS IN SEA WATER OF BOKA KOTORSKA BAY

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ABSTRACT

In this work, of main and same biogenic and trace elements in the sea water were determined from different sampling points from Boka Kotorska Bay.

The content of (Mg, Ca, Sr, K, Na, Li, Rb, Zn, Fe, Ni, Mn, Cu, Cd, Pb, Cr and Co) have been determined AAS method, for determination of Hg the technique of cold mercury and for determination of As and Se the hydride technique has been used. The analytical results were compared with the published date.

Key words: metals, sea water, FAAS, hydride technique, technique cold mercury.

MAKRO I MIKRO ELEMENTI U MORSKOJ VODI BOKOKOTORSKOG ZALIVA

REZIME

U ovom radu, glavni i neki biogeni i teški elementi u morskoj vodi određeni su na različitim pozicijama Bokokotorskog zaliva.

Sadržaj Mg, Ca, Sr, K, Na, Li, Rb, Zn, Fe, Ni, Mn, Cu, Cd, Pb, Cr i Co određen je AAS metodom, za određivanje Hg korišćena je tehnika hladne živine pare, a za određivanje As i Se hidridna tehnika. Rezultati određivanja upoređivani su sa objavljenim literaturnim podacima.

Ključne riječi: metali, morska voda, FAAS, hidridna tehnika, tehnika hladne živine pare.

INTRODUCTION

Seas and oceans cover about 71 % or 36,1 10⁷ km² of Earth surface, containing about 1,37 10⁹ km³ or 1,413 10¹⁸ tons of water. Sea water is an important and endless supply of certain elements and compounds (Mg, Br, table

salt), although the concentration of certain metals is so low that regardless the huge reserves their extraction from sea water is not commercially useful.

As well as in other natural water sources, several groups of elements may be determined with in the chemical content of sea water.

1. Main or basic ions (Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , Br^- , Na^+ , Mg^{2+} , Ca^{2+} and K^+) and additional ions. The main or basic elements, not counting oxygen and hydrogen, represent about 3,5 % of total mass of water.
2. Biogene elements: mineral compounds of nitrogen (NH_4^+ , NO_2^- , NO_3^-), mineral compounds of phosphorus (PO_4^{3-}) and mineral compounds of silicium (silicates).
3. Micro elements (Li, Rb, Ba, Al, Fe, Mo, Zn, Se, As, Cu, Sn, V, Mn, Ni, U, Ti, Co, Cs, Sb, Ag, La, Bi, Cd, Pb, W, Cr and Hg).
4. Gasses (O_2 , N_2 , CO_2 , CH_4 , H_2S)

Volume of water mass in whole Boka Kotorska Bay is only 2,41 km³. Besides atmospheric falls, flow of water from the flowing area and the fresh water there is also a vast amount of wastewater deposited in Boka Kotorska Bay annually (about 0,2% of the total water content of Boka Botorska Bay) which disturbs the ecological balance in the bay.

The aim of this paper was to determine the content of certain macro, micro and biogene elements in the sea water from different sampling points of Boka Kotorska Bay (Kotor, Plagenti, IBM, Orahovac, Risan, Morinj, Verige, Sv.Nedelja, Tivat, Kukuljina, Solila, Bijela, H.Novi and Mamula).

MATERIALS AND METHODS

Apparatus. Atomic absorption spektrometer equipped with a deuterium-are background corrector and Perkin Elmer MHS-10 hydride generator were used. Standard holow cathode lamps were used for all elements except arsenic and selenium, for which a Electrodes Discharge (EDLs) lamp was used.

Reagents. High-purity certified reagents were used for all analyse ("Merck"): Calcium-carbonate CaCO_3 , Magnesium-oxide, MgO , Pottasium-carbonate, K_2CO_3 , Sodium-chloride NaCl , Hydrochloric acid $\text{HCl}(1+1)$, Hydrochloric acid HCl , redistilled, Methyl-isobutil-ketone (MIBK), redistilled, Sodium-borhydrid, 3% in 1% NaOH .

Amonium pyrolidine dithiocarbamate (APDC) solution, 1% (w/v) in distilled, deionized water. Prepared the APDC solution fresh daily and purify as follows: shake the APDC solution with an equal volume of MIBK, allow the phases to separate and retain the aqueous (lower) phase.

Artificial sea-water solution. Transfer 0.9990 g CaCO_3 , 2.074 g MgO , 1.414 g K_2CO_3 and 25.41 g NaCl to a 1-liter volumetric flask. Dissolve in a minimum volume of (1+1) HCl and dilute to volume with deionized water.

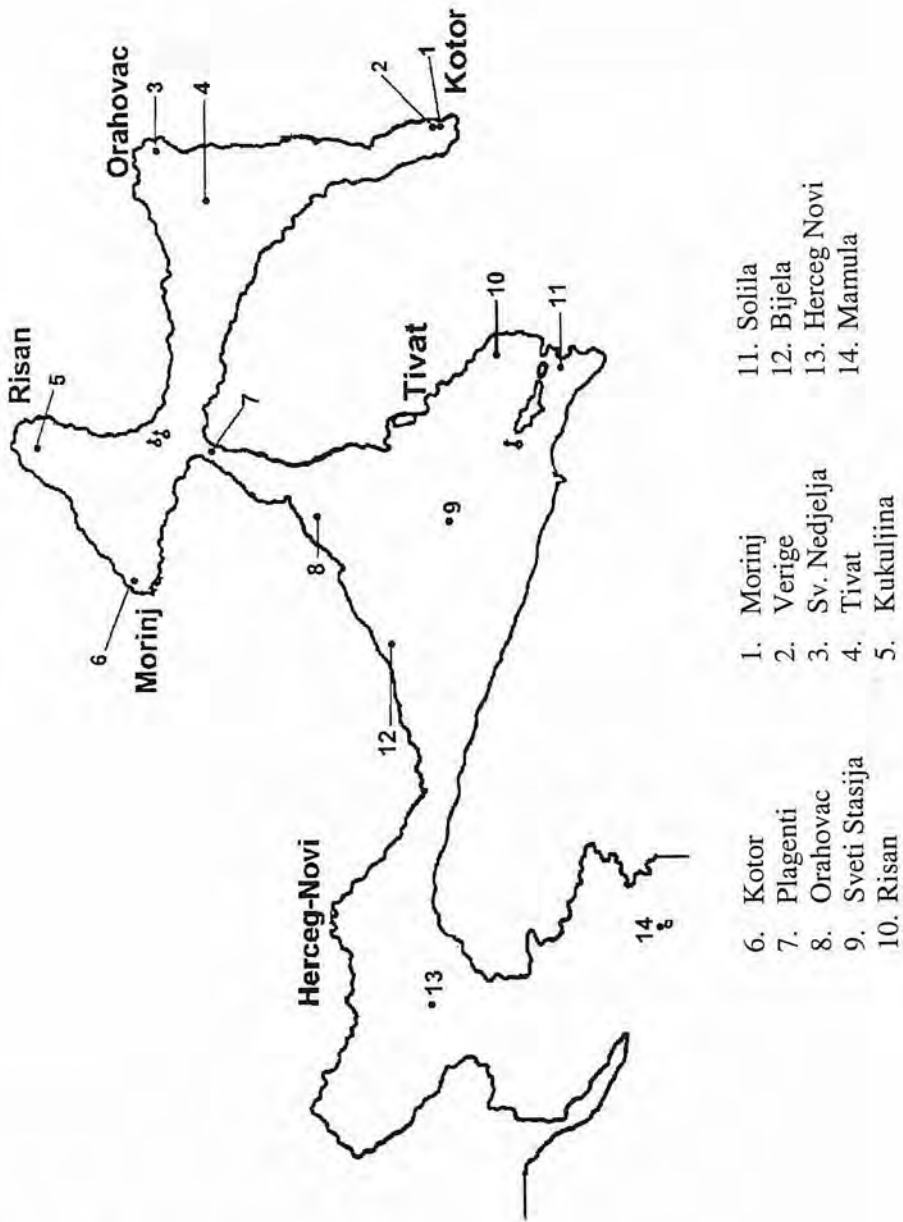


Figure 1. Investigated area

The final solution contains 10.000 µg/mL Na, 1.250 µg/mL Mg, 400 µg/mL Ca and 400 µg/mL K.

All standards were prepared from certified atomic absorption reference standards. Working solutions were prepared freshly every day by diluting appropriate aliquots of the stock solution. For trace elements (Li, Rb and Sr), dilute the stock standard solution to appropriate concentration level with the artificial seawater solution.

Procedure. Samples of sea water were taken in 6 localities in year 1997 and 14 localities in year 2001, covering the whole Boka Kotorska Bay: Kotor, Plagenti, IBM, Orahovac, Risan, Morinj, Verige, S.Nedelja, Tivat, Kukuljina, Solila, Bijela, H.Novi and Mamula (Figure 1.).

Determination of Ca and Mg was done with absorption AAS, after the water sample was diluted (1:2000), for Mg (1:100) and for Ca (1:100). Potassium was determined with emission AAS (1:200) with addition of RbCl as a radiation buffer.

Strontium, lithium and rubidium were also determined by emission technique AAS by direct aspiration of the sample by flame. When determined Li, Rb and Sr use the synthetic sea water solution as reagent blank. Silicon was determined with AAS method in $N_2O-C_2H_2$ flame. Lead, nickel, cobalt, iron and copper were also determined with AAS method. Complex of these metals with APDC on pH=4,5 were extracted with MIBK and the extract was directly aspirated in C_2H_2 -air flame. In order to determine As and Se, we used the hydride technique, and in order to determine mercury, the technique of cold mercury vapors.

RESULTS AND DISCUSSION

Choice of methods used in order to determine metal content in sea water was dictated by metal concentration in water and the minimal amount needed for detection with certain instrumental method. In the Table 1. are presented the middle values of content of certain metals in sea water as well as some literature data, while Table 2. shows smallest amounts of some metals present in sea water that can be detected by certain instrumental methods.

Macro and micro elements in sea water

Table 1. Content of some metals in the sea water

Element	Found values	Literature data			
		1	2	3	4
Na (mg/L)	-	10556	10500	-	-
Mg (mg/L)	1216.3-1372	1272	1350	-	-
Ca(mg/L)	348.7-400.1	400	400	-	-
K (mg/L)	407.5-580.8	380	380	-	-
Sr (mg/L)	7.19-9.47	8	8	-	-
Si (mg/L)	2.85-3.21	3	3	-	-
Li (mg/L)	0.164-0.29	0.2	0.2	-	-
Rb (mg/L)	0.1-0.127	0.12	0.12	-	-
Zn (µg/L)	0.0-2.0	10	0.01	0.17-0.18	1.9-5.3
Fe (µg/L)	0.9-2.4	7	0.01	1.6-3.7	-
Ni (µg/L)	0.25-0.47	5	2	0.33	0.049-0.096
Mn (µg/L)	-	4	2	0.46	-
As (µg/L)	1.36-2.16	3	3	1.60	-
Cu (µg/L)	0.60-1.10	2	3	2.50	0.050-0.054
Cd (µg/L)	-	11	0.10	0.5-0.6	0.018-0.025
Se (µg/L)	0.0-1.08	10	4	0.50-0.02	-
Cr (µg/L)	-	5	0.05	-	-
Hg (µg/L)	-	3	0.03	0.029	-
Co (µg/L)	0.0-1.1	0.5	0.5	0.015-0.18	-
Pb (µg/L)	0.0	0.3	1	0.06-0.22	0.012-0.068

Table 2. Instrumental limits of the detection for some metals

ELEMENT	PLAMEN FAAS µG/L	- GF AAS µG/L	ICP-AAS µG/L	HG-AAS µG/L
As	20	0.2	45	0.20
Ca	1	0.05	0.1	
Cd	0.5	0.003	2	
Co	6	0.02	7	
Cr	2	0.01	4	
Cu	1	0.02	3	
Fe	5	0.02	3	
Hg	200	2	20	0.02
K	1	0.002	60	
Li	0.5	0.2	3	
Mg	0.1	0.004	0.2	
Mn	1	0.01	0.6	
Na	0.2	0.01	0.2	
Mi	4	0.2	8	
P	50 000	30	20	
Pb	10	0.05	30	
Rb	2	0.2	300	
Se	100	0.5	60	0.20
Si	50	0.1	10	
Sr	2	0.05	0.2	
Zn	1	0.01	2	

It is obvious that the concentration of K, Na, Ca, Mg, Pb, Li, Si and Sr in sea water was larger than the minimal needed concentration for use of both AAS and ICP- AES methods, so in order to determine these metals, both methods can successfully be used. The concentration of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in sea water are much lower than the minimal amount needed in order for these metals by AAS. Therefore these elements can be detected by AAS flame only after the previously done concentration of the sample. The best way to increase concentration of sea water sample is to extract the complexes of these metals with APDK in IMBK.

Minimal amount needed for detection by flame AAS is 30 µg/L for arsenic and 100 µg/L for selen and mercury. Therefore none of these elements can be detected by AAS flame. The minimal amounts needed in order to use thermal AAS and HGAAS are approximately the same. However, as HGAAS is much less expensive than thermal AAS in order to detect these elements in sea water, it is the best to apply the hydride technique and technique of cold mercury vapours. The results of the research are given in Table 3.

Our results were compared with literature data. Results of our research show that the concentration of Mg, Ca, K, Sr, Si, Li and Rb in sea water of Boka Kotorska Bay is approximately the same as the medium concentration cited for these elements in sea and ocean water. Concentration of Zn, Fe, Ni, Cu, Co and Pb is similar to that given in literature data..

Concentration of selen, mercury and arsenic matches the middle concentration of these elements in sea and ocean water.

Data presented in table 3 are the result of a single sampling of sea water at depth of 1-2 .

CONCLUSION

In order to make valuable conclusion on content of sea water in Boka Kotorska Bay, research should be done throughout the year, in all seasons, and in various depths, as the concentration of certain elements in various depths differs 2-100 -fold. The concentration of researched elements in sea water of Boka Kotorska Bay is not differing much from the middle values of concentration of same elements in other sea and ocean waters.

Macro and micro elements in sea water

Table 3. Content of analysed metals in the sea water

Param.	Mg mg/L	Ca mg/L	K mg/L	Li mg/L	Rb mg/L	Sr mg/L	Si mg/L	Pb µg/L	Ni µg/L	Zn µg/L	Co µg/L	Fe µg/L	Cu µg/L	As µg/L	Hg µg/L	Se µg/L
Kotor	1336,3	376,7	563,3	0,28	0,16	6,68	-	-	-	-	-	-	-	1,69	0,00	-
Plagen.	1322	348,7	501	0,263	0,1	7,38	3,21	0,00	0,55	0,00	0,10	0,90	0,60	1,73	0,00	0,20
IBM	1325	400,1	564,5	0,28	0,127	-	-	-	-	-	-	-	-	-	0,00	-
Orahov.	1333,3	381	509,3	0,283	0,111	7,83	2,86	0,00	0,25	2,00	0,00	2,40	1,10	1,81	0,00	0,00
Risan	1341	380,1	407,5	0,28	0,111	-	-	-	-	-	-	-	-	-	0,00	-
Morinj	1364,3	392	566,8	0,268	0,10	7,19	2,85	0,00	0,47	0,00	0,00	2,40	0,90	1,36	0,52	0,88
Verige	1309	374,1	478,8	0,28	0,10	-	-	-	-	-	-	-	-	-	0,00	-
S.Ned.	1353,3	375,8	503,8	0,277	0,11	-	-	-	-	-	-	-	-	-	0,00	-
Tivat	1342	385,3	536,5	0,28	0,127	-	-	-	-	-	-	-	-	2,11	0,00	0,84
Kukulj.	1291,3	369	504,4	0,274	0,108	-	-	-	-	-	-	-	-	-	0,00	-
Sotila	1216,3	369,3	548	0,27	0,108	-	-	-	-	-	-	-	-	-	0,00	-
Bijela	1274	377,5	580,8	0,164	0,104	-	-	-	-	-	-	-	-	-	0,00	-
H. Novi	1344	381,8	557,8	0,279	0,115	9,48	-	-	-	-	-	-	-	2,11	0,00	0,90
Mamula	1372	393,5	564,8	0,291	0,103	-	-	-	-	-	-	-	-	-	0,00	-

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