

**DETERMINATION OF LEAD AND COPPER IN SALT LAKE
«PANONNICA» BY DIFFERENTIAL PULSE ANODIC STRIPPING
VOLTAMMETRY**

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ABSTRACT

One of the most serious problems facing the world today is the contamination of the environment by inorganic, organic and organometallic species. One area of particular interest is the detection of heavy metals and metalloids in environmental matrices. In the city of Tuzla recently was built an artificial salt lake filled with natural salt brine mixed with natural water from Modrac lake called «Panonnica». Due to high mineral and salt contents it has good healing effects and for that reason monitoring of heavy metals is necessary and was the main task of this work. Differential Pulse Anodic Stripping Voltammetry was used for determination lead and copper contents in salt lake, as well as other inorganic species relevant to the existence of lead and copper compounds.

Key words: Heavy metals, salt lake, Differential Pulse Anodic Stripping Voltammetry, inorganic species.

1. INTRODUCTION

One of the most serious problems facing the world today is the contamination of the environment by inorganic, organic and organometallic species. One area of particular interest is the detection of heavy metals and metalloids in environmental matrices.

Metals are defined chemically as „elements which conduct electricity, have a metallic luster, are malleable and ductile, form cations and have basic oxides“.¹

Metal and metalloid ions can be divided into three groups, based on their toxicity:

The metal/metalloids of the first group are toxic at all concentrations and have no known biological functions; this group includes lead, cadmium, and mercury.

The ions of the second group which includes arsenic, bismuth, indium, antimony, and thallium also have no known biological functions, but are less toxic; however, they are still toxic if present in more than trace concentrations.

The final group includes essential metal/metalloids such as copper, zinc, cobalt, selenium and iron, which are required for various biochemical and physiological processes and are toxic above certain concentrations.²

The heavy metals are biodegradable and are present in nature and cause continual damage of organisms. As a result of biodegradability of heavy metals, they accumulate in vital organs of human body and are toxic effect increasing progressive. The most dangerous and the most important heavy metals are lead, mercury, cadmium, arsenic, thallium and selenium. Heavy metals are toxic even if present in trace concentrations. The most toxic form is free hydrated metallic ion. The main aim of this work was determine the total concentrations of lead and copper in salt lake as well as chemical forms in which they exist.

Lead (Pb) occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Lead can enter (drinking) water through corrosion of pipes. The lead in its compounds is often in divalent or tetravalent, but compounds in which it is

monovalent. Lead is accumulating in bone and different internal organs (kidney, liver and spleen), muscles and nervous tissue. Lead can cause several unwanted effects, such as: disruption of the biosynthesis of haemoglobin and anaemia, a rise in blood pressure, kidney damage, disruption of nervous systems, brain damage and behavioural disruptions of children, impulsive behavior and hyperactivity.³ By the Law on water (BiH) maximal allowed concentration of lead in water of second class is 0,05 mg/L and whole concentration above this value caused different toxic effect on living organisms.

Copper (Cu) is reddish colored metal. In nature copper is occurs in the form of sulfide, carbonate and oxide. In very low concentrations copper have a very importante function in organism in the process of producing of blood, but it is very toxic when it is present in high concentrations. The Recommended Dietary Allowances (RDA) for copper in normal healthy adults is 0.9 mg/day. Because of its role in facilitating iron uptake, copper deficiency can often produce anemia like symptoms. Maximal allowed concentration of copper in water second class is 0,05 mg/L.

2. MATERIAL AND METHODS

Samples of salt lake „Panonnica“ were taken at four different locations ei. (the East, the West, the North and the South). Chemical analysis was performed for the content of: salt (NaCl), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}) and magnesium (Mg^{2+}). For determination of heavy metals (Pb and Cu) electroanalytical method differential pulse anodic stripping voltammetry (DPASV) was used. Chemicals of high purity (producer, Merck, Germany) were used. Analyte solutions were prepared by dilluting 1000 ppm copper and lead nitrate standard solutions (Merck, Germany) in the supporting electrolyte. The concentration of analyte solutions were in the range 10^{-4} to 10^{-6} M. DPASV was performed with the following equipment: Radiometer MDE 150, Polarographic stand, electrochemical cell, Princenton Applied Research (EG & G) model 303 A, Potenciostat (PAR, model 263A) interfaced to an Pentium II computer system with Computrace software Model 270/250 Research Electrochemistry, version 4.3, for monitoring the voltammetric measurement. The electrochemical experiments were carried out at room temperature, with deoxygenation in electrochemical cell, containing a platinum auxiliary electrode, a Ag/AgCl reference electrode and a Hanging Mercury Drop Electrode, HMDE as the working electrode.

3. RESULTS

Table 1. The results of chemical analysis

Compound	Concentration, gL^{-1}			
	Sample I	Sample II	Sample III	Sample IV
NaCl	30,79	30,79	30,79	30,79
HCO_3^-	0,3355	0,4575	0,3355	0,3843
SO_4^{2-}	0,2017	0,3073	0,1825	0,1536
Ca^{2+}	0,0921	0,0881	0,0921	0,1002
Mg^{2+}	0,0729	0,0802	0,0729	0,0753

Instrumenatal parameters:

- Purge time 120 s
- Deposition time 300 s
- Equal time 15 s
- Scan rate 2 mV/s
- Stirring rate 300 °/min
- Working electrode, HMDE
- Reference elektrode, Ag/AgCl

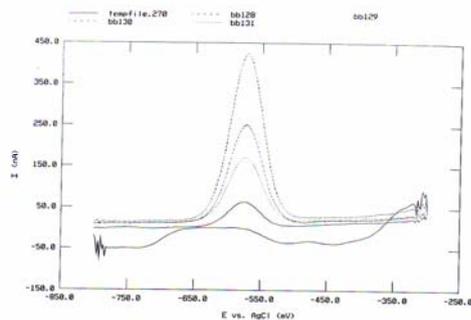


Figure 1. Voltammogram of Pb^{2+} in 0,1M KCl; pH 2,0

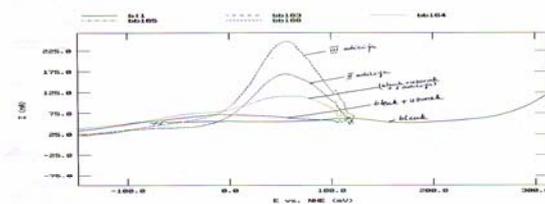


Figure 2. Voltammogram of Cu^{2+} , in 0,1M KNO_3 ; pH 6,5

Table 2. The results of voltammetric determination

Sample	Middle concentration, gL^{-1}	
	Pb	Cu
I	$8,09 \times 10^{-6}$	$2,46 \times 10^{-6}$
II	1×10^{-4}	$1,11 \times 10^{-7}$
III	$3,08 \times 10^{-5}$	$4,64 \times 10^{-6}$
IV	$1,72 \times 10^{-5}$	$5,85 \times 10^{-6}$

The results of inorganic species of lead and copper were obtain by computrace software VISUAL MINTEQA2:

I = 0,006 M
 $[SO_4^{2-}]_{TOT} = 2.10 \text{ mM}$
 $[CO_3^{2-}]_{TOT} = 5.50 \text{ mM}$
 $[Cl^-]_{TOT} = 527.00 \text{ mM}$

$[Pb^{2+}]_{TOT} = 0.29 \text{ }\mu\text{M}$
 $[Mg^{2+}]_{TOT} = 3.00 \text{ mM}$
 $[Ca^{2+}]_{TOT} = 2.30 \text{ mM}$

I = 0,006 M
 $[SO_4^{2-}]_{TOT} = 2.10 \text{ mM}$
 $[CO_3^{2-}]_{TOT} = 5.50 \text{ mM}$
 $[Cl^-]_{TOT} = 527.00 \text{ mM}$

$[Cu^{2+}]_{TOT} = 92.10 \text{ nM}$
 $[Mg^{2+}]_{TOT} = 3.00 \text{ mM}$
 $[Ca^{2+}]_{TOT} = 2.30 \text{ mM}$

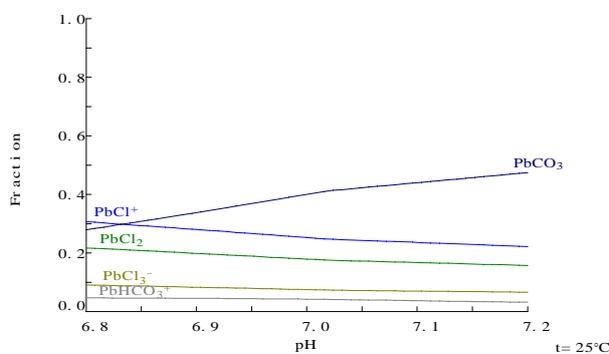


Figure 3. Inorganic species of lead (Pb)

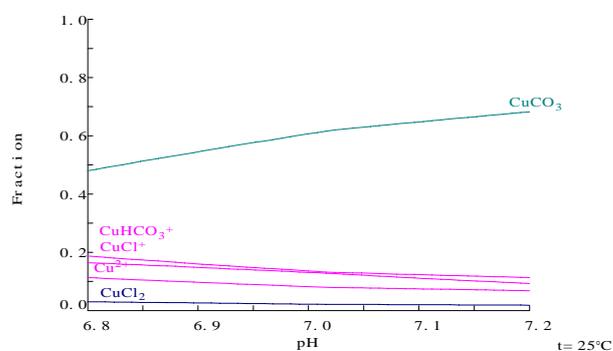


Figure 2. Inorganic species of copper (Cu)

4. DISCUSSION

DPASV was used for the determination of heavy metals. The preconcentration parameters (deposition potential and deposition time) and solution pH have been optimized for determination of lead and copper in aqueous samples. The deposition potential of -0.8 V do -0,3 V is identified to be suitable in determination of lead with HMDE. The deposition potential of -0.3 V do +0,25 V is identified to be suitable in determination of copper with HMDE. Physical-chemical determinations showed that content of inorganic compounds followed maximal allowed concentration in salt lake „Panonnica“ by regulations directive EU and WHO.⁴ Voltammetric determinations are based on the current response of an analyte to an applied potential waveform and the current was plotted as a function of the applied potential, as shown in figure 1 and figure 2. The magnitude of the peak current is proportional to the concentration of the analyte in solution.⁵ The results of inorganic species showed that carbonate compounds were present in the highest amounts.

5. CONCLUSION

The main aim of this work was the determination of total concentrations of lead and copper in the salt lake „Panonnica“ as well as chemical forms in which they exist. For determination of total concentration of lead and copper electro-analytical method Differential Pulse Anodic Stripping Voltammetry was used and for determination of chemical forms inorganic species was used computer software VISUAL MINTEQA2. Differential Pulse Anodic Stripping Voltammetry showed to be as reliable and exact technique for the determination of heavy metals in water samples because of its low (nanogram per liter) detection limits. Necessity of continuous monitoring of content of heavy metals because of toxic effect on live organism, even if present in trace concentrations, is obvious and polarographic technique with additional computer programs proved to be very useful and accurate.

6. REFERENCES

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