

Original Research Article

# Simultaneous Determination of Copper and Lead in Environmental Samples by Anodic Stripping Voltammetry

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Anodic stripping voltammetry has been developed for the simultaneous determination of copper (II) and lead (II) in environmental samples – drinking, lake and sea waters, sea lye and sea salt. The stripping peaks were obtained at -50 to -200 mV for copper and at -400 to -500 mV for lead ions, supporting electrolyte 0.01 M HNO<sub>3</sub>. The concentrate was stripped by changing the potential from -1300 to +400 mV, at a potential sweep rate 25 mV/s. The standard addition method was applied for the determination of the analytes. The concentrations of metals determined are below the international permissible limits and do not pose a health concern to use these natural objects in Bourgas region, Bulgaria.

**Keywords:** Voltammetry, Copper and Lead determination, Environmental waters, Lye and salt.

## INTRODUCTION

Anodic stripping voltammetry (ASV) has been widely used for the analysis of heavy metal ions at trace levels because of its excellent characteristics, such as good selectivity, portability, low cost, fast analysis speed and high sensitivity [1–9]. The metals are electrodeposited onto the electrode surface via an electrodeposition process and then stripped off the electrode surface via a stripping process [10]. The concentration of the metals is proportional to their stripping peak currents, which flows during the stripping process [11]. The type of the metal can be identified by the potential at which the stripping initiates.

Heavy metals are the most toxic inorganic pollutants and can be of both natural and anthropogenic origin associated with various sources of harmful emissions. The effects of toxic and heavy metals are particularly pronounced in areas with developed chemical or metallurgical industries [12, 13]. Major sources of intoxication include air, soil and water. In international practice, the term "environmental disease" has been officially recognized, associated with acute toxic changes in the blood, nervous diseases, and interference with the genetic structure of the cell. As a result, mutagenic and carcinogenic damage to the immune system occurs [13].

Researches on heavy metal content surveys have been done more than 35 years in Bulgaria, mainly in areas with intensive industries, where 5 "hot spot" in the country have been established [12]. Bourgas region is also an ecologically endangered area whose problems are due to industrial production, the high growth of production and domestic waste, the growth and physical aging of the fleet.

Depending on the degree of danger to human health, heavy metals are divided into three groups (see table 1). The most dangerous for human health are the metals of the first group [13]. The poisonous action of heavy metals on humans and animals is as great as their compounds are more soluble in water and in fats. Diluted, they are easier to digest and show their toxicity. The water that reaches our home usually comes either from surface water (water that comes from small rivers, streams or lakes) or underground water. About 80% of the tap water in Bulgaria comes from lakes, rivers or other sources on the surface. Underground water sources and municipal wells provide about 20% and the rest are from private wells.

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**Table 1.** Groups of elements according to their harmfulness [13]

Group	Elements
I group	Hg, Cd, Pb, As, Zn, Ti
II group	Co, Ni, Mo, Cu, Cr
III group	Ba, V, Mn, Sr, Al

The most common chemical pollutants in waters are nitrates, pesticides, petroleum products and heavy metals due to different sources [14, 15]:

- Depending on the original source of the water;
- When it is due to human activity, agriculture, industry or water supply network;
- Drinking water may also be contaminated by contact with water supply.

Water quality can be assessed by various parameters such as Biochemical oxygen demand (BOD, also called biological oxygen demand), temperature, electrical conductivity, nitrate, phosphorus, potassium, dissolved oxygen, etc. Heavy metals such as Pb, Cu, etc. are of special concern because they produce water or chronic poisoning in aquatic animals. The World Health Organization recommends the maximum level of copper in drinking water should not exceed 2 mg/l (2 ppm), as well as the maximum level of lead in drinking water should not exceed 0.01 mg/l (10 ppb) [16].

According to the Bulgarian State Standard [17], basic methods for determining the metals studied are:

- Copper - photometric and polarographic (ISO 17.1.4.1980);
- Lead - photometric and polarographic (ISO 17.1.4.2080).

For the determination of heavy metals in water such as Cu and Pb, photometric and polarographic methods are recommended [17]. Photometric methods in the presence of turbid or colored solutions are inapplicable or less applicable. In some cases, multiple filtration or searching for a clarification solution is necessary, which prolongs the analysis.

Voltammetry allows simultaneous determination of several metals with sufficient accuracy and sensitivity which is characteristics of atomic absorption [18], as well as it is comparable to the sensitivity of neutron activation analysis [19]. Another advantage of the voltampermetric method is that it is safe and the cost of the analysis is comparatively lower. Its resolution is greater than the standard polarographic method for heavy metal analysis in water. Examples of determinations of Cu and Pb by Anodic Stripping Voltammetry (ASV) are given in the literature [20-24].

The goal of this work is to determine the concentrations of copper and lead ions in various environmental samples by Anodic stripping voltammetry, using a standard addition method and to characterize the method of ASV in terms of accuracy, reproducibility and sensitivity in Cu and Pb analysis in these specified natural objects.

## EXPERIMENTAL

### Instrumentation

Voltammograms are recorded using an Ekotest –VA (Ekoniks-Ekspert, RF) computer-controlled voltammetric analyzer connected to a three-electrode cell. The electrode system is a three-in-one transducer designed as a single body electrochemical cell with a polycarbon indicator electrode, an auxiliary electrode and a reference electrode located in the same plane [25]. The combination «3 in 1» electrode is a whole voltammetric 3-electrode cell in a single body. All component electrodes (work, auxiliary and reference electrodes) are placed coplanarly on top of the sensor. The indicator electrode surface is regenerated by polishing it with an ashless paper filter wetted with ethanol. Voltammograms are recorded in an alternating-current mode with alternating voltage amplitude. The pH is measured using an Ekspert 001, model 3 (0.1) pH meter/potentiometer (Ekoniks-Ekspert, RF) with a glass electrode.

Thermo Scientific Evolution 300 UV-Vis and Specol-11 spectrophotometers were used.

### Reagents and solutions

All chemicals (Merck, Germany, high purity >99 %) are of analytical-reagent grade and employed without further purification. Double-distilled water was used in the preparation of the various solutions. The following reagents are used: HNO<sub>3</sub>; Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O; CuSO<sub>4</sub>·2H<sub>2</sub>O; Pb(NO<sub>3</sub>)<sub>2</sub>; KCl. A stock solution of Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> at a concentration of 5 g/l; a working solution of Hg<sup>2+</sup> - 100 mg/l; a stock solution of Pb<sup>2+</sup> - 25 mg/l; a Cu<sup>2+</sup> stock solution - 25 mg/l. The working solutions of standard lead and copper additives are at a concentration of 1.25 mg/l. The concentrated supporting electrolyte solution is prepared as 50 ml of 0.01 M HNO<sub>3</sub> and 50 ml of 0.01 M Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> are placed in a 250 ml flask and then it is diluted to the mark with double-distilled water. Concentrated HNO<sub>3</sub> supporting electrolyte solution is prepared as 50 ml of 0.01 M HNO<sub>3</sub> is transferred to a 250 ml flask and then it is diluted to the mark with double-distilled water (ddH<sub>2</sub>O). Diluted solution is prepared as 200 ml of concentrated supporting electrolyte solution is poured into a 1 dm<sup>3</sup> flask and brought to the mark with ddH<sub>2</sub>O.

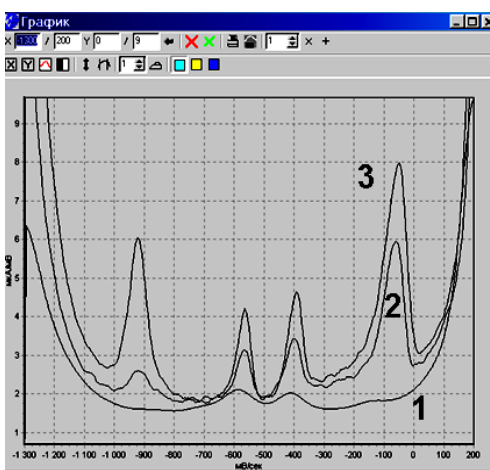
### Analytical procedure

#### Drinking and lake waters

1 liter water sample was filtered and evaporated to 150 ml. 80 cm<sup>3</sup> water sample was pipetted and transferred into 100 ml volumetric flask. Then 20 ml concentrated supporting electrolyte was added and the solution was homogenized. 25 ml from this solution was transferred in the glass vessel and 8 drops of 100 mg/l Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O were put in the vessel.



**Fig. 1.** The set for the measurements of the heavy metals in the laboratory and field conditions.



**Fig. 2.** Examples of measurement of zinc, cadmium, lead, copper with the complexes «Ecotest-VA- heavy metals». Samples: 1 - blank, 2 - tested sample, 3 - tested sample with standard additions [25].

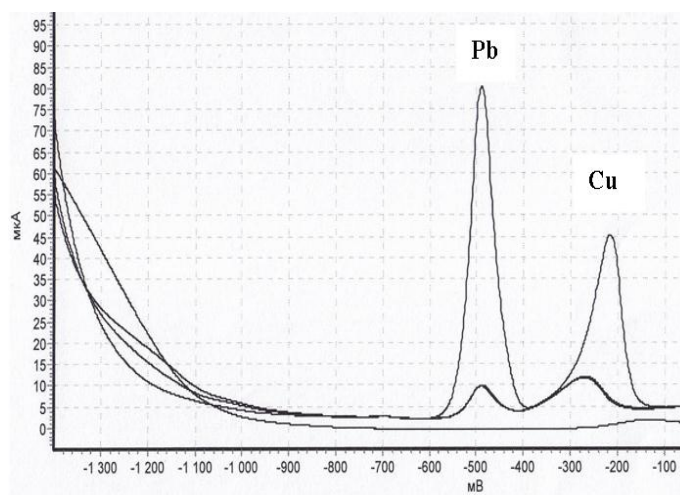
**Table 2.** Optimal conditions for voltammetric measurements using a three-in-one transducer.

Stage of analysis	Solution composition	Potential of the working electrode, $E_w$ , mV	The time of exposing the electrode, $t_{exp}$ , s
1. Electrochemical cleaning of the electrode	0.1M HNO <sub>3</sub>	+100	100
2. Formation of the mercury film	Hg(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O 100 mg/l, 0.1M HNO <sub>3</sub>	-600	200
3. Electrochemical pre-concentration of copper and lead	0.1M HNO <sub>3</sub> 0.01M HNO <sub>3</sub>	-600	200
4. Electrostripping of the concentrate	0.01M HNO <sub>3</sub> + sample	-1300...+400; potential sweep rate, 25 mV/s	300

The electrode was immersed into the solution and the analytes were pre-concentrated. The voltammograms were recorded. Consequently 1, 2 and 3 ml of standard additives of copper and lead (1.25 mg/l) solutions were added and voltammograms were recorded. The program calculates the areas of the peaks and gives the concentrations. All measurements were carried out at room temperature.

### Seawater, lye and salt

In samples of seawater and lye it is necessary to carry out the decomposition of the organic substances, interfering the determination of the metal ions. The decomposition is carried out by the mineralization method to wet salts. Sample preparation of seawater and lye involves incinerating the residue in a muffle furnace at a temperature of about 400° C for 30-40 minutes. The same procedure is followed for analysis of sea salt.



**Fig. 3.** Voltammograms of Pb and Cu in drinking water with standard additions of lead and copper

**Table 3.** Determination of copper (II) in environmental waters

Samples	Cu(II) found $\bar{x} \pm tS/\sqrt{n}$ ( $\mu\text{g/l}$ )	RSD $S_r = (S/\bar{x}) \times 100$ (%)
Drinking water	$66.0 \pm 5.6$	7.34
Lake water	$105.4 \pm 6.4$	1.37

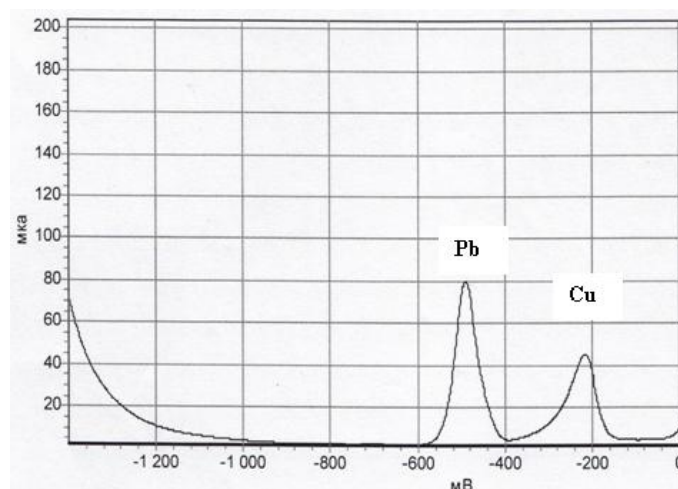
**Table 4.** Determination of lead (II) in environmental waters.

Samples	Pb(II) found $\bar{x} \pm tS/\sqrt{n}$ ( $\mu\text{g/l}$ )	RSD $S_r = (S/\bar{x}) \times 100$ (%)
Drinking water	$5.7 \pm 0.4$	6.35
Lake water	$9.5 \pm 0.7$	6.36

Number of determination  $n=5$ ;  $t$  - Students  $t$ -value at 95% probability;  $S$  - standard deviation;  $\bar{x}$ , an average

**Table 5.** Results for the determination of copper and lead in seawater, lye and salt. (n=5)

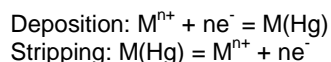
Sample	Analyte	Supporting electrolyte	Sample quantity, g	Found		$\bar{x}$ μg/l	RSD (%)
				$\bar{x}$ %	$\bar{x}$ g/ml		
Sea salt (Bulgaria)	Pb	HNO <sub>3</sub>	3.0	1,6.10 <sup>-6</sup>	-	-	13
	Cu	HNO <sub>3</sub>	3.0	0,5.10 <sup>-6</sup>	-	-	15
Sea salt (Tunis)	Pb	HNO <sub>3</sub>	1,5	0,7.10 <sup>-6</sup>	-	-	9
	Cu	HNO <sub>3</sub>	1,5	2,1.10 <sup>-6</sup>	-	-	13
Medical lye	Pb	HNO <sub>3</sub>	2.0	-	1,0.10 <sup>-8</sup>	10	9
	Cu	HNO <sub>3</sub>	2.0	-	1,7.10 <sup>-8</sup>	17	10
Seawater, density 1,023 g/ml	Pb	HNO <sub>3</sub>	10.0	-	7,0.10 <sup>-9</sup>	7	6
	Cu	HNO <sub>3</sub>	10.0	-	3,1.10 <sup>-8</sup>	31	7

**Fig. 4.** Voltammograms of Pb and Cu in Black sea salt.

The sampling for medical lye is 2 ml, for seawater is 10 ml and for sea salts 1-3 g. Samples of seawater and lye are evaporated to moist salts in quartz dishes. 20 ml of bi-distilled water are added and quantitatively transferred to the electrolysis cell. 5 ml of diluted supporting electrolyte solution is added and the analyses starts.

## RESULTS AND DISCUSSION

Anodic stripping voltammetry is used to determine the concentration of Pb and Cu in the water samples. The method consists of a deposition potential that is more negative than the half-wave potential  $E_{1/2}$  of the metals to be determined and an anodic scan to oxidize the reduced metal back into solution:



During deposition, an amalgam is formed by the elemental metal and the mercury on the electrode. Scan in the positive

direction peak current is proportional to the concentration of the metal M. The sensitivity of the method arises due to the pre-concentration of the analyte species. The analytes can be determined simultaneously because the difference of their potentials is sufficient to avoid overlapping individual peaks. This is one of the advantages of ASV compared to standard spectrophotometry method.

The maximum analytical signal of copper was found to be from -50 to -200 mV and this one for lead from -400 to -500 mV at a rate of 25 mV/s in an alternating-current mode. The optimum current range was 2-200 μA. The optimal conditions for voltammetric measurements are given in Table 2.

Linear calibration graphs were obtained in a concentration range 10-500 μg/l for Cu<sup>2+</sup>, and 30-500 μg/l for Pb<sup>2+</sup>. The detection limit for copper ions is 0.5 μg/l (RSD=12%) and for lead ions is 0.1 μg/l (RSD=10%). The accuracy and precision of the voltammetric procedure were verified by standard spectrophotometric method for determination of copper and lead ions in waters. The results obtained are given in Tables 3 and 4. According to the literature [26], the threshold limit value

(TLV) for coastal marine waters is 30 µg/l. The content of copper in seawater is below the TLV. Certain interest in terms of sanitary monitoring is the determination of lead in seawater. TLV of lead in coastal marine waters is 10 µg/l. The content of lead determined in seawater lies within this range.

Of great importance for this work is the determination of lead and copper in important products obtained during the salt production process, which are widely used in a number of industries. Due to the widespread use of these products, it is necessary to carry out sanitary monitoring of copper and lead contamination. An analysis of sea salt used for food purposes was therefore carried out. Figure 4 presents the voltammetric curves of lead and copper in sea salt.

The reproducibility of determining the concentrations of Cu and Pb in sea salt in Bulgaria is  $\pm 15\%$  and  $\pm 13\%$  respectively, and in Tunisian sea salt is respectively  $\pm 13$  for copper and for lead  $\pm 9\%$ . Data from sea salt analysis shows that analyte concentrations are in the range of  $n \cdot 10^{-6}\%$  (table 5). According to the Ordinance on the Quality of Marine Salt for Food [27], the TLV for lead is 2 mg/kg, respectively. Analyzed marine salts are compliant with the Bulgarian state standard, as the copper and lead TLVs are in the range of  $n \cdot 10^{-6}\%$ .

The concentrations of copper and lead in various environmental samples were found to be lower than the water contamination standards issued by the World Health Organization.

## CONCLUSIONS

Anodic stripping voltammetry has been developed for the simultaneous determination of copper (II) and lead (II) in environmental samples - drinking, lake and sea waters, sea lye and salt. Under the optimal conditions, alternating-current voltammograms were recorded and the concentration of copper and lead ions were determined by standard addition method. The results obtained are in agreement with those of spectrophotometry standard method.

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## CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest related to this study.

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