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Original Research Article

Simultaneous Determination of Cadmium and Zinc in Environmental Samples by Anodic Stripping Voltammetry

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The concentrations of Cd and Zn metal ions in various environmental samples were simultaneously determined with anodic stripping voltammetry technique at mercury-film electrode. The stripping peaks were obtained at -600 to -700 mV for cadmium(II) and at -900 to -1100 mV for zinc(II), supporting electrolyte 0.1 M HNO_3. The concentrate was stripped by changing the potential from -1400 to +200 mV, at a potential sweep rate 25 mV/s. Under the optimum experimental conditions, the calibration curves for Cd and Zn ions were obtained in the linear range of 0.5-400 ppb and 0.5-500 ppb, respectively. The detection limits and quantitation limits are as follow: for Cd 0.67 µg/L and 2.23 µg/L, and for Zn 0.56 µg/L and 1.86 µg/L. The proposed method has a good reproducibility and was successfully applied to the determination of Cd(II) and Zn(II) in drinking, lake and sea waters, sea lye and sea salt. The concentrations of metals determined are lower than the international permissible limits and there is no health-threatening concern due to the consumption of water and sea salt in this region.

Keywords: Voltammetry, Cadmium and Zinc determination, Environmental waters, Sea lye and sea salt.

INTRODUCTION

Over the last decade, Stripping Voltammetry has been widely used in various fields as a very versatile and powerful electroanalytical technique. This method is aimed to extend the scope of the sensitivity and selectivity of analysis toward numerous analytes [1-11]. Electrochemical methods include stripping voltammetric techniques, principally anodic stripping (ASV) and adsorptive cathodic stripping (AdSV) voltammetry, which show numerous advantages, such as minimum sample pretreatment, high speed of analysis, good performance with saline matrix, low cost [2].

The problem of environmental pollution with heavy metals is relevant both globally and in our country due to the fact that they are not biodegradable, they remain in the soil for an extended period of time and the process of their purification is difficult and prolonged. 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. Cadmium is one of the most toxic metals. Zinc is not toxic, but its salts have some toxic action. Therefore, conducting ecological monitoring in environmental sites is of great importance for protecting the health of the population.

The World Health Organization recommends the maximum level of zinc in drinking water should not exceed 5 mg/L (5 ppm) as well as the maximum level of cadmium in drinking water should not exceed 0.005 mg/L (5 ppb) [14-16]. According to the Bulgarian State Standard [17], basic methods for determining the metals studied are:

- cadmium - photometric and polarographic (BSS 7320-69, BSS 16777, ISO 8288);
- zinc - photometric and polarographic (BSS 15107-80, BSS 16777, ISO 8288).

Photometric methods in the presence of turbid or colored solutions are inapplicable or less applicable.

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Although numerous methods are already established for detecting heavy metals, such as atomic absorption spectroscopy, atomic emission spectroscopy, mass spectroscopy and x-ray fluorescence spectroscopy, voltammetry is preferred over spectroscopic techniques due to some advantages related to their cost, simplicity and the possibility of on-site application. ASV allows simultaneous determination of several metals with sufficient accuracy and sensitivity which are characteristics of atomic absorption, as well as it is comparable to the sensitivity of neutron activation analysis. Examples of determinations of Cd and Zn by Anodic Stripping Voltammetry are given in the literature [18-22].

The present paper describes an ASV study for determination of cadmium and zinc in drinking and lake waters. The goal of the work is to characterize the method of ASV in terms of selectivity, accuracy, reproducibility and sensitivity for analyses of Cd and Zn in these samples. The parameters studied were: variation of pH solution, accumulation potential and accumulation time. To determine the precision, accuracy, sensitivity, and linearity of method, relative standard deviation (RSD), limit of detection and limit of quantitation were determined. The method at optimum condition was applied for the direct determination of Cd(II) and Zn(II) in waters.

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 [23-25]. 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 place 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 were used: HNO_3; $Hg_2(NO_3)_2{\times}H_2O$; $Zn(NO_3)_2{\times}6H2O$; Na_2SO_3, $Cd(NO_3)_2{\times}4H_2O$. A stock solution of $Hg_2(NO_3)_2$ at a concentration of 5 g/L; a working solution of Hg^{2+} - 100 mg/L; a stock solution of Cd^{2+} - 1 g/L; a Zn^{2+} stock solution - 1 g/L. The working solutions of standard cadmium and zinc solutions having concentrations 100-500 ppb were prepared with appropriate dilution.

Analytical procedure

Drinking and lake waters. Water samples were filtered. Then 1 mL water sample was pipetted and transferred in glass vessel containing 25 mL 0.1N HNO_3 supporting electrolyte and 100 µg/L Hg^{2+} solution to form a Hg-film during electrolysis (7 drops of 100 mg/L $Hg(NO_3)_2.H_2O$ were put in the vessel). The electrode was immersed in the solution and the analytes were pre-concentrated. The voltammograms were recorded. Calibration graphs: 1, 2, 3, 4, 5 mL of standard solutions of Cd and Zn (100 ppb) were added in the glass vessel containing 25 mL 0.1N HNO_3 supporting electrolyte and 100 µg/L Hg^{2+} solution and voltammograms were recorded at optimal conditions (table 1). The concentrations were calculated by the equations of the calibration graphs. All measurements were carried out at room temperature and 5 duplicates.

Sea water, lye and salt. The decomposition was carried out by the mineralization method to wet salts. Sample preparation of seawater and lye involved incinerating the residue in a muffle furnace at a temperature of about 400° C for 30-40 minutes. Sea salt samples were dried at 110 ° C, tempered in a desiccator and the exact mass was dissolved in an accurate volume of distilled water. The concentration of all samples prepared was 1 g/L.

RESULTS AND DISCUSSION

Anodic stripping voltammetry has been developed to determine the concentrations of Cd and Zn at ppb level. The preconcentration step is key for achieving these low detection limits. During the accumulation, the metal is reduced and forms an amalgam in the mercury film.

1. Electrochemical deposition – preconcentration of analyte at the electrode thin film surface under forced convective conditions (stirring solution):

   $$M^{2+} + 2e- + Hg = M(Hg)$$

2. Quiet time – the potential is still applied, but the stirring is stopped for 30 seconds prior to analysis.
3. Stripping – the potential is scanned to oxidize the metal back to its original state:

$$M(Hg) = M^{2+} + 2e- + Hg$$

Scan in the positive direction peak current is proportional to the analyte concentration.

Results from the ASV show that the signals from both cadmium and zinc increased linearly with concentration. The linearity of the calibration curves obtained yielded correlation values (R) close to 1. Peak currents were obtained at the potentials between −600 and −700 mV for cadmium(II) and at −900 to −1100 mV for zinc(II), supporting electrolyte 0.1 M HNO3 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, reported earlier by us [24], are given in table 1.

Linear calibration graphs were obtained in a concentration range 10−400 µg/L for $Cd^{2+,}$ and 10−500 µg/L for Zn^{2+}. The detection limit (LOD = 3. δ/S) and quantitation limit (LOQ = 10.δ/S), where δ is the standard deviation of the reagent blank (n=5) and S is the slope of the calibration curve for cadmium ions are 0.67 µg/L and 2.23 µg/L and for zinc ions are 0.56 µg/L and 1.86 µg/L, respectively.

The accuracy and precision of the voltammetric procedure were verified by analyses of model solutions (table 2). The results obtained for the determination of Cd and Zn in environmental waters are given in tables 3 and 4.

Cd^{2+} was not found in any water samples. Zn^{2+} was in the order of 2.2−350 ppb in the samples, which is bellow international permissible limits. According to the literature [25, 26], the threshold limit value (TLV) of zinc for coastal marine waters is 50 µg/L.

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

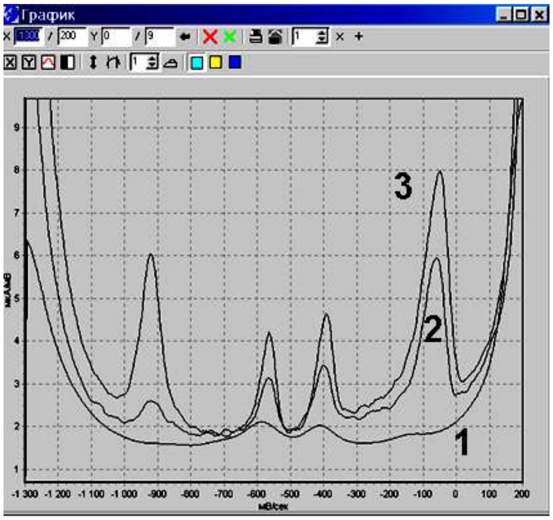

Fig. 2. Examples of measurement of zinc, cadmium, lead, copper with the complexes «Ecotest-VA- heavy metals». Samples: 1 - blank, 2 - tested sample, 3 - tested sample with standard additions [23].

Table 1. 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_3	+100	100
2.Formation of the mercury film	$Hg(NO_3)_2.H_2O$ 100 mg/l, 0.1M HNO_3	-600	200
3.Electrochemical pre-concentration of cadmium and zinc	0.1M HNO_3 0.01M HNO_3	-600	200
4.Electrostripping of the concentrate	0.1M HNO_3 + sample	-1400…+200; potential sweep rate, 25 mV/s	300

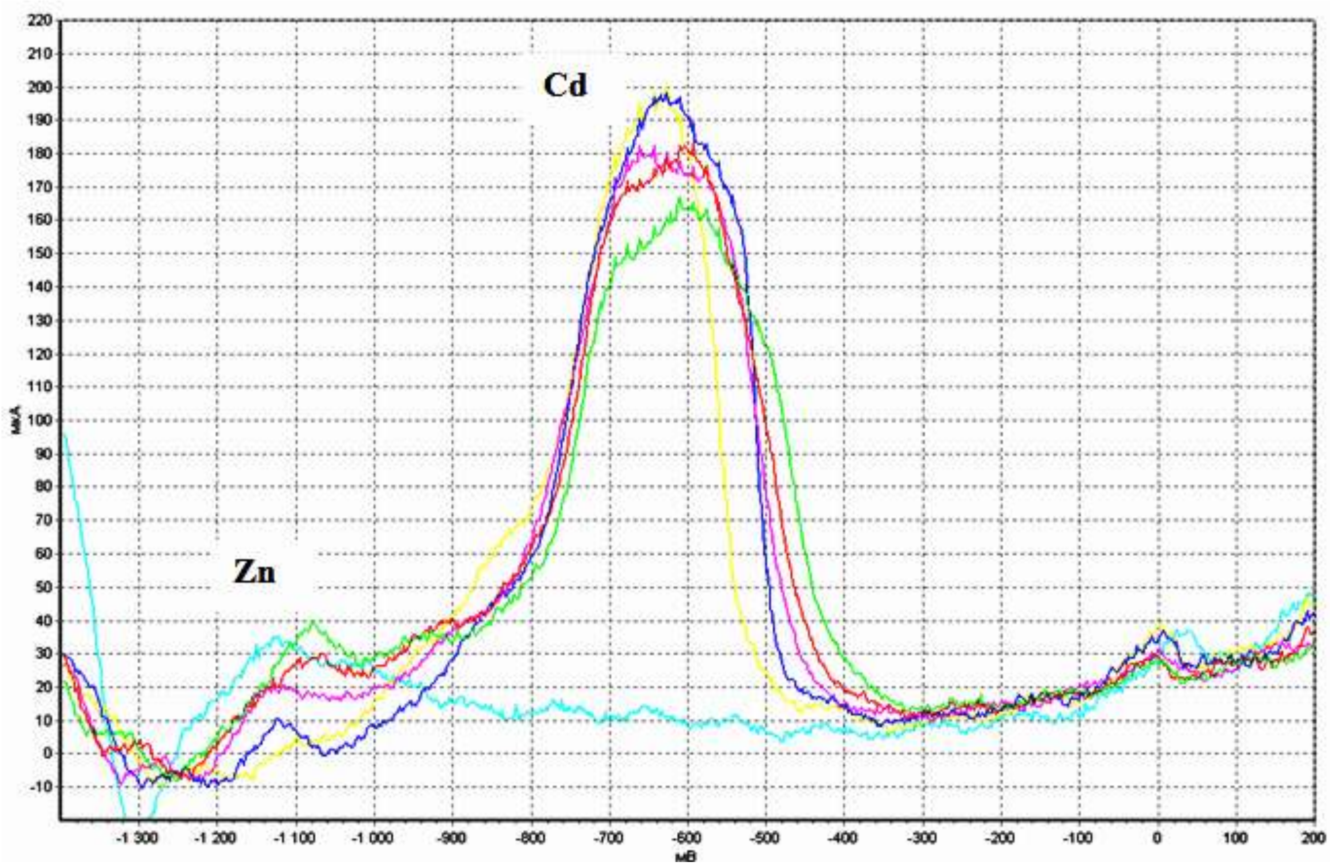

Fig. 3. Voltammograms of sea water without additions of Zn standard and with additives of 300 □g/L Cd standard solution – 5 duplicates.

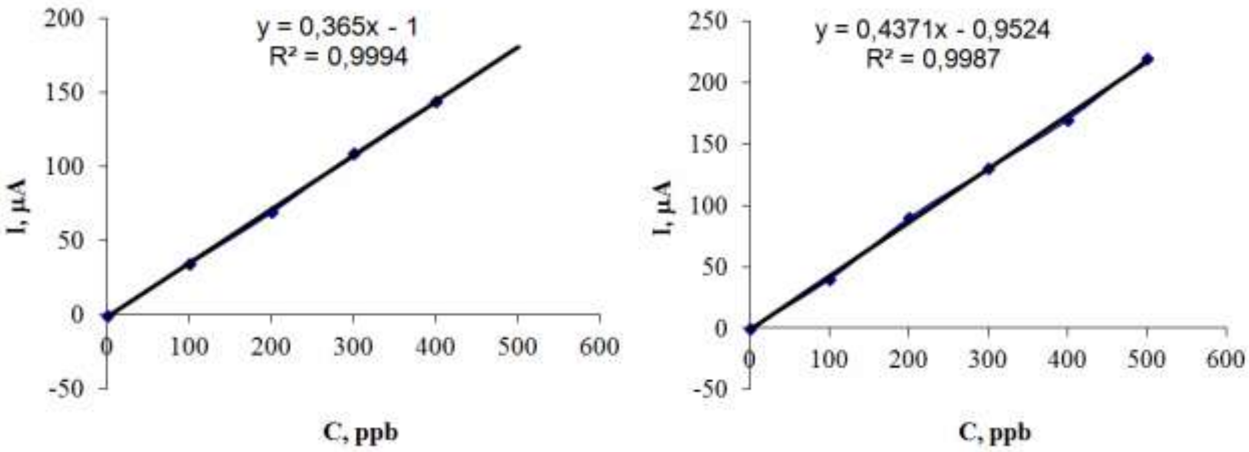

Fig. 4. Calibration graphs of: 1) cadmium(II) and 2) zinc(II) standard solutions.

Table 2. Analyses of model solutions having additions of standards of Cd and Zn

Samples	Found $\bar{x} \pm tS/\sqrt{n}$ (μg/L)	RSD $S_r = (S/\bar{x})\times100$ (%)
Cd addition 100 μg/L	99.8 ± 1.3	1.10
Cd addition 200 μg/L	199.4 ± 3.1	1.26
Zn addition 100 μg/L	99.6 ± 1.5	1.21
Zn addition 200 μg/L	200.2 ± 2.2	0.89

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

Table 3. Determination of Cd(II) in waters with 100 ppb addition of Cd standard.

Sample	Cd(II) found $\bar{x} \pm tS/\sqrt{n}$ (μg/L)	RSD $S_r = (S/\bar{x})\times100$ (%)
Tap water	98.2 ± 2.7	2.21
Mineral water Hyssar	96.0 ± 3.7	3.13
Mineral water Bankya	97.6 ± 3.9	3.20
Spring water	96.8 ± 5.0	4.16
Lake water	99.2 ± 2.5	2.06

Table 4. Determination of Zn(II) in waters having 100 ppb addition of Zn standard.

Sample	Zn(II) found $\bar{x} \pm tS/\sqrt{n}$ (μg/L)	RSD $S_r = (S/\bar{x})\times100$ (%)
Tap water	291.4 ± 4.0	1.10
Mineral water Hyssar	118.2 ± 6.4	4.12
Mineral water Bankya	102.2 ± 5.1	3.99
Spring water	99.6 ± 5.4	4.41
Lake water	450.0 ± 7.0	1.26

Table 5. Results for the determination of cadmium(II) in sea water, lye and salt.

Sample	Found with addition of 300 ppt Cd^{2+}, $\bar{x} \pm tS/\sqrt{n}$, (μg/l)	Cd^{2+} found $\bar{x} \pm tS/\sqrt{n}$ (μg/l)	RSD $S_r = (S/\bar{x})\times100$ (%)
1. Sea water	302.7 ± 1.7	2.7 ± 1.7	0.45
2. Sea lye	304.1 ± 2.1	4.1 ± 2.1	0.55
3. Black sea salt	-	31.8 ± 1.4	3.68
4. Iodized salt Black sea	303.6 ± 2.8	3.6 ± 2.8	0.74

Table 6. Results for the determination of zinc(II) in sea water, lye and salt.

Sample	Zn^{2+} found $\bar{x} \pm tS/\sqrt{n}$ (μg/l)	RSD $S_r = (S/\bar{x})\times100$ (%)
1. Sea water	26.9 ± 2.3	6.98
2. Sea lye	20.0 ± 1.6	6.51
3. Black sea salt	291.3 ± 3.2	0.89
4. Iodized salt Black sea	57.6 ± 2.4	3.34

The content of zinc in seawater is below the TLV. Certain interest in terms of sanitary monitoring is the determination of cadmium in seawater. TLV of cadmium in coastal marine waters is 5 µg/L. The content of cadmium determined in seawater lies within this range (table 5).

It is of great importance the determination of cadmium and zinc in important products obtained during the salt-making process, which are widely used in a number of areas. For example, sea salt is used in the food, pharmaceutical, chemical and other industries. Medical lye is included in a number of pharmaceutical preparations and drugs. In view of the widespread use of these products, it is necessary to carry out a sanitary monitoring of their contamination with cadmium and zinc. An analysis of sea salt used for food purposes was therefore carried out. According to the Ordinance on the Quality of Marine Salt for Food Purposes, the TLV of cadmium(II) in sea salt is 0.1 mg kg (100 µg/kg) and the TLV of zinc(II) in sea salt is 10 mg/kg. The concentrations we set are far below the cadmium and zinc content in the Black sea salt.

The method proposed is easy and fast and it requires minimal sample pre-treatment. It is generally not affected by salt content. The concentrations of Cd and Zn in various water samples were found to be lower than the drinking water contamination standards issued in the World Health Organization.

CONCLUSIONS

Anodic stripping voltammetry has been developed for the simultaneous determination of cadmium(II) and zinc(II) in environmental samples - drinking, lake and sea waters, sea lye and sea salt. Under the optimal conditions alternating-current voltammograms were recorded and the concentrations were determined by calibration graph method. The results obtained show that the method offers advantages as easy sample pretreatment, good selectivity, sensitivity, reproducibility and linearity.

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