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Direct Determination of Zn Heavy Metal in Tap Water of Canakkale (TURKEY) by Anodic Stripping Voltammetry Technique

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In this work, the direct determination of zinc heavy metal in the tap water was carried out by differential pulse anodic stripping voltammetry (DPASV) technique at the glassy carbon electrode (GCE). The zinc ions were deposited by reduction at -1.5 V on a bare glassy carbon surface. Then, the deposited metal was oxidized by scanning the potential of the electrode surface from -1.5 to -0.8 volt using a differential puls mode. The stripping current arising from the oxidation of metal was connected with the concentration the metal in the sample. The concentration of zinc heavy metal found in tap water sample was determined to be 180 μg L^{-1} using 0.2 mol L^{-1} acetate buffer (pH: 3.50).

Keywords: Anodic stripping voltammetry; Glassy carbon electrode; Zinc; Heavy metal; Tap water

1. INTRODUCTION

Knowledge of the concentration of free metal in tap water is essential to understand the role of nutrient and pollutant elements. Investigations of toxic heavy metals such as Pb, Cd, Cu, Zn and Cr place special importance on environmental samples [1,2]. Thus, there is a pressing need to develop trace element analysis techniques that allow separation of the different element species prior to trace element analysis. "Industrial and household waste discharges, directly or indirectly through leakages in sewage systems into water sources, cause excessive pollution in surface and underground water" [3]. Water quality also changes in relation to the properties of physical, chemical and biological components of water.

Anodic stripping voltammetry (ASV) is a powerful technique used for rapid determination of trace levels of metal ions. For determination of zinc by ASV, bismuth-film electrodes [4,5], thick-film modified graphite-containing electrode (TFMGE) [6], gallium film electrode [7], an anion-exchange perfluorinated polymer Tosflex mercury film electrodes (TMFE's) [8] and the hanging mercury drop electrode [9,10] have been used. However, because of the toxicity of mercury, the alternative electrodes used in environmentally-friendly analytical techniques should be improved to determine the trace metals in samples of environmental, clinical and industrial origin. Moreover, it is known that mercury or mercury plated electrodes, used to determine the heavy metals in the samples, is affected by organic substances. These substances can form non-labile complexes with the analyte element and adsorb on the electrode. Therefore, the alternative electrodes are widely utilized in determining many heavy metals.

In this study, DPASV technique was used to determine of zinc heavy metal in tap water sample on a bare GC electrode. Consequently, the most appropriate conditions were fixed to determine zinc amount as an analytical application of DPASV on a bare GC electrode. DPASV technique, new, rapid, simple, selective and inexpensive for qualitative and quantitative determinations of heavy metals, was successfully applied.

2. MATERIAL AND METHODS

2.1. Instrumentation and operating conditions

Voltammetric determinations of Zn(II) were performed with Metrohm 757 VA Computrace (Herisau, Switzerland) with a three-electrode system consisting of a glassy carbon working electrode (GCE; 3 mm diameter, Metrohm), a platinum wire auxiliary electrode and Ag/AgCl (NaCl/ 3 M, Metrohm) reference electrode. The operating parameters are given in Table 1.

After the experimental parameters were recorded, the sample in the voltametric cell was sprayed with argon for 5 minutes. The zinc ions were deposited by reduction at -1.5 V on a bare glassy carbon surface. Then, the deposited metal was oxidized by scanning the potential of the electrode surface from -1.5 to -0.8 volt using a differential puls mode.

All pH measurements were made with Model Metrohm 744 pH meter (Herisau, Switzerland) at ambient temperature of the laboratory (25-30 °C).

2.2. Reagents

The standard zinc solution of 10 mg L^{-1} for the voltammetric investigations was prepared from the stock solution of 1000 mg L^{-1}. A 0.2 mol L^{-1} acetate buffer (pH 3.5), prepared by mixing the appropriate amounts of glacial CH_3COOH (Riedel, Seelze, Germany, 100 m/m %) and NaOH (Riedel, Seelze, Germany), was used to prepare solutions of the supporting electrolyte. Ultra pure-deionize water was obtained from Sartorius Arium model Ultra Pure Water Systems and was used to prepare to buffer. Other chemicals and all of analytical-reagent grades (Merck) were used.

Table 1. Instrument operating parameters for the analysis of Zn(II) in tap water by anodic stripping voltammetry

Parameter	Description
Working electrode	(Glassy Carbon,GC)
Mode	(Differential Pulse, DP)
Calibration	Standard addition
Blank purge time (s)	300
Purge time before each measurement (s)	10
Accumulation potential(V)	-1.50
Accumulation time (s)	300
Pulse amplitude (V)	0.05
Start potential (V)	-1.50
End potential (V)	-0.80
Obtained peak potential (V)	-0.98
No of replication	3
Sweep rate (V/s)	0.015

2.3. Sample Preparation and Anodic Stripping Voltammetric Measurements

Tap water sample was collected from our research laboratory for the determination of Zn(II). Then 10 mL of this water sample and 10 mL of 0.2 mol L^{-1} acetate buffer (pH 3.5) were put into voltammetric cell. After the solution was deaerated by purging with argon, Zn heavy metal was analyzed at the operating condition which was applied to the deposition potential of -1.5 V. At the same time, the solution was stirred at the adsorption period of the deposition time of 300 s. After a period of 10 s, the potential scan was started in the anodic direction using the differential pulse mode. The other parameters are given in Table 1. After the addition of 100 µl Zn(II) standard solution, the procedure was repeated two times. The peak potentials of Zn(II) was obtained at -0.980 V for the all voltammetric measurements.

3. RESULTS AND DISCUSSION

3.1. Determination of Zn in tap water sample

In this study, the concentration of the zinc metal in the tap water was successfully determined by ASV technique. DPAS voltammograms of zinc obtained from standard addition technique are given in Fig 1. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation (Fig 2). (Used voltammetric apparate on quantitative mode automatically requires one sample to be added to the voltammetric cell and then two standards to be added and finally, the machine plots the value of the current- concentration. Therefore, there are only three plots on calibration curve). Consequently, linear calibration range was automatically obtained as being related to quantitative mode of the voltammetric unit.

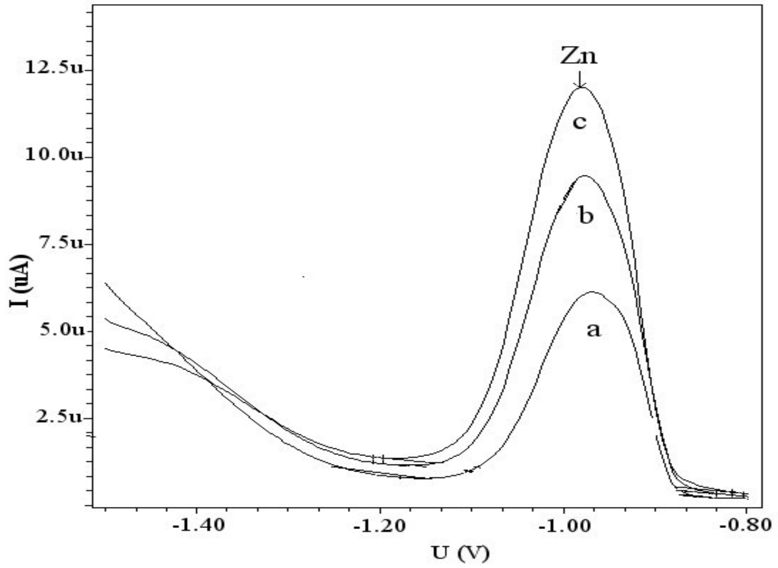

Figure 1. DPAS voltamograms of the Zn obtained from standart addition technique a) 10 ml acetate buffer (pH = 3.5) + 10 ml tap water b) a + 100 μL c) b + 100 μL standart solution of Zn (10 mg L^{-1}).

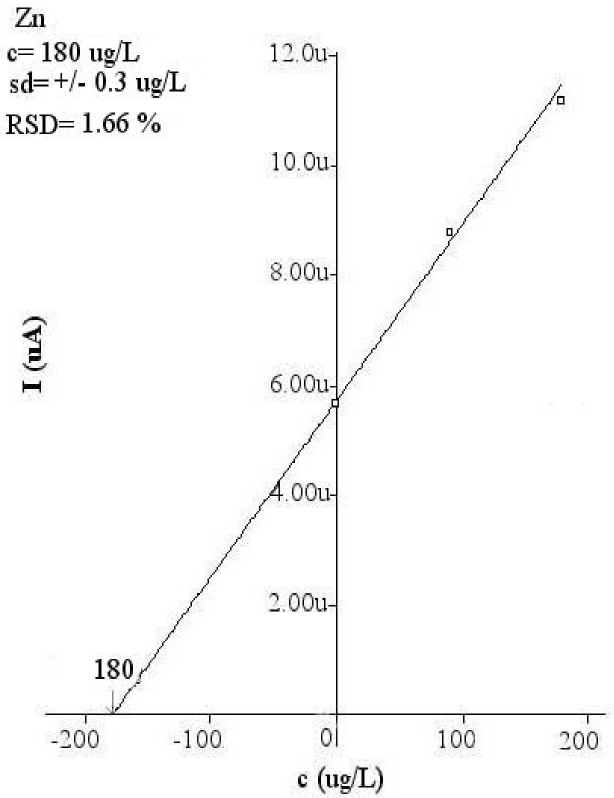

Figure 2. The calibration plot of Zn(II) obtained from standard addition by DPASV technique.

As can be seen from the Fig. 2, the current of oxidation peak of zinc increased by the addition of the standard solution. A further increase in sensitivity of peak currents was achieved by increasing the deposition time to 300 s. In addition, to increase sensitivity, the optimum pH value in acetate tampon was determined to be 3.5. Under these conditions, the concentration of Zn(II) in tap water of Canakkale was found to be 0.180 mg L^{-1}. This value is between the limit values suggested by WHO, TSE and EPA (Table 2). In addition, the concentration of Zn(II) found indicates to be “the first quality water” of the tap water according to the inland water quality classification (Table 3) [11,12]. Consequently, it is understood that the concentration of Zn(II) in tap water have no influence on the human health.

Table 2. Limit value (according to TSE, WHO, EPA: [11, 12]) and the found value of zinc heavy metal in tap water of Canakkale City (TURKEY)

Heavy metals	Limit values of Zn TSE 266 (mg L^{-1})	WHO (mg L^{-1})	EPA (mg L^{-1})	Found value of Zn(II) in tap water (mg L^{-1})
Cd	0.010	0.010	0.010	
Pb	0.050	0.050	0.050	
Cu	3.000	-	-	
Zn	**5.000**	**-**	**5.000**	**0.180**
Cr	0.050	0.050	0.050	
Fe	0.300	0.100	0.300	
Ni	0.020	0.020	0.020	

Table 3. Limit value (µg L^{-1}, according to the inland water quality classification: [11, 12]) and the found value of Zn heavy metal in tap water of Canakkale City (TURKEY)

	Limit values of the Water Quality Classes (µg L^{-1})				Found value of Zn in tap water (µg L^{-1})
Heavy Metals	I. Quality	II. Quality	III. Quality	IV. Quality	
Cd	3	5	10	>10	
Pb	10	20	50	>50	
Cu	20	50	200	>200	
Zn	**200**	**500**	**2000**	**>2000**	**180**
Cr^{+6}	<20	20	50	>50	
Cr (total)	20	50	200	>200	
Fe	300	100	5000	>5000	
Ni	20	50	200	>200	

Determination of zinc by ASV, especially at the mercury film and bismuth film electrodes, is affected by the presence of copper in the analysed samples. The problem of a copper interference with a zinc determination by ASV is discussed in a number of papers [13-18]. The various analytical applications to solve these problems are recommended [7,19,20]. However, the interferences with copper or the other heavy metals on zinc determination in the tap water sample in our work have not been observed. Therefore, a bare GC surface can be recommended to determine zinc in the tap water samples. Also, the analysis in some papers has been determined without the interferences in the applied voltammetric method [21-24]. The advantages of the proposed voltammetric method over the other known techniques were sample preparation, sensitivity, rapidity and cost.

4. CONCLUSIONS

In this work, the most appropriate conditions were fixed to determine the amount of zinc as an analytical application of DPASV on a bare GC electrode. Direct determination of Zn(II) in the tap water sample is possible by DPASV. A bare GC electrode surface can be recommended for the analytical application of DPASV. Under working conditions to be 3.5 of pH using acetate tampon and 300 s of the deposition time, zinc amount in the tap water sample has been successfully determined.

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