

Simultaneous Determination of Traces of Cadmium and Zinc by Adsorptive Stripping Voltammetry

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Abstract

A procedure for the simultaneous determination of cadmium and zinc by adsorptive differential pulse cathodic stripping voltammetry has been developed in this work. The complexes of cadmium and zinc ions with PTT are accumulated onto a hanging mercury drop electrode (HMDE). Optimal conditions were obtained at pH 9.0, PTT concentration of 3.5×10^{-5} M, deposition potential of 0.1 V, deposition time of 30 s, scan rate of 12 mV/s and pulse height of 50 mV. The linear range of cadmium (II) and zinc (II) were observed over the concentration range 5-230 and 5-370 ng/mL, respectively. The detection limit ($S/N=3$) was 1.1 ng/mL (cadmium) and 1.6 ng/mL (zinc). The method has been successfully applied for determination of both ions in real samples.

Keywords: Adsorptive cathodic stripping voltammetry; Cadmium; Zinc; PTT

Résumé

Dans ce travail, nous avons développé une procédure pour la détermination simultanée du cadmium et du zinc par voltampérométrie impulsions différentielle adsorbante après redissolution cathodique. Les complexes PTT des ions cadmium et zinc PTT ont été accumulés sur une électrode de mercure à goutte pendante (HMDE). Les conditions optimales ont été obtenues à pH 9.0, et ce pour une concentration en PTT de 3.5×10^{-5} M, un potentiel de dépôt de 0.1 V, une temps de dépôt de 30 s, une vitesse de balayage de

12 mV/s et une amplitude d'impulsion de 50 mV. Les gammes de mesure linéaire du cadmium (II) et du zinc (II) ont été observées sur des concentrations de 5-230 et 5-370 ng/mL, respectivement. La limite de détection ($S/N=3$) se situait à 1.1 ng/mL (cadmium) et 1.6 ng/mL (zinc). La méthode a pu être appliquée avec succès pour la détermination des deux ions dans des échantillons réels.

Introduction

Cadmium is known to be a hazardous environmental pollutant with toxic effects for the living organisms in aquatic ecosystems (1). Adsorptive effects of cadmium are produced not only because of its high toxicity even at trace concentrations, but also due to bioaccumulation processes along the food chain. As water plays an important role in nature as carrier, among others, the anthropogenic inputs of cadmium can be easily widespread over the aquatic medium (2).

Zinc is among the most important of the trace elements in human nutrition. It is vital for the immune system, the expression of genes and the transfer of nervous signals (3). Zinc is chemically active and can easily make alloys with other metals. This is why it is used so often in industry. The widespread use of zinc has led to increased monitoring of zinc levels in the environment to safeguard human life (4).

There are several methods that can determine cadmium (5-6) or zinc (7-9) at trace levels in a variety of samples e.g. UV-Visible spectrophotometry, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), neutron activation analysis (NAA) and X-ray fluorescence analysis. These methods are too expensive to be used in routine analysis and furthermore, need complicate

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procedure and enrichment steps for analysis.

The low cost and the high sensitivity of electrochemical methods make them very appealing for the detection and quantitation of heavy metals. Indeed, detection limits comparable to (and sometimes even lower than) those of the more expensive electrothermal atomic absorption spectrometry (ETAAS) can be attained easily by techniques such as stripping voltammetry. In particular adsorptive cathodic stripping voltammetry (AdSV) is a powerful analytical technique for the determination of ppb levels of metal ions. The technique is based upon adsorptive accumulation of the metal ion complex with a suitable ligand at the electrode scanning in the negative direction. The advantages of AdSV for trace analysis are high sensitivity and low instrumentation and running costs. The possibility of analyzing various samples without the need of a prior separation is also convenient. Thus, adsorptive stripping analysis (10-12) is becoming a widely accepted tool for trace amount measurements of heavy metal ions. Several adsorptive stripping methods have been reported for the determination of Cd (II) and Zn (II), separately, with different reagents (13-17). These methods have some advantages and disadvantages with respect to sensitivity and selectivity. Zinc is frequently present at trace levels in cadmium compounds, which occur widely in nature in a close association, therefore, simultaneous determination of these two ions is very important.

In this study, we have examined the application of PTT to the simultaneous determination of cadmium and zinc by adsorptive cathodic stripping voltammetry on a hanging mercury drop electrode (HMDE). The method relies on the effective accumulation of the Cd (II) and Zn (II) complexes with PTT onto the HMDE. The method is extremely sensitive, selective and simple for the determination of trace levels of cadmium and zinc in real samples.

Experimental

Apparatus

A Metrohm 746/747 VA processor with a three-electrode system consisting of a HMDE as the working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode were used to obtain the voltammograms. All potentials reported were referred to the Ag/AgCl electrode. A Metrohm 691 pH meter using a combined glass electrode was used to determine the pH of solutions. A Varian AA-50 atomic absorption spectrometer equipped with cadmium and zinc hollow

cathode lamps was used for atomic absorption measurements.

Reagents and Solutions

All solutions were prepared with doubly distilled water. The stock solutions of Cd (II) and Zn (II) of 1000 mg/L were prepared by dissolving the appropriate amount of cadmium nitrate and zinc nitrate (Merck) in distilled water into two 100 mL volumetric flasks.

The ligand of 5-phenyl-1,2,4-triazol-3-tion (PTT) was synthesized and purified according to a previously reported procedure (18). A stock solution of 1.0×10^{-3} M PTT was prepared by dissolving 0.0177 g of the compound in ethanol. The molecular structure of PTT is shown in Fig.1.

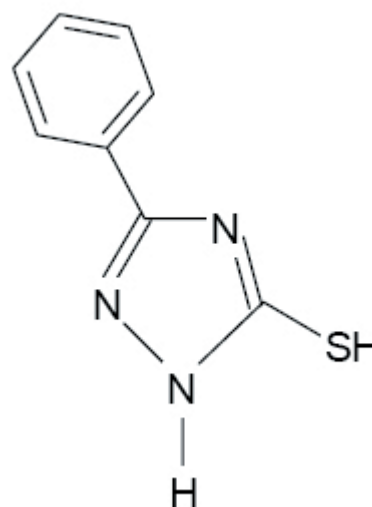


Figure 1. Structural formula of PTT.

The supporting electrolyte was a Tris buffer solution (pH 7.4-9.5). By mixing tris(hydroxy methyl)amino methane, 0.1 M, and hydrochloric acid, 0.1 M, in a 50-mL volumetric flask, different Tris buffers were prepared.

Procedures

The supporting electrolyte solution (10 mL Tris buffer pH 9.0) containing 3.5×10^{-5} M PTT was pipetted into the cell and purged with nitrogen for 4 min. The deposition potential (0.1 V vs. Ag/AgCl) was applied to a fresh mercury drop while the solution was stirred for 30 s. At the end of deposition time the stirrer was switched off, and after 10 s had elapsed to allow the solution to become quiescent, the potential was scanned in a negative direction from -0.5 to -1.2 V using differential pulse stripping voltammetry, with a scan rate of 12 mV/s and a pulse height of 50 mV. Each scan was repeated three

times with a new drop for each analyzed solution and the mean value was obtained.

After recording the background voltammogram, by adding aliquots of cadmium and zinc standard solution into the cell and following the described procedure, the sample voltammogram was achieved. Cadmium and zinc-stripping peaks were registered at about -0.665 V and -0.976 V and their currents were used as a measure of cadmium and zinc concentration. All experiments were carried out at room temperature.

Results and Discussion

Preliminary experiments were performed to characterize the suitability of PTT for the determination of cadmium and zinc ions. Figure 2 shows cathodic stripping differential pulse voltammograms of the Cd and Zn-PTT systems at pH 9.0 (Tris buffer), after deposition at 0.1 V for 30 s on a HMDE. The blank solution (the ligand without metal ions) in pH of 9.0 (curve a) did not show any peak in this potential range. The metal ions in buffer solutions showed small peak currents in the absence of the ligand. Curve 2b shows the voltammogram of a solution containing 150 ng/mL of cadmium and 120 ng/mL of zinc in the absence of ligand under similar conditions. The sample solution containing the metal ions with the ligand are represented by two peaks (curve c) at -0.665 and -0.976 V that correspond to the reduction of Cd (II) and Zn (II) complexes with PTT in pH of 9.0. These peak currents increased with increasing deposition time before the potential scan. The effects of the potential scan rate on the current of the adsorbed metal ions-PTT complexes showed that the cathodic peak

increased with increasing scan rate from 2 to 12 mV/s, thereafter the peak heights decreased. In addition, the presence of small amount of surfactants such as Triton X-100 suppressed the peak currents. These phenomena indicate that the complexes were strongly adsorbed on mercury electrode surface.

For the best sensitivity in simultaneous determination of cadmium and zinc the influence of different parameters such as pH, ligand concentration, deposition time and potential and scan rate were investigated.

Effect of supporting electrolyte and pH

Preliminary experiments were carried out with different types of buffers such as citrate, borate, phosphate, acetate, Briton-Robinson and Tris. The best results were achieved in Tris buffer solution. Thus, Tris buffer was used as supporting electrolyte for further experiments. The influence of pH on the sensitivity of method in the range from 7.4 to 9.5 of Tris buffer was investigated. The results are shown in Figure 3. The results show that the peak current for cadmium decreased with increasing pH, whereas for zinc the peak current increased. It appears that pH 9.0 is adequate in obtaining sufficient sensitivity for both cadmium and zinc ions. Thus, this pH value was used for further studies.

Effect of PTT concentration

The effect of the PTT concentration on the cathodic stripping peak heights of Cd and Zn at pH 9.0 in Tris buffer at a deposition potential of -0.2 V for 120 s was also studied (Figure 4). Variation of PTT concentration showed that the stripping peak height for cadmium and zinc increased up to 3.5×10^{-5} M and in higher PTT

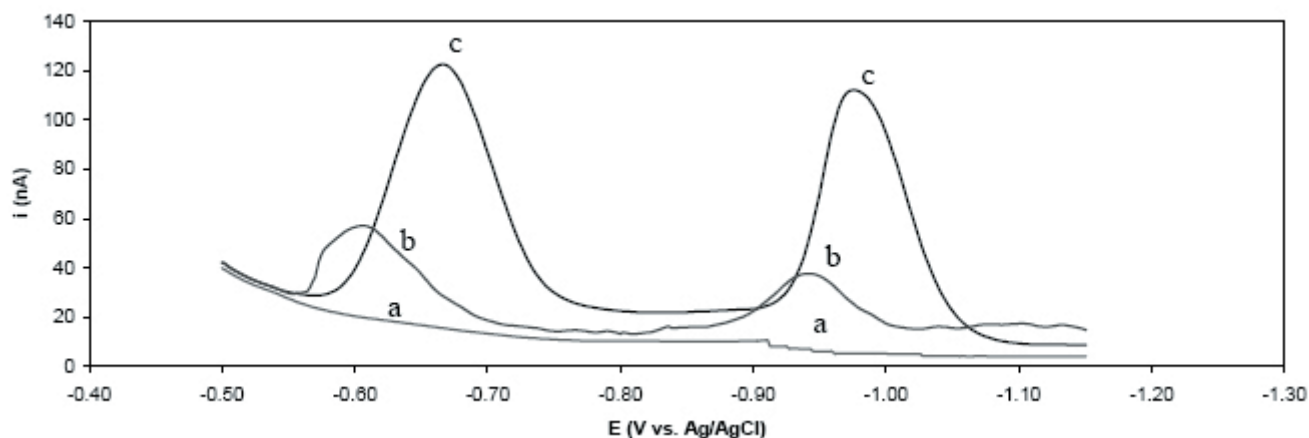


Figure 2. Differential pulse voltammograms of a) Blank solution; b) Cd^{2+} (150 ng/mL) and Zn^{2+} (120 ng/mL) ions without the ligand; and c) Cd^{2+} (100 ng/mL) and Zn^{2+} (80 ng/mL) complexes with ligand (PTT). Conditions: pH, 9.0; PTT, 3.5×10^{-5} M; deposition potential, 0.1 V; deposition time, 30 s; pulse height, 0.05 V; scan rate, 12 mV/s.

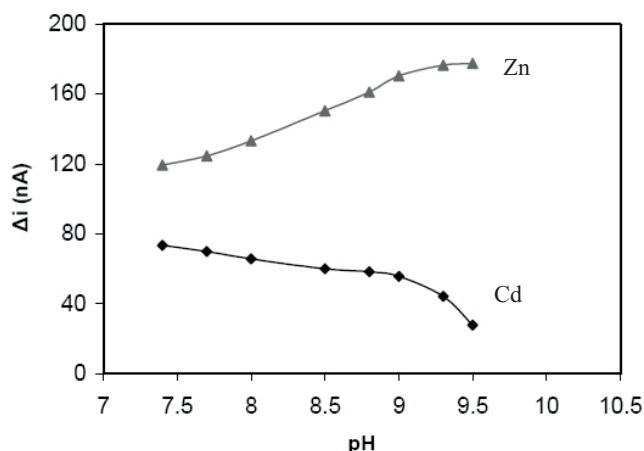


Figure 3. Effect of pH on sensitivity. Conditions: Cd^{2+} , 150 ng/mL; Zn^{2+} , 150 ng/mL; PTT, 1.0×10^{-4} M; deposition potential, -0.2 V; deposition time, 120 s; pulse height, 0.05 V; scan rate, 12 mV/s.

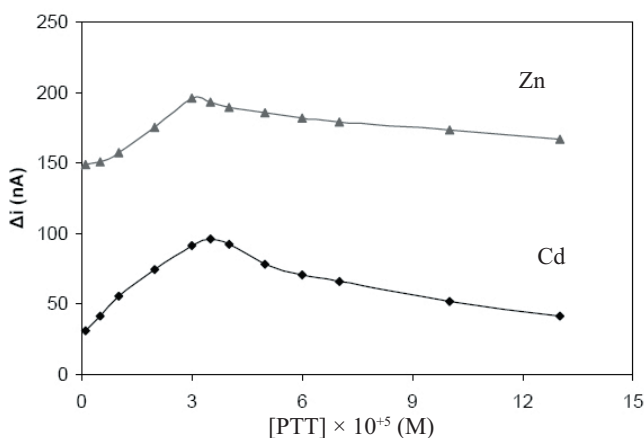


Figure 4. Effect of ligand concentration on the sensitivity. Conditions: Cd^{2+} , 150 ng/mL; Zn^{2+} , 150 ng/mL; pH 9.0; deposition potential, -0.2 V; deposition time, 120 s; pulse height, 0.05 V; scan rate, 12 mV/s.

concentration the peak current heights decreased due to the competition of PTT with Cd (II)-PTT and Zn (II)-PTT complexes for adsorption onto the mercury drop electrode. Therefore, the PTT concentration of 3.5×10^{-5} M was selected as optimum value for further experiments.

Effect of deposition time

Figure 5 shows that the influence of preconcentration time on the stripping peak currents of Cd and Zn in the range 0-150 s. The peak current increased rapidly for both Cd (II) and Zn (II) up to 30 s and at that point the Zn (II) current continued to increase while the Cd (II) current decreased. The 30 s range shows the point where adsorptive equilibrium was reached. Thus, a deposition time of 30 s was selected for next experiments.

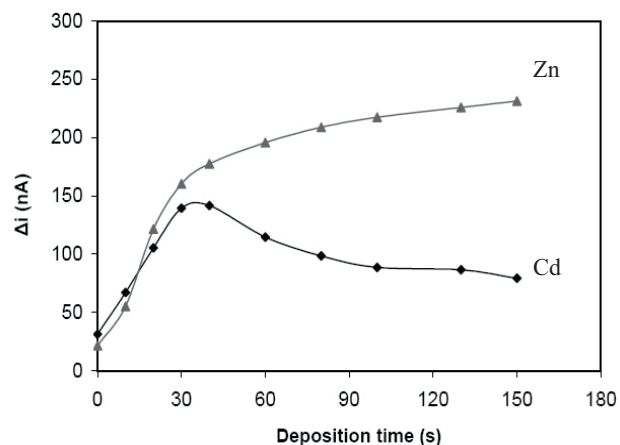


Figure 5. Effect of deposition time on the sensitivity. Conditions: Cd^{2+} , 150 ng/mL; Zn^{2+} , 150 ng/mL; pH, 9.0; PTT, 3.5×10^{-5} M; deposition potential, -0.2 V; pulse height, 0.05 V; scan rate, 12 mV/s.

Effect of deposition potential

The effect of varying adsorption potential on the peak height for cadmium and zinc is shown in Figure 6. The adsorption potential was varied between 0.3 and -1.5 V. The peak current was found to increase with decreasing deposition potential up to 0.1 V for both Cd and Zn. The peak currents decreased in more negative potentials thereafter. Thus, a deposition potential of 0.1 V was chosen.

Effect of scan rate

The dependence of peak currents on the scan rate under the optimal conditions was also investigated in the range of 2-30 mV/s. The peak height for cadmium and zinc increased with increasing scan rate until about 12 mV/s. In larger scan rates, the sensitivity decreased. The scan rate of 12 mV/s was then selected as an optimum value.

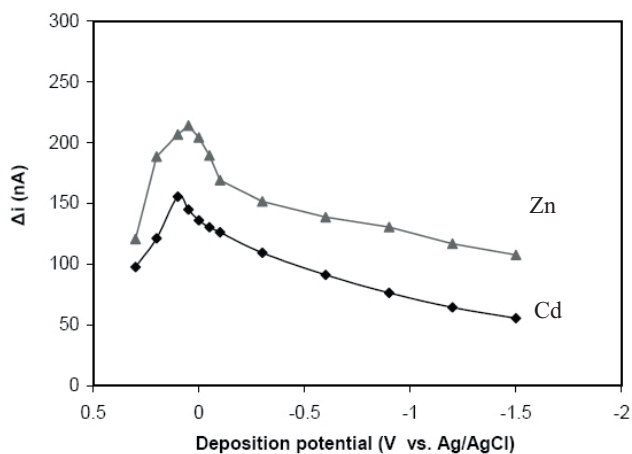


Figure 6. Effect of deposition potential on the sensitivity. Conditions: Cd^{2+} , 150 ng/mL; Zn^{2+} , 150 ng/mL; pH, 8.0; PTT, 3.5×10^{-5} M; deposition time, 30 s; pulse height, 0.05 V; scan rate, 12 mV/s.

Linear Range, Detection Limit and Precision of the Method

To verify the linear relationship between peak currents and metal concentrations, two calibration graphs were plotted under optimum conditions (3.5×10^{-5} M PTT, pH 9.0, a deposition potential of 0.1 V and 30 s deposition time) and are shown in Figure 7.

The calibration equation, obtained by least-squares method, is: $\Delta i = 0.89C + 16.36$ ($r^2 = 0.9991$) for Cd^{2+} and $\Delta i = 1.32C + 6.01$ ($r^2 = 0.9995$) for Zn^{2+} determination, where C is the concentration of metal ions (ng/mL) and Δi is the peak current (nA). The stripping peak current of Cd (II)-PTT and Zn (II)-PTT complexes were found to be directly proportional to the cadmium and zinc concentration in the range of 5-230 and 5-370 ng/mL, respectively.

The relative standard deviation for 10 replicate analysis of a solution containing 20 and 50 ng/mL Cd (II) were 2.4%, 2.6% and for 20 and 30 ng/mL Zn (II) were 2.6%, 2.1%, respectively.

A detection limit of 1.1 and 1.6 ng/mL of Cd^{2+} and Zn^{2+} , respectively, was estimated from 10 replicate determination of blank solution under optimum conditions ($Y_{\text{Lod}} = Y_{\text{B}} + 3S_{\text{B}}$, where Y_{Lod} refers to the signal due to the limit of detection, and Y_{B} and S_{B} are the average signal due to the blank and the standard deviation of the blank signal, respectively) (19).

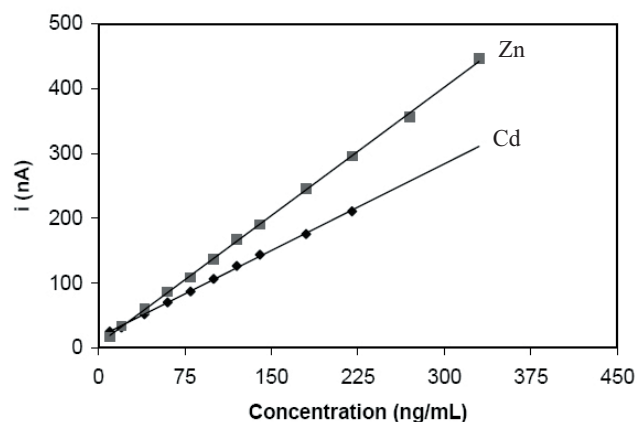


Figure 7. Calibration curves for the determination of cadmium and zinc under optimum conditions: PTT, 3.5×10^{-5} M; pH, 9.0; deposition potential, 0.1 V; deposition time, 30 s; pulse height, 0.05 V; scan rate, 12 mV/s.

Interference Studies

Possible interference of other species in the adsorptive stripping voltammetric determination of cadmium and zinc was studied by addition of the interfering ion to a solution containing 100 ng/mL of Cd (II) and Zn (II) using the optimized conditions (the criterion for interference was a 5% error in the peak heights of Cd and Zn). The results of this study are summarized in Table 1. It was found that most of foreign ions did not interfere for cadmium and zinc determination.

Table 1. Interference study for cadmium and zinc determination.

Species	Tolerance limit mass ratio (ion:Cd)	Tolerance limit mass ratio (ion:Zn)
Pb (II), K^+ , Cs^+ , Mg^{2+} , Ba^{2+} , HCO_3^- , I, F, Br, Cl, WO_4^{2-} , N_3^- , BrO_3^- , ClO_3^- , ClO_4^- , NO_3^- , OAc, Na^+ , Al^{3+} *	1000	1000
SO_4^{2-} , IO_3^- , CO_3^{2-}	1000	500
NO_2^- , SCN^-	500	1000
Sr^{2+} , Ca^{2+}	500	250
Mn (II)	250	500
$\text{S}_2\text{O}_3^{2-}$	100	500
Fe(II)	100	50
Fe(III)	100	10
Ni^{2+}	50	250
Co^{2+} , Hg(II), Pd(II), Ce(IV)	20	50
Rh(III), CN^-	20	20
Cu^{2+}	10	20

*after adding 50 $\mu\text{g/mL}$ of F⁻.

Table 2. Determination of cadmium and zinc in synthetic mixtures.

Sample	Added (ng/mL)		Found (ng/mL)		Recovery (%)	
	Cd	Zn	Cd	Zn	Cd	Zn
1	20	20	19.1(±0.5)	19.4(±0.8)	95.5	97.0
2	60	100	62.2(±2.2)	102.8(±3.5)	103.7	102.8
3	100	180	96.6(±2.6)	185.9(±7.8)	96.6	103.3
4	140	260	143.8(±5.6)	248.0(±6.9)	102.7	95.4
5	80	60	77.1(±2.5)	62.5(±1.7)	96.4	104.2
6	180	150	183.1(±6.4)	146.1(±6.2)	101.7	97.4

Number in parenthesis is the standard deviation for four replicate measurements.

Table 3. Determination of cadmium and zinc in natural water samples.

Sample	Added (ng/mL)		Found by AAS (ng/mL)		Found by Proposed Method (ng/mL)		% Recovery	
	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn
Tap water (Tehran, Iran)	-	-	-	28.8 (±1.1)	-	29.7 (±1.3)	-	103.1
	20.0	20.0	-	-	19.5 (±0.7)	48.4 (±1.9)	97.5	98.0
	40.0	40.0	-	-	38.6 (±1.3)	69.9 (±3.1)	96.5	102.8
Spring water	-	-	-	158.1 (±4.6)	-	154.7 (±7.0)	-	97.8
	30.0	30.0	-	-	31.2 (±1.1)	187.4 (±6.1)	104.0	97.7
	60.0	30.0	-	-	59.0 (±2.2)	188.6 (±8.7)	98.3	101.7
Under- ground water	-	-	-	1214 (±43)	-	1263 (±64)	-	104
	40.0	40.0	-	-	38.3 (±1.6)	1255 (±49)	95.8	102.5
	40.0	70.0	-	-	38.9 (±1.5)	1282 (±56)	97.3	97.1

Number in parenthesis is the standard deviation for four replicate measurements.

Table 4. Determination of zinc in two industrial alloys.

Alloy	% Zn (II) Certified value	Zn (II) Found	% Recovery
LTD (MBH C51X)	0.15	0.146 (±0.005)	97.3
Si/Cu/Al (MBH-C55X)	2.46	2.43 (±0.09)	98.8

Number in parenthesis is the standard deviation for four replicate measurements.

Alloy contents: LTD (0.13% Cu, 0.04% Mg, 0.48% Si, 0.41% Fe, 0.2% Mn, 0.12% Ni, 0.15% Zn, 0.08% Pb, 0.008% Sn, 0.09% Ti, 0.06% Cr, 98.23% Al); Si/Cu/Al (3.16% Cu, 0.1% Mg, 8.78% Si, 0.64% Fe, 0.18% Mn, 0.67% Ni, 2.46% Zn, 0.19% Pb, 0.26% Sn, 0.09% Ti, 0.11% Cr, 83.36% Al)

Applications

The utility of the developed method was tested by determining cadmium and zinc in some synthetic mixtures (Table 2). The method was also applied to natural water sources such as tap water, spring water and underground water (Table 3). The method was applied to the determination of zinc in two alloy samples (Table 4) as well. The alloy samples were analyzed after dissolution of the sample in HNO₃-HCl (1:3) plus several drops of conc. HF acid by heating. The natural water samples were also analyzed for cadmium and zinc contents by atomic absorption (AAS) method (Cadmium ions in water samples could not be detected by AAS without spiking). In order to eliminate the matrix effect, the standard addition method was used. The obtained data for samples spiked with cadmium and zinc showed good recoveries (Table 2 and 3) and the ability of proposed method for the determination of those elements in different real samples.

Conclusion

The present study demonstrates that the adsorptive stripping voltammetry of cadmium and zinc in the presence of PTT is an excellent method for determination of trace amounts of these two metal ions in real samples. The above system offers a practical potential for the simultaneous determination of cadmium and zinc, in addition, this method has high sensitivity, high selectivity, simplicity and speed.

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References

1. T.R. Crompton, "Toxicants in the aqueous Eco-system", Wiley, Chinchester, 1997, p. 91-135.
2. R.M. Atlas, R. Bartha, "Ecologia Microbiana y Microbiologia Ambiental", Pearson Education, 2002, p. 544-545.
3. www.zincworld.org, International Zinc Association, Brussels, Belgium.
4. O.-W. Lau, O.-M. Cheng, *Anal. Chim. Acta*, **376**, 197 (1998).
5. C.J. Menendez-Botet, M.K. Schwartz, *Anal. Chem.*, **63**, 196R (1991).
6. R.F.M. Herber, H.G. Seiler, A. Sigel, H. Sigel, Eds., "Handbook on Metals in Clinical and Analytical Chemistry", Marcel Dekker, New York, 1994, p. 283-297.
7. A.D. Eaton, L.S. Clescer, A.E. Greenberg, Eds., "Standard Methods for the Examination of Water and Wastewater", 19th ed., American Public Health Association, Washington DC, 1995, p. 3-13, 3-103, 3-104.
8. L. Percelay, P. Appriou, H. Handel, R. Guglielmetti, *Anal. Chim. Acta*, **209**, 249 (1988).
9. S. Mukhtar, S.J. Haswell, A.T. Ellis, O.T. Hawke, *Analyst*, **116**, 333 (1991).
10. J. Wang, in: A.J. Bard (Eds.), "Electroanalytical Chemistry", vol. 16, Marcel Dekker, New York, 1989, p. 1-89.
11. C.M.G. van den Berg, *Analyst*, **114**, 1527 (1989).
12. R. Kalvoda, M. Kopanica, *Pure Appl. Chem.*, **61**, 209 (1984).
13. M. Stozik, W.W. Kubiak, Z. Kowalski, *Chem. Anal.*, **40**, 1 (1995).
14. P. Suci, M. Vega, L. Roman, *J. Pharm. and Biomed. Analysis*, **23**, 99 (2000).
15. J.A. Jurado-Gonzalez, M.D. Galindo-Riano, M.G. Garcia-Vergas, *Anal. Chim. Acta*, **487**, 229 (2003).
16. A.A. Ensafi, K. Zarei, *Talanta*, **52**, 435 (2000).
17. K.W. Cha, C.I. Park, S.H. Park, *Talanta*, **52**, 983 (2000).
18. E. Hoggarth, *J. Chem. Soc.*, **1163** (1949).
19. J.C. Miller, J.N. Miller, "Statistics for Analytical Chemistry", 3rd ed., Ellis Horwood, New York, 1993.