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SIMULTANEOUS DETERMINATION OF TRACE AMOUNTS OF LEAD AND ZINC BY ADSORPTIVE CATHODIC STRIPPING VOLTAMMETRY

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Abstract

A selective and sensitive method for simultaneous determination of lead and zinc by adsorptive differential pulse cathodic stripping voltammetry is presented. The method is based on adsorptive accumulation of the complexes of Pb (II) and Zn(II) ions with Dopamine onto hanging mercury drop electrode (HMDE), followed by reduction of adsorbed species by differential pulse cathodic stripping voltammetry. Optimal conditions were obtained at pH 10.0, Dopamine concentration of 1.0×10^{-4} M, accumulation potential of 0.0 V (vs. Ag/AgCl), accumulation time of 10 s, scan rate of 10 mV/s. Under the optimized conditions, a linear calibration curve was established for the concentration of Pb (II) and Zn (II) in the range of 5-150 and 5-250 ng/mL, respectively, with a detection limit of 0.5 ng/mL Pb (II) and 1.8 ng/mL Zn (II). The procedure was successfully applied to the simultaneous determination of both ions in some real samples.

Keywords: lead; Zinc; Dopamine; Adsorptive stripping voltammetry

Introduction

Heavy metals such as lead, mercury and cadmium are toxic when absorbed in the body. Their accumulative behavior causes poisoning, cancer, brain damage, etc. Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semipermanent brain damage in young children. Lead has the ability to replace calcium in bone to form sites for long-term replace [1]. Because of the increased industrial use of lead and its serious hazardous effect to human health, the development of new sensitive methods for quantifying trace amount of lead is required

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 [2]. 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 [3].

On the other hand, metallic ions of lead and zinc frequently exist together in many real environmental and food samples. It is necessary to determine these metallic ions simultaneously in most instances [4]. Typical simultaneous analyses have usually been based on chromatography having detection systems based on spectrometry, anodic stripping voltammetry or potentiometric stripping [5, 6]. Although chromatographic techniques were successfully used, they are tedious, expensive and the separation step involved is usually time consuming and not precise, with the result that these techniques are not convenient for routine analysis of large sets of samples where rapid analysis is needed.

Alternatively multielement analysis for several analytes has successfully been done with energy dispersive X-ray fluorescence spectrometry [7], atomic spectrometry [8], ICP-AES and ICP-MS. However, these techniques have some disadvantages, such as complicated operation, high cost of maintenance, expensive apparatus and requiring well-controlled experimental conditions.

For the above reason electrochemical methods such as stripping voltammetry for the determination of heavy metal ions, including lead and zinc, is one of the most favorable techniques, because of its low cost, high sensitivity, easy operation and ability of analyzing element speciation [9-11]. Stripping voltammetry (SV) comprises a variety of electrochemical approaches, having a step of pre-concentration onto the electrode surface prior to the voltammetric measurements. The major advantage of SV compared with direct voltammetric measurement and other analytical techniques is the pre-concentration factor. Anodic stripping voltammetry (ASV) that is the most popular stripping voltammetric method is an effective technique in trace and multielement analysis for heavy metals [12-15]. Although anodic stripping voltammetry is a powerful tool for the determination of trace amounts of these two important elements but the application of ASV for the determination of analytes in complex sample matrices is complicated because of the adsorption of interfering components onto the electrode surface with the result that electrode activity is lost and non-reproducible results are obtained. However the selectivity and sensitivity have further been also improved based on adsorption rather than electrolytic accumulation. Stripping analysis following adsorptive accumulation of metal chelates is becoming a widely accepted analytical tool, as it extends the scope of stripping analysis toward additional trace metals, and offers an effective alternative method for monitoring other metals. The history, theoretical background and application of adsorptive stripping voltammetry (AdSV) for the determination of lead [20-23] and zinc [24,25] with different reagents. These methods either have short linear dynamic range or suffer from much interference.

The present study describes a new adsorptive cathodic stripping procedure for simultaneous determination of trace amounts of lead and zinc by using of Dopamine as a complexing agent. The method relies on the effective accumulation of the Pb (II) and Zn (II) complexes with Dopamine onto the hanging mercury drop electrode (HMDE). This method has large dynamic range, low detection limits and is able to determine lead and zinc in different 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 (saturated KCl) reference electrode, and a platinum counter electrode was used differential pulse voltammetry. All potentials reported were referred to the Ag/AgCl electrode. Differential pulse voltammetry was carried out with pulse amplitude of 50 mV. pH measurements were performed with a Metrohm 691 pH meter using a combined glass electrode. A Varian AA-50 atomic absorption spectrometer equipped with lead and zinc hollow cathode lamps were used for atomic absorption measurements.

Reagents and Solutions

All solutions were prepared with doubly distilled water. The stock solutions of Pb (II) and Zn (II), 1000 mg/L, were prepared by carefully weighting solid lead nitrate and zinc nitrate (Merck) and dissolving in distilled water in two 100 ml volumetric flasks. A stock solution of 1.0×10^{-3} Dopamine (Merck) was prepared by dissolving 0.0192 g of the compound in 100.0 mL water. Ammonia buffer solutions (pH 7.5-10.5) were prepared by mixing different amounts of ammonium chloride, 0.2 M, and ammonia, 0.2 M, in a 100.0 mL volumetric flask.

Procedures

The supporting electrolyte solution (10 ml of 0.2 M NH_3/NH_4^+ buffer solution, pH 10.0) containing 1.0×10^{-4} M Dopamine was transferred into the electrochemical cell and purged with nitrogen for at least 4 min. The accumulation potential (0.0 V vs. Ag/AgCl) was applied to a fresh mercury drop while the solution was stirred for a period of 10 s. After 10 s of accumulation time, the stirring was stopped, and after equilibration for 10 s, voltammogram was recorded from -0.35 V to -1.25 V with a potential scan rate of 10 mV/s and pulse amplitude of 50 mV. After the background voltammograms has been obtained, aliquots of the lead and zinc standard solution were introduced into the cell and the obtained solution was deoxygenated with nitrogen gas for 1 min. Then a differential pulse voltammograms was recorded according to described procedure to give the sample peak current. Each scan was repeated three times with a new drop for each analyzed solution and the mean value was obtained. Lead and zinc stripping peaks were registered at about -0.527 V and -1.031 V and their currents were used as a measure of lead and zinc concentrations. All data were obtained at room temperature. Calibration graph were prepared the peak current against lead (II) and zinc (II) concentrations.

Results and Discussion

Preliminary experiments were performed to identify the general features, which characterize the behavior of Pb- and Zn-Dopamine systems on mercury electrode. Figure 1 shows cathodic stripping differential pulse voltammograms of the Cd-and Zn-PTT systems at pH 10.0 (ammonia buffer), after accumulation at 0.0 V for 10s on a HMDE. The Blank solution (the ligand without metal ions) in pH of 10.0 (curve a) doesn’t show any peak in this potential range. The metal ions in buffer solutions showed small peak currents in the absence of the ligand. Curve b shows the voltammogram of a solution containing 40 ng/ml of lead and zinc in the absence of ligand under similar conditions. The sample solution containing the metal ions with the ligand shows two peaks (curve c) at -0.527 and -1.031 V that correspond to the reduction of Pb (II) and Zn (II) complexes with Dopamine in pH of 10.0. These peak currents increased with increasing accumulation time before the potential scan. The effects of the potential scan rate on the current of the adsorbed metal ions-Dopamine complexes showed that the cathodic peak increase 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.

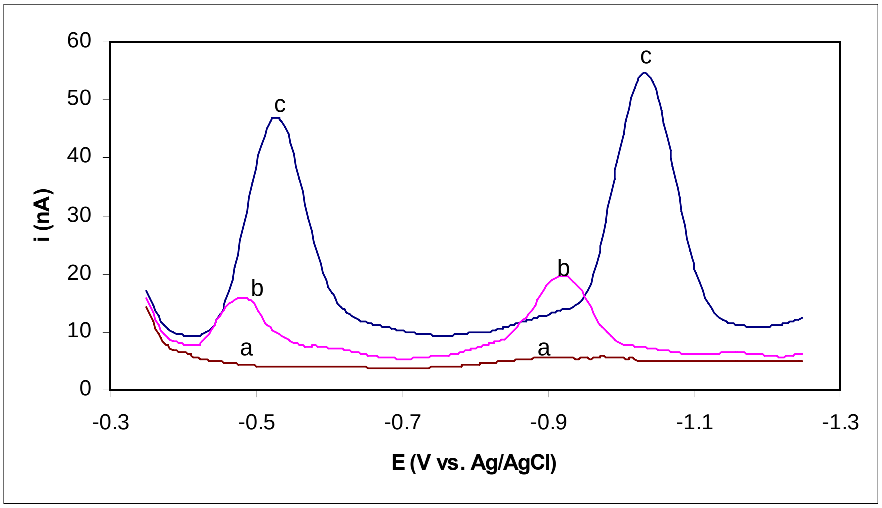

Fig 1: Differential pulse voltammograms of a) Blank solution; b) Pb^{2+} (40 ng/ml) and Zn^{2+} (40 ng/ml) ions without the ligand; and c) Pb^{2+} (40 ng/ml) and Zn^{2+} (40 ng/ml) complexes with ligand (Dopamine); Conditions: pH, 10; Dopamine, 1.0×10^{-4} M; accumulation potential, 0.0 V; accumulation time, 10 sec; scan rate, 10 mV/sec.

Influence of supporting electrolyte and pH

Preliminary experiments were carried out with different types of buffers such as acetate, phosphate, citrate, borate, Phthalate, Britton-Robinson, ammonia-ammonium and Tris. The results showed that the peaks shape for lead and zinc were improved in the presence of ammonia-ammonium buffer solution. Therefore, ammonia-ammonium buffer was used for optimization of pH. The influence of pH on the cathodic stripping peak currents of lead and zinc was studied in the pH range of 7.5-10.5 of ammonia buffer. The results are shown in Figure 2. The results show that the peak currents for lead and zinc increase with increasing the pH to about 10.0. This phenomenon is due to the enhanced complexing ability of Dopamine in large pH values. Thus, pH of 10.0 was adopted for further studies.

Influence of Dopamine concentration

The influence of Dopamine concentration on the sensitivity of proposed method was also studied. The obtained results (Figure 3) show that the cathodic stripping peak currents of Pb- and Zn-Dopamine complexes increased with increasing the Dopamine concentration up to about 1.0×10^{-4} M, leveling off at higher concentrations. This is due to the competition of Dopamine with Pb- and Zn-Dopamine complexes for adsorption on the HMDE. So, an optimum Dopamine concentration of 1.0×10^{-4} M was selected for further experiments.

Influence of accumulation time

The effect of the accumulation time on the stripping peak currents for Pb and Zn in the range 0-120 s is illustrated in Figure 4. The peak currents increased initially with increasing pre-concentration time, indicating that before adsorptive equilibrium is reached, the longer accumulation time, the more metal-Dopamine were adsorbed and thus the peak currents become larger. However, after a specific period of accumulation time, the peak currents tend to level-off slowly as the equilibrium surface concentration of the adsorbed complexes was approached. Therefore, an accumulation time of 10 s was selected for further investigations.

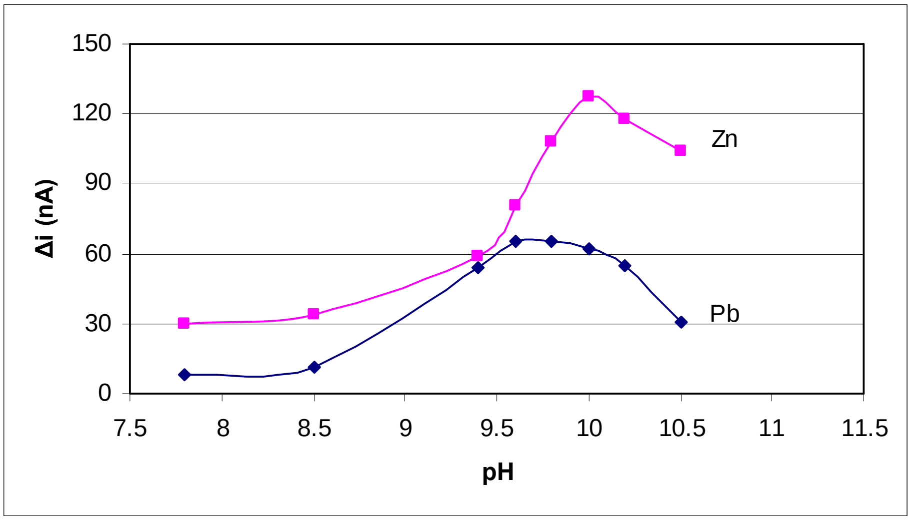

Fig 2: Influence of pH on the peak currents; conditions: Pb^{2+}, 100 ng/mL; Zn^{2+}, 100 ng/mL; Dopamine, 0.5×10^{-4} M; accumulation potential, 0.0 V; accumulation time, 60 sec; scan rate, 10 mV/sec.

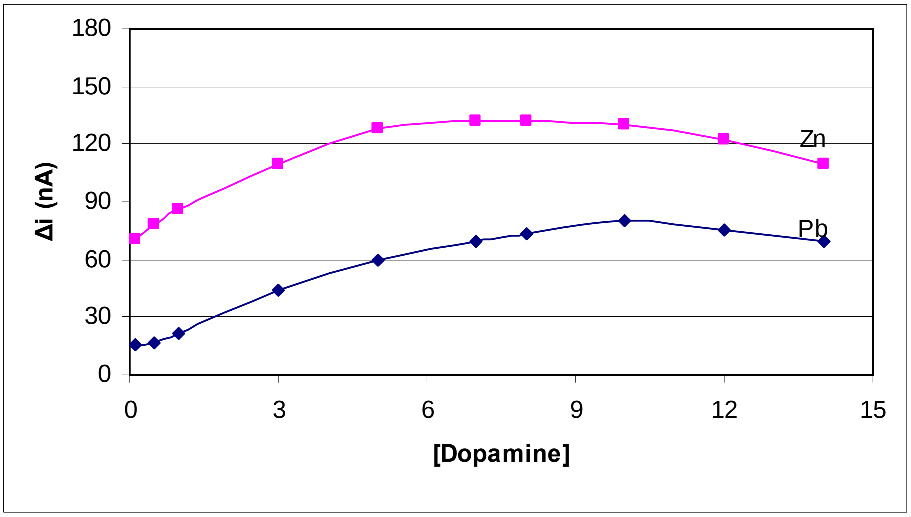

Fig 3: Influence of Dopamine concentration on the peak currents; Conditions: Pb^{2+}, 100 ng/mL; Zn^{2+}, 100 ng/mL; pH, 10; accumulation potential, 0.0 V; accumulation time, 60 sec; scan rate, 10 mV/sec.

Influence of accumulation potential

The effect of the accumulation potential on the peak heights on Pb and Zn was studied in the range from 0.3 to -0.6 V and is shown in Figure 5. As it can be seen the accumulation potential of 0.0 V has better sensitivity for both metal ions, so an accumulation potential of 0.0 V was used for the optimized analytical procedure.

Influence of scan rate

Figure 6 depicts the effect of scan rate on the stripping peaks of Pb and Zn in the optimal conditions that described before. The results show that the peak heights for both Pb and Zn increase nearly from 2 to 10 mV/s and in larger scan rates the sensitivity decreases. Therefore, a scan rate of 10 mV/s was selected.

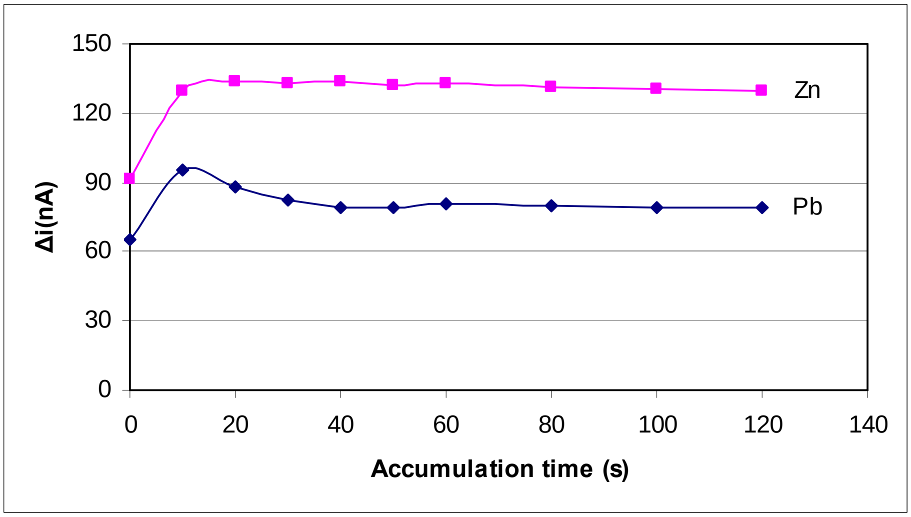

Fig 4: Influence of accumulation time on the peak currents; Conditions: Pb^{2+}, 100 ng/mL; Zn^{2+}, 100 ng/mL; pH, 10; Dopamine, $1.0{\times}10^{-4}$ M; accumulation potential, 0.0 V; scan rate, 10 mV/sec.

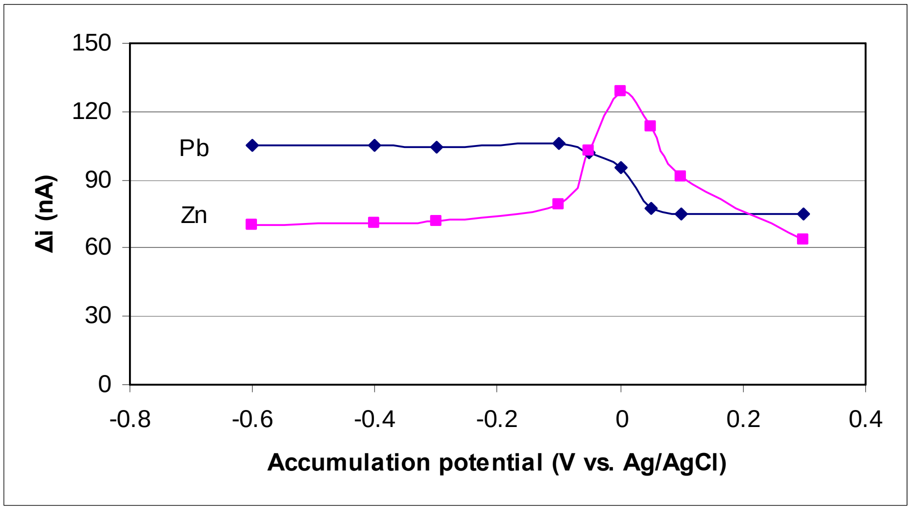

Fig. 5: Influence of accumulation potential on the peak currents; Conditions: Pb^{2+}, 100 ng/mL; Zn^{2+}, 100 ng/mL; pH, 10; Dopamine, $1.0{\times}10^{-4}$ M; accumulation time, 10 sec; scan rate, 10 mV/sec.

Linear range, detection limit and precision

Using the optimized conditions (1.0×10^{-4} M of Dopamine, pH 10.0, an accumulation potential of 0.0 V and 10 s accumulation time) the calibration graphs were found to be linear in the concentration range of 5-150 and 5-250 ng/ml for lead and zinc, respectively Figure 7 The correlation equations for the dependence of cadmium and zinc peak currents on their concentration are:

$\Delta i = 0.93C + 3.74$ (r^2=0.9994) for Pb^{2+} concentration,

and $\Delta i = 1.27C + 0.53$ (r^2=0.9992) for Zn^{2+} concentration,

where C is concentration of metal ions in ng/ml and Δi is the peak current vs. nA.

A detection limit (the blank signal plus three times of its standard deviation) of 0.5 ng/ml Pb (II) and 1.8 ng/ml Zn (II) was obtained. Repeated voltammograms after 10 s accumulation time showed that the relative standard deviation for 30 and 60 ng/ml lead is 2.8% and 2.5% ng/ml and for 80 and 30 ng/ml zinc is 2.7% and 3.1% ng/ml, respectively.

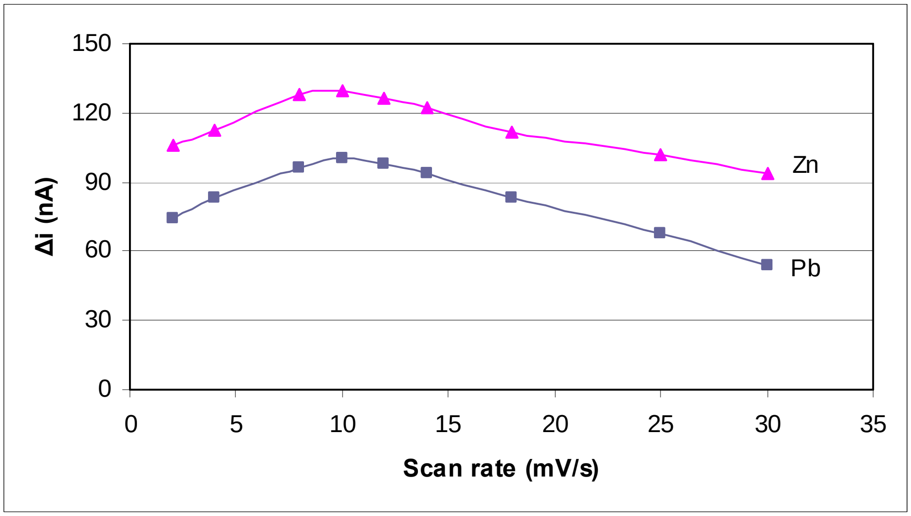

Fig. 6: Influence of scan rate on the peak currents; Conditions: Cd^{2+}, 100 ng/ml; Zn^{2+}, 100 ng/ml; pH, 10; Dopamine, 1.0×10^{-4} M; accumulation potential, 0.0 V; accumulation time, 10 s.

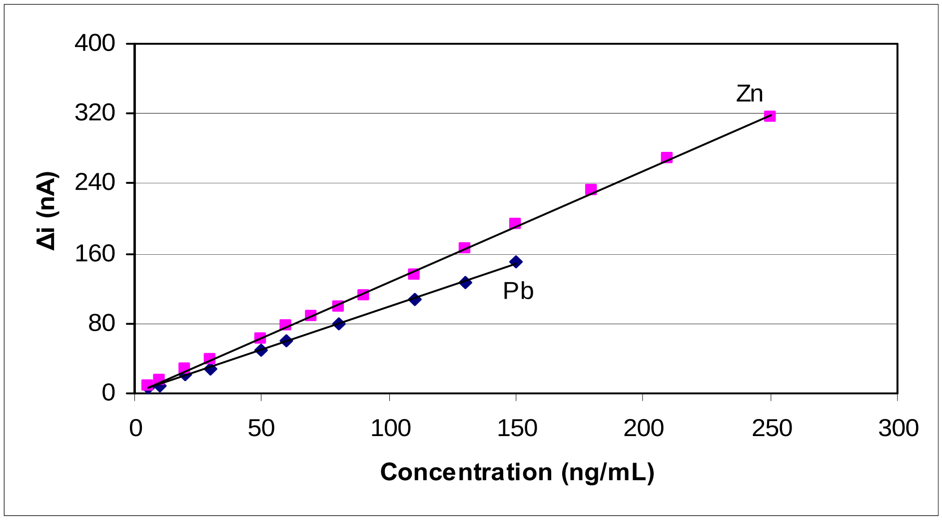

Fig. 7: Calibration curve under optimum conditions; Conditions: pH, 10; Dopamine, 1.0×10^{-4} M; accumulation potential, 0.0 V; accumulation time, 10 sec; scan rate, 10 mV/sec.

Interferences studies

In the AdSV determination of lead and zinc, interferences may be caused by the competitive adsorption of ions on the HMDE, forming a complex with Dopamine, or producing a reduction current at potentials near that of Pb (II)- or Zn(II)-Dopamine complexes. The effect of co-existing ionic species and surface-active substances on the determination of lead and zinc was investigated. First, surfactants are the most serious interference in stripping analysis. Triton X-100 was used to simulate the effect of a non-ionic surfactant. Adding of 4 µg/ml Triton X-100 to the solution containing 50 ng/ml Pb and Zn, completely suppressed their peaks. In addition, metal ions can also interfere (the criterion for interference was a 5% error in the peak heights of Pb and Zn) with the measurement. A number of metal ions and anions that could potentially interfere were examined. The results are summarized in Table 1. From The result, it can be concluded that the method for the determination of lead and zinc is free from much interference of foreign ions.

Table 1: Interference study for lead and zinc determination

Species	Tolerance limit $W_{ion}/W_{Pb(II)}$	Tolerance limit $W_{ion}/W_{Zn(II)}$
K^+, Na^+, Cs^+, HCO_3^-, I^-, Br^-, Cl^-, WO_4^{2-}, N_3^-, ClO_3^-, ClO_4^-, NO_3^-, NO_2^-, F^-, CO_3^{2-}, IO_3^-, OAC^-, BrO_3^-, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn(II), Al^{3+}*	1000	1000
Zn^{2+}	1000	–
Pb^{2+}	–	1000
Sr^{2+}	500	1000
SO_4^{2-}	500	500
$S_2O_3^{2-}$	250	500
Rh(III)	250	20
CrO_4^{2-}	250	100
Co^{2+}	250	50
Ce(IV)	250	50
CN^-	100	50
Cu^{2+}, Ni^{2+}, Fe(III)	50	50
Pd(II)	20	250
Fe(II), Hg(II)	20	50
Al^{3+}	1	5

*After adding 40 µg/ml F^-.

Applications

The utility of the developed method was tested by determining cadmium and zinc in some synthetic mixtures (Table 2). The method was applied to natural water sources such as tap water, spring water and well water for determination of lead and zinc (Table 3). The proposed method was also used to determine lead and zinc in three standard reference alloy materials including Al/Cu/Si (MBH-C55X), LTD (MBH-C51X), NBS SRM 85b, (Table 4). The alloy samples were analyzed after dissolution of the sample in HNO_3-HCl (1:3) plus several drops of conc. HF acid by heating. The natural water samples were also analyzed for lead and zinc contents by atomic absorption method. In order to eliminate the matrix effect, the standard addition method was used. The results obtained by the proposed method show good recoveries and reveal the capability of the method for determination of cadmium and zinc in real samples.

Table 2: Determination of lead and zinc in synthetic mixtures.

Sample	Added (ng/ml)		Found (ng/ml)		Recovery (%)	
	Pb	Zn	Pb	Zn	Pb	Zn
1	15	15	14.5(±0.4)	14.6(±0.6)	96.7	97.3
2	40	60	38.8(±1.1)	61.9(±1.9)	97.0	103.2
3	80	140	82.9(±2.6)	136.9(±4.1)	103.6	97.8
4	90	50	93.1(±2.6)	51.3(±2.1)	103.4	102.6
5	120	80	117.1(±4.1)	82.1(±2.2)	97.6	102.6

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
Underground 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)	97.2	97.1

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

Conclusion

The adsorption of Pb (II)-Dopamine and Zn (II)-Dopamine complexes on mercury electrode can be utilized for simultaneous determination of trace amounts of lead and zinc by adsorptive stripping voltammetry. This new method offers a practical potential for trace determination of lead and zinc, with high selectivity and sensitivity, simplicity and speed relative to other methods. This method was successfully applied for determination of Cd and Zn in real samples such as water and alloys.

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