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## **Simultaneous Adsorptive Stripping Differential Pulse Voltammetric Measurements of Trace Lead, Cadmium and Nickel in the Presence of 2-aminobenzoic Acid**

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### **Abstract**

In this study, 2-aminobenzoic acid (ABA) has been used as complexing ligand for simultaneous determination of metal ions by adsorptive cathodic stripping voltammetry (AdCSV), for the first time. Thus, a selective and sensitive procedure was presented for simultaneous determination of lead, cadmium and nickel using ABA and differential pulse-adsorptive cathodic stripping voltammetry (DP-AdCSV). The method was based on adsorptive accumulation of the complexes of Pb(II), Cd(II) and Ni(II) ions with ABA onto hanging mercury drop electrode (HMDE), followed by reduction of adsorbed species by differential pulse cathodic stripping voltammetry. The effect of experimental parameters such as pH, ABA concentration, accumulation time and potential and scan rate on the electrode response was examined. Under the optimized conditions, linear calibration curves were established for the concentration of Pb(II), Cd(II) and Ni(II) in the ranges of 5-150, 5-120 and 5-150 ng mL<sup>-1</sup>, respectively. Detection limits of 1.78, 2.26 and 1.78 ng mL<sup>-1</sup> were obtained for Pb(II), Cd(II) and Ni(II), respectively. An application of the proposed method was reported for determination of these elements in tap water and industrial waste water of as real samples.

**Keywords:** *2-aminobenzoic acid, Heavy metals, Adsorptive cathodic stripping voltammetry, Water samples.*

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## **Introduction**

The pollution of heavy metals such as lead, cadmium and nickel is one of the most serious environmental problems [1]. They are highly toxic to many organs of both humans and animals, including nervous, immune, reproductive, and gastrointestinal systems [2,3]. Sensitive methods for the determination of trace amount of lead, cadmium and nickel have received much attention and many techniques have been employed for the determination of heavy metals. Flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry and inductively coupled plasma-optical emission spectrometry are widely used as analytical techniques for detection of nickel [4-8], lead [8-14] and cadmium [15-18]. Anodic stripping voltammetry (ASV) and adsorptive cathodic stripping voltammetry (AdCSV) techniques have shown numerous advantages including speed of analysis, good selectivity, sensitivity and good performance with different matrices [19]. Application of ASV to the samples with complex matrices is limited due to the adsorption of the interfering components onto the electrode surface and, consequently, the loss of electrode activity and irreproducible results.

AdCSV is an alternative stripping voltammetric method to determine trace metals [20,21]. This technique is based on adsorptive accumulation of a complex of the element with an added specific ligand onto the electrode followed by electrochemical reduction of the adsorbed metal complex [19]. Some chelating reagents such as morin [22], mixture of dimethylglyoxime and oxine [23] and carbidopa [24] have been used for voltammetric determination of the lead. Also, a large number of ligands such as tetramethylenedithiocarbamate [25], alizarin [26] and aluminon [27] already has been applied for determination of cadmium and several organic compounds such as N,N'-bis(salicylaldehyde)4-carboxyphenylenediamine [28], dimethylglyoxime [29,30], Dowex 50W x 12 [31], mixture of dimethylglyoxime and catechol [32] and 1-nitroso-2-naphthol [33] as complexing agent have been reported for voltammetric determination of nickel. AdCSV was successfully used for individual and simultaneous determination of heavy metals. In other researches, AdCSV methods for the simultaneous determination of Ni-Cd [28], Ni-Co [29], Pb-Cd [34], Cu-Ni-V [32], Pb-Cd-Ni [35] using different ligands have been described.

On the best of our knowledge, there is no report about the application of 2-aminobenzoic acid as complexing ligand in determination of metal ions using AdCSV technique. Therefore, in this work, an AdCSV procedure for simultaneous determination of  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Ni^{2+}$  ions by using 2-aminobenzoic acid as complexing agent has been presented. Also, various factors influencing the method were investigated. Furthermore, this method was used for determination  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Ni^{2+}$  ions in tap water and industrial waste water samples.

## **Experimental**

### *Apparatus*

Differential pulse voltammetry experiments were carried out with pulse amplitude of 50 mV using 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. 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 applied for atomic absorption measurements.

### *Chemicals*

All solutions were prepared with doubly distilled water. The stock solutions of Pb(II), Cd(II) and Ni(II) 1000 mg L<sup>-1</sup>, were prepared by carefully weighting solid lead nitrate, cadmium nitrate and nickel nitrate (Merck) and dissolving in aqueous 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>. 2-aminobenzoic acid (ABA) was purchased from Merck and its solution was prepared by dissolving an appropriate amount in 96% ethanol and was diluted by doubly distilled water, in different 100 mL volumetric flasks.

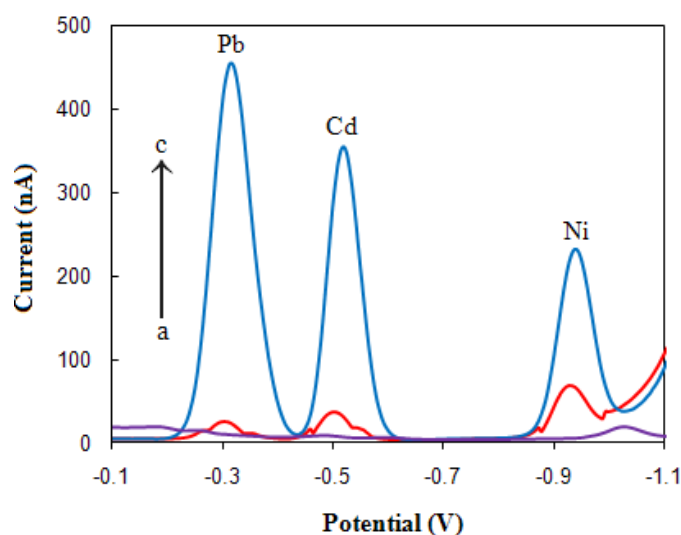
### *Procedures*

The supporting electrolyte solution (phosphate buffer with pH 7.4) was transferred into the electrochemical cell and purged with nitrogen for at least 4 min. The accumulation potential (0.0 V vs. Ag/AgCl/KCl (3M)) 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 0.1 V to -1.1 V with a potential scan rate of 10 mV s<sup>-1</sup> and pulse amplitude of 50 mV. After the background voltammogram has been obtained, aliquots of the copper, lead and cadmium standard solutions were introduced into the cell and the obtained solution was deoxygenated with nitrogen gas for 1 min. Then a differential pulse voltammogram was recorded according to described procedure to give the sample peak current. Each scan was repeated five times with a new drop for each analyzed solution and the mean value was obtained. Lead, cadmium and nickel stripping peaks were registered at about -0.319, -0.520 and -0.940 V and their currents were used as the method of measuring the magnitude of the analytical signals of lead, cadmium and nickel. All data were obtained at room temperature. Calibration graphs were prepared the peak current against lead(II), cadmium(II) and nickel(II) concentrations.

## **Results and discussion**

Preliminary experiments were carried out to identify the general features that characterize the behaviour of the Pb(II)-ABA, Cd(II)-ABA and Ni(II)-ABA systems on HMDE. Figure 1a displays

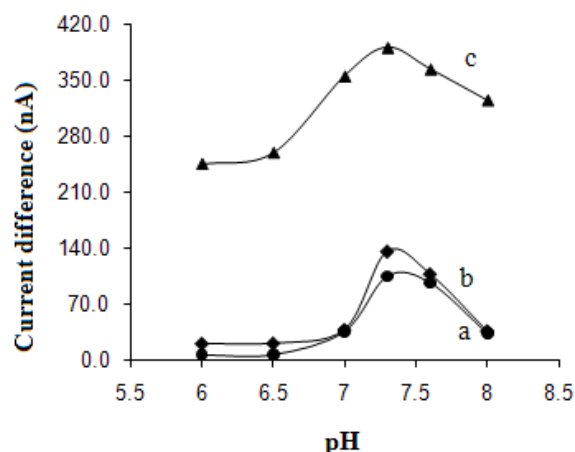
differential pulse voltammograms of phosphate buffer (pH 7.0) on the HMDE surface with scan rate  $10 \text{ mV s}^{-1}$ . Figure 1b represent the voltammograms of a solution containing  $70 \text{ ng mL}^{-1}$  of lead(II), cadmium(II) and nickel(II) in absence of ABA ligand under similar conditions as Figure 1a. By addition of  $0.40 \text{ mmol L}^{-1}$  ABA to solution of Figure 1b the corresponding reduction peak for lead, cadmium and nickel complexes with ABA ligand were amplified by several times after 60 s accumulation at  $-0.25 \text{ V}$  in phosphate buffer with pH 7.0 (Figure 1c). The comparison of the voltammograms shows that the height of metal ion reduction peaks depends on the presence and absence of ABA, which reveals the adsorptive nature of the responses. In order to simultaneous determination of lead(II), cadmium(II) and nickel(II) effects of various variables were examined and the optimum procedural conditions were identified.



**Figure 1.** DP-AdCS voltammograms of a) blank (phosphate buffer with pH 7.0), b) blank containing  $70 \text{ ng mL}^{-1}$  of each of Pb(II), Cd(II) and Ni(II) c) b +  $0.40 \text{ mM}$  ABA ligand on the HMDE surface. Conditions: accumulation potential  $-0.25 \text{ V}$ ; accumulation time  $60 \text{ s}$  and scan rate  $10 \text{ mV s}^{-1}$ .

#### *Effect of pH solution*

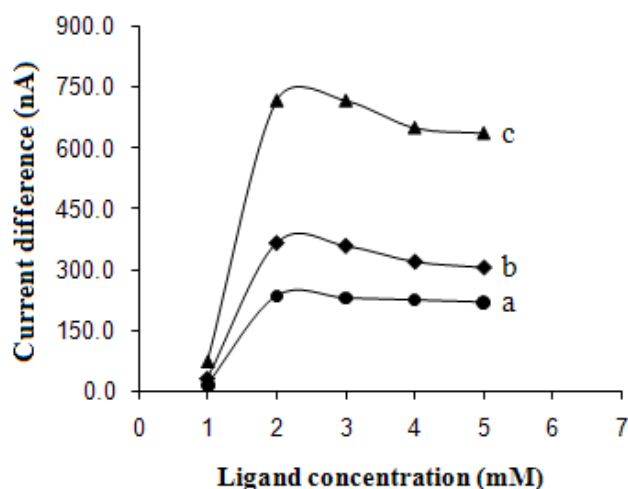
The influence of pH on the cathodic stripping peaks current of lead, cadmium and nickel was studied in the pH range of 6-8 in a solution containing  $70 \text{ ng mL}^{-1}$  of lead(II), cadmium(II) and nickel(II) in the presence of  $0.40 \text{ mmol L}^{-1}$  ABA using recording DP-AdCS voltammograms onto the HMDE by adsorptive accumulation at  $-0.25 \text{ V}$  for  $60 \text{ s}$ . Figure 2 shows the dependence of the peak heights on pH. As it is seen the peak height of metal ions increased in the pH range 6-7.4 and decreased at pH values greater than 7.4 and smaller than 6.5 that may be due to hydroxocomplex formation of metal ions and ABA protonation respectively. In spite of this the maximum peaks current were obtained at pH 7.4 for both metal ions that, it was selected for subsequent experiments.



**Figure 2.** DP-AdCS voltammetric peak current as a function of pH on the HMDE surface for a solution containing  $70 \text{ ng mL}^{-1}$  of each of Pb(II), Cd(II) and Ni(II) in the presence of  $0.40 \text{ mM}$  ABA. Conditions: accumulation potential,  $-0.25 \text{ V}$ ; accumulation time,  $60 \text{ s}$  and scan rate,  $10 \text{ mV s}^{-1}$ .

#### *Effect of ligand concentration*

The dependence of the Pb(II)-ABA, Cd(II)-ABA and Ni(II)-ABA peaks current on the complexing agent concentration was tested. DP-AdCS voltammograms of  $70 \text{ ng mL}^{-1}$  of lead (II), cadmium(II) and nickel(II) in the presence of increased amount of ABA ( $0.2\text{--}5.3 \text{ mM}$ ) were recorded in aqueous phosphate buffer of pH 7.4 following preconcentration of these metal ions as metal-ABA complexes onto the HMDE at  $-0.25 \text{ V}$  by adsorptive accumulation for  $60 \text{ s}$ . The obtained results (Figure 3) showed that the peaks currents of Pb(II)-ABA, Cd(II)-ABA and Ni(II)-ABA complexes increase along with increasing of the ligand concentration up to  $0.45 \text{ mM}$ . Beyond this concentration, the peak height decreases gradually, probably due to some competition of the ligand for adsorption at the electrode surface. Consequently, an optimum ABA concentration of  $0.45 \text{ mM}$  was selected for further experiments.

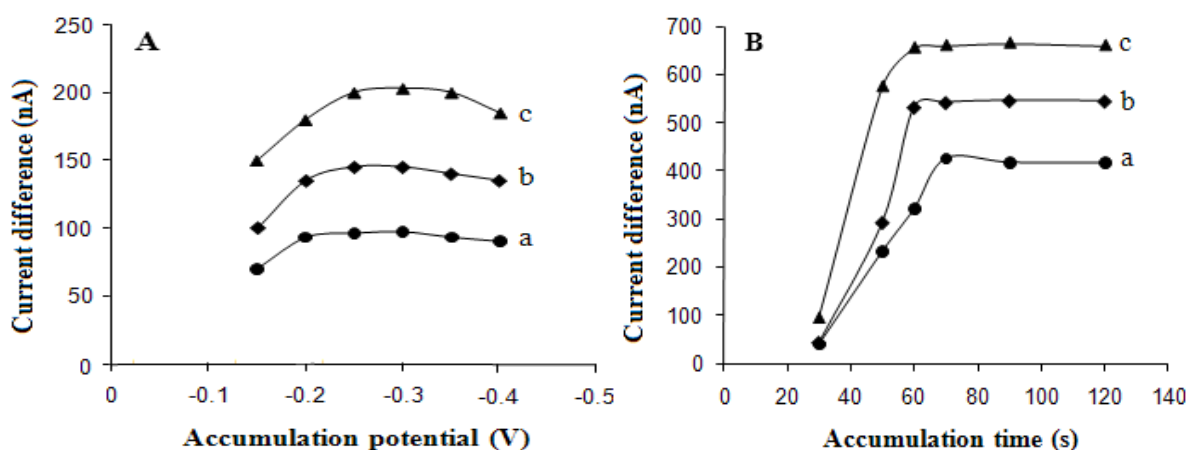


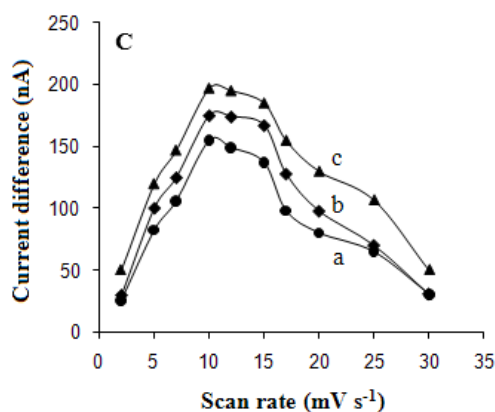
**Figure 3.** The effect of ligand concentration on the  $70 \text{ ng mL}^{-1}$  of each of Pb(II), Cd(II) and Ni(II) determination. Conditions: pH, 7.4; accumulation potential,  $-0.25 \text{ V}$ ; accumulation time,  $60 \text{ s}$  and scan rate,  $10 \text{ mV s}^{-1}$ .

*Effect of accumulation parameters*

The charge on the surface of mercury electrode plays an important role in the absorption efficiency of the interesting metal complexes [36]; whereas, the applied potential and composition of solution actually affect significantly the charge on the mercury electrode. Therefore, in this study, the influence of accumulation potential on the stripping peaks current of metal ions complexes with ABA ligand was examined individually over the potential range of  $-0.15$  to  $-0.40$  V. The plots of stripping peaks current of both metal ions as a function of pre-concentration potential are shown in Figure 4A. As it is obvious the peaks current increased up to about  $-0.2$  for all metal ions and slightly decreased with going toward more negative values. This behaviour is due to competitive adsorption behaviour between complex and ligand in the adsorption on the electrode surface. Subsequently, the accumulation potential of  $-0.2$  V was used in all further DP-AdCSV measurements.

On the other hand, DP-AdCS voltammograms of  $70 \text{ ng mL}^{-1}$  of each of lead (II), cadmium(II) and nickel(II) solutions in the presence of  $0.45 \text{ mM}$  ABA were recorded under the optimum conditions following increased pre-concentration time (30-120 s) by adsorptive accumulation potential at  $-0.2$  V. As shown in Figure 4B, the peak current of all metal ions-ABA complexes increases with accumulation time over the investigated period. At higher ion concentrations adsorptive saturation of the mercury electrode surface (adsorption equilibrium) was reached and hence the peak current levelled off. Therefore an accumulation time of  $65 \text{ s}$  was selected for further study. The effect of the scan rate was also tested in the range  $2\text{-}30 \text{ mV s}^{-1}$  (Figure 4C). The current (metal ions-ABA complexes) was found constant at scan rate higher than  $10 \text{ mV s}^{-1}$ . This scan rate was selected for the simultaneous determination of lead, cadmium and nickel.

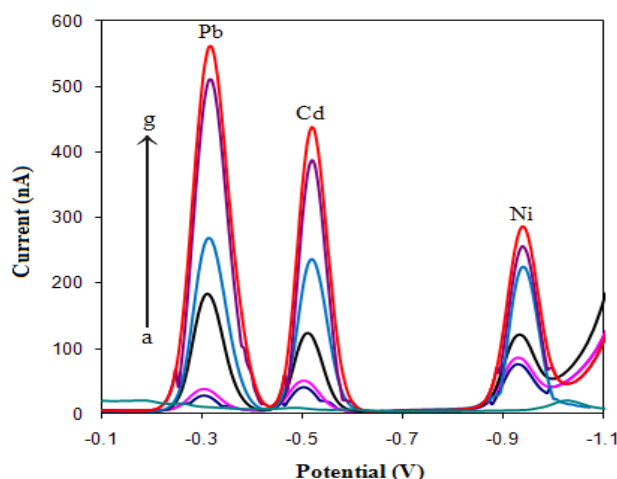




**Figure 4.** The influence of A) accumulation potential, B) accumulation time and C) sweep rate on the cathodic adsorptivity stripping peak current of  $70 \text{ ng mL}^{-1}$  of each of Pb(II), Cd(II) and Ni(II) in phosphate buffer of pH 7.4 containing  $0.45 \text{ mM}$  ABA. Other conditions: A) accumulation time,  $60 \text{ s}$  and scan rate,  $10 \text{ mV s}^{-1}$ , B) accumulation potential,  $-0.2 \text{ V}$  and scan rate,  $10 \text{ mV s}^{-1}$ , C) accumulation potential,  $-0.2 \text{ V}$  and accumulation time,  $65 \text{ s}$ .

#### *Simultaneous determination of Pb(II), Cd(II) and Ni(II)*

DP-AdCS voltammograms of various concentrations of the metal ions were recorded under the optimum procedural conditions (Figure 5). Rectilinear relations between peak current ( $I_p$ ) and concentrations of each of Pb(II), Cd(II) and Ni(II) were obtained over the ranges indicated in Table 1. The results shown in Table 1 confirmed the reliability of the described DP-AdCS voltammetry method for simultaneous determination of Pb(II), Cd(II) and Ni(II) within the indicated linear ranges.



**Figure 5.** DP-AdCS voltammograms of HDME in the presence of various concentrations of each of Pb(II), Cd(II) and Ni(II): a) 0, b) 5, c) 20, d) 50, e) 60, f) 70 and g) 80 ppb in phosphate buffer of pH 7.4 containing  $0.45 \text{ mM}$  ABA following pre-concentration at  $-0.2 \text{ V}$  onto the HMDE by adsorptive accumulation for  $65 \text{ s}$  at sweep rate  $10 \text{ mV s}^{-1}$ .

**Table 1.** Characteristics of the calibration curves of the described DP-AdCS voltammetric method for simultaneous determination of Pb(II), Cd(II) and Ni(II) as ABA complexes under optimum conditions.

Metal ions	Linearity range (ng mL <sup>-1</sup> )	Linear square equation	R <sup>2</sup>	Detection limit (ng mL <sup>-1</sup> )
Pb <sup>2+</sup>	5-150	$y = 1.1523x + 4.0683$	0.9976	1.78
Cd <sup>2+</sup>	5-120	$y = 1.0412x - 2.5793$	0.9945	2.26
Ni <sup>2+</sup>	5-150	$y = 2.0396x + 4.685$	0.9986	1.78

### Interference studies

In multi-elemental determinations at mercury electrode, the effect of interference between metal ions is potentially important because the ions compete for complexation with the same ligand and for adsorption into or onto the mercury drop. Moreover, formation of inter-metallic compounds among the investigated metal ions may cause an error in their determination. Possible interference by other metal ions with the cathodic adsorptive stripping voltammetry of Pb(II), Cd(II) and Ni(II) was investigated by the addition of the interfering ion to a solution containing these metals using the optimized conditions. The results of this study are summarized in Table 2. The tolerance limit was defined as the concentration, which gave an error of 3% in the determination of Pb(II), Cd(II) and Ni(II). Based on the results shown in Table 2 it can be concluded that the method is free from much interference of the foreign ions. However, 1-fold concentration of Al(III) had significantly influence on the determination of Pb(II), Cd(II) and Ni(II) and 20-fold concentration of Fe(II) had major interference for determination of Pb(II) and Cd(II). Interference from Al<sup>3+</sup> and Fe<sup>2+</sup> ions can be minimized by addition of 400 and 500-fold concentration of F<sup>-</sup> and SCN<sup>-</sup> ions respectively, if necessary.

### Analysis of tap water and waste water samples

The described DP-AdCS voltammetry method was successfully applied for simultaneous determination of Pb(II), Cd(II) and Ni(II) in tap water of semnan city sample and industrial waste water samples of some alloy producer companies (Table 3). The same water samples were also analyzed for these metal ions by flame atomic absorption spectrometry (FAAS). Comparison of the results obtained by the described DP-AdCS voltammetry method with those obtained by FAAS revealed the capability of the stripping voltammetry method for determination of Pb(II), Cd(II) and Ni(II) at trace concentrations. The results correspond to the mean values of five replicate determinations.



**Table 2.** The effect of foreign ions on determination of 70 ng mL<sup>-1</sup> of each metal ion under optimum conditions.

Foreign ions	Tolerance limited		
	[W(M)/W(Pb)] [W(M)/W(Ni)]	[W(M)/W(Cd)]	
NO <sub>2</sub> <sup>-</sup> , Cl <sup>-</sup> , IO <sub>3</sub> <sup>-</sup> , WO <sub>4</sub> <sup>2-</sup> , N <sub>3</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , Cs <sup>+</sup> , Mg <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , F <sup>-</sup> , Br <sup>-</sup> , SCN <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> , Cu <sup>2+</sup> , Al <sup>3+</sup> [a], Fe <sup>2+</sup> [b] BrO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , I <sup>-</sup>	1000	1000	1000
Sr <sup>2+</sup> , Ba <sup>2+</sup>	100	100	250
CN <sup>-</sup> , Co <sup>2+</sup> , Mn <sup>2+</sup> , Rh <sup>3+</sup> , Ca <sup>2+</sup> , Ce(IV)	50	50	100
Fe <sup>2+</sup>	20	20	50
Ni <sup>2+</sup>	1000	1000	–
Cd <sup>2+</sup>	1000	–	1000
Pb <sup>2+</sup>	–	1000	1000
Cu <sup>2+</sup>	1000	1000	1000
Al <sup>3+</sup>	1	1	1

[a] After addition of 400-fold concentration of F<sup>-</sup> ions to solution[b] After addition of 500-fold concentration of SCN<sup>-</sup> ions to solution**Table 3.** Determination of Pb(II), Cd(II) and Ni(II) in some tap and industrial waste water samples by the described DP-AdCSV voltammetry method under optimum conditions and FAAS.

Sample	Pb(II) (ppm)		Cd(II) (ppm)		Ni(II) (ppm)	
	AdCSV	FAAS	AdCSV	FAAS	AdCSV	FAAS
Tap water [a]	0.98	1	19.8 [b]	–	0.54	0.56
Abzar Mahdi Co.	1.55	1.5	0.811	0.82	1.31	1.30
Fenarlol Iran Co.	1.97	2.0	0.289	0.3	11.97 [c]	–
Abkaran Co.	1.61	1.5	0.319	0.32	0.84	0.86

[a] Concentrated by 25-fold

[b] No found, added 20 ppb and found 19.80 ppb with recovery percentage of 99.0%

[c] No found, added 20 ppb and found 11.97 ppb with recovery percentage of 98.0%

## Conclusion

The present study demonstrates that the adsorptive stripping analysis of lead, cadmium and nickel in the presence of 2-aminobenzoic acid is an excellent method for determination of trace amounts of these three cations. In conclusion, the above system, offers a practical potential for the simultaneous determination of lead, cadmium and nickel, especially having advantages of high sensitivity, high selectivity, simplicity and speed with minimum interference from other ions. This method can probably be used to measure other ions such as zinc and iron in aqueous media.

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