Simultaneous determination of trace lead and cadmium in water samples by adsorptive stripping voltammetry using gallic acid as a selective chelating agent
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ABSTRACT

This work describes a procedure for the simultaneous determination of cadmium and lead in some food and water samples using an adsorptive stripping voltammetric method. The method is based on the adsorptive accumulation of 2,3,4-trihydroxybenzoic acid (gallic acid (GA)) complexes of these elements onto a hanging mercury drop electrode, followed by the reduction of the adsorbed species. Optimal analytical conditions were found to be 0.10 M borate buffer (pH 6.2), 2.5 × 10⁻⁵ M GA, an accumulation potential of −0.1 V (Versus SCE), an accumulation time of 80 s and a scan rate of 60 mV/s. The peak current is proportional to the concentration of lead and cadmium over the range of 0.50–70.00 ng mL⁻¹ and 0.20–35.00 ng mL⁻¹, respectively, and the detection limit is 0.014 ng mL⁻¹ and 0.011 ng mL⁻¹ for lead and cadmium, respectively, for an 80 s adsorption time. The proposed method was applied to the determination of lead and cadmium in water and food samples with satisfactory results.

Key words | adsorptive stripping voltammetry, cadmium, lead, water samples

INTRODUCTION

Lead is an ubiquitous environmental pollutant with no known biological functions which has strong chemical toxicity at low concentrations (Arancibia et al. 2009). Acute lead poisoning in humans causes severe damage in the liver, brain, kidneys, reproductive system and central nervous system and sometimes causes death. Mild lead poisoning causes anemia, headaches, and the victim may feel fatigued and irritable. Besides, chronic exposure to lead causes nephritis, scarring and the shrinking of kidney tissues (Espada et al. 2009).

Cadmium is known as a hazardous environmental pollutant with toxic effects on living organisms (Ensafi et al. 2006). Cadmium ions are easily absorbed by vegetables, as well as in animal-based food, and are principally distributed in the liver and kidneys (Oymak et al. 2009). Heavy metals such as lead and cadmium are toxic when absorbed into the body (Abbasi et al. 2011). Owing to the low concentrations of these metals in food and biological samples, the development of new methods for quantifying trace metals is required and challenged. Several analytical methods have been reported to quantitatively determine the lead and cadmium at trace levels in a variety of samples including atomic absorption spectrometry (Karadjova et al. 2000; Baranowska et al. 2002) and inductively coupled plasma optical emission spectroscopy (Vassileva & Furuta 2001). However, these techniques have some disadvantages such as expensive apparatus, complicated operation, high cost of maintenance, and requiring well-controlled experimental conditions. For these reasons, electrochemical methods such as differential pulse polarography (Sreedhar et al. 2009), cathodic stripping voltammetry (Locatelli & Torsi 1999) for the determination of heavy metal ions, including lead and cadmium, is one of the most favorable techniques. Some of the advantages of adsorptive stripping voltammetry (AdSV) for trace analysis include high sensitivity, high selectivity, low instrumentation and possibility of convenient
analyzing of various samples without the need for a prior separation.

The present study attempts to describe a new adsorptive cathodic stripping procedure for simultaneous determination of trace amounts of lead and cadmium by using gallic acid (GA) as a complexing agent. GA (3,4,5-trihydroxybenzoic acid) is a natural polyphenolic compound which is coordinated to the metal ions (Li et al. 2007) through hydroxyl groups. The method is based on the effective accumulation of the Pb(II) and Cd(II) complexes with GA onto the hanging mercury drop electrode (HMDE). This method has low detection limits and is able to determine lead and cadmium in different water samples.

MATERIALS AND METHODS

Apparatus

The voltammetric experiments were carried out with a Metrohm Instrument model 746 VA processor equipped with 747 VA stand using a HMDE as the working electrode. The reference electrode was double junction, Ag/AgCl, saturated with 3.0 M KCl, and the counter electrode was a platinum wire. A rotating Teflon rod stirred solutions in the voltammetric cell. The mercury was triple-distilled quality, and the medium drop size of the HMDE was selected. All experiments were done at room temperature. The pH values were adjusted employing a Metrohm model 827 (Switzerland) using a combined glass electrode. Eppendorf Vary-Pipettes (10–100, 100–1,000 μL) were used to deliver accurate volumes. All glassware and storage bottles were soaked in 10% HNO₃ overnight and thoroughly rinsed with deionized water prior to use.

Reagents

Solutions were prepared by dissolving analytical-reagent grade reagents in double distilled water. A 1.00×10⁻³ M GA (Merck) was prepared by dissolving an appropriate amount of GA in 100.0 mL double distilled water. Stock solutions of lead and cadmium (1,000 mg L⁻¹) was prepared by dissolving appropriate amounts of lead and cadmium nitrate salts in water and diluting to 100.0 mL in a volumetric flask (to prevent the hydrolysis of lead and cadmium nitrate salts, two drops of nitric acid 0.02% was added). Standard solutions of lead and cadmium were prepared daily by dilution (1,000 mg L⁻¹). Borate buffer solutions (pH 6.0–10.0) were prepared by mixing different amounts of boric acid, 0.10 M, and NaOH (0.1 M) in a 100.0 mL volumetric flask.

Procedures

The supporting electrolyte solution (10 mL of 0.1 M NaOH/H₂BO₃ buffer solution, pH 6.2) containing 2.5×10⁻⁵ M of GA was transferred into the electrochemical cell and purged with nitrogen for at least 3 min. The accumulation potential (−0.1 V vs. Ag/AgCl) was applied to a fresh mercury drop, while the solution was stirred for a period of 80 s. After 80 s of accumulation time, the stirring was stopped, and after equilibration for 10 s voltammograms were recorded from +0.05 to −0.6 V with a potential scan rate of 60 mV/s and pulse amplitude of 50 mV. After the background voltammograms have been obtained, aliquots of the lead and cadmium standard solutions were introduced into the cell. Then voltammograms were recorded according to described procedure to give the sample peak current. After each scan was repeated three times with a new drop for each analyzed solution, the mean value was obtained. Lead and cadmium stripping peaks were registered at about −0.471 and −0.576 V and their currents were used as a measure of lead and cadmium concentrations. All data were obtained at room temperature. Calibration graph was prepared for the peak current against lead (II) and cadmium (II) concentrations.

Sample preparation and determination

To demonstrate its application in a practical analysis, the procedure employed to detect lead and cadmium ions in rice, soya, sugar and tea samples was prepared as follows.

Determination of lead and cadmium in rice

Rice (Iranian agricultural farms) was purchased from a local supermarket and 20.0 g of each sample was accurately weighed and placed into a quartz crucible. A total of 10 mL
of concentrated sulfuric acid was then added and evaporated to near dryness; then 10.0 mL of nitric acid (1:1, volume ratio) was added and evaporated to dryness. Under the heating conditions, concentrated hydrogen peroxide was added by drop until the solution became clear and evaporated. Water was added and continued to be heated to remove the hydrogen peroxide. The residue was then cooled and was transferred into a 50-mL calibrated flask and diluted to the mark with water (Abbasi et al. 2009). Volumes of 2.0 mL of each aliquot were taken for the determination of lead and cadmium via the recommended procedure under the established optimum conditions.

**Determination of lead and cadmium in soya and sugar**

A total of 1 g each of soya and sugar samples were accurately weighed and transferred into a 25 mL Teflon high-pressure microwave acid-digestion vessel. A total of 4.5 mL of concentrated nitric acid and a 6.0 mL of 30% H₂O₂ were added. The vessels were tightly sealed and then positioned in the carousel of the microwave oven. The system was operated at full power for 3 min. The digest was evaporated to dryness. The residue was dissolved with 10.0 mL of 5% nitric acid and was then filtered. After cooling, the solution was neutralized using NH₃ 1.00 M, and transferred to a volumetric flask and diluted to 25 mL with water (Hosseinzadeh et al. 2007).

**Determination of lead and cadmium in tea**

Each tea sample (Chakosh sabz, 3.9883 g) was accurately weighed and placed into a ceramic crucible. A total of 6 mL of concentrated nitric acid (65%, w/w, Merck) and 2.0 mL of concentrated hydrochloric acid (37%, w/w, Merck) were added. After 20 min, the sample was gently heated to digest until it reached near dryness. It was transferred into a muffle furnace for ashing at 600 °C for 1 hour. The sample was taken out to cool and 5.0 mL of nitric acid (1:1, volume ratio) was added and evaporated to near dryness by gentle fire heating. A total of 2 g ammonium peroxydisulfate (Merck) was added to cover the residue. The sample was transferred to a muffle furnace at 800 °C for ashing for 1 hour. It was cooled and was taken out. A total of 10 mL nitric acid (1:99, volume ratio) was used to dissolve the residue and the sample was transferred to a 100 mL calibrated flask and diluted to the mark with water (Abbasi et al. 2009).

**RESULTS AND DISCUSSION**

Preliminary experiments were performed to identify the general features which characterize the behavior of Pb and Cd-GA systems on mercury drop electrode. Figure 1 shows cathodic stripping differential pulse voltammograms of the Pb- and Cd-GA systems at pH 6.2 (borate buffer), after accumulation at −0.1 V for 80 s on a HMDE. The blank solution (the ligand without metal ions) for pH of 6.2 (curve ‘a’) does not show any peak in this potential range. The metal ions in the buffer solutions showed small peak currents in the absence of the ligand. Curve ‘b’ shows the voltammograms of a solution containing 60.00 ng mL⁻¹ of lead and 30.00 ng mL⁻¹ cadmium in the absence of ligand under similar conditions. The sample solution containing the metal ions with the ligand shows two peaks (curve ‘c’) at −0.471 and −0.576 V which correspond to the reduction of Pb(II) and Cd(II) complexes with GA in pH of 6.2. These peak currents increased with increasing accumulation time before the potential scan. As illustrated in Figure 1, the sensitivity of cadmium and lead reduction currents was enhanced due to the addition of GA to the solution. These responses increased when an accumulation time preceded...
the potential scan. The reduction currents increased linearly with increasing metal concentrations. Comparison of the voltammograms shows that the height of lead and cadmium reduction peaks depends on the reduction of preconcentration steps and also on the presence and absence of GA, which reveals the adsorptive nature of the response. For the best sensitivity in simultaneous determination of lead and cadmium the influence of different parameters, such as pH, ligand concentration, deposition time and potential and scan rate, were investigated.

**Effects of the variables**

The experimental variables were optimized as below.

**The influence of supporting electrolyte and pH**

The 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 peak shape for lead and cadmium were improved in the presence of borate buffer solution. Therefore, borate buffer was used for optimization of pH. The influence of pH on the cathodic stripping peak currents of lead and cadmium was studied in the pH range of 5.5–9.0 of borate buffer. The results are shown in Figure 2. It was found that, at pH 6.2, the peak currents of cadmium and lead were at maximum values. Owing to metal hydroxide formation and protonation of ligand at higher and lower pH values the pH 6.2 was selected for subsequent uses.

**Effect of chelating agent concentration**

The influence of GA concentration on the sensitivity of the proposed method was also studied. The obtained results (Figure 3) show that with increasing GA concentration up to about $2.5 \times 10^{-5}$ M, the cathodic stripping peak currents of Pb- and Cd-GA complexes increased and then levelled off at higher concentrations. This is due to the competition of GA with Pb- and Cd-GA complexes for adsorption on the HMDE. Therefore, an optimum GA concentration of $2.5 \times 10^{-5}$ M was selected for further experiments.

**The influence of accumulation potential**

The effect of the accumulation potential on the peak heights of Pb and Cd (shown in Figure 4) was studied in the range from +0.05 to –0.6 V. As it can be seen, the accumulation potential of –0.1 V has better sensitivity for both metal ions, so an accumulation potential of –0.1 V was used for the optimized analytical procedure.

**The influence of accumulation time**

The effect of the accumulation time on the stripping peak currents for Pb and Cd in the range 20–120 s was studied. With increasing pre-concentration time the peak currents initially increased, indicating that before adsorptive equilibrium is reached, the longer accumulation time, the more metal-GA were adsorbed and thus the peak currents become larger. However, after a specific period of accumulation time, the peak currents tended to level off slowly as...
the equilibrium surface concentration of the adsorbed complexes was approached. Thus, a deposition time of 80s was used throughout, as it combined good sensitivity and relatively short analysis time.

**The influence of scan rate**

The effect of scan rate on the stripping peaks of Pb and Cd under the optimal conditions was examined. The results show that the peak heights for both Pb and Cd increase nearly from 20 to 60 mV/s while for larger scan rates the sensitivity decreases. Therefore, a scan rate of 60 mV/s was selected.

**Linear range, detection limit and precision**

To verify the linear relationship between peak currents and metal concentrations, two calibration graphs were plotted under optimum conditions (2.5 × 10⁻⁵ M GA, pH 6.2, a deposition potential of −0.1 V and 80s deposition time). The linearity of the calibration curves were maintained in the range of 0.50–70.00 ng mL⁻¹ Pb(II), with regression equation of: \( I = 5.3986C + 9.1969 \) (\( r^2 = 0.9987 \)) and 0.20–35.00 ng mL⁻¹ Cd(II) with regression equation of \( I = 8.6727C + 7.3907 \) (\( r^2 = 0.9992 \)), where \( I \) is the net peak current in nano amperes (nA) and \( C \) is the concentration in ng/mL. The relative standard deviation for 10 replicate analyses of a solution containing 3.00 and 30.00 ng mL⁻¹ Pb(II) were 1.03%, 2.21% and for 3.00 ng mL⁻¹ and 30.00 ng mL⁻¹ Cd(II) were 2.86%, 1.73%, respectively. The detection limits which were calculated from three times the standard deviation of the blank divided by the slope of the calibration graph were 0.014 ng mL⁻¹ for lead and 0.011 ng mL⁻¹ for cadmium.

**Interference study**

Possible interference of other species in the adsorptive stripping voltammetric determination of lead and cadmium was studied by addition of the interfering ion to a solution containing 60.00 ng mL⁻¹ of Pb(II) and 30.00 ng mL⁻¹ Cd(II), using the optimized conditions (the tolerance limit was defined as the concentration of foreign species which produces a change in peak heights of Pb and Cd less than 5%). The results of this study are summarized in Table 1. It was found that most of the foreign ions did not interfere with lead and cadmium determination, so the proposed method has a very high selectivity.

**Application**

The proposed method was directly applied to the determination of lead and cadmium in some water samples without any separation steps. Lead and cadmium was determined in water and food samples (rice, soya and sugar) by using the standard addition method. The recovery results for analyses of some real samples are shown in Table 2. The data obtained for samples spiked with known amounts of lead and cadmium showed good recovery.

**CONCLUSIONS**

The present study demonstrates that in the presence of GA the AdSV of lead and cadmium is an excellent method for

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Interferences study for lead and cadmium determination</th>
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<tbody>
<tr>
<td>Species</td>
<td>Pb(II) ((W_{inter}/W_{Pb})^a)</td>
</tr>
<tr>
<td>Cs⁺, Mg²⁺, ClO₃⁻, Al³⁺, Ni²⁺, CH₃COO⁻, K⁺, C₂O₄⁻, NO₃⁻, SO₄²⁻</td>
<td>500</td>
</tr>
<tr>
<td>Sn²⁺, Zn²⁺</td>
<td>150</td>
</tr>
<tr>
<td>SCN⁻, I⁻, Cl⁻, F⁻, Cu²⁺, Fe³⁺, CO₃²⁻</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^a\)The relative weight of interfering ion to the weight of Pb²⁺ and Cd²⁺.
the determination of trace amounts of these two metal ions in food samples. The above system offers a practical potential for the simultaneous determination of lead and cadmium; in addition, this method has high sensitivity, selectivity, simplicity and speed. Table 3 shows some critical properties of the present work compared with previous studies using adsorptive cathodic voltammetry for simultaneous determination of lead and cadmium. Comparison of the present work with the results in this table shows a good analytical figure of merits compared with other studies.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Working electrode</th>
<th>Detection limit (ng/mL)</th>
<th>Linear dynamic range (ng/mL)</th>
<th>Accumulation time (s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quercetin-5'-sulfonic acid</td>
<td>HMDE</td>
<td>0.3 0.1</td>
<td>0.5–40.0 0.5–45.0</td>
<td>30 30</td>
<td>Nagles et al. (2012a)</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole</td>
<td>HMDE</td>
<td>0.02 0.01</td>
<td>0.5–70.0 0.1–30.0</td>
<td>160 160</td>
<td>Abbasi Khodarahmiyan &amp; Abbasi (2011)</td>
</tr>
<tr>
<td>Pyrogallol red</td>
<td>Nafion-coated antimony film electrode</td>
<td>0.4 0.9</td>
<td>0.9–12.0 0.9–12.0</td>
<td>100 100</td>
<td>Arancibia et al. (2013)</td>
</tr>
<tr>
<td>Xylenol orange</td>
<td>HMDE</td>
<td>1.0 1.2</td>
<td>5–200 10–200</td>
<td>30 30</td>
<td>Ensafi et al. (2006)</td>
</tr>
<tr>
<td>Pyrogallol red</td>
<td>Nafion–mercury coated glassy carbon electrode</td>
<td>0.05 0.01</td>
<td>1.0–16.0 1.0–13.0</td>
<td>100 100</td>
<td>Nagles et al. (2012b)</td>
</tr>
<tr>
<td>Carbamoyl phosphonic acid</td>
<td>Carbon paste electrode</td>
<td>0.5 0.5</td>
<td>10–200 10–200</td>
<td>1,800 1,800</td>
<td>Yantasee et al. (2004)</td>
</tr>
<tr>
<td>8-Hydroxyquinoline</td>
<td>HMDE</td>
<td>0.06 0.1</td>
<td>0.06–12.4 0.1–28.1</td>
<td>600 600</td>
<td>Van den Berg (1986)</td>
</tr>
<tr>
<td>Clioquinol</td>
<td>HMDE</td>
<td>0.1 0.06</td>
<td>0.1–10.0 0.06–31.0</td>
<td>90 60</td>
<td>Herrero et al. (2014)</td>
</tr>
<tr>
<td>Gallic acid</td>
<td>HMDE</td>
<td>0.01 0.01</td>
<td>0.5–70.0 0.2–35.0</td>
<td>80 80</td>
<td>This work</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENT

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REFERENCES


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