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Simultaneous determination of Pb^{2+} , Cd^{2+} and Zn^{2+} by adsorptive stripping voltammetry using Clioquinol as a chelating-adsorbent agent



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ABSTRACT

A sensitive and selective method for the simultaneous determination of lead, cadmium and zinc based on the formation of their complexes with Clioquinol (5-chloro-7-iodo-8-hydroxyquinoline, CQ) is described. These studies were carried out using separate copper, lead, cadmium and zinc solutions and also mixtures of them. The optimum pH values were 2.3; 5.1; 5.3 and 5.2 for copper, lead, cadmium and zinc respectively (Britton Robinson buffer 0.03 mol L⁻¹). In addition to optimum pH values, copper not interfere, but simultaneous determination of four elements is not possible. A pH of 5.3, a CQ concentration of 3.6 μmol L⁻¹ and an accumulation potential of -0.65 V were chosen for the analysis. Copper, lead, cadmium and zinc complexes peak currents were observed at -0.30; -0.41; -0.59 and -0.95 V whereas the free CQ is reduced at -0.80 V. For individual analysis, the relationship between the peak current and metal concentration is linear until 40.0; 31.0 and 70.0 μg L⁻¹ for lead, cadmium and zinc respectively. However in the simultaneous determination, the relationship is linear until 15.0 μg L⁻¹ for lead and cadmium and 25.0 μg L⁻¹ for zinc and the detection limits were found to be 0.10; 0.06 and 0.06 μg L⁻¹ for lead, cadmium and zinc respectively. The relative standard deviation for 6 replicates determination of 5.0 μg L⁻¹ lead, cadmium and zinc is equal to 1.8%, 0.9% and 1.6% respectively. The method was validated by determining lead, cadmium and zinc in spiked synthetic sea water (ASTM D665), Ontario lake reference water (TMDA-61.2) and was applied to the determination of these metal ions in tap water, sea water, and mineral water samples.

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1. Introduction

8-Hydroxyquinolines are compounds of great interest in the field of analytical, inorganic and bioinorganic chemistry. They are characterized by the presence of an N,O-binding system that is suitable for interacting strongly with ions like Cu²⁺, Zn²⁺, Fe²⁺, Al³⁺, Mo⁶⁺, V⁵⁺, Ti⁵⁺ and Co²⁺. Clioquinol (5-chloro-7-iodo-8-hydroxyquinoline, CQ) is the best known member of this family. CQ was first prepared early in the last century and was widely used as an antibiotic. In the 1970s it was banned in many countries because it was linked to outbreaks of subacute myelo-optic neuropathy in Japan. However, this conclusion was not supported by subsequent epidemiologic studies [1–3]. Recent animal studies have shown that CQ can reverse the progression of Alzheimer's, Parkinson's and Huntington's diseases. Its biological effects are most likely ascribed to complexation of specific metal ions, such as Cu²⁺ and Zn²⁺, critically associated with protein aggregation

and degeneration processes in the brain. The high lipophilicity of free CQ may explain its ready access to the brain (log P is 3.5, while log P for 8-HQ is 1.84), and selective metal chelation may account for its effects against neurodegeneration. CQ selectively binds Zn²⁺ and Cu²⁺ with greater affinity than it binds Ca²⁺ and Mg²⁺ (log K₁(Zn) = 7.0, log K₁(Cu) = 8.9, log K₁(Ca) = 4.9, log K₁(Mg) = 5.0) [4–6]. Budimir et al. [7] carried out a physicochemical study of the coordination properties of CQ with Cu²⁺, Zn²⁺, Ni²⁺, Co²⁺ and Mn²⁺ using electrospray mass spectrometry, absorption spectrophotometry, and potentiometric techniques, reporting stability constants of log K₁(Zn) = 8.5, log K₁(Cu) = 12.5, log K₁(Ni) = 10.3, log K₁(Co) = 9.4, and log K₁(Mn) = 7.1 (methanol:water). Di Vaira et al. [8] reported the structural characterization of the Zn²⁺ and Cu²⁺ complexes with CQ. A ligand to metal stoichiometry of 2:1 was found in both cases, though in the presence of quite different coordination polyhedral (Zn(CQ)₂(H₂O); Cu(CQ)₂).

Due to their toxicity, even at low concentrations, lead and cadmium are metals of prime environmental concern, but copper and zinc are important as they may play a vital or a toxic role depending on their concentration. For their determination, adsorptive

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stripping voltammetry (AdSV) is very suitable owing to its high sensitivity, relative simplicity, no need for previous separation, and because only very simple pretreatment of the sample is required. One of the future trends in AdSV is multielement analysis. AdSV requires the presence of a ligand with adsorptive properties and the complexes must be formed quantitatively and quickly in solution, they must be adsorbed on the electrode's surface, and later the ligand or the metal are oxidized or reduced [9–13]. Their sensitivity and selectivity depends on the working electrode as well as on the choice of a suitable ligand. Despite the toxicity of mercury, the hanging mercury drop electrode (HMDE) is a nearly ideal electrode, especially for cathodic processes and mainly due to good adsorptive properties [14,15]. The sensitivity of the method is directly related to the adsorption of the complex, and the adsorption of the complex is related to its net charge, size, and solubility. The favorable pharmacological effects of CQ are probably related to its lipophilicity as well as to its ability to form relatively stable complexes with Zn^{2+} and Cu^{2+} ions. Due to these characteristics, CQ may be a good ligand which can be adsorbed on a mercury electrode to determine these and other metal ions at trace levels.

The aim of this study was to optimize the adsorptive stripping voltammetry technique to determine Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} simultaneously using CQ as complexing and adsorbing agent. Neither the use of this ligand in AdSV with analytical purposes nor the simultaneous determination of some trace metals have been reported yet.

2. Experimental

2.1. Apparatus

Stripping voltammetry measurements were obtained with a Metrohm 797 VA Computrace Stand. The hanging mercury drop electrode (HMDE) or modified glassy carbon electrode (NHgFE, disc diameter of 2 mm), were used as working electrodes with a Ag/AgCl/KCl 3 mol L^{-1} reference electrode, and a platinum wire auxiliary electrode. Solutions were stirred during the purging and deposition steps with a rotating PTFE rod. The solutions were deaerated using high-purity nitrogen. pH was measured with an Orion model 430 pH meter. UV-irradiation of water samples was performed in quartz tubes using a 705 UV-digester (Metrohm).

2.2. Chemical and samples

Deionized water, Emsure quality, Merck (Darmstadt, Germany), was used for sample the preparation, dilution of the reagents, and rinsing purposes. All the chemicals (nitric acid, hydrochloric acid, peroxide, ethanol, etc.) were analytical grade from Merck. The 0.1 and 1.0 mg L^{-1} standard solutions of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} (separate or mixtures of them) were prepared by appropriate dilution of the stock standard solutions (1000 mg L^{-1} , CertiPUR, Merck). Nafion (5%w/v solution in a mixture of water and lower alcohols) and Clioquinol (CQ) were purchased from Aldrich (Milwaukee, WI). The stock solution of CQ in ethanol (1.2 mmol L^{-1}) was freshly prepared every two or three days. Britton Robinson (BR) buffer solutions were used to investigate pH in the 2.0–10.2 range. These buffers (0.3 mol L^{-1}) were prepared by mixing equal volumes of orthophosphoric acid, acetic acid, and boric acid, adjusting to the required pH with 30% NaOH solution. All the chemicals used were of suprapur quality (Merck). The usefulness of the present method was also evaluated by determining lead, cadmium and zinc in spiked synthetic sea water (ASTM D665) and Ontario lake reference water (TMDA-61.2) purchased from Environment Canada, containing Cu 63.5; Pb 61.4; Cd 58; Zn 71.3; Mo 72.2; Al 57.9; As

34.4; Bi 22.7; Co 63; Fe 79.7; Mn 75.7; Ni 57.5; V 71.1 $\mu\text{g L}^{-1}$, and others. Finally, the method was applied to the determination of Pb(II), Cd(II) and Zn(II) in tap water, sea water and mineral water after UV digestion. Domestic tap water samples were collected in our laboratory, sea water samples were obtained from a beach close to several industries and near to a populated area with much tourism (Quintero) and were introduced in plastic bottles previously washed with 1% HNO_3 solution. Mineral water (Puyehue, Liv, Chanqueahue) were purchased in a supermarket. Before the analysis all the samples and reference material were digested for 90 min at 90 °C in the presence of H_2O_2 (10.0-mL of sample with 100 μL of 30% H_2O_2) to decompose organic substances.

2.3. Adsorptive stripping voltammograms

Aliquots of separate Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} solutions (0.1 or 1.0 mg L^{-1}) or of mixtures of them, 1.0 mL of BR buffer (0.3 mol L^{-1}), 30 μL of CQ (1.2×10^{-3} mol L^{-1}) and 9.0 mL of water, were pipetted into the voltammetric cell. The solution was stirred and purged with nitrogen gas for 5 min. After a new HMDE was formed, the adsorption process was started according to the conditions chosen for each experiment. At the end of the accumulation time the stirrer was switched off. After resting for 10 s, the differential pulse voltammogram was ran, scanning the potential from -0.20 to -1.10 V (modulation time, 40 ms; modulation amplitude, 50 mV; interval time, 0.1 s; potential step, 5 mV, resulting in a scan rate of 50 mV s^{-1}). Each scan was repeated two or three times. The calibration curves were obtained and linear regression and detection limits were calculated. The standard addition method was used to eliminate matrix effects.

2.4. Procedure for the preparation of NHgFE

Before measurement, the glassy carbon electrode was thoroughly polished using a polishing pad with a 0.3 mm Al_2O_3 slurry, rinsed with ethanol and water in an ultrasonic bath and dried with N_2 . A drop of the Nafion solution (10 μL) was placed on the electrode surface and the solvents were left to evaporate at room temperature for 10 min. The electrode was then transferred into the plating solution containing 200 mg L^{-1} Hg(II) and the Hg film was formed by holding the working electrode potential at -1.30 V for 150 s.

2.5. Detection limits (DL)

The detection limit was calculated from the first 5 or 6 points of the calibration curve $y_{\text{DL}} = a + 3\sigma_{x/y}$ and $y_{\text{DL}} = a + bx_{\text{DL}}$, where a is the intercept, $\sigma_{x/y}$ is the random error in x and y , and b is the slope ($\text{DL} = x_{\text{DL}} = 3\sigma_{x/y}/b$) [16].

3. Results and discussion

The introduction of Cl, Br, or I into the oxine molecule increases its acid strength, and the extraction of some metals can be made under more acidic solutions. The pK_a values of CQ are 2.7 and 7.9 while the pK_a of oxine are 5.0 and 9.7. It has been reported that Clioquinol forms neutral complexes with Cu^{2+} and Zn^{2+} with a 1:2 metal:ligand stoichiometry, and it also forms complexes with Pb^{2+} and Cd^{2+} , but their stoichiometry has not been reported. Under our working conditions we found that CQ forms complexes with all the metal ions studied: Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} .

3.1. Effect of operational parameters

3.1.1. Influence of pH

The formation of the complexes, their stability, net charge and adsorptive properties depends largely on the pH of the system. The influence of pH on the peak current of copper, lead, cadmium and zinc were studied in the pH range of 2.0–10.2 using BR buffer (0.3 mol L^{-1}) for solutions containing $10.0 \mu\text{g L}^{-1}$ of each ion separately and $2.4 \times 10^{-6} \text{ mol L}^{-1}$ of CQ ($E_{\text{ads}} = -0.70 \text{ V}$ and $t_{\text{ads}} = 30 \text{ s}$). As can be seen in Fig. 1, the peak current of the Cu–CQ complex decreased from pH 2.3 to 7.0, while the peak current of the Pb–CQ, Cd–CQ and Zn–CQ complexes increased up to 5.1–5.3 and then it decreased. The maximum peak currents were obtained at pH: 2.3; 5.1; 5.3 and 5.2 for copper, lead, cadmium and zinc, respectively. Therefore, a pH of 5.3 was chosen for the study, giving copper, lead, cadmium and zinc peak currents at -0.30 ; -0.41 ; -0.59 and -0.95 V , while the free ligand is reduced at -0.80 V . Simultaneous determination including copper was not possible, however it is not presents interference. At pH 5.3 the peak current of copper is very low and when aliquots of standard Cu(II) solution were added the peak current decreased because of the slow precipitation of neutral $\text{Cu}(\text{CQ})_2$ complex [7]. A study as a function of buffer concentration was carried out adding aliquots of 0.3 mol L^{-1} BR buffer, obtaining no considerable difference of peak current of complexes when 700–1000 μL were added (total volume on cell was $\approx 10.0 \text{ mL}$). Then, BR buffer of pH 5.3 (0.3 mol L^{-1}) was replaced by acetic acid/acetate buffer of the same pH and concentration, finding lower values of peak current of complexes than those obtained with BR buffer.

3.1.2. Influence of ligand concentration

The concentration of CQ plays an important role in the adsorptive determination of lead, cadmium and zinc. This study was carried out with each ion separately and together. Fig. 2 shows the individual influence of CQ concentration on the peak current for $10.0 \mu\text{g L}^{-1}$ lead, cadmium and zinc (pH 5.3, $E_{\text{ads}} = -0.70 \text{ V}$; $t_{\text{ads}} = 30 \text{ s}$). It is seen that for lead, cadmium and zinc the peak current increases gradually with increasing CQ concentration up to $6.0 \mu\text{mol L}^{-1}$. However, in the simultaneous determination the peak current for lead and cadmium increases linearly with increasing CQ concentration up to 4.3 – 5.5 and 4.9 – $6.8 \mu\text{mol L}^{-1}$ respectively and then decreases slightly. For zinc, however, maximum peak heights were reached at a very low CQ concentration

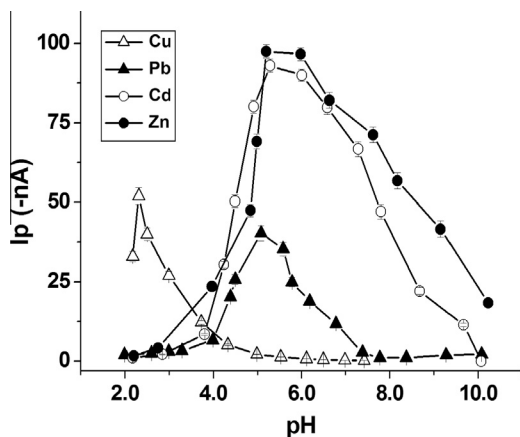


Fig. 1. Influence of pH on the peak current of the Cu–CQ, Pb–CQ, Cd–CQ, and Zn–CQ complexes (0.03 mol L^{-1} BR buffer) separately. Conditions: $C_{\text{Cu,Pb,Cd,Zn}} 10.0 \mu\text{g L}^{-1}$; $C_{\text{CQ}} 2.4 \mu\text{mol L}^{-1}$; $t_{\text{ads}} 30 \text{ s}$; $E_{\text{ads}} -0.70 \text{ V}$. Differential pulse voltammograms were obtained with modulation time: 40 ms ; modulation amplitude: 50 mV ; interval time: 0.1 s ; potential step: 5 mV ; and scan rate: 50 mV s^{-1} .

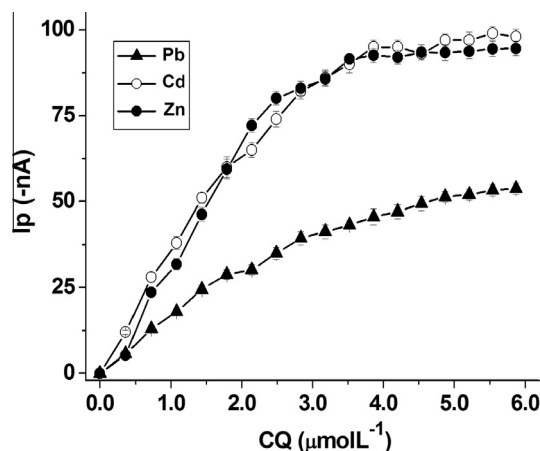


Fig. 2. Influence of CQ concentration on the peak current of the Pb–CQ; Cd–CQ and Zn–CQ complexes separately. Conditions: pH 5.3; $C_{\text{Pb,Cd,Zn}} 10.0 \mu\text{g L}^{-1}$; $t_{\text{ads}} 30 \text{ s}$; $E_{\text{ads}} -0.70 \text{ V}$. Other conditions as in Fig. 1.

($1.2 \mu\text{mol L}^{-1}$) and they decrease when additional CQ was added. This slightly different behavior is due to competition of the ions by CQ or competition of CQ with complexes for adsorption on the HMDE. To determine lead, cadmium and zinc simultaneously a CQ concentration of $3.6 \mu\text{mol L}^{-1}$ was chosen.

3.1.3. Influence of accumulation potential and time

The effect of the adsorption potential on the stripping peak current was studied in the 0.00 to -1.20 V range using $10.0 \mu\text{g L}^{-1}$ metal ion concentrations (pH 5.3, $C_{\text{CQ}} 3.6 \mu\text{mol L}^{-1}$, $t_{\text{ads}} 30 \text{ s}$, Fig. 3). The peak currents are almost constant from 0.00 to -0.70 for lead, cadmium, and zinc, and they decreased when the accumulation potentials were more negative. The same results were obtained when the study was carried out with individual or simultaneous analysis. An accumulation potential of -0.65 V was chosen for further measurements.

On the other hand, the effect of accumulation time was examined in the 0 – 300 s range ($C_{\text{Pb,Cd,Zn}} 10.0 \mu\text{g L}^{-1}$, pH 5.3, $C_{\text{CQ}} 3.6 \mu\text{mol L}^{-1}$, $E_{\text{ads}} -0.65 \text{ V}$). Peak current increased with increasing accumulation time prior to the potential scan, indicating that the CQ and the complexes are readily adsorbed on the HMDE. The results were different when the study was carried out for individual or simultaneous analysis. When the study was carried out

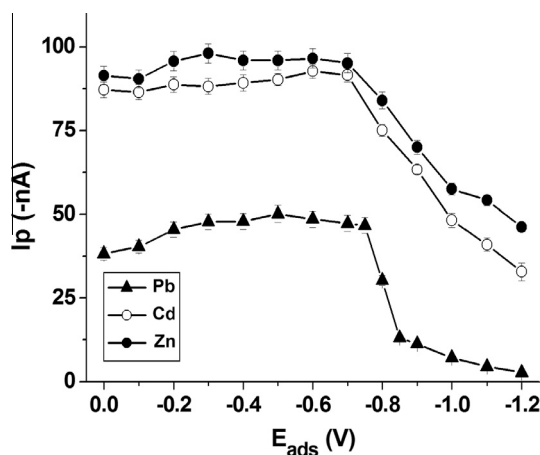


Fig. 3. Influence of E_{ads} on the peak current of the Pb–CQ; Cd–CQ and Zn–CQ complexes. Conditions: pH 5.3; $C_{\text{Pb,Cd,Zn}} 10.0 \mu\text{g L}^{-1}$; $C_{\text{CQ}} 3.6 \mu\text{mol L}^{-1}$; $t_{\text{ads}} 30 \text{ s}$. Other conditions as in Fig. 1.

individually the peak current of lead, cadmium and zinc complexes increased almost linearly until 300 s. However, in the simultaneous determination the peak current of lead, cadmium and zinc increased almost linearly with accumulation time until 90, 60 and 150 s, respectively and then decreased. On the other hand, the peak current of free CQ increased with accumulation time until 50 s and then decreased abruptly. This may be due to the fact that with increasing accumulation time Zn–CQ was competitive with Pb–CQ and Cd–CQ or consumes free CQ because it forms the more stable complex. Considering the speed of the measurement, t_{ads} between 30 and 60 s were used for further studies, but in the analysis of real samples with low analyte concentration longer times may be needed to achieve good sensitivity.

3.1.4. Comparison with others techniques and electrodes

Anodic stripping voltammetry (ASV), the most popular stripping voltammetric technique, is effective for the determination of trace amounts of metal ions. In adsorptive voltammetry higher sensitivity could be achieved in the presence of adequate ligand. In anodic voltammograms (Fig. 4A), the oxidation peaks of zinc, cadmium and lead are seen at -0.99 ; -0.59 and -0.41 V with peak currents of 21.8; 49.4 and 9.4 nA while in adsorptive voltammograms, the reduction peaks are seen at -0.95 ; -0.62 and -0.45 V with peak currents of 62.4; 286.0 and 54.3 nA for the same solution ($C_{\text{Pb,Cd,Zn}}$ $10.0 \mu\text{g L}^{-1}$, pH 5.3 (0.03 mol L^{-1} BR buffer), C_{CQ}

$3.6 \mu\text{mol L}^{-1}$, $E_{\text{AdSV}} -0.65$ V, $E_{\text{ASV}} -1.20$ V, t_{acc} 30 s). Later measurements were carried out using a Nafion coated mercury film electrode on glassy carbon electrode (NHgFE) and applying the optimal analytical conditions obtained with HMDE: $C_{\text{Pb,Cd,Zn}}$ $10.0 \mu\text{g L}^{-1}$, pH 5.3, C_{CQ} $3.6 \mu\text{mol L}^{-1}$, $E_{\text{ads}} -0.65$ V, t_{ads} 30 s). Fig. 4B shows anodic and adsorptive voltammograms obtained with this electrode. In anodic voltammograms (Fig. 4B), the oxidation peaks of zinc, cadmium and lead are seen at -1.18 ; -0.77 and -0.59 V with peak currents of 5.1; 1.2 and $0.77 \mu\text{A}$ while in adsorptive voltammograms, the reduction peaks are seen at -1.15 ; -0.73 and -0.55 V with peak currents of 0.79; 0.20 and $0.20 \mu\text{A}$. With HMDE the peak currents obtained with AdSV were higher than ASV, whereas with NHgFE the peak currents obtained with ASV were higher than AdSV for the same solution. On the other hand, in AdSV with NHgFE the free CQ peak was not observed due to the fact that nafion (negative membrane) prevents the adsorption of organic compounds. With glassy carbon unmodified non signals were observed.

3.1.5. Influence of instrumental variables

Another not minor parameter is stirring speed in the accumulation step; normally, if the complex is weakly adsorbed, a low stirring speed is recommended. A linear increase of the peak current of the complexes were seen when the stirring speed varied from 800 to 2000 rpm and then tended to a steady value. A stirring speed of 2000 rpm was used for further studies. The effect of pulse amplitude, voltage step, pulse time and voltage step time on the peak current were varied from 25 to 100 mV; 5 to 25 mV; 0.02 to 0.08 s and 0.05 to 0.2 s, respectively. It was found that by increasing pulse amplitude, voltage step, pulse time and voltage step time up to 50 mV; 5 mV; 0.04 s and 0.1 s (scan rate of 50 mV s^{-1}) the peak currents increased without losing resolution, and these values were chosen for the further measurements.

3.2. Linear range, detection limit, and repeatability of the method

Optimal analytical conditions were found to be a CQ concentration of $3.6 \mu\text{mol L}^{-1}$, pH 5.3 (BR buffer 0.03 mol L^{-1}), and accumulation potential of -0.65 V (stirring speed 2000 rpm; modulation time, 40 ms; modulation amplitude, 50 mV; interval time, 0.1 s; potential step, 5 mV; scan rate 50 mV s^{-1}). Under these conditions calibration plots were recorded. The results were different if the study was carried out with each ion separately or together. When the study was carried out with each ion the peak current of lead, cadmium and zinc complexes increased almost linearly with the concentration until 40.0; 31.0 and $70.0 \mu\text{g L}^{-1}$ respectively. However, in the simultaneous determination the linear calibration plot extends up to a concentration of $15.0 \mu\text{g L}^{-1}$ for lead and cadmium and $25.0 \mu\text{g L}^{-1}$ for zinc with an accumulation time of 60 s. When Cu^{2+} solution was added the peak current decreased because the low solubility of the Cu–CQ complex. The calibration plots, the standard deviation of the replicates and the differential pulse voltammograms of solutions containing copper, lead, cadmium and zinc are shown in Fig. 5. The detection limits ($3\sigma_{\text{xy}}/b$) were found to be 0.10, 0.06 and $0.06 \mu\text{g L}^{-1}$ for lead, cadmium and zinc, respectively (t_{ads} 30 s). Six repeated differential pulse voltammograms after 60 s accumulation time showed that the relative standard deviation for $5.0 \mu\text{g L}^{-1}$ of lead, cadmium and zinc were 1.8%, 0.9% and 1.6%, respectively. Over the last years the popularity of AdSV has been increasing, however the majority of the published applications on the simultaneous determination of lead and cadmium and/or zinc have utilized ASV.

The simultaneous determination of lead, cadmium and zinc by AdSV was carried out recently by del Valle et al. [17] using a graphite electrode modified with peptides however this authors reported sensitivity rather than detection limits. On the other

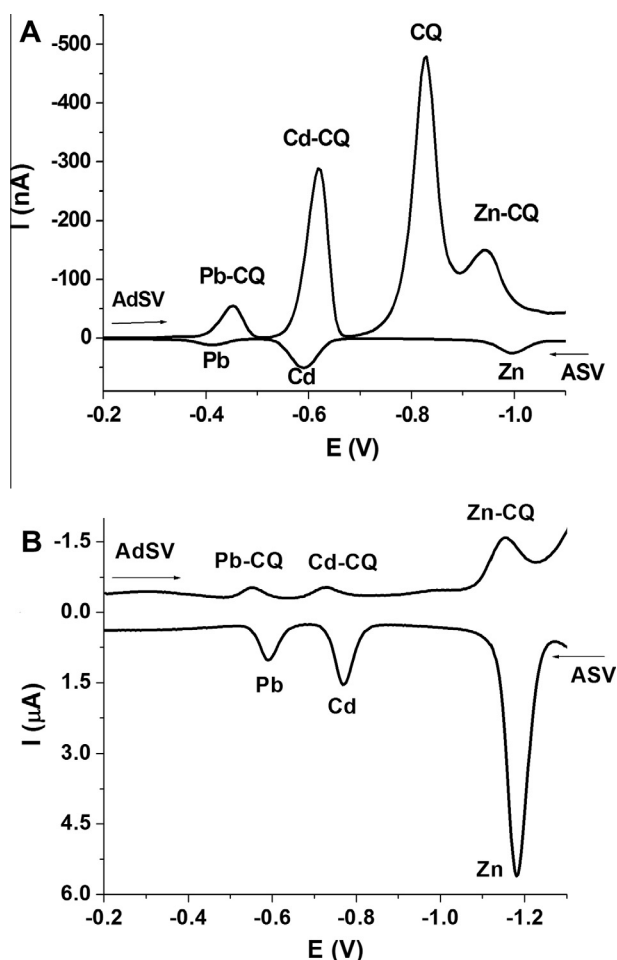


Fig. 4. Adsorptive and anodic stripping voltammograms of a solution of Pb, Cd and Zn in the presence of CQ with (A) HMDE and (B) NHgFE. Conditions: pH 5.3; $C_{\text{Pb,Cd,Zn}}$ $10.0 \mu\text{g L}^{-1}$; C_{CQ} $3.6 \mu\text{mol L}^{-1}$; t_{acc} 30 s; E_{ads} -0.65 V (E_{dep} -1.20 V). Other conditions as in Fig. 1.

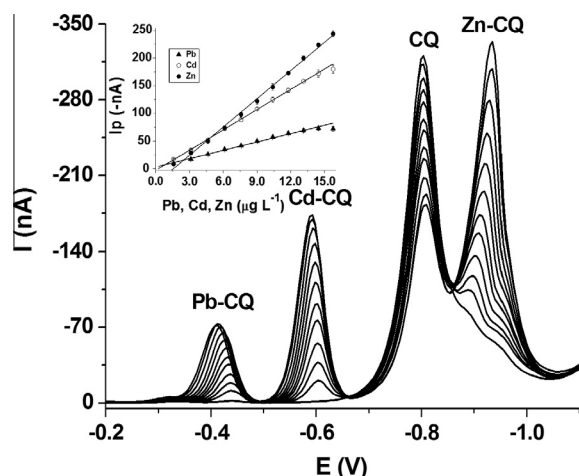


Fig. 5. DPV and calibration curve for increasing concentration of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} . Conditions: pH 5.3; C_{CQ} : $3.6 \mu\text{mol L}^{-1}$; E_{ads} : -0.65 V ; t_{ads} : 30 s. Other conditions as in Fig. 1.

hand, Galindo-Riaño et al. [18] studied the individual and simultaneous determinations of cadmium, lead and copper and reported detection limits of 0.28, 0.026 and $0.038 \mu\text{g L}^{-1}$ for individual determination and 0.107, 0.17 and $0.053 \mu\text{g L}^{-1}$ for simultaneous determination respectively. In this study the calibration curves were linear over the range $0.5\text{--}10 \mu\text{g L}^{-1}$ for cadmium and lead, and over the range $0.5\text{--}9 \mu\text{g L}^{-1}$ for copper. These results are similar to those obtained by us.

3.3. Interference studies and validation of the method

Metal ions can interfere with the measurement by complexing with CQ, and this consumes the ligand or both by complexing and producing reduction peaks that overlap with, or even completely suppress, the Pb-CQ, Cd-CQ or Zn-CQ complexes peak. The first problem was solved by adding excess ligand and using the standard addition method for the determination. Has been reported CQ and oxine forms complex with aluminum, but under our experimental conditions (pH 5.3; C_{CQ} $3.6 \mu\text{mol L}^{-1}$; E_{ads} -0.65 V), Al (III) was added until $50.0 \mu\text{g L}^{-1}$ and no signal was observed. Similar results were obtained with Co(II) and Ni(II).

A 9.0 mL aliquot of synthetic sea water (ASTM D665) contaminated with a standard solution containing lead, cadmium and zinc ($5.0 \mu\text{g L}^{-1}$), was added to the electrochemical cell that contained 1.0 mL of BR buffer and $30 \mu\text{L}$ of CQ 1.2 mmol L^{-1} adjusting to the 5.3 pH with NaOH solution. The analysis of these metal ions was carried out using the standard addition method. The values obtained were 4.8 ± 0.3 ; 5.0 ± 0.1 ; $4.9 \pm 0.2 \mu\text{g L}^{-1}$; (RE -4.0% , 0.0% and -2.0%) respectively for lead, cadmium and zinc. The usefulness of the present method was also evaluated by determining these analytes in certified reference water TMDA-61. Fig. 6 shows differential pulse voltammograms and calibration plot obtained when 0.5 mL of TMDA-61 sample was added to 8.5 mL of deionized water, 1.0 mL of BR buffer pH 5.3 (0.3 mol L^{-1}) and $30 \mu\text{L}$ of 1.2 mmol L^{-1} CQ. The values obtained for lead, cadmium and zinc were 65.6 ± 1.2 ; 59.5 ± 0.6 ; $69.9 \pm 0.9 \mu\text{g L}^{-1}$; (RE 6.8%, 2.6% and -2.0%). These values are satisfactory because this reference lake Ontario water contains about 28 metal ions with concentrations between 3.2 and $113 \mu\text{g L}^{-1}$.

3.4. Real water samples analysis

The proposed method was applied to the determination of lead, cadmium and zinc tap water, sea water (Quintero) and mineral

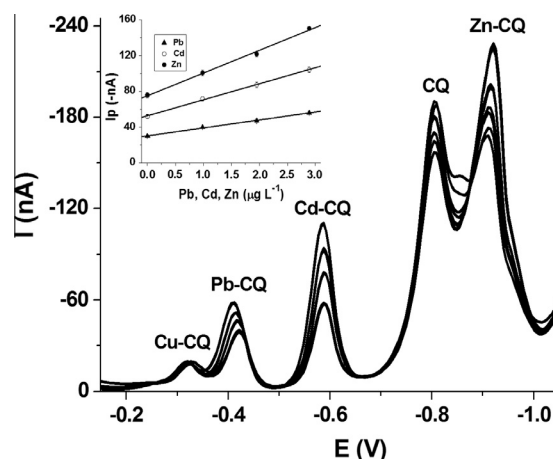


Fig. 6. DPV of certified reference water (TMDA-61.2) and standard addition curve. Conditions: pH 5.3; C_{CQ} : $3.6 \mu\text{mol L}^{-1}$; E_{ads} : -0.65 V ; t_{ads} : 60 s. Other conditions as in Fig. 1.

Table 1

Determination of lead, cadmium and zinc in tap water, sea water and mineral water (three samples).

Sample	Mass of added			Achieved		
	Pb	Cd	Zn ($\mu\text{g L}^{-1}$)	Pb	Cd	Zn ($\mu\text{g L}^{-1}$)
Tap water	0	0	0	1.2 ± 0.3	–	16.3 ± 0.3
	5.0	5.0	5.0	6.1 ± 0.2	4.9 ± 0.2	21.8 ± 0.3
Sea water	0	0	0	1.5 ± 0.2	–	26.3 ± 0.3
	5.0	5.0	5.0	6.3 ± 0.2	5.1 ± 0.3	31.9 ± 0.3
Puyehue	0	0	0	0.4 ± 0.1	–	2.9 ± 0.3
	5.0	5.0	5.0	5.5 ± 0.3	4.8 ± 0.2	7.7 ± 0.3
Chanqueahue	0	0	0	0.4 ± 0.1	–	1.4 ± 0.2
	5.0	5.0	5.0	5.6 ± 0.2	4.8 ± 0.2	6.6 ± 0.2
Liv	0	0	0	0.2 ± 0.1	–	1.0 ± 0.2
	5.0	5.0	5.0	5.0 ± 0.1	5.3 ± 0.2	6.2 ± 0.2

water (Puyehue, Liv, Chanqueahue). Dissolved organic matter present in seawater could interfere with the determination of trace metals by AdSV due to competition with the added ligand for the metal, this effect was eliminated by ultraviolet irradiation [19]. For quantization of cadmium and lead in water samples, a volume of 9.0 mL was analyzed, while for zinc determination an inferior volume was necessary. Three replicate analyses were performed for each sample. Cd(II) was not detected in any of these samples. Fortunately in our country this ion is present in very low concentrations. To check the reliability of the method the samples were analyzed by ICP-AES, but the results obtained with this technique for cadmium were below $5.0 \mu\text{g L}^{-1}$. The results are given in Table 1.

4. Conclusions

An alternative method is developed using Clouquinol for the determination of trace amounts of lead, cadmium and zinc in one run by adsorptive stripping voltammetry. In the analyzed water samples the concentration of cadmium is too low. The sensitivity can be increased by choosing only the optimum experimental conditions for this element, such as higher CQ concentration and longer t_{ads} . The proposed method is more sensitive than atomic absorption spectrometry and inductively coupled plasma with emission spectrometry. The resolution between the signals of the complexes was optimum.

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