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ORIGINAL PAPER

Simultaneous determination of trace aluminum (III), copper (II) and cadmium (II) in water samples by square-wave adsorptive cathodic stripping voltammetry in the presence of oxine

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Abstract A validated adsorptive cathodic stripping voltammetry method is described for simultaneous determination of Al(III), Cu(II) and Cd(II) in water samples. In acetate buffer (pH 5) containing 10 μM oxine, these metal ions were determined as oxine complexes following adsorptive accumulation onto the HMDE at −0.05 V versus Ag/AgCl/KCl$_s$. The best signal to noise ratio was obtained using a square wave of scan increment 10 mV, frequency 120 Hz, and pulse-amplitude 25 mV. Limits of detection as low as 0.020 μg L^{-1} Al(III), 0.012 μg L^{-1} Cu(II) and 0.028 μg L^{-1} Cd(II) were achieved. Interference due to various cations (K(I), Na(I), Mg(II), Ca(II), Mn(II), Fe(III), Bi(III), Sb(III), Se(IV), Pb(II), Zn(II), Ni(II), Co(II)), anions (Cl^{-}, NO^{3-}, SO$_4{}^{2-}$, PO$_4{}^{3-}$) and ascorbic acid was minimal as the measured signals change by 4% at the maximum. The stripping voltammetry method was successfully applied for simultaneous determination of Al(III), Cu(II) and Cd(II) in tap and natural bottled water samples.

Keywords Aluminum · Copper · Cadmium · Oxine · Determination · Square-wave adsorptive stripping voltammetry

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1 Introduction

Trace elemental analysis has become an area of particular concern and high priority in environmental research and protection. Aluminum is an element of considerable biological, environmental and industrial significance and to which humans are frequently exposed, as it is widely found in the air, water of low pH values, plants and consequently in food. Interest in aluminum has considerably increased as a result of knowledge of its potential toxic effects, particularly in patients with chronic renal failure [1]. Aluminum has also been implicated in a number of human pathologies including encephalopathy/dialysis dementia, Parkinson's disease and Alzheimer's disease [2]. Excess deposits of aluminum in the skeleton may result in a syndrome commonly referred to as "Al-induced bone disease" [3, 4].

Copper is a widely distributed element and is essential in the nutrition of plants and animals. Chronic deficiency of copper causes anemia of a microcytic type [5]. Although copper is not considered to be a cumulative systemic poison, excess of copper may cause symptoms of gastroenteritis with nausea, hypercupremia, vomiting, myalgia and hemolysis.

Cadmium is known to be a hazardous environmental pollutant with toxic effects for living organisms in aquatic ecosystems [6]. Adverse effects of cadmium are produced not only because of its high toxicity in humans and animals, even at trace concentrations, but also due to bioaccumulation processes in almost all organs. The main target organs affected by cadmium are lungs, kidney, bones and teeth.

Flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma-optical emission spectrometry (ICPOES) are the widely used analytical techniques for detection of aluminum [7–16], copper [17–22] and cadmium [17, 23–28]. 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 [29]. The utility of direct voltammetric approaches for determination of aluminum is limited by the very negative reduction potential of the Al(III) which is very close to the reduction potential of hydrogen, potassium, sodium and barium [30]. In order to shift the reduction potential of Al(III) to more positive potentials (less negative potentials), its complexation with some ligands has been employed prior to the analysis. These include 1,2-dihydroxy-anthraquinone-3-sulphonic acid [30, 31], solochrome violet [32–35], cupferron [36, 37], alizarin S [38], morin [39], pyrogallol red [40] and norepinephrine [41]. Anodic stripping voltammetric determination of copper is not very sensitive due to the closeness of its anodic peak potential to that of mercury oxidation and the broadness of its anodic peak [42, 43]. However, cathodic stripping voltammetry was successfully used for determination of copper complexed with different ligands [44–56]. In addition, anodic and adsorptive cathodic stripping voltammetric methods have been reported for determination of cadmium [43–45, 50, 56–65].

Oxine (8-hydroxyquinoline) is a ligand capable of forming complexes with several metal ions. It was used as a complexing agent for determination of Cd(II) by ICPOES [66] and AdSV [67, 68], Cu(II) by AdSV [56, 69], Al(III) by HPLC [70], FAAS and ICPOES [71] and spectrofluorimetry [72], Mo(VI) by AdSV [69, 73, 74] and Sn(II) by AdSV [75]. However, no adsorptive cathodic stripping voltammetry method is reported in literature yet for determination of Al(III) as oxine-complex at the HMDE. Moreover, there is no any analytical method reported in literature yet for the simultaneous determination of Al(III), Cu(II) and Cd(II).

In this work a sensitive square-wave adsorptive cathodic stripping voltammetry method was described for simultaneous determination of Al(III), Cu(II) and Cd(II) in water samples as metal–oxine complexes.

2 Experimental

2.1 Apparatus

A computerized Electrochemical Trace Analyzer Model 394-PAR (Princeton Applied Research, Oak Ridge, TN, USA) controlled via 270/250 PAR software was used for the voltammetric measurements. The electrode assembly (Model 303A-PAR) incorporating a micro-electrolysis cell, a three electrode system comprising of a hanging mercury drop electrode as a working electrode (area: 0.026 cm^2), an Ag/AgCl/KCl$_s$ reference electrode and a platinum wire counter electrode, was used. Stirring of the solution was performed using a magnetic stirrer (305-PAR) to provide convective transport during the preconcentration step. The measurements were automated and controlled through the programming capacity of the apparatus.

A Shimadzu Flame Atomic Absorption Spectrometer (FAAS) Model AA-670 interfaced with a data processor was used for determination of the metal ions in various water samples.

A Mettler balance (Toledo-AB104, Greifensee, Switzerland) was used for weighing the solid materials. A pH-meter (Crison, Barcelona, Spain) was used for measuring the pH of solutions. A micopipetter (Eppendorf-Multipette® plus) was used for transferring the analyte solutions.

2.2 Reagents and solutions

Britton-Robinson (B-R) universal buffer (pH 2–11), acetate buffer (pH 4.5–5.5), and phosphate buffer (pH 2–7.5) were prepared in de-ionized water and were used as supporting electrolytes. A 1×10^{-3} M 8-Hydroxyquinoline (Oxine) solution was prepared by dissolving an appropriate amount of the compound (Merck) in spec-pure methanol. Desired standard solutions of Al(III), Cu(II), Cd(II), Pb(II), Sb(III), Bi(III), Se(IV), Zn(II), Mn(II), Ni(II), Co(II) and Fe(III) were prepared by accurate dilution of their standard stock solutions (1,000 mg L^{-1} dissolved in aqueous 0.1 M HCl, supplied from Cica, Japan) by de-ionized water. Standard solutions of Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} (Each of 100 mg L^{-1}) were prepared by dissolving appropriate amounts of KCl, KNO_3, Na_2SO_4 and Na_3PO_4 in de-ionized water, respectively. Solutions of 1,000 mg L^{-1} ascorbic acid and 1% Triton X-100 were prepared in de-ionized water. All chemicals used were of analytical grade and were used without further purification.

The de-ionized water was supplied from a Purite-Still Plus Deionizer connected to a Hamilton-Aqua Matic bidistillation water system (Hamilton Laboratory Glass LTD, Kent, UK). The water samples subjected to analysis by means of the described square-wave adsorptive cathodic stripping voltammetry method were bottled natural water with Trademarks: Siwa®, Baraka®, Aquafina® and Hayate®, obtained from the local market.

2.3 Recommended analytical method

Five mL of the water sample containing the examined metal ions, 5 mL of the acetate buffer (pH 5) and 10 μM oxine were introduced into the micro-electrolysis cell. After de-oxygenation with pure nitrogen for 8 min, a selected accumulation potential was then applied to the

HMDE for a selected accumulation time, while the solution was stirred at 400 rpm. At the end of the accumulation time, the stirring was stopped and a 10 s rest period was allowed for the solution to become quiescent. The voltammogram was then recorded by scanning the potential in the negative direction using the square-wave potential waveform. All measurements were carried out at room temperature. Recoveries of Al(III), Cu(II) and Cd(II) in the analyzed water samples were estimated using the calibration curve and standard addition methods.

3 Results and discussion

3.1 Electrochemical behavior of various metal ions in presence of oxine

Figure 1 displays square-wave adsorptive cathodic stripping (SW-AdCS) voltammogram of free oxine in acetate buffer of pH 5 and those of various metal ions in the absence and the presence of oxine. Free oxine was found electroactive at the HMDE and its SW-AdCS voltammogram in buffered solutions of various pH values exhibited a single cathodic peak (Fig. 1, curve a) corresponding to reduction of the N=C double bond of the pyridine ring [76, 77]. SW-AdCS voltammogram of 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II), Sb(III), Bi(III), Se(IV), Zn(II), Mn(II), Ni(II), Co(II), Fe(III) and Al(III) in acetate buffer (pH 5) in the absence of oxine exhibited no voltammetric peak over the studied potential range (Fig. 1, curve b). This behavior may be attributed to the low concentration level of these ions, the non-optimized pH value of the medium and/or the close reduction potential of some of these metal ions to that of the hydrogen evolution (e.g. in case of Al(III)). When 10 μM oxine were added to the solution of various metal ions, only four ill-defined cathodic peaks were obtained (Fig. 1, curve c). However, following preconcentration onto the HMDE by adsorptive accumulation for 30 s the voltammogram exhibited four well resolved and much enhanced cathodic peaks ($E_p = -0.20$, -0.49, -0.78 and -1.34 V, Fig. 1, curve d). The first three cathodic peaks (first, second and third peaks) were attributed, respectively, to reduction of the adsorbed Al(III), Cu(II) [56, 69] and Cd(II) [67, 68] oxine-complexes, while the fourth cathodic peak was attributed to reduction of the N=C double bond of the pyridine ring of the rest of the free oxine enhanced by adsorption onto the HMDE. The earlier appearance of a cathodic peak of Al–oxine complex at a less negative potential ($E_p = -0.20$ V versus Ag/AgCl/KCl_s) may be due to formation of the cationic complex species $Al(Ox)^{++}$ and/or $Al(Ox)_2^+$ [78], which are much more easily reduced at the HMDE than the neutral $Cu(Ox)_2$ and $Cd(Ox)_2$ complex species. Cathodic peaks for the rest of the ions present in the solution were absent because of their non-complexing character with oxine under the experimental conditions. The peak current (i_p) of each of Al(III), Cu(II) and Cd(II) as oxine-complex increased with increase in preconcentration time (Fig. 1, curve d) confirming the interfacial adsorption of Al(III), Cu(II) and Cd(II)–oxine complexes onto the HMDE which is a behavior essential for the adsorptive stripping voltammetry determination of these metal ions as metal–oxine complexes.

The general formation reaction of the metal (M^{n+})–oxine (HOx) complexes (Eq. 1), their preconcentration by adsorptive accumulation onto the HMDE at −0.05 V (Eq. 2) and then their cathodic stripping reaction at the HMDE (Eq. 3) can be expressed as:

$$M^{n+} + yHOx \Leftrightarrow M(Ox)_y + yH^+ \quad (1)$$

$$M(Ox)_y \Leftrightarrow M(Ox)_{y(ad)} \quad (2)$$

$$M(Ox)_{y(ad)} + ne^- + yH^+ \Leftrightarrow M(Hg) + yHOx \quad (3)$$

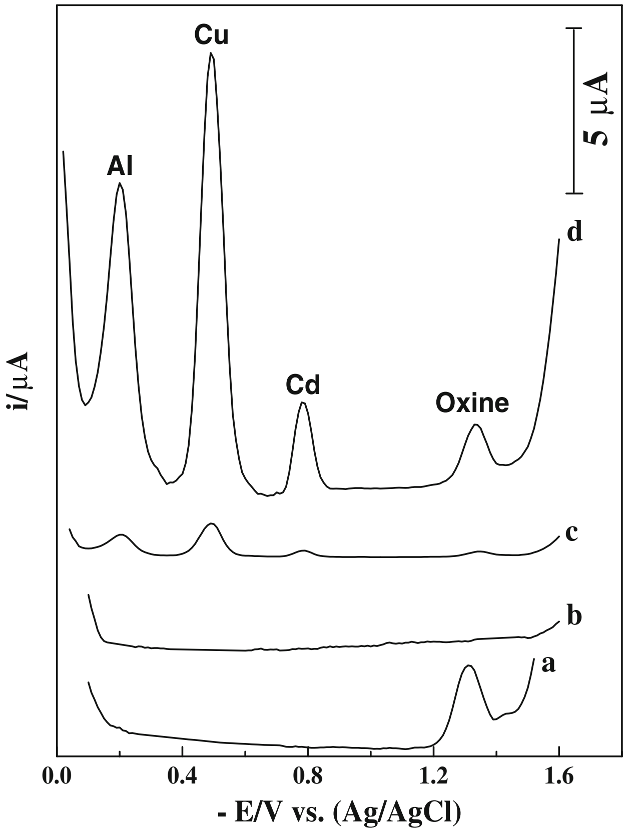

Fig. 1 SW-AdCS voltammograms at the HMDE in acetate buffer of pH 5 for: (a) 10 μM oxine, (b) 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II), Sb(III), Bi(III), Se(IV), Zn(II), Mn(II), Ni(II), Co(II), Fe(III) and Al(III) solution in the absence of oxine, $t_{acc} = 0$ s, (c) the same solution of (b) in the presence of 10 μM oxine, $t_{acc} = 0$ s and (d) the same solution of (c) following preconcentration at −0.05 V by adsorptive accumulation for 30 s; frequency $f = 120$ Hz, scan increment $\Delta E_i = 10$ mV and pulse-amplitude $a = 25$ mV

SW-AdCS voltammetry peak potentials of Al(III), Cu(II) and Cd(II)–oxine complexes shifted linearly to more negative values upon increase in pH of the medium. This behavior is in accordance with the cathodic stripping reaction (Eq. 3) where reduction of the adsorbed metal–oxine complexes seems to be much difficult upon pH increase. Stoichiometries of 1:2 Cu(II)–oxine ($Cu(Ox)_2$) and Cd(II)–oxine ($Cd(Ox)_2$) complexes with stability constants of 1.60×10^{26} [79] and 1.26×10^{17} [67, 79], respectively, have been reported. On the other hand, 1:1 or 1:2 Al(III)–oxine cationic complexes ($Al(Ox)^{++}$ or $Al(Ox)_2{}^{+}$) were most probable in slightly acidic to slightly alkaline media [78], while the 1:3 water insoluble complex form ($Al(Ox)_3$) was formed in alkaline medium [78].

The electrode surface coverage Γ^o (adsorption density) of each of Al(III), Cu(II) and Cd(II)–oxine complexes onto the HMDE was estimated using the expression: $\Gamma^o = Q/nFA$, where (Q) is the amount of charge (μC) consumed in the surface process estimated from the integration of the cyclic voltammetry peak area of each analyte [80], n is the total number of electrons consumed in the reduction process, A is the surface area of the mercury electrode (0.026 cm^2). The estimated electrode surface coverage of Al(III), Cu(II) and Cd(II)–oxine complexes were found to be 6.106×10^{-10}, 6.458×10^{-10} and 4.937×10^{-10} mol cm^{-2}, respectively. Thus, the area occupied by each adsorbed molecule of Al(III), Cu(II) or Cd(II)–oxine complex was found to be 0.272, 0.257 or 0.336 nm^2, respectively.

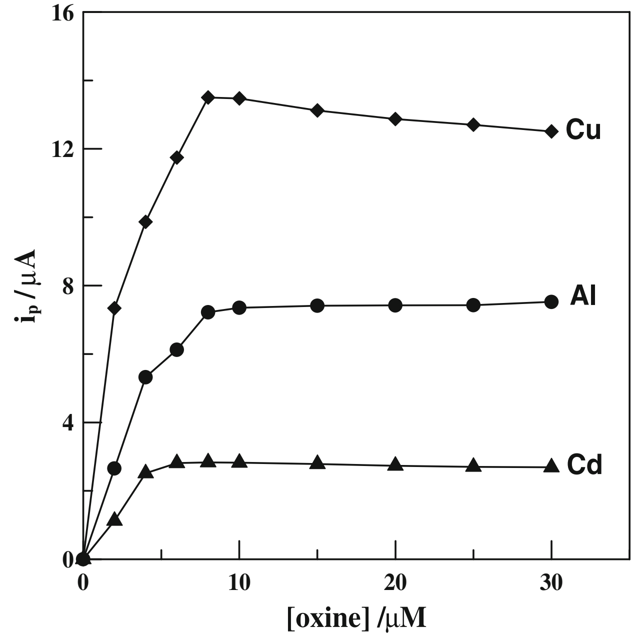

Fig. 2 SW-AdCS voltammetric peak current (i_p) as a function of oxine concentration for a solution containing 0.1 mg L^{-1} of each of Al(III), Cu(II) and Cd(II). Other conditions are as those given in Fig. 1

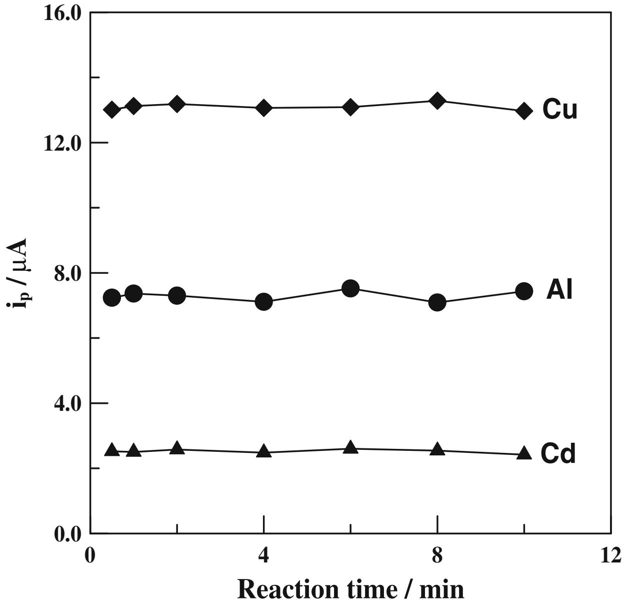

Fig. 3 SW-AdCS voltammetric peak current (i_p) as a function of reaction time for a solution containing 0.1 mg L^{-1} of each of Al(III), Cu(II) and Cd(II) in the presence of 10 μM oxine. Other conditions are as those given in Fig. 1

3.2 Simultaneous determination of Al, Cu and Cd

Based on the foregoing results of the metal–oxine system at the HMDE, a square-wave adsorptive cathodic stripping

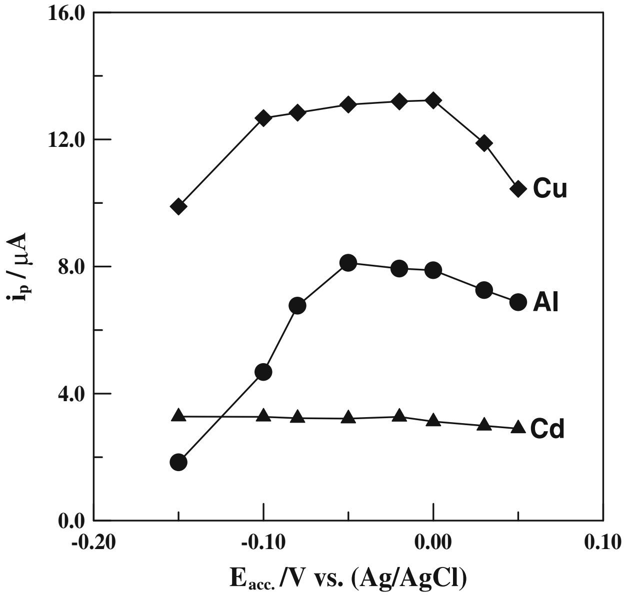

Fig. 4 SW-AdCS voltammetric peak current (i_p) as a function of preconcentration potential (E_{acc}) for a solution containing 0.1 mg L^{-1} of each of Al(III), Cu(II) and Cd(II) in presence of 10 μM oxine. Other conditions are as those given in Fig. 1

(SW-AdCS) voltammetry method was optimized for simultaneous trace determination of Al(III), Cu(II) and Cd(II) as adsorbed oxine complexes onto the HMDE. Effects of various variables were examined and the optimum procedural conditions were identified.

3.2.1 Effect of varying concentration of oxine

SW-AdCS voltammograms of 0.1 mg L^{-1} of each of Al(III), Cu(II) and Cd(II) in the presence of increased amount of oxine (0–30 μM) were recorded in aqueous acetate buffer of pH 5 following preconcentration of these metal ions as metal–oxine complexes onto the HMDE at −0.05 V by adsorptive accumulation for 30 s. The voltammograms showed that the peak current (i_p) of the examined metal–oxine complexes increased with concentration of oxine up to ∼10 μM (Fig. 2). Kinetics of reactions of Al(III), Cu(II) and Cd(II) with oxine were identified from their voltammograms recorded after different mixing time of reactants. The peak currents (i_p) of the examined complexes were practically constant with the reaction time (Fig. 3), indicating the immediate formation of metal–oxine complexes within the mixing time of reactants in the electrochemical cell; therefore, heating of the reactants solution was not required in the present work.

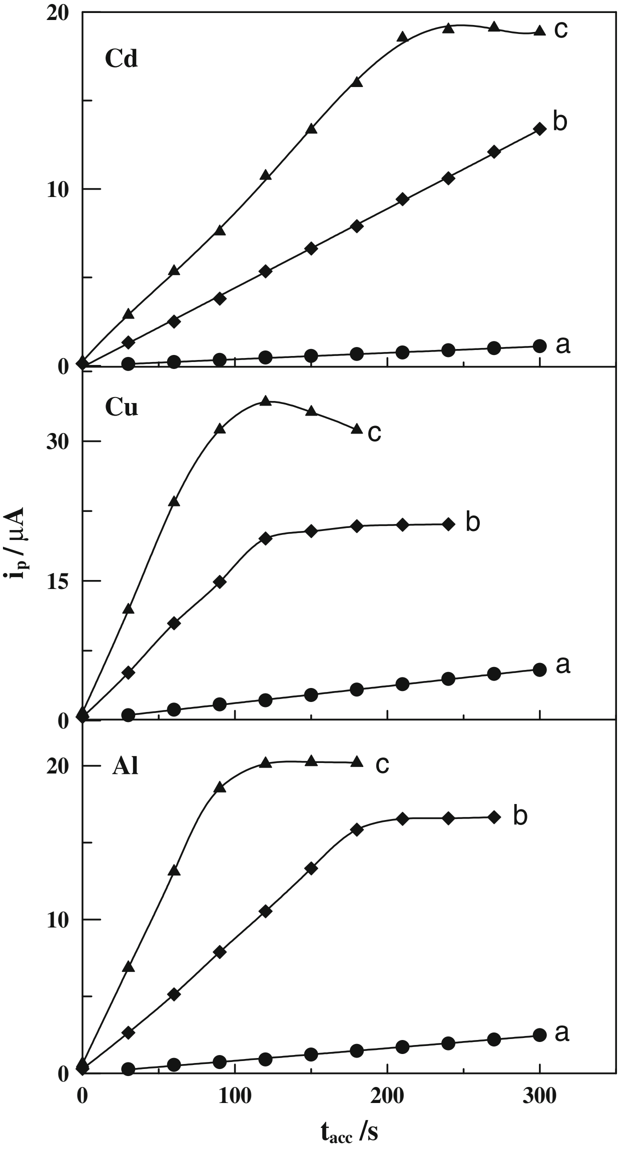

Fig. 5 SW-AdCS voltammetric peak current (i_p) as a function of the preconcentration time (t_{acc}) for a solution containing; (a) 0.01, (b) 0.05 and (c) 0.1 mg L^{-1} of each of Al(III), Cu(II) or Cd(II) in the presence of 10 μM oxine. Other conditions are as those given in Fig. 1

3.2.2 Effect of supporting electrolyte and pH

SW-AdCS voltammograms of 0.1 mg L^{-1} of each of Al(III), Cu(II) and Cd(II) in the presence of 10 μM oxine were recorded in various supporting electrolytes namely: Britton-Robinson universal buffer (pH 2–11), acetate buffer (pH 3.8–6.2) and phosphate buffer (pH 2–7.5) following preconcentration of the metal–oxine complexes onto the HMDE by adsorptive accumulation at −0.05 V (versus Ag/AgCl/KCl_s) for 30 s. Three peaks of enhanced peak currents were obtained over the pH range 5–7. However, sharper peaks and much enhanced peak currents

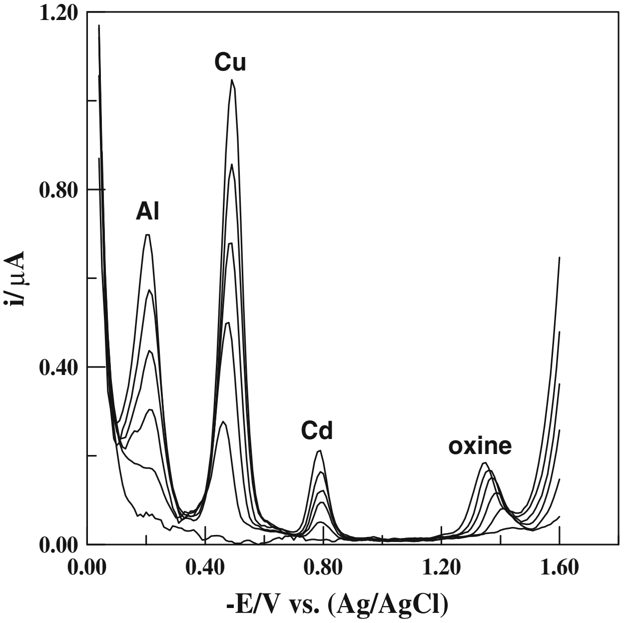

Fig. 6 SW-AdCS voltammograms for successive additions of Al(III), Cu(II) and Cd(II) solutions, recorded in acetate buffer of pH 5 containing 10 μM oxine following preconcentration at −0.05 V onto the HMDE by adsorptive accumulation for 300 s. Each addition affected a 1 μg L^{-1} of each metal ion. Dotted line represents the blank solution. Other conditions are as those given in Fig. 1

were achieved when using the acetate buffer of pH 5 as a supporting electrolyte, therefore, it was chosen in the rest of the present analytical study. This agrees well with the previously reported study [78] in which moderately acidic media (pH 4–5) were found to be the most preferable for the formation of metal–oxine complexes.

3.2.3 Square-wave pulse parameters

In order to obtain well developed and separated voltammetric peaks for 0.1 mg L^{-1} of each of Al(III), Cu(II) and Cd(II) in the presence of 10 µM oxine in acetate buffer of pH 5, following preconcentration onto the HMDE at 0.0 V by adsorptive accumulation for 30 s, the square-wave pulse parameters were optimized by varying the frequency f (20–120 Hz), scan increment ΔE_i (2–10 mV) and pulse-amplitude a (20–60 mV). Although the peak current (i_p) increases linearly with increase in frequency, scan increment or pulse-amplitude, the best signal to noise ratio was obtained on using a square wave of scan increment 10 mV, frequency of 120 Hz, and pulse-amplitude of 25 mV.

3.2.4 Preconcentration (accumulation) conditions

Effect of varying the preconcentration (accumulation) potential E_{acc} (+0.05 to −0.15 V versus Ag/AgCl/KCl_s) on the peak current of the SW-AdCS voltammograms for 0.1 mg L^{-1} of each of Al(III), Cu(II) and Cd(II) in acetate buffer solution of pH 5 in the presence of 10 µM oxine was evaluated, following preconcentration onto the HMDE for 30 s (Fig. 4). The results showed that much enhanced peak currents for the investigated metal–oxine complexes were achieved at −0.05 V. However, a significant decrease in the peak height of Al–oxine complex occurred at preconcentration potentials more negative than −0.05 V. Therefore, preconcentration potential of −0.05 V was used throughout the present study.

On the other hand, SW-AdCS voltammograms of solutions of 0.01, 0.05 and 0.10 mg L^{-1} of each of Al(III), Cu(II) or Cd(II) in the presence of 10 µM oxine were recorded under the optimum conditions following increased preconcentration time (30–300 s) by adsorptive accumulation at −0.05 V. As shown in Fig. 5, the peak current of each of 0.01 mg L^{-1} Al(III), 0.01 mg L^{-1}

Table 1 Characteristics of the calibration curves of the described SW-AdCS voltammetric method for simultaneous determination of Al(III), Cu(II) and Cd(II) as oxine complexes; $E_{acc} = -0.05$ V and $t_{acc} = 300$ s

Metal ion	Linearity range (µg L^{-1})	Least square equation[a]		(r)	LOD (µg L^{-1})	LOQ (µg L^{-1})
		Intercept (µA)	Slope (µA/µg L^{-1})			
Al(III)	0.08–25	0.107	0.136	0.995	0.020	0.067
Cu(II)	0.05–10	0.135	0.211	0.996	0.012	0.040
Cd(II)	0.12–40	0.158	0.044	0.999	0.028	0.093

[a] Average of three determinations

Table 2 Accuracy and precision of the described SW-AdCS voltammetry method as recovery (%R) and standard deviation (%SD) for simultaneous determination of various concentrations of Al(III), Cu(II) and Cd(II) as oxine complexes

Metal ions	[Taken] (µg L^{-1})	SW-AdCS voltammetry method (%R ± SD)		FAAS method (%R ± SD) A	F-statistic	t-test
		A	B			
Al(III)	10.0	100.74 ± 0.44	99.18 ± 0.83	99.86 ± 1.03	5.48	1.76
	1.00	98.13 ± 1.64	97.94 ± 1.88	*	–	–
	0.10	96.89 ± 2.77	96.23 ± 3.01	*	–	–
Cu(II)	10.0	100.73 ± 0.61	99.75 ± 0.27	101.23 ± 0.83	1.85	1.09
	1.00	100.06 ± 0.79	98.61 ± 1.63	*	–	–
	0.1	98.33 ± 2.02	96.75 ± 3.07	*	–	–
Cd(II)	10.0	100.50 ± 0.82	99.36 ± 1.11	99.27 ± 1.73	4.45	1.44
	1.00	98.12 ± 1.03	98.53 ± 2.54	*	–	–
	0.10	95.73 ± 3.79	96.07 ± 4.10	*	–	–

A: using the calibration curve method and B: using the standard addition method

Theoretical F-statistic = 6.39 and t-test = 2.3 at 95% confidence limit for $n_1 = n_2 = 5$

* Under limit of detection

Cu(II) and 0.01–0.05 mg L^{-1} Cd(II)–oxine complexes increases linearly with preconcentration 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. Accordingly, the preconcentration time should be chosen according to the concentration level of the metal ions in the investigated solution.

3.3 Method validation

3.3.1 Linearity

SW-AdCS voltammograms of various concentrations of the metal ions were recorded under the optimum procedural conditions (Fig. 6). Rectilinear relations between peak current (i_p) and concentrations (C) of each of Al(III), Cu(II) and Cd(II) were obtained over the ranges indicated in Table 1. The results shown in Table 1 confirmed the reliability of the described SW-AdCS voltammetry method for determination of Al(III), Cu(II) and Cd(II) within the indicated linear ranges.

Table 3 Interferences of some inorganic species and ascorbic acid in the simultaneous determination of 0.01 mg L^{-1} of each of Al(III), Cu(II) and Cd(II) as oxine-complexes by the described SW-AdCS voltammetry method

Foreign ions	Concentration (mg L^{-1})	Relative error[a] (%)		
		Al(III)	Cu(II)	Cd(II)
K^+	100	+2.6	+1.9	+0.9
Na^+	100	+0.7	+0.2	−0.1
Mg^{2+}	100	−1.7	−1.4	−0.5
Ca^{2+}	100	−0.5	−0.7	−0.2
Mn^{2+}	5	−0.3	−0.4	−0.1
Fe^{3+}	5	−1.5	−0.9	−0.6
Bi^{3+}	0.10	−0.1	−0.2	+0.1
Sb^{3+}	0.10	+0.3	+0.7	+1.1
Se^{4+}	0.10	−0.2	−0.6	−0.1
Pb^{2+}	0.10	−1.1	−1.5	−0.8
Zn^{2+}	0.10	−2.8	−3.6	−2.2
Ni^{2+}	0.10	+0.9	+0.4	+0.4
Co^{2+}	0.10	+1.7	+0.6	+1.8
Cl^-	100	+2.7	+1.9	+2.1
NO^{3-}	100	+1.5	+3.4	+1.1
SO_4^{2-}	100	−1.2	−1.1	−0.4
PO_4^{3-}	100	−1.5	−1.2	−1.2
Ascorbic acid	3	−2.9	−3.8	−3.3

[a] Calculated using the calibration curve method

3.3.2 Limits of detection and quantitation

Limits of detection (LOD) and quantitation (LOQ) of Al(III), Cu(II) and Cd(II) as oxine complexes were estimated using the expression: k SD/b [81], where $k = 3$ for LOD and 10 for LOQ, SD is the standard deviation of intercept (or blank) and b is the slope of the calibration curve. The achieved LOD and LOQ (Table 1) following preconcentration of the investigated metal–oxine complexes onto HMDE for 300 s under the optimum procedural conditions confirmed the reliability of the described SW-AdCS voltammetry method for ultra-trace determination of the metal ions. Limits of detection of the investigated metal ions by the described SW-AdCS voltammetry method (Table 1) indicated its high sensitivity

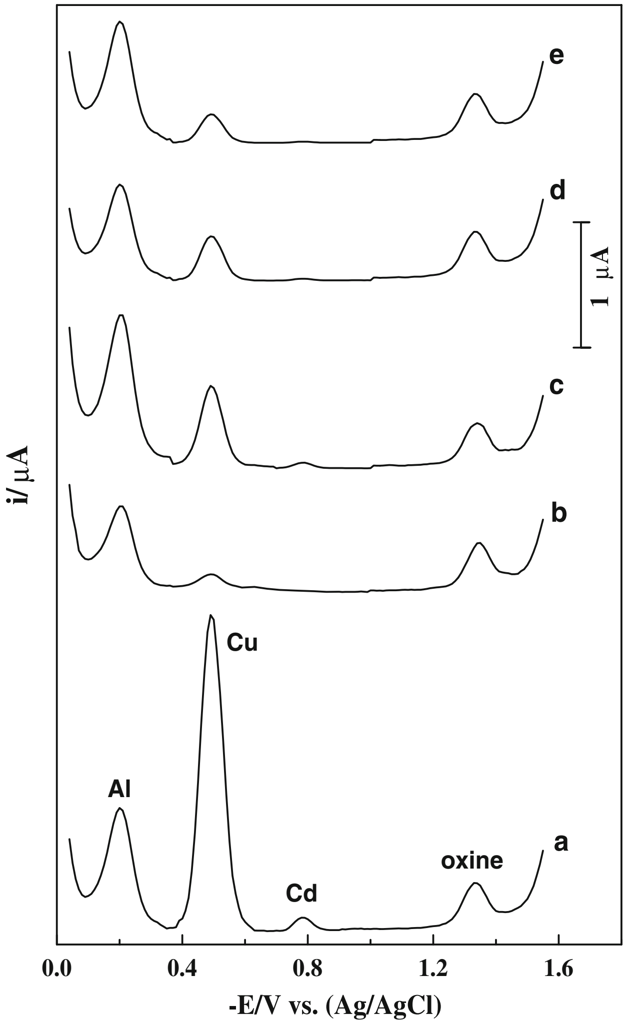

Fig. 7 SW-AdCS voltammograms of various water samples: (a) tap water, (b) Siwa®, (c) Baraka®, (d) Aquafina® and (e) Hayat® bottled natural water, recorded in acetate buffer of pH 5 containing 10 μM oxine, following preconcentration onto the HMDE at −0.05 V by adsorptive accumulation for 300 s; Other conditions are as those given in Fig. 1

Table 4 Simultaneous determination of Al(III), Cu(II) and Cd(II) in some tap and bottled natural water samples by the described SW-AdCS voltammetry method ($t_{acc} = 300$ s) and flame atomic absorption spectrometry (FAAS)

Sample	Al(III) (μg L^{-1})		Cu(II) (μg l^{-1})		Cd(II) (μg L^{-1})	
	AdCSV	FAAS	AdCSV	FAAS	AdCSV	FAAS
Tap water	13 ± 0.8	11 ± 1.3	24.3 ± 1.3	21 ± 2.5	0.5 ± 0.1	*
Bottled water						
Siwa®	10 ± 0.7	12 ± 1.5	0.9 ± 0.1	*	*	*
Baraka®	17 ± 1.1	20 ± 2.2	5.7 ± 0.4	7 ± 0.5	0.2 ± 0.03	*
Aquafina®	11 ± 0.7	7 ± 0.7	3.4 ± 0.2	2 ± 0.9	*	*
Hayat®	13 ± 0.7	10 ± 0.9	1.7 ± 0.1	*	*	*

* Under limit of detection

over most of the reported methods for determination of Al(III) (0.03–69 μg L^{-1}) [30–41], Cu(II) (0.016–4.2 μg L^{-1}) [51, 53, 54] and Cd(II) (0.067–1.4 μg L^{-1}) [65, 68].

3.3.3 Accuracy and precision

Accuracy and precision of the described SW-AdCS voltammetry method for simultaneous determination of Al(III), Cu(II) and Cd(II) as oxine-complexes were estimated as recovery (%R) and standard deviation (%SD) by analyzing their various reference standard solutions for three times (Table 2). Mean recoveries and standard deviations obtained by applying the calibration curve and standard addition methods (Table 2) indicated the accuracy and precision of the described SW-AdCS voltammetry method for simultaneous determination of Al(III), Cu(II) and Cd(II) as oxine-complexes. Moreover, the results obtained by the described stripping method, applying calibration curve method, were statistically compared with those obtained by the flame atomic absorption spectrometry method (FAAS). Since the calculated value of the *F*-statistic does not exceed the theoretical value (Table 2), there was no significant difference between the described SW-AdCS voltammetry and FAAS methods with respect to reproducibility [82]. Also, no significant differences were noticed between the two methods regarding accuracy and precision as revealed by *t*-values [82], Table 2.

3.3.4 Interferences

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. Results of the possible interferences of some inorganic species are summarized in Table 3. The cations, (K(I), Na(I), Mg(II), Ca(II) (up to 100 mg L^{-1}), Mn(II), Fe(III) (each 5 mg L^{-1}), Bi(III), Sb(III), Se(IV), Pb(II), Zn(II), Ni(II), Co(II) (each 0.10 mg l^{-1})), anions (Cl^{-}, NO^{3-}, SO_4^{2-}, PO_4^{3-} (up to 100 mg L^{-1})) and ascorbic acid up to 3 mg L^{-1}) change the signals of 0.01 mg L^{-1} Al(III), Cu(II) and Cd(II) by 4% at the maximum.

Interference from Triton X-100 (a non-ionic surfactant) was also evaluated. Insignificant interference was obtained in the presence of Triton X-100 up to 0.001%. High concentration levels of the surfactant caused a strong deformation and suppression of the voltammetric peaks, making their determination impossible. The influence of surfactants can be completely eliminated by a thorough mineralization of a water sample prior to the analysis. However the presence of surfactants in tap and bottled natural water is very rare.

3.4 Analysis of tap and bottled natural water

The described SW-AdCS voltammetry method was successfully applied for simultaneous determination of Al(III), Cu(II) and Cd(II) in tap and bottled natural water samples (Fig. 7). The same water samples were also analyzed for these metal ions by FAAS. Comparison of the results obtained by the described SW-AdCS voltammetry method with those obtained by FAAS (Table 4) revealed the capability of the stripping voltammetry method for simultaneous determination of Al(III), Cu(II) and Cd(II) at trace and ultra-trace concentrations.

4 Conclusion

A simple, fast, highly sensitive and specific square-wave adsorptive cathodic stripping voltammetry method was developed for simultaneous determination of Al(III), Cu(II) and Cd(II) as oxine-complexes in water samples without significant interference from foreign cations, anions and organics. The method was successfully applied for simultaneous determination of Al(III), Cu(II) and Cd(II) in tap water and bottled natural water samples. The limits of detection using the described SW-AdCS voltammetry method (0.020 μg L^{-1} Al(III), 0.012 μg L^{-1} Cu(II) and 0.028 μg L^{-1} Cd(II)) indicate its high sensitivity compared with most previously reported methods for determination of Al(III) (0.03–69 μg L^{-1}) [30–41], Cu(II) (0.016–4.2 μg L^{-1}) [51, 53, 54] and Cd(II) (0.067–1.4 μg L^{-1}) [65, 68].

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