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Simultaneous determination of Mn(II), Cu(II) and Fe(III) as 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol complexes by adsorptive cathodic stripping voltammetry at a carbon paste electrode

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ABSTRACT

A simple and precise square-wave adsorptive cathodic stripping voltammetry (SW-AdCSV) method has been described for simultaneous determination of Mn(II), Cu(II) and Fe(III) in water samples using a carbon paste electrode. In 0.1 mol L^{-1} acetate buffer (pH 5) containing 50 μmol L^{-1} of 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), Mn(II), Cu(II) and Fe(III) were simultaneously determined as metal-complexes with 5-Br-PADAP following preconcentration onto the carbon paste electrode by adsorptive accumulation at +1.0 V (*vs.* Ag/AgCl/3 M KCl). Insignificant interference from various cations (K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Bi^{3+}, Sb^{3+}, Se^{4+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, V^{5+}, Ti^{4+} and $NH_4{}^+$), anions ($HCO_3{}^-$, Cl^-, NO^{3-}, $SO_4{}^{2-}$ and $PO_4{}^{3-}$) and ascorbic acid was noticed. Limits of detection of 0.066, 0.108 and 0.093 μg L^{-1} and limits of quantitation of 0.22, 0.36 and 0.31 μg L^{-1} Mn(II), Cu(II) and Fe(III), respectively, were achieved by the described method. The described stripping voltammetry method was successfully applied for simultaneous determination of Mn(II), Cu(II) and Fe(III) in ground, tap and bottled natural water samples.

1. Introduction

Simultaneous determination of various metal ions at trace and ultra trace concentrations in real matrices is one of the main aims of new selective, high sensitive and environmentally safe analytical methods. Manganese is an essential element, which plays an important role in activation of many enzymes involved in metabolic processes of man, animals and plants [1–3]. Manganese is involved in many physiological processes particularly in metabolism of proteins, carbohydrates, lipids and in the production of steroids sexual hormones. It is the cofactor of enzymes such as RNA synthetase, glutamine synthetase and pyruvate decarboxylase [4]. Acute exposure to manganese containing dust may lead to chemical pneumonitis while chronic exposure may lead to a Parkinson-like dementia [5].

Copper is essential in the nutrition of plants and animals. Chronic deficiency of copper causes anemia of a microcytic type [6]. 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 [6]. On the other side, iron is an essential constituent of the human body, necessary for haemoglobin formation and the oxidative processes of living tissues. Most of iron present in human body as haemoglobin and the remainder exist in storage forms, such as ferritin or haemosiderin, in the reticuloendothelial system or as myoglobin with smaller amounts occurring in haem-containing enzymes or in plasma bound to transferrin [7].

Flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma-optical emission spectrometry (ICPOES) are the widely used analytical techniques for determination of manganese [8–12], copper [8,9,13–17] and iron [8,18–21]. However, most of these methods are relatively expensive and not accurately reliable for the determination of ultra trace concentrations of metal ions. Moreover, these methods suffer from serious matrix interferences.

Electrochemical methods including stripping voltammetry, particularly anodic and cathodic stripping voltammetry methods have shown numerous advantages including speed of analysis, good selectivity, sensitivity and inexpensive for determination of various metal ions [22]. However, anodic stripping voltammetric determination of Mn(II) at the hanging mercury drop electrode (HMDE) suffers from the low solubility of manganese in mercury, the closeness of its reduction potential to that of hydrogen ion (−1.7 V *vs.* SCE) and the formation of intermetallic compounds at the mercury electrode [23]. Anodic stripping voltammetric determination of copper ions is not sensitive enough due to the closeness of its anodic peak potential to that of mercury oxidation, besides the broadness of its anodic peak [24,25]. On the other side, the reduction poten-

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tial of iron(III) ions to metal (≈−1.5 V *vs.* SCE) is un-exploitable for polarographic or voltammetric measurements, since its signal in acidic solutions overlaps with that of hydrogen reduction, besides it hydrolyzes in weakly acidic to alkaline media. Moreover, its determination using stripping voltammetry via Fe^0 is limited by the low solubility of iron in mercury [26].

Selectivity of determination of metal ions by adsorptive stripping voltammetry was improved by their complexation or chelation with specific ligands [22]. Cathodic stripping voltammetry technique was successfully used for the determination of manganese [27–30], copper [31–36] and iron [37–40] as metal-complexes with different ligands at mercury, glassy carbon, carbon paste, carbon film and bismuth film electrodes.

2-(5′-Bromo-2′-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) is a ligand capable of forming complexes with several metal ions. It was successfully used as a complexing agent for cathodic stripping voltammetric determination of Mn(II) [30], Cu(II) [31], Fe(III) [38], V(V) [41,42], Bi(III) [43], Cr(III) [44], Co(II) [45] and Ti(IV) [46] at the mercury electrodes. However, 5-Br-PADAP ligand has never been used before as a complexing agent for voltammetric determination of metal ions using the carbon paste electrode (CPE). The achieved limits of detections of Mn(II), Cu(II) and Fe(III) as metal-complexes by the reported electrochemical methods using some solid and the mercury electrodes [27–40] were: 0.20–5.5 $\mu g\,L^{-1}$ Mn(II), 0.20–1.0 $\mu g\,L^{-1}$ Cu(II) and 0.10–0.56 $\mu g\,L^{-1}$ Fe(III). Nowadays, applications of analytical methods using the mercury electrodes are avoided in many countries due to the toxicity of mercury and its impact on the environment.

This work aimed to describe a simple and precise square-wave adsorptive cathodic stripping voltammetric (SW-AdCSV) method for the simultaneous determination of Mn(II), Cu(II) and Fe(III) in water samples as 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol complexes using a carbon paste electrode.

2. Experimental

2.1. Reagents and solutions

Britton–Robinson (B–R) universal buffer (pH 2–11), acetate buffer (pH 4.0–6.0), and phosphate buffer (pH 2–7.5) were prepared in de-ionized water and were tested as supporting electrolytes. A solution of 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol (1×10^{-3} mol L^{-1}) was prepared by dissolving an appropriate amount of the compound (Sigma) in spec-pure methanol. Desired standard solutions of K(I), Na(I), Mg(II), Ca(II), Al(III), Cu(II), Cd(II), Pb(II), Sb(III), Bi(III), Se(IV), Zn(II), Mn(II), V(V), Ti(IV), Ni(II), Co(II) and Fe(III) were prepared by accurate dilution of their standard stock solutions (1000 mg L^{-1} dissolved in aqueous 0.1 mol L^{-1} HCl, supplied from Cica, Japan) by de-ionized water. Standard solutions of Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$ and $PO_4{}^{3-}$ (each of 1000 mg L^{-1}) were prepared by dissolving appropriate amounts of KCl, KNO_3, Na_2SO_4 and Na_3PO_4, respectively, in de-ionized water. 1000 mg L^{-1} ascorbic acid and 1% Triton X-100 solutions were prepared in de-ionized water. All chemicals used were of Analytical-grade reagents and were used without further purification.

The de-ionized water used throughout the present work was obtained from a Purite-Still Plus Deionizer connected to a Hamilton-Aqua Matic bi-distillation water system (Hamilton Laboratory Glass Ltd., Kent, UK).

2.2. Preparation of the carbon paste electrode

The carbon paste was prepared by thoroughly hand mixing 5 g of graphite powder (Aldrich, Milwaukee, WI, USA 1–2 μm) with 1.8 mL of Nujol oil (Sigma, d = 0.84 g/mL) in an agate mortar with pestle. The Nujol-carbon paste was packed into the well of the electrode and its surface was manually smoothed by polishing on clean paper. The carbon paste electrode (CPE) was then immersed in the supporting electrolyte placed in the electrolysis cell and several sweeps were applied until a low background current was achieved.

2.3. 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. A micro-voltammetric cell consisting of a C-2 stand (BASi Model MF-2063) with a carbon paste working electrode, an Ag/AgCl/3 M KCl reference electrode (BASi Model MF-2079) and a platinum wire counter electrode (BASi Model MW-4130) was used. The body of the carbon paste electrode was a Teflon rod with end cavity (3 mm diameter and 1 mm deep) at one end for paste filling (BASi Model MF-2010). Contact was made with a copper wire through the center of the Teflon rod. A magnetic stirrer (PAR-305) with a Teflon-coated magnet was used to provide the convective transport during the preconcentration step. The whole 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 examined 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 measurements of pH of the solutions. A micropipetter (Eppendorf – Multipette® plus) was used for transferring the solutions throughout the present experimental work.

2.4. Recommended analytical method

5 mL of the water sample containing the examined metal ions, 5 mL of the acetate buffer (pH 5) and 50 μmol L^{-1} of 5-Br-PADAP ligand were introduced into the micro-voltammetric cell. A selected preconcentration (accumulation) potential was then applied to the CPE for a selected time period, while the solution was stirred at 400 rpm. At the end of the preconcentration time, 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 towards the less positive direction using the square-wave potential-waveform. All the measurements were carried out at room temperature. Recoveries of Mn(II), Cu(II) and Fe(III) in the analyzed water samples were estimated using the calibration curve and standard addition methods.

3. Results and discussion

3.1. Voltammetric response of metal ions–5-Br-PADAP system

Square-wave voltammograms of a solution containing 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), Al(III), V(V) and Ti(IV) in the acetate buffer of pH 5 at the CPE exhibited no any voltammetric peak either without prior preconcentration (Fig. 1, curve a) or following preconcentration onto the CPE by adsorptive accumulation at +1.0 V for 60 s (Fig. 1, curve b). On the other side, square-wave cathodic voltammograms of 50 μmol L^{-1} 5-Br-PADAP free ligand in the acetate buffer of pH 5 showed no any voltammetric peak without prior preconcentration (curve c) or even following preconcentration onto the CPE by adsorptive accumulation at +1.0 V for 60 s (curve d). This means that the 5-Br-PADAP ligand

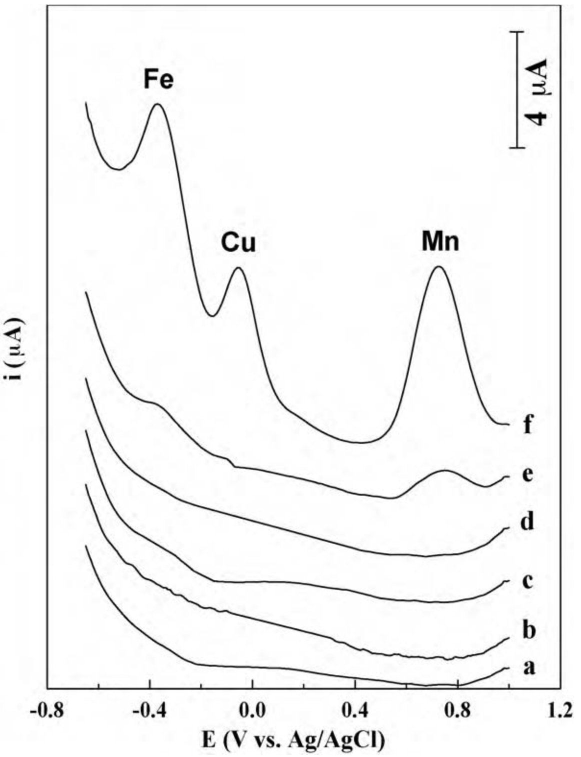

Fig. 1. SW voltammograms for a solution containing 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II), Sb(III), Bi(III), Se(IV), Zn(II), Mn(II), Ni(II), Co(II), Fe(III), Al(III), V(V) and Ti(IV) recorded without prior preconcentration (a) and following preconcentration onto the CPE (b); SW voltammograms for a solution of 50 μmol L^{-1} free 5-Br-PADAP recorded without prior preconcentration (c) and following preconcentration onto the CPE (d); and SW voltammograms for a solution containing 0.1 mg L^{-1} of each of all the examined metal ions in the presence of 50 μmol L^{-1} 5-Br-PADAP recorded without prior preconcentration (e) and following preconcentration onto the CPE by adsorptive accumulation at +1.0 V for 60 s (f). The supporting electrolyte was 0.1 mol L^{-1} acetate buffer (pH 5) and the instrumental conditions were: f = 100 Hz, ΔE_i = 10 mV and a = 20 mV.

is electro-inactive at the CPE under the experimental conditions. For a solution containing 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), Al(III), V(V) and Ti(IV) in addition to 50 μmol L^{-1} 5-Br-PADAP, the voltammogram exhibited only three ill-defined cathodic peaks (Fig. 1, curve e). However, following their preconcentration onto the CPE by adsorptive accumulation at +1.0 V for 60 s the voltammogram exhibited the same three cathodic peaks (Fig. 1, curve f) but in better resolved and enhanced forms (E_p = +0.73, −0.05 and −0.36 V *vs.* Ag/AgCl/3 M KCl). SW-AdCS voltammograms recorded for successive additions of a standard solution of each of all the preliminary examined metal ions to their solution in the electrochemical cell in the presence of 50 μmol L^{-1} 5-Br-PADAP ligand indicated that the enhanced cathodic peaks {1st (+0.73 V), 2nd (−0.05 V) and 3rd (−0.36 V)} are due to the reduction of the adsorbed Mn(II), Cu(II) and Fe(III)–5-Br-PADAP complexes, respectively (Fig. 1, curve f). No voltammetric peaks were appeared for the rest of metal ions present in the analyzed sample which may be at least due to their non-complexing character with 5-Br-PADAP ligand under the experimental conditions.

The SW-AdCS voltammetric peak current (i_p) of each of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes increased along with the increase of preconcentration time (Fig. 1, curves e and f), indicating the adsorptive nature of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes onto the CPE. Addition of small amount of 1% Triton X-100 to the solution of the examined metal ions in the electrochemical cell leads to strong suppression of the SW-AdCS voltammetric peak currents of the investigated metal-complexes, confirming again the adsorptive nature of the examined metal-complexes onto the CPE. As reported in the literature, the compositions of Mn(II), Cu(II) and Fe(III) complexes formed with 5-Br-PADAP ligand were 1:2 [47], 1:1 [48] and 1:1 [38], respectively.

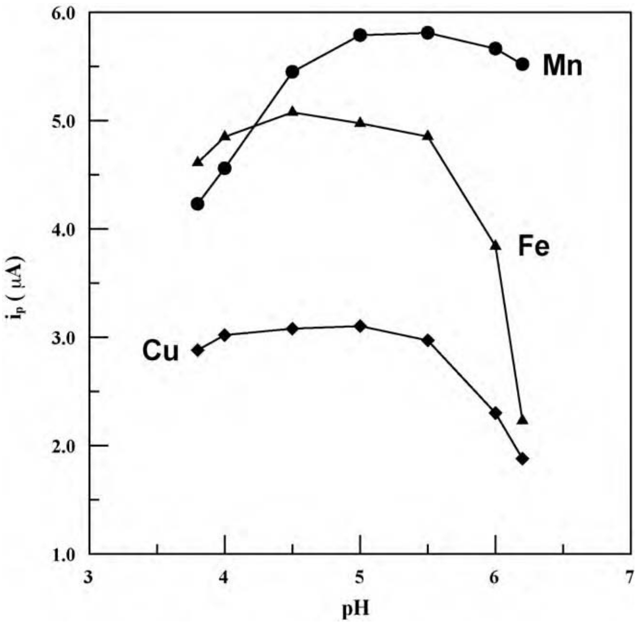

Fig. 2. Plots of SW-AdCSV peak currents (i_p) *vs.* pH of 0.1 mol L^{-1} acetate buffer for a solution containing 0.1 mg L^{-1} of each of Mn(II), Cu(II) and Fe(III) in the presence of 50 μmol L^{-1} 5-Br-PADAP; $E_{acc.}$ = +1.0 V, $t_{acc.}$ = 60 s, f = 100 Hz, ΔE_i = 10 mV and a = 20 mV.

3.2. Simultaneous determination of Mn(II), Cu(II) and Fe(III)

Based on the adsorptive behavior and voltammetric response of Mn(II), Cu(II) and Fe(III)–5-Br-PADAP system at the CPE, a square-wave adsorptive cathodic stripping voltammetry (SW-AdCSV) method has been optimized for simultaneous trace determination of these metal ions in water samples as shown in the following.

3.2.1. Effect of supporting electrolyte and pH

SW-AdCS voltammograms of a solution containing 0.1 mg L^{-1} of each of Mn(II), Cu(II) and Fe(III) in addition to 50 μmol L^{-1} 5-Br-PADAP were recorded in various supporting electrolytes {Britton–Robinson (pH 2–11), acetate (pH 4–6) and phosphate (pH 2–7.5) buffers} following preconcentration of the metal–5-Br-PADAP complexes onto the CPE by adsorptive accumulation at +1.0 V (*vs.* Ag/AgCl/3 M KCl) for 60 s. Three enhanced SW-AdCSV peaks for Mn(II), Cu(II) and Fe(III) were obtained over the pH range 4–5.5. However, sharper peaks of much better enhanced peak currents were achieved in the acetate buffer especially of pH 5 (Fig. 2). At higher pH values the peak currents of the investigated metal ions were decreased; this may be attributed to the precipitation of metal hydroxides [49]. Moreover, the influence of ionic strength of the acetate buffer solution (0.05–0.20 mol L^{-1}) has been also studied while keeping the pH value at 5.0. Better enhanced peak currents were achieved in 0.10 mol L^{-1} acetate buffer of pH 5.0, therefore, it has been chosen as a supporting electrolyte in the rest of the present analytical study.

3.2.2. Effect of concentration of 5-Br-PADAP as a ligand

SW-AdCS voltammograms of a solution containing 0.1 mg L^{-1} of each of Mn(II), Cu(II) and Fe(III) in 0.10 mol L^{-1} acetate buffer

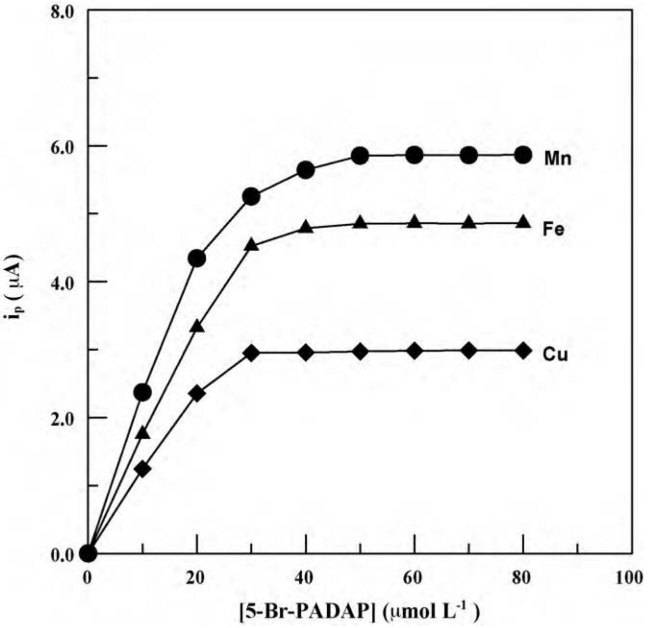

Fig. 3. Plots of SW-AdCSV peak currents (i_p) *vs.* concentration (C) of 5-Br-PADAP for a solution containing 0.1 mg L^{-1} of each of Mn(II), Cu (II) and Fe(III) in 0.1 mol L^{-1} acetate buffer (pH 5); $E_{acc.}$ = +1.0 V, $t_{acc.}$ = 60 s, f = 100 Hz, ΔE_i = 10 mV and a = 20 mV.

(pH 5) in the presence of increasing concentration of 5-Br-PADAP (0–80 μmol L^{-1}) were recorded following preconcentration of the metal ions as 5-Br-PADAP complexes onto the CPE by adsorptive accumulation at +1.0 V for 60 s. The voltammograms showed that the peak currents (i_p) of the examined metal-complexes increased with concentration of 5-Br-PADAP up to ~50 μmol L^{-1}, and then leveled off (Fig. 3). Kinetics of reactions of Mn(II), Cu(II) and Fe(III) with 5-Br-PADAP were identified from their voltammograms recorded after different times of mixing the reactants. The peak currents (i_p) of the examined metal-complexes were practically constant with reaction time, indicating the immediate formation of metal–5-Br-PADAP complexes on mixing the reactants in the electrochemical cell; therefore, heating of the reactants solution was not required in the present work.

3.2.3. Square-wave pulse-parameters

Pulse-parameters (frequency f, scan increment ΔE_i and pulse-amplitude a) were optimized to obtain well-developed and better separated SW-AdCSV peaks for a solution containing 0.1 mg L^{-1} of each of Mn(II), Cu(II) and Fe(III) in addition to 50 μmol L^{-1} 5-Br-PADAP in the acetate buffer (pH 5) following preconcentration onto the CPE by adsorptive accumulation at +1.0 V for 60 s. The results indicated that the peak currents of the examined metal-complexes were increased linearly with the increase of frequency within the range 20–120 Hz; the corresponding regression equations for the investigated metal-complexes were:

$$\text{Mn(II)}: \quad i_p(\mu\text{A}) = 0.0513f\,(\text{Hz}) - 0.688 \qquad (r = 0.996)$$

$$\text{Cu(II)}: \quad i_p(\mu\text{A}) = 0.0158f\,(\text{Hz}) + 1.644 \qquad (r = 0.995)$$

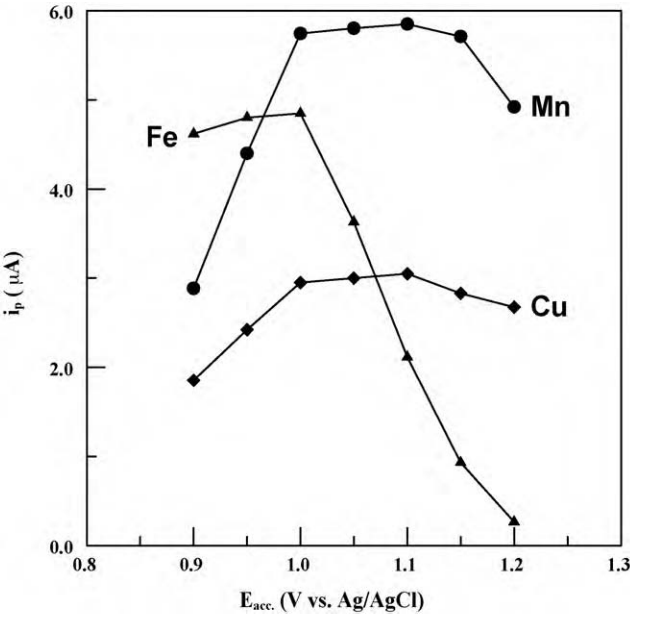

Fig. 4. Plots of SW-AdCSV peak currents (i_p) *vs.* preconcentration potential ($E_{acc.}$) for a solution containing 0.1 mg L^{-1} of each of Mn(II), Cu(II) and Fe(III) in 0.1 mol L^{-1} acetate buffer (pH 5) in the presence of 50 μmol L^{-1} 5-Br-PADAP; f = 120 Hz, ΔE_i = 10 mV and a = 25 mV.

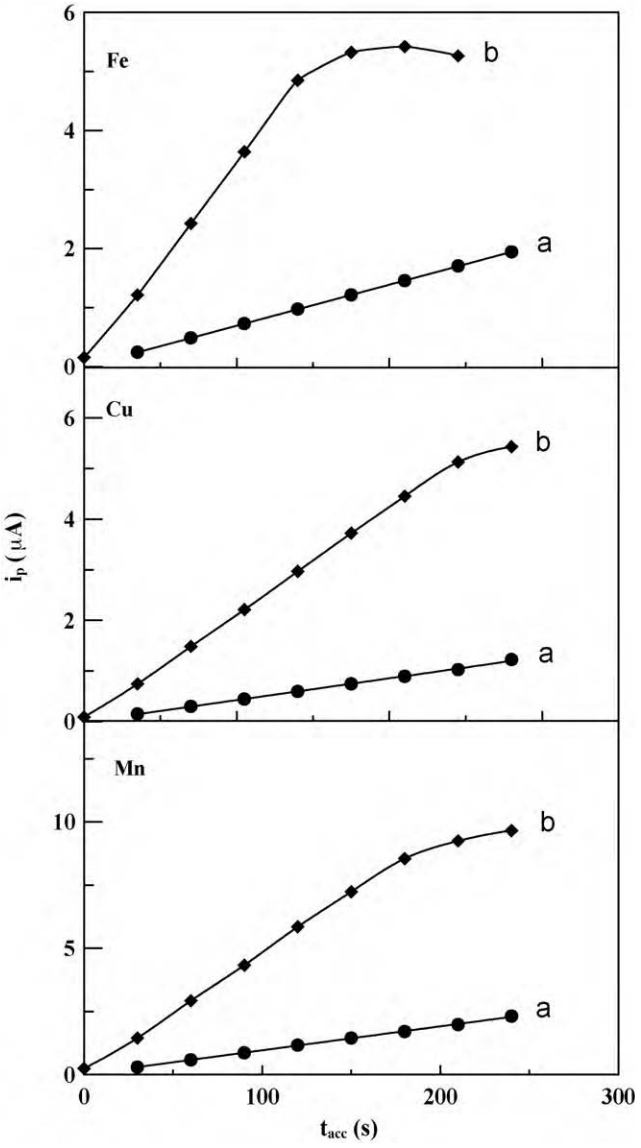

Fig. 5. Plots of SW-AdCS voltammetric peak currents (i_p) *vs.* preconcentration time ($t_{acc.}$) for solutions of (a) 0.01 and (b) 0.05 mg L^{-1} of each of Mn(II), Cu (II) and Fe(III) in 0.1 mol L^{-1} acetate buffer (pH 5), in the presence of 50 μmol L^{-1} 5-Br-PADAP; f = 120 Hz, ΔE_i = 10 mV and a = 25 mV.

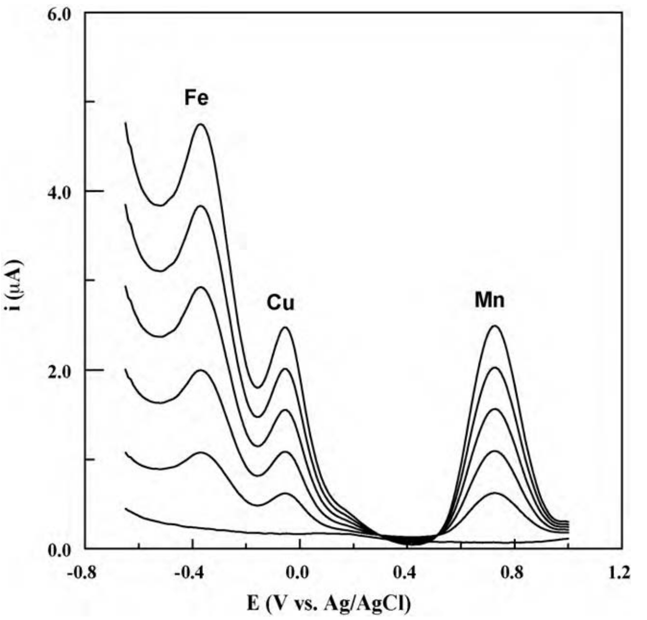

Fig. 6. SW-AdCS voltammograms for successive additions of Mn(II), Cu(II) and Fe(III) solutions in 0.1 mol L^{-1} acetate buffer (pH 5) containing 50 µmol L^{-1} 5-Br-PADAP recorded following preconcentration onto the CPE by adsorptive accumulation at +1.0 V for 240 s. Each addition affected a 2 µg L^{-1} of each of the examined metal ions. Dotted line represents the blank solution; $f = 120$ Hz, $\Delta E_i = 10$ mV and $a = 25$ mV.

$$\text{Fe(III)}: \quad i_p(\mu A) = 0.0334 f(\text{Hz}) - 0.128 \qquad (r = 0.999)$$

On increasing the scan increment within the range 2–10 mV, the peak currents of the investigated metal-complexes were also increased linearly; the corresponding regression equations were:

$$\text{Mn(II)}: \quad i_p(\mu A) = 0.3333\,\Delta E_i\,(\text{mV}) + 2.580 \qquad (r = 0.995)$$

$$\text{Cu(II)}: \quad i_p(\mu A) = 0.0379\,\Delta E_i(\text{mV}) + 4.019 \qquad (r = 0.994)$$

$$\text{Fe(III)}: \quad i_p(\mu A) = 0.3733\,\Delta E_i(\text{mV}) + 0.409 \qquad (r = 0.993)$$

Although the peak currents (i_p) were increased with the increase of pulse-amplitude within the range 20–60 mV, the best peak morphology with lowest baseline was obtained at a pulse-amplitude of 25 mV. Accordingly, the optimal pulse-parameters which were used over the rest of the present investigation were: frequency $f = 120$ Hz, scan increment $\Delta E_i = 10$ mV and pulse-amplitude $a = 25$ mV.

Table 3
Interferences of some inorganic and organic species on the simultaneous determination of 10 µg L^{-1} of each of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes by the described SW-AdCSV method.

Foreign species	Tolerance level[a] (mg L^{-1})
K^+, Na^+, Mg^{2+}, Cl^-, HCO_3^-	100
Ca^{2+}, NO^{3-}, SO_4^{2-}, PO_4^{3-}	50
NH_4^+	1.0
Al^{3+}, Bi^{3+}, Sb^{3+}, Se^{4+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, V^{5+}, Ti^{4+}	0.1
Ascorbic acid	5.0

[a] For 6% error.

3.2.4. *Preconcentration conditions (potential and time)*

SW-AdCS voltammograms of a solution containing 0.1 mg L^{-1} of each of Mn(II), Cu(II) and Fe(III) in addition to 50 µmol L^{-1} 5-Br-PADAP in the acetate buffer (pH 5) were recorded under the optimized pulse-parameters, following preconcentration onto the CPE by adsorptive accumulation for 60 s at varying preconcentration potentials ($E_{acc.}$ = +1.20 to +0.90 V *vs.* Ag/AgCl/3 M KCl). As shown in Fig. 4 better enhanced peak currents of the investigated metal-complexes were achieved at +1.0 V. Therefore, a preconcentration potential of +1.0 V (*vs.* Ag/AgCl/3 M KCl) was used throughout the present analytical study.

On the other side, SW-AdCS voltammograms of solutions of 0.01 and 0.05 mg L^{-1} of each of Mn(II), Cu(II) or Fe(III) in the presence of 50 µmol L^{-1} Br-PADAP were recorded under the optimum operational conditions following preconcentration onto the CPE by adsorptive accumulation at +1.0 V for varying preconcentration times (30–240 s). As shown in Fig. 5, the peak current of each of 0.01 mg L^{-1} Mn(III), Cu(II) and Fe(III) as 5-Br-PADAP complexes has increased linearly with preconcentration time over the examined time period. At higher concentration of each of the investigated metal ions, adsorptive saturation of the electrode surface (adsorption equilibrium) was reached and hence the peak currents leveled off. Accordingly, the preconcentration time should be chosen according to the concentration level of metal ions in the investigated solution ($t_{acc.} \leq 240$ s).

Table 1
Characteristics of the calibration curves of the described SW-AdCSV method for simultaneous determination of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes; $E_{acc.}$ = +1.0 V and $t_{acc.}$ = 240 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})			
Mn(II)	0.22–40	0.048 ± 0.0011	0.235 ± 0.005	0.998	0.066	0.22
Cu(II)	0.36–45	0.032 ± 0.0010	0.123 ± 0.004	0.997	0.108	0.36
Fe(III)	0.31–25	0.027 ± 0.0008	0.195 ± 0.007	0.995	0.093	0.31

[a] Average of three determinations.

Table 2
Accuracy and precision of simultaneous determination of 10 µg L^{-1} of each of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes by means of the described SW-AdCV method in comparison to those obtained by a reported FAAS method [8].

Metal ions	SW-ASCSV (%$R \pm S.D.$)		FAAS (%$R \pm S.D.$) (A)	F-statistic	t-Test
	(A)	(B)			
Mn(II)	99.21 ± 1.30	100.63 ± 0.34	98.84 ± 1.58	1.48	0.40
Cu(II)	98.53 ± 1.12	98.91 ± 1.01	99.41 ± 0.83	1.82	1.41
Fe(III)	100.72 ± 0.75	100.53 ± 0.50	99.95 ± 1.11	2.19	1.29

(A) Calibration curve method and (B) standard addition method. Theoretical F-statistic = 6.39 and t-test = 2.3 at 95% confidence limit for $n_1 = n_2 = 5$.

Table 4
Simultaneous determination of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes in various water samples by the described SW-AdCSV ($E_{acc.}$ = +1.0 V and $t_{acc.}$ = 240 s) and a reported flame atomic absorption spectrometry (FAAS) methods.

Analyzed sample	Mn(II) (μg L^{-1})		Cu(II) (μg L^{-1})		Fe(III) (μg L^{-1})	
	SW-AdCSV	FAAS	SW-AdCSV	FAAS	SW-AdCSV	FAAS
Ground water	730 ± 5.5[a]	715 ± 7.0	33.2 ± 1.6	31 ± 2.0	103 ± 3.7	106 ± 4.0
Tap water	155 ± 3.6[a]	160 ± 3.5	21.3 ± 1.1	23 ± 1.8	53 ± 2.4	50 ± 3.1
Bottled water:						
Siwa®	8.2 ± 1.0	10 ± 1.3	1.0 ± 0.3	[b]	5.1 ± 0.8	4 ± 1.2
Delta®	28.5 ± 1.7	30 ± 2.6	9.5 ± 0.8	11 ± 1.1	10.4 ± 0.8	12 ± 2.4
Aquasiwa®	15.6 ± 0.7	15 ± 1.8	5.8 ± 0.7	5 ± 0.8	9.5 ± 0.5	11 ± 1.8
Safi®	5.4 ± 0.8	7 ± 1.1	1.3 ± 0.5	[b]	5.5 ± 0.5	7 ± 2.1

[a] Preconcentration time = 60 s.
[b] Under limit of detection.

3.3. Method validation

3.3.1. Linearity rang, limits of detections and limits of quantitations

SW-AdCS voltammograms of various concentrations of the examined Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes were recorded following their preconcentration onto the CPE for 240 s under the optimum operational conditions (Fig. 6). Rectilinear relations between peak current (i_p) and concentrations (C) of each of Mn(II), Cu(II) and Fe(III) were obtained over the ranges indicated in Table 1. Limits of detection (LOD) and quantitation (LOQ) of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes were also estimated using the expression: $kS.D./b$ [50], where $k = 3$ for LOD and 10 for LOQ, $S.D.$ is the standard deviation of intercept (or blank) and b is the slope of the calibration curve. The results reported in Table 1 confirmed the reliability of the described SW-AdCSV method for determination of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes. The achieved LOD of the examined metal ions (Table 1) indicated that the developed SW-AdCSV method is sensitive compared to the reported electrochemical methods using some solid and the mercury electrodes [27–40] for the determination of Mn(II), Cu(II) and Fe(III) as metal-complexes.

3.3.2. Accuracy and precision

Accuracy and precision of assay of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes by means of the described SW-AdCSV method were estimated as recovery (%R) and standard deviation (%$S.D.$). This was performed by analyzing reference standard solutions of each of the investigated metal ions for three times. The results reported in Table 2 indicated the accuracy and precision of the described SW-AdCSV method for simultaneous determination of Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes. Moreover, the results obtained by the described SW-AdCSV method, applying calibration curve method, were statistically compared with those obtained by a flame atomic absorption spectrometry (FAAS) method [8]. Since the calculated value of F-statistic does not exceed the theoretical value (Table 2); there was no significant difference between the described SW-AdCSV and the reported FAAS [8] methods with respect to reproducibility [51]. Also, no significant differences were noticed between the two methods regarding accuracy and precision as revealed by t-values [51] (Table 2).

3.3.3. Interferences

Interferences from some foreign cations (K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Bi^{3+}, Sb^{3+}, Se^{4+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, V^{5+}, Ti^{4+} and $NH_4{}^+$), inorganic anions ($HCO_3{}^-$, Cl^-, NO^{3-}, $SO_4{}^{2-}$ and $PO_4{}^{3-}$) and ascorbic acid to the assay of 10 μg L^{-1} of each of Mn(II), Cu(II) and Fe(III) by the described SW-AdCSV method were evaluated. As shown in Table 3, the investigated foreign species, below tolerance level, have insignificant effect on the magnitudes of the peak currents of 10 μg L^{-1} of each of Mn(II), Cu(II) and Fe(III) since the relative errors were below 6%. Interference from Triton X-100 (a non-ionic surfactant) up to 0.001% to the assay of the investigated metal ions was insignificant. Higher concentrations of the surfactant cause deformation and suppression of the voltammetric peaks of the investigated metal ions making impossible their determination. However, the presence of Triton X-100 in ground, tab or bottled natural water samples is very rare.

3.4. Applications

The described SW-AdCSV method was successfully applied for simultaneous determination of Mn(II), Cu(II) and Fe(III) in ground, tap and bottled natural water samples collected from Tanta City, Egypt. A flame atomic absorption spectrometer (FAAS) method [8] was applied also for analysis of Mn(II), Cu(II) and Fe(III) in the same examined water samples and the obtained results are reported in Table 4. A comparison of the results obtained by the described SW-AdCV method with those obtained by FAAS one [8] (Table 4) revealed the capability of the described stripping voltammetry method for simultaneous determination of Mn(II), Cu(II) and Fe(III) at trace and ultra trace concentrations. Moreover, the described stripping voltammetry method is much more sensitive than the FAAS one since concentrations <1 μg L^{-1} of metal ions could not be detected by FAAS.

4. Conclusion

A simple, specific and precise square-wave adsorptive cathodic stripping voltammetry (SW-AdCSV) method has been described for simultaneous determination of Mn(II), Cu(II) and Fe(III) as 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol complexes in water samples with insignificant interferences from foreign inorganic and organic species. Limits of detection of 0.066, 0.108 and 0.093 μg L^{-1} Mn(II), Cu(II) and Fe(III) as 5-Br-PADAP complexes, respectively, were achieved by the described method. The results confirmed that the described SW-AdCSV method using the CPE is sensitive compared to the reported electrochemical methods using some solid and the mercury electrodes [27–40] for determination of Mn(II), Cu(II) and Fe(III) as metal-complexes.

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References

[1] T.M. Florence, Analyst 111 (1986) 489.
[2] J. Labuda, M. Vanickova, E. Beinrohr, Microchim. Acta 1 (1989) 113.
[3] B. Chiswell, M.B. Mokhtar, Talanta 33 (1986) 669.
[4] F.C. Wedler, in: G.P. Ellis (Ed.), Progress in Medicinal Chemistry, vol. 30, Elsevier, Amsterdam, 1993, pp. 89–133.
[5] N.V. Hue, S. Vega, J.A. Silva, J. Am. Soil Sci. Soc. 65 (2001) 153.
[6] J.D. Hem, Study and Interpretation of the Chemical Characteristics of Natural Water, 2nd edn., US Department of the Interior, US Government Printing Office, Washington, 1960.
[7] Martindale, The Extra Pharmacopoeia, 29th edn., The Pharmaceutical Press, London, 1989, pp. 1189–1195.
[8] P. Pohl, I. Sergiel, Microchim. Acta 168 (2010) 9.
[9] N. Tokman, J. Hazard. Mater. 143 (2007) 87.
[10] A.R. Rod, S. Borhani, F. Shemirani, Eur. Food Res. Technol. 223 (2006) 649.
[11] Ç.A. Şahin, M. Efeçınar, N. Şatıroğlu, J. Hazard. Mater. 176 (2010) 672.
[12] R.G.O. Araujo, F.S. Dias, S.M. Macedo, W.N.L. dos Santos, S.L.C. Ferreira, Food Chem. 101 (2007) 397.
[13] F. Sabermahani, M.A. Taher, Microchim. Acta 159 (2007) 117.
[14] A. Zacharia, S. Gucer, B. Izgi, A. Chebotarev, H. Karaaslan, Talanta 72 (2007) 825.
[15] A. Caballo-Lopez, M.D.L. de Castro, Talanta 71 (2007) 2074.
[16] E.Z. Jahromi, A. Bidari, Y. Assadi, M.R.M. Hosseini, M.R. Jamali, Anal. Chim. Acta 585 (2007) 305.
[17] H. Matusiewicz, M. Krawczyk, Microchem. J. 83 (2006) 17.
[18] A. Ohashi, H. Ito, C. Kanai, H. Imura, K. Ohashi, Talanta 65 (2005) 525.
[19] M.H. Mashhadizadeh, M.S. Azimi, M. Pesteh, I. Sheikhshoaei, M.M. Ardakani, M.A. Karimi, Spectrochim. Acta B 63 (2008) 889.
[20] M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, M. Montazerozohori, M. Soylak, J. Hazard. Mater. 166 (2009) 1441.
[21] A. Desaulty, C. Mariet, P. Dillmann, J.L. Joron, P. Fluzin, Spectrochim. Acta B 63 (2008) 1253.
[22] J. Wang, Stripping Analysis: Principles, Instrumentation and Application, VCH, Deerfield Beach, 1985.
[23] Y. Jin, F. Xu, T. Miwa, Electroanalysis 12 (2000) 610.
[24] R. Hajian, E. Shams, Anal. Chim. Acta 491 (2003) 63.
[25] M.M. Ghoneim, A.M. Hassanein, E. Hammam, A.M. Beltagi, Fresenius J. Anal. Chem. 367 (2000) 378.
[26] F. Vydra, K. Štulík, E. Juláková, Electrochemical Stripping Analysis, Ellis Horwood, Chichester, 1976.
[27] O.M.S. Filipe, C.M.A. Brett, Talanta 61 (2003) 643.
[28] J.S. Roitz, K.W. Bruland, Anal. Chim. Acta 344 (1997) 175.
[29] M. Rievaj, P. Tomcik, Z. Janosikova, D. Bustin, R.G. Compton, Chem. Anal. 53 (2008) 153.
[30] J. Wang, J. Lu, Talanta 42 (1995) 331.
[31] S. Tanaka, K. Sugawara, M. Taga, Talanta 37 (1990) 1001.
[32] A.A. Ensafi, T. Khayamian, A. Benvidi, E. Mirmomtaz, Anal. Chim. Acta 561 (2006) 225.
[33] A.G. Fogg, A. Rahim, H.M. Yusoff, R. Ahmad, Talanta 44 (1997) 125.
[34] L. Jin, N.J. Gogan, Anal. Chim. Acta 412 (2000) 77.
[35] A.A. Ensafi, T. Khayamian, S.S. Khaloo, Anal. Chim. Acta 505 (2004) 201.
[36] A.A. Ensafi, T. Khayamian, M. Atabati, Talanta 57 (2002) 785.
[37] A. Komersová, M. Bartoš, K. Kalcher, K. Vytřas, J. Pharm. Biomed. Anal. 16 (1998) 1373.
[38] J. Zhao, W. Jin, J. Electroanal. Chem. 267 (1989) 271.
[39] R. Segura, M.I. Toral, V. Arancibia, Talanta 75 (2008) 973.
[40] N.A. El-Maali, Y.M. Temerk, M.S. Abd El-Azizb, Anal. Chim. Acta 353 (1997) 313.
[41] J. Lu, W. Jin, S. Wang, Anal. Chim. Acta 238 (1990) 375.
[42] W. Jin, S. Shi, J. Wang, J. Electroanal. Chem. 291 (1990) 41.
[43] J. Zhao, W. Jin, J. Electroanal. Chem. 256 (1988) 181.
[44] J. Lu, W. Jin, S. Wang, T. Sun, J. Electroanal. Chem. 291 (1990) 49.
[45] J. Wenrui, L. Xixia, Anal. Chim. Acta 236 (1990) 453.
[46] J. Zhou, R. Neeb, Fresenius J. Anal. Chem. 338 (1990) 905.
[47] X.C. Qiu, Y.S. Zhang, Y.Q. Zhu, Soil Sci. 138 (1984) 432.
[48] N. Menek, S. Topçu, M. Uçar, Anal. Lett. 34 (2001) 1733.
[49] H. Alemu, B.S. Chandravanshi, Anal. Chim. Acta 368 (1998) 165.
[50] M. Swartz, I.S. Krull, Analytical Method Development and Validation, Marcel Dekker, New York, 1997.
[51] G.D. Christian, Analytical Chemistry, 5th edn., Willey, Hoboken, NJ, 1994.