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Simultaneous determination of cadmium (II), lead (II), copper (II) and mercury (II) by square-wave anodic stripping voltammetry at a montmorillonite-calcium modified carbon paste electrode

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A simple and efficient montmorillonite-calcium modified carbon paste electrode (MMT-Ca modified CPE) was constructed for simultaneous trace determination of Cd(II), Pb(II), Cu(II) and Hg(II). The MMT-Ca modified CPE significantly enhances the voltammetric stripping peak current magnitudes of the investigated metal ions compared to the bare CPE due to the large cation-exchange capacity and the strong adsorptive property of montmorillonite-Ca clay. A fully validated simple, sensitive, selective and precise square-wave anodic stripping voltammetric method was developed for the simultaneous trace determination of Cd(II), Pb(II), Cu(II) and Hg(II) in various water samples using a fabricated 10% (w/w) MMT-Ca modified CPE. The achieved limits of detection of Cd(II) $0.54 \mu\text{g L}^{-1}$, Pb(II) $0.30 \mu\text{g L}^{-1}$, Cu(II) $0.75 \mu\text{g L}^{-1}$ and Hg(II) $1.05 \mu\text{g L}^{-1}$ indicating the high sensitivity of the described SW-AS voltammetry method for the assay of these metal ions in aqueous solutions. The method was successfully applied for analysis of tap water, bottled natural water and seawater samples.

Keywords: cadmium; lead; copper; mercury; simultaneous determination; montmorillonite-Ca clay; modified carbon paste electrode

1. Introduction

Determination of concentration levels of different metal ions in fresh water, underground water, food stuff and soil has become an area of particular concern and high priority in environmental research and protection. The most commonly used techniques for determination of various metal ions are atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), and inductively coupled plasma atomic emission spectrometry (ICP-AES). These techniques are highly sensitive, selective and have wide range of linearity, but they have some intrinsic drawbacks since they require complicated and expensive instruments, high cost and they are not applicable for *in situ* measurements. Moreover, these techniques also require specific standards and careful sample preparation [1]. Electrochemical methods are also attractive for determination of various metal ions since they exhibit high sensitivity, good selectivity, rapid response, easy data read-out and low cost [2]. Besides, the instruments employed are relatively simple and conveniently miniaturised for *in situ* and automated detection. Solid electrodes based on carbon are

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currently in widespread use in electro-analysis because of their broad potential window, low background current, rich surface chemistry, low cost, chemical inertness, and suitability for various sensing and detection applications. Carbon-paste electrode is a mixture of an electrically conducting graphite powder and a pasting liquid (e.g. Nujol mineral oil); it offers easily renewable, porous surface and low background current contributions [2]. However, the sensitivity of carbon paste electrode (CPE) is relatively poor in the determination of metal ions. In order to improve this, a fascinating and effective way is to modify it with a unique substance. Clay minerals have become attractive electrode modifier since the first example of the use of clay as modifier was reported [3]. Montmorillonite (MMT) is a kind of clay of a layer lattice which becomes an attractive electrode modifier for the voltammetric determination of metal ions due to its high chemical and mechanical stability, well-layered structure, high cationic exchange capacity and strong adsorptive properties attributed to the expandability of its internal layers. MMT was used successfully as a modifier in carbon paste electrode for the individual determination of each of Cu(II) [4], Au(III) [5,6], Hg(II) [7,8], Eu(III) [9] and Pb(II) [10]. To the best of our knowledge, Cd(II) was never determined electrochemically at MMT modified CPE. Besides, no voltammetric method is reported in literature to date for the simultaneous trace determination of metal ions at MMT-Ca modified CPE. Several electrodes modified with different modifiers were also used for the determination of Cd(II), Pb(II), Cu(II) and/or Hg(II) [11–22] (Table 1).

Cadmium, lead and mercury are known to be hazardous environmental pollutants with toxic effects for the living organisms in aquatic ecosystems even at low concentrations [23–28]. Adverse effects of these heavy metals 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. Copper is an essential element in the nutrition of plants and animals and not considered to be a cumulative systemic poison, but excess of copper may cause symptoms of gastroenteritis with nausea, hypercupremia, vomiting, myalgia and haemolysis [29]. It is therefore crucial and of importance to develop a simple and sensitive analytical method for trace determination of at least these four metal ions.

This work describes a simple and high sensitive square-wave anodic stripping voltammetry method for simultaneous determination of cadmium (II), lead (II), copper (II) and mercury (II) at trace concentrations in water samples utilising a constructed montmorillonite-calcium modified carbon paste electrode.

2. Experimental

2.1 Apparatus

All voltammetric measurements were performed with Princeton Applied Research (PAR, Oak Ridge, TN, USA) Potentiostats Model 273 A. A voltammetric cell consisting of a C-2 stand with a carbon paste working electrode body (BAS model mf-2010, 3 mm in diameter and 1 mm in depth), an Ag/AgCl/saturated KCl reference electrode (BAS model MF-2063) and a platinum wire counter electrode (BAS model MW-1032) was used. A magnetic stirrer (PAR - 305) with a Teflon-coated magnet was used to provide the convective transport during the preconcentration step. The data were treated through a personal computer connected to the potentiostat and loaded with the 270/250 Research Electrochemistry software version 4.41 (PerkinElmer Instruments Inc.).

Table 1. List of some modified electrodes which have been reported for determination of Cd(II), Pb(II), Cu(II) and Hg(II) in aqueous solutions.

Electrode	Medium	Technique	Metal ion	LOD	Ref.
Montmorillonite-Na modified CPE	Acetate buffer (pH = 3.6)	DPV	Cu(II)	$4 \times 10^{-8} \text{ mol L}^{-1}$	[4]
Montmorillonite modified CPE	Acetate buffer (pH = 3.6)	ASV	Hg(II)	$4.98 \times 10^{-8} \text{ mol L}^{-1}$	[7]
Montmorillonite-Na modified CPE	0.1 mol L ⁻¹ tartaric acid (pH = 1.0)	DP-SV	Hg(II)	$1 \times 10^{-10} \text{ mol L}^{-1}$	[8]
Montmorillonite-Ca modified CPE	0.01 mol L ⁻¹ HCl (pH = 2)	ASV	Pb(II)	$6 \times 10^{-9} \text{ mol L}^{-1}$	[10]
Bismuth/glassy carbon composite electrode	0.1 mol L ⁻¹ acetate buffer (pH = 4.5)	ASV	Pb(II)	0.41 $\mu\text{g L}^{-1}$	[11]
Diacyldioxime modified CPE	0.1 mol L ⁻¹ NaH ₂ PO ₄ buffer (pH = 5.0)	DP-SV	Cd(II)	0.49 $\mu\text{g L}^{-1}$	[12]
Antimony film CPE	0.01 mol L ⁻¹ HCl (pH = 2)	SW-ASV	Cd(II)	$4 \times 10^{-8} \text{ mol L}^{-1}$	[13]
Ca ₁₀ (PO ₄) ₆ (OH) ₂ -modified CPE	1.0 mol L ⁻¹ HClO ₄ (pH = 8)	SWV	Pb(II)	0.8 $\mu\text{g L}^{-1}$	[14]
Nafion-coated bismuth film electrode	0.1 mol L ⁻¹ acetate buffer (pH = 4.5)	DP-ASV	Pb(II)	0.2 $\mu\text{g L}^{-1}$	[15]
Bismuth/poly(<i>p</i> -amino benzene sulfonic acid) film electrode	0.1 mol L ⁻¹ acetate buffer (pH = 5.3)	DP-ASV	Pb(II)	$7.68 \times 10^{-10} \text{ mol L}^{-1}$	[16]
Bismuth-modified carbon nanotube electrode	0.1 mol L ⁻¹ acetate buffer (pH = 4.5)	ASV	Cd(II)	0.63 $\mu\text{g L}^{-1}$	[17]
CPE modified with SBA-15 nanostructured silica organofunctionalised with 2-benzothiazolethiol	0.1 mol L ⁻¹ phosphate buffer (pH = 3.0)	DP-ASV	Pb(II)	1.3 $\mu\text{g L}^{-1}$	[18]
Bismuth-modified zeolite doped CPE	0.1 mol L ⁻¹ acetate buffer (pH = 4.5)	DP-SV	Cu(II)	$2 \times 10^{-7} \text{ mol L}^{-1}$	[19]
CPE modified with 1-furoylthioureas	Britton-Robinson buffer (pH = 4.0)	DP-ASV	Cd(II)	$4 \times 10^{-7} \text{ mol L}^{-1}$	[20]
GCE modified with Langmuir-Blodgett film of <i>p</i> - <i>tert</i> -butylthiacalix[4]arene	0.1 mol L ⁻¹ acetate buffer (pH = 4.8)	ASV	Cd(II)	0.08 $\mu\text{g L}^{-1}$	[21]
CPE modified with zirconium phosphated amorphous silica	citrate buffer (pH = 3.5)	ASV	Pb(II)	0.1 $\mu\text{g L}^{-1}$	[22]

A Shimadzu Flame Atomic Absorption Spectrometer (FAAS) Model AA-670 interfaced with a data processor was used for comparative 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 the pH measurements. An automatic micropipette (Eppendorf–Multipette® plus) was used for transfer of the analyte solutions throughout the present experimental work. The de-ionised water used throughout the present study was supplied from a Purite-Still Plus de-ioniser connected to an Aqua Matic bi-distillation water system (Hamilton Laboratory Glass, Margate, Kent, UK).

2.2 Reagents and solutions

Desired standard solutions of Cd(II), Pb(II), Cu(II), Hg(II), Sb(III), Bi(III), Se(IV), Zn(II), Mn(II), Ni(II), Co(II), Al(III) and Fe(III) were prepared by accurate dilution of their standard stock solutions (each 1000 mg L⁻¹ dissolved in aqueous 0.1 M HCl, supplied from Cica, Japan) by de-ionised water. Standard solutions of Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, HCO₃⁻ and NH₄⁺ (each of 1000 mg L⁻¹) were prepared by dissolving appropriate amounts of KCl, KNO₃, Na₂SO₄, Na₃PO₄, NaHCO₃ and NH₄Cl in de-ionised water, respectively. Solutions of 1000 mg L⁻¹ ascorbic acid and 1% Triton X-100 were prepared in de-ionised water. A stock solution of 1 × 10⁻³ mol L⁻¹ EDTA (di-sodium salt) was prepared in de-ionised water.

Britton-Robinson (B-R) universal buffer (pH 2–5), 0.1 M HClO₄ and 0.01–0.2 M HCl solutions were prepared in de-ionised water and were used as supporting electrolytes. All chemicals used were of analytical grade and were used without further purification.

2.3 Preparation of the modified carbon paste electrodes

An amount of 4.5 g of graphite powder (1–2 μm, Aldrich, Milwaukee, WI, USA) and 0.5 g of montmorillonite-calcium clay (fine powder <5 μm, ECC America Inc., Southern Clay Products Subsidiary, Gonzales, Texas, USA) were mixed uniformly by milling in a small agate mortar, then 1.8 mL Nujol oil (Sigma, $d = 0.84 \text{ g mL}^{-1}$) was added and milled again to give a homogenous MMT-Ca modified carbon paste (10% w/w). Various modified carbon pastes containing different mass ratio of MMT-Ca clay (0, 5, 15 and 20% (w/w)) were similarly prepared. An amount of the prepared MMT-Ca modified carbon paste was pressed into the end cavity (3 mm in diameter, 1 mm in depth) of the electrode body. Surface of the constructed MMT-Ca carbon paste electrode (MMT-Ca CPE) was manually smoothed by polishing on clean paper before use.

2.4 General analytical procedure

A 10 mL volume of 0.1 M HCl solution (pH = 1) was transferred to the micro-electrolysis cell and the smoothed MMT-Ca modified CPE was then immersed in the supporting electrolyte and several sweeps were applied to obtain a low background current. After that, aliquots of the investigated metal ions were introduced into the electrolysis cell and a selected preconcentration potential was then applied to the developed MMT-Ca modified

CPE for a selected preconcentration time, while the solution was stirred at 400 rpm. At the end of the preconcentration time, the stirring was stopped and a 5 s rest period was allowed for the solution to become quiescent. The voltammogram was then recorded by scanning the potential towards the positive direction using the square-wave potential waveform. After each measurement, the used modified carbon paste was carefully removed from the end of the cavity and a new MMT-Ca modified CPE was constructed from the prepared stock modified carbon paste.

2.5 Analysed real water samples

Various water samples were subjected to analysis by means of the described square-wave anodic stripping voltammetry method at the constructed montmorillonite-calcium modified carbon paste electrode. These include tap water, bottled natural water (available in the Egyptian market) and coastal seawater samples (obtained from Alexandria City coast, Egypt). The coastal water sample was taken a few meters from the coast where the water was 3–4 m deep. Then, the seawater sample was UV-digested (3 h) after acidification with HCl to pH 1 with a 1 KW high-pressure mercury-vapour lamp to avoid possible interferences caused by natural organic compounds and to breakdown organic-metal complexes.

3. Results and discussion

3.1 Electrochemical response of MMT-Ca modified CPE

Figure 1 shows the square-wave anodic stripping (SW-AS) voltammograms of 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II), Hg(II), Sb(III), Bi(III), Se(IV), Zn(II), Mn(II), Ni(II), Co(II), Fe(III) and Al(III) in 0.1 M HCl at a bare carbon paste electrode (CPE) and at montmorillonite-Calcium modified CPE (MMT-Ca modified CPE). The voltammogram recorded at CPE following preconcentration at open circuit conditions exhibited no anodic peaks (curve a), while that recorded following preconcentration by electrolytic deposition at -0.9 V for 60 s exhibited two broad ill-defined peaks (curve b) corresponding to oxidation of deposited Pb and Cu metals. However, voltammograms of the same solution following preconcentration by electrolytic deposition at -0.9 V for 60 s at CPE modified with 5% MMT-Ca (curve c), 10% MMT-Ca (curve d) and 15% (w/w) MMT-Ca (curve e) exhibited four well-defined anodic peaks at -0.65 , -0.34 , -0.05 V and $+0.19 \text{ V}$ (vs. Ag/AgCl/KCl_s) corresponding to oxidation of the deposited Cd, Pb, Cu and Hg, respectively. This may be attributed to the huge cation-exchange capacity and strong adsorptive ability of MMT-Ca. No more peaks were observed for the rest of metal ions present in the investigated solution, which may be attributed to the non-optimised pH value of the medium and/or the potential window of the MMT-Ca modified CPE under the experimental conditions. This behaviour indicated that modification of the CPE with MMT-Ca significantly enhances the stripping peak current magnitudes of Cd(II), Pb(II), Cu(II) and Hg(II) under the experimental conditions. Following exchange, adsorption and then preconcentration of the four metal ions by electrolytic deposition at the MMT-Ca modified CPE surface (Step 1), they re-oxidised and stripped out from the electrode surface by scanning the potential towards the positive direction (Step 2), resulting in the

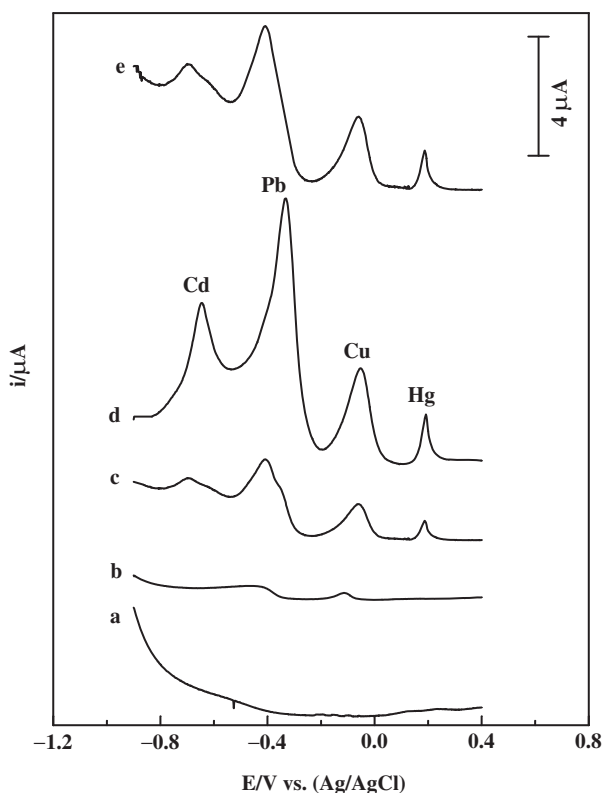
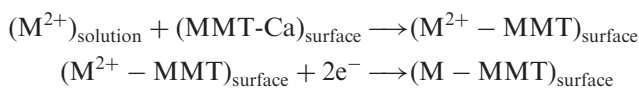


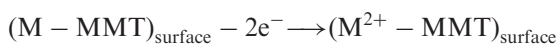
Figure 1. SW-AS voltammograms of 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II), Hg(II), Sb(III), Bi(II), Se(II), Zn(II), Mn(II), Ni(II), Co(II), Fe(III) and Al(III) in 0.1 M HCl solution (pH 1), recorded following preconcentration by electrolytic deposition at a bare CPE under open circuit conditions (a), then at -0.90 V for 60 s (b) and those following preconcentration at 5% MMT-Ca modified CPE (c), 10% MMT-Ca modified CPE (d) and 15% MMT-Ca modified CPE (e); Frequency $f = 120 \text{ Hz}$, scan increment $\Delta s = 2 \text{ mV}$ and pulse-amplitude $E_{\text{sw}} = 25 \text{ mV}$.

obvious anodic voltammetric peaks (Figure 1, curves c–e). The overall electrode process may be expressed as:

- (1) Exchange, adsorption and electrolytic deposition step:



- (2) Stripping step:



On the other side, as shown in Figure 1, the stripping peak current magnitudes of the investigated four metal ions firstly increased upon the increase of percentage of MMT-Ca up to 10% (curve d) in the graphite powder of the CPE, and then decreased (curve e). This behaviour was expected because as the amount of MMT-Ca increased (0–10%), the exchange sites for Cd(II), Pb(II), Cu(II) and Hg(II) into the MMT-Ca clay are increased

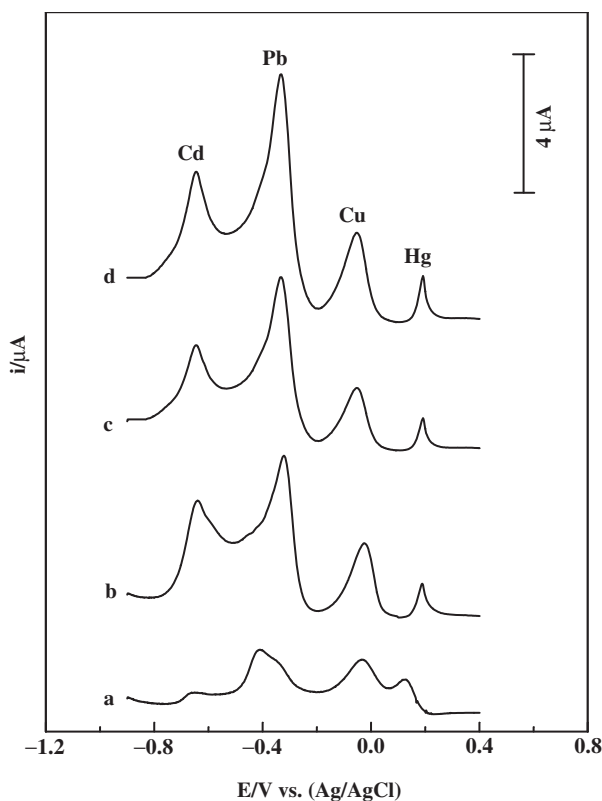


Figure 2. SW-AS voltammograms of 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II) and Hg(II) recorded following preconcentration by electrolytic deposition at -0.90 for 60 s at the 10% MMT-Ca modified CPE in B-R buffer of pH 2 (a), 0.1 M HClO_4 (b), 0.01 M HCl (c) and 0.1 M HCl (d). Other parameters are as those given in Figure 1.

leading to better preconcentration efficiency and consequently enhancing the voltammetric peak current magnitudes. Higher mass ratios of the non-conductive MMT-Ca clay in the CPE lead to a significant decrease of conductivity of CPE (blocking the electron transfer of the investigated metal ions) and hence, increasing the background current and consequently decreasing the voltammetric peak current magnitudes. Therefore, a mass ratio of 1:10 MMT-Ca: graphite powder was used in preparing the modified CPE throughout this study.

3.2 Effect of supporting electrolyte and pH

SW-AS voltammograms of 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II) and Hg(II) were recorded in various supporting electrolytes namely Britton-Robinson buffer (pH 2–5), 0.1 M HClO_4 and 0.01 – 0.20 M HCl solutions. Better enhanced peak current magnitudes were obtained in 0.1 M HCl solution (pH = 1) as a supporting electrolyte (Figure 2, curve d), therefore, it was used throughout the rest of the present analytical study. Previous electro-analytical studies [30–34] revealed that hydrochloric acid solution of pH 1 is the most suitable supporting electrolyte for the simultaneous determination of Cd(II),

Pb(II), Cu(II) by anodic stripping voltammetry at mercury electrodes. This is due to the easy formation of their metal-chlorocomplexes of different formation constants and hence they reduced to their metallic forms at different potentials providing good peak separation. Moreover, Hg(II) was preferred to be determined as a chloro-complex [8].

3.3 Square-wave pulse parameters

In order to obtain better developed and well-separated voltammetric peaks for the simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl, following preconcentration by electrolytic deposition at the MMT-Ca modified CPE, the square-wave pulse parameters were optimised by varying the frequency f (20–120 Hz), scan increment Δs (2–10 mV) and pulse-amplitude E_{sw} (20–60 mV). Although, the peak current magnitudes of the investigated metal ions increased linearly with increasing frequency, scan increment and pulse amplitude, better enhanced peak currents with the best peak separation at the modified CPE were achieved at square-wave pulse parameters of $f=80$ Hz, $\Delta s=2$ mV and $E_{sw}=25$ mV.

3.4 Electrolytic deposition conditions

Effect of varying the preconcentration potential E_d (–1.0 to –0.84 V vs. Ag/AgCl/KCl_s) on the electrolytic deposition of 0.1 mg L^{–1} of each of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl solution for 60 s at the MMT-Ca modified CPE and consequently on their SW-AS voltammetric peak current magnitudes was evaluated (Figure 3). The results

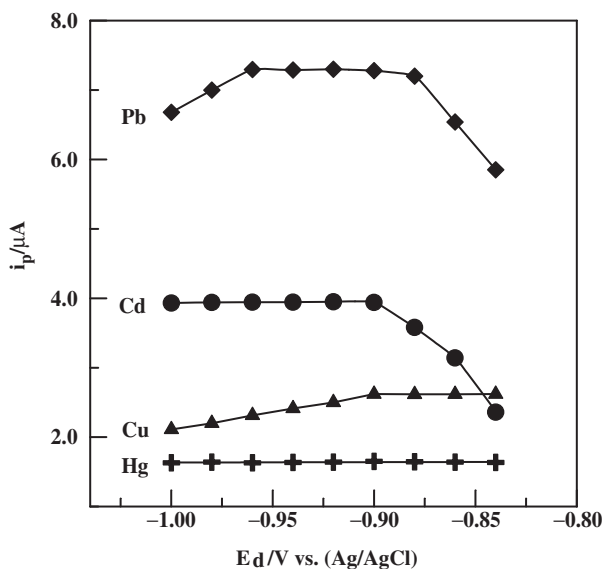


Figure 3. SW-AS voltammetric peak current magnitudes (i_p) as a function of preconcentration potential (E_d) for a solution containing 0.1 mg L^{–1} of each of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl following preconcentration by electrolytic deposition at the 10% MMT-Ca modified CPE. Frequency $f=80$ Hz, scan increment $\Delta s=2$ mV and pulse-amplitude $E_{sw}=25$ mV.

showed that better enhanced peak current magnitudes for the investigated metal ions were achieved at -0.90 V. However, significant decrease in the peak current magnitudes of Cd(II) and Pb(II) occurred at preconcentration potentials less negative than -0.90 V (Figure 3). Therefore, -0.90 V was the optimal preconcentration potential for the simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl solution and it was used throughout the present analytical study.

On the other hand, SW-AS voltammograms of 0.05 and 0.1 mg L⁻¹ of each of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl solution were recorded under the optimum procedural parameters following preconcentration by electrolytic deposition at -0.90 V for increased preconcentration time (0 to 420 s). As shown in Figure 4, the peak current

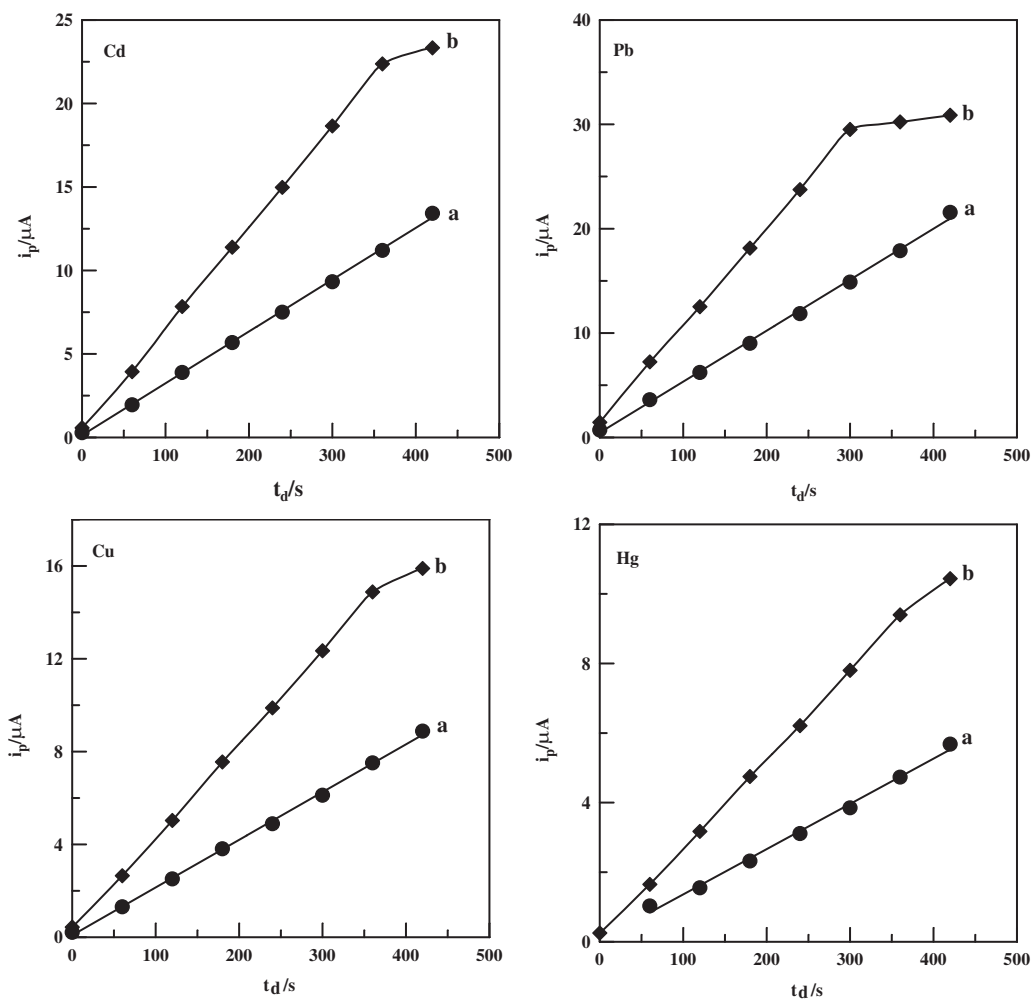


Figure 4. SW-AS voltammetric peak current magnitudes (i_p) as a function of the preconcentration time (t_d) for solutions containing 0.05 mg L⁻¹ (a) and 0.1 mg L⁻¹ (b) of each of Cd(II), Pb(II) and Cu(II) in 0.1 M HCl following preconcentration by electrolytic deposition at -0.90 V at the 10% MMT-Ca modified CPE. Other parameters are as those given in Figure 3.

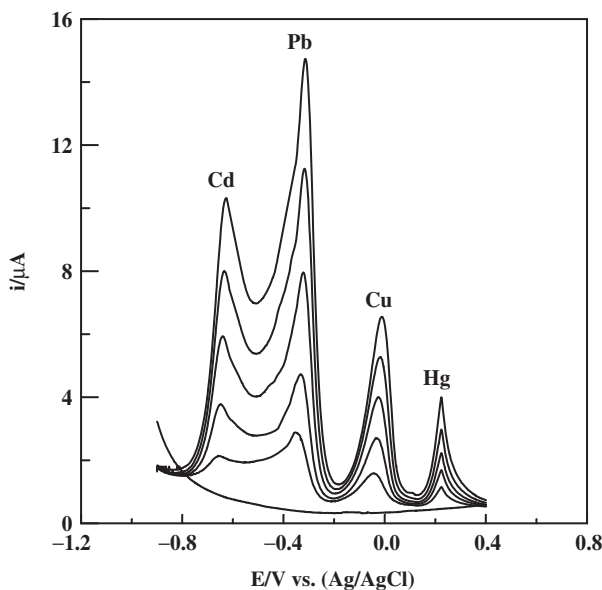


Figure 5. SW-AS voltammograms for successive additions of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl solution, following preconcentration by electrolytic deposition at -0.90 V for 300 s at the 10% MMT-Ca modified CPE. Each addition affected $10 \mu\text{g L}^{-1}$ of each metal ion. Other conditions are as those given in Figure 3.

magnitudes of 0.05 mg L^{-1} of each of Cd(II), Pb(II), Cu(II) and Hg(II) increased linearly with preconcentration time over the investigated period. For 0.1 mg L^{-1} of each of Cd(II), Pb(II), Cu(II) and Hg(II), the peak current magnitudes showed linear increase up to 300–360 s. At longer preconcentration periods, saturation of the MMT-Ca modified CPE surface by the deposited metals 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.

3.5 Validation of the method

3.5.1 Linearity

SW-AS voltammograms of various concentrations of the investigated metal ions were recorded under the optimum procedural conditions (Figure 5). Rectilinear relations between peak current (i_p) and concentrations (C) of each of Cd(II), Pb(II), Cu(II) and Hg(II) were obtained over the ranges indicated in Table 2. The results shown in Table 2 confirmed the reliability of the described SW-AS voltammetry method for determination of the investigated metal ions within the indicated linear ranges.

3.5.2 Limits of detection and quantitation

Limits of detection (LOD) and quantitation (LOQ) of each of Cd(II), Pb(II), Cu(II) and Hg(II) by applying the described SW-AS voltammetry method were estimated using the expression: $k \cdot S.D/b$ [35], 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 plot. The achieved

Table 2. Characteristics of the calibration plots of the described SW-AS voltammetric method for simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl solution at the constructed 10% (w/w) MMT-Ca modified CPE; $E_d = -0.90$ V and $t_d = 300$ s.

Metal ion	Linearity range ($\mu\text{g L}^{-1}$)	Least square equation*			LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)
		Intercept (μA)	Slope ($\mu\text{A}/\mu\text{g L}^{-1}$)	(r)		
Cd(II)	1.8–120	0.102	0.216	0.996	0.54	1.80
Pb(II)	1.0–100	0.175	0.324	0.998	0.30	1.00
Cu(II)	2.5–130	0.049	0.129	0.999	0.75	2.50
Hg(II)	3.5–150	0.009	0.078	0.999	1.05	3.50

Note: *Average of three determinations.

LOD and LOQ values (Table 2) following preconcentration of the investigated metal ions by electrolytic deposition at the MMT-Ca modified CPE for 300 s under the optimum procedural conditions confirmed the reliability of the described method for ultra-trace determination of these metal ions. The achieved limits of detection of Cd(II) $0.54 \mu\text{g L}^{-1}$ ($4.80 \times 10^{-9} \text{ mol L}^{-1}$), Pb(II) $0.30 \mu\text{g L}^{-1}$ ($1.45 \times 10^{-9} \text{ mol L}^{-1}$), Cu(II) $0.75 \mu\text{g L}^{-1}$ ($1.18 \times 10^{-8} \text{ mol L}^{-1}$) and Hg(II) $1.05 \mu\text{g L}^{-1}$ ($5.24 \times 10^{-9} \text{ mol L}^{-1}$) indicated the high sensitivity of the described SW-AS voltammetry method over those previously reported for determination of Pb(II) ($6 \times 10^{-9} \text{ mol L}^{-1}$) [10], Cu(II) ($4 \times 10^{-8} \text{ mol L}^{-1}$) [4] and Hg(II) ($4.98 \times 10^{-8} \text{ mol L}^{-1}$) [7] at the MMT modified CPE. Besides, Cd(II) was never determined at the MMT-Ca modified CPE. This means that the described method provides a novel scheme for the assay of Cd(II), Pb(II), Cu(II) and Hg(II) simultaneously at 10% MMT-Ca modified CPE with a very good sensitivity compared with those previously cited methods using various kinds of modified electrodes and even applying different voltammetric techniques (Table 1).

3.5.3 Accuracy and precision

Accuracy and precision of the described SW-AS voltammetry method for simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl at the MMT-Ca modified CPE were estimated as recovery (%R) and standard deviation (%SD) by analysing reference standard solutions of $10 \mu\text{g L}^{-1}$ of each of the investigated metal ions for five replicate times (Table 3). Mean percentage recoveries and standard deviations obtained by applying the calibration plot and standard addition methods (Table 3) indicated the accuracy and precision of the described SW-AS voltammetry method for simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) at the MMT-Ca modified CPE. Moreover, the results obtained by the described stripping method, applying calibration plot method, were statistically compared with those obtained by flame atomic absorption spectrometry method (FAAS). Since the calculated value of F -statistic does not exceed the theoretical value (Table 3), there was no significant difference between the described SW-AS voltammetry and FAAS methods with respect to reproducibility [36]. Also, no significant differences were noticed between the two methods regarding accuracy and precision as revealed by t -values [36], Table 3.

Table 3. Accuracy and precision of the described SW-AS voltammetry method as recovery (%R) and standard deviation (%SD) for simultaneous determination of $10 \mu\text{g L}^{-1}$ of each of Cd(II), Pb(II), Cu(II) and Hg(II) in 0.1 M HCl solution at the constructed 10% (w/w) MMT-Ca modified CPE.

Metal ions	SW-ASV method (% R \pm SD)		FAAS method (%R \pm SD) calibration curve	F-statistic	t-test
	Calibration curve	Standard addition			
Cd(II)	99.55 \pm 1.02 97.78 \pm 1.51*	98.95 \pm 0.77	99.21 \pm 1.03	0.98	0.53
Pb(II)	100.04 \pm 0.57 99.31 \pm 1.03*	99.32 \pm 0.53	101.23 \pm 1.13	3.93	2.10
Cu(II)	99.75 \pm 0.38 98.21 \pm 0.70*	100.13 \pm 0.09	99.83 \pm 0.84	4.89	0.19
Hg(II)	99.88 \pm 0.24 101.36 \pm 1.52*	100.07 \pm 0.22	–	–	–

Notes: *Obtained from a solution of each metal ion present alone.

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

3.5.4 Interferences

Interferences in multi-elemental analysis may be caused either by the formation of intermetallic compounds between the investigated metal ions itself or by foreign inorganic and/or organic species which may present in the analysed solutions. The possibility of intermetallic compounds formation was investigated by applying the described method for the assay of reference standard samples of $10 \mu\text{g L}^{-1}$ of each of Cd(II), Pb(II), Cu(II) and Hg(II) present individually in the solution and mixed with the same concentration of the other investigated metal ions (Table 3). The results shown in Table 3 indicated no intermetallic compound were formed between the elements deposited at the 10% MMT-Ca modified CPE under the optimal operational conditions.

Interferences from some foreign cations (K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Bi^{3+} , Sb^{3+} , Se^{4+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Fe^{3+} and NH_4^+), inorganic anions (HCO_3^- , Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) and organics (e.g. ascorbic acid) to the assay of $10 \mu\text{g L}^{-1}$ of each of Cd(II), Pb(II), Cu(II) and Hg(II) by the described SW-AS voltammetry method were evaluated. As shown in Table 4, the investigated foreign inorganic and organic species have insignificant effect on the peak current magnitudes of $10 \mu\text{g L}^{-1}$ of each of Cd(II), Pb(II), Cu(II) and Hg(II) since the relative error values are below 6%. Effect of different concentrations of EDTA (as a complexing agent) on the peak current magnitudes of the investigated metal ions was also evaluated. Analysis of $10 \mu\text{g L}^{-1}$ of each of Cd(II), Pb(II), Cu(II) and Hg(II) solution in the presence of $1 \times 10^{-5} \text{ mol L}^{-1}$ EDTA indicated the suppression of their peak currents to 51.2%, 63.6%, 56.4% and 92.5%, respectively. Interference from Triton X-100 (as a non-ionic surfactant) up to 0.003% 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. Influence of surfactants, if present in the analysed water samples, can be completely eliminated by a thorough mineralisation of water sample prior to the analysis.

Table 4. Interferences of some inorganic species in the simultaneous determination of $10 \mu\text{g L}^{-1}$ of each of Cd(II), Pb(II) and Cu(II) in 0.1 M HCl solution at the constructed 10% (w/w) MMT-Ca modified CPE by the described SW-AS voltammetry method.

Foreign species	Tolerance level* (mg L^{-1})
Na^+ , Mg^{2+} , Ca^{2+} , HCO_3^-	100
K^+ , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-}	50
Mn^{2+} , Fe^{3+} , Ascorbic acid	5
NH_4^+	1
Al^{3+} , Bi^{3+} , Sb^{3+} , Se^{4+} , Zn^{2+} , Ni^{2+} , Co^{2+}	0.1

Note: *For 6% error.

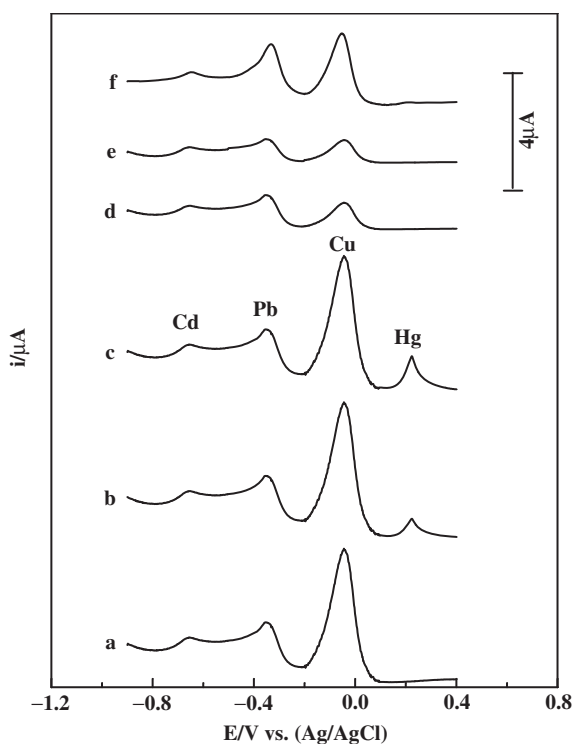


Figure 6. SW-AS voltammograms of various water samples: tap water (a), tap water spiked with $10 \mu\text{g L}^{-1}$ (b) and $20 \mu\text{g L}^{-1}$ Hg(II) (c), Baraka[®] (d) and Nahl[®] (e) bottled natural water and fresh coastal seawater (f) recorded in 0.1 M HCl, following preconcentration by electrolytic deposition at -0.90 V for 300 s at the 10% MMT-Ca modified CPE; other conditions are as those given in Figure 3.

3.6 Analysis of various water samples

The described SW-AS voltammetry method was successfully applied for simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) in tap water, some bottled natural water samples and a coastal seawater sample, at the constructed 10% MMT-Ca modified CPE (Figure 6). FAAS was used as a comparative method for determination of the investigated

Table 5. Simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) in some tap and bottled natural water samples by the described SW-AS voltammetry method at the constructed 10% (w/w) MMT-Ca modified CPE ($t_d = 300$ s) and flame atomic absorption spectrometry (FAAS).

Sample	Cd(II)/ $\mu\text{g L}^{-1}$		Pb(II)/ $\mu\text{g L}^{-1}$		Cu(II)/ $\mu\text{g L}^{-1}$	
	SW-AS	FAAS	SW-AS	FAAS	SW-AS	FAAS
Tap water	3.4 ± 0.4	*	4.9 ± 0.6	*	36.2 ± 0.9	33 ± 1.6
<i>Bottled water</i>						
Aquafina [®]	*	*	1.9 ± 0.3	*	3.7 ± 0.3	2 ± 0.5
Aquasiwa [®]	*	*	1.2 ± 0.4	2 ± 0.7	3.6 ± 0.6	4 ± 0.7
Baraka [®]	2.4 ± 0.1	2 ± 0.4	3.4 ± 0.5	2 ± 0.9	6.9 ± 0.6	8 ± 1.2
Hayat [®]	*	*	1.8 ± 0.3	*	2.0 ± 0.5	3 ± 0.6
Nahl [®]	2.5 ± 0.2	3 ± 0.7	2.1 ± 0.7	3 ± 0.5	6.0 ± 0.4	8 ± 1.0
Safi [®]	*	*	1.7 ± 0.2	*	5.5 ± 0.3	8 ± 0.7
Siwa [®]	*	*	1.3 ± 0.1	*	*	*
Seawater	2.3 ± 0.6	3 ± 0.5	5.2 ± 0.8	6 ± 1.0	15.3 ± 1.1	15 ± 1.5

Notes: *Under limit of detection.

Hg(II) was not detected by both the described SW-ASV and FAAS methods.

Table 6. Analysis of tap water sample spiked with various concentrations of Hg(II) by the described SW-AS voltammetric method at the constructed 10% (w/w) MMT-Ca modified CPE.

Spiked ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Relative error (RE%)
5	4.88	-2.4
10	10.16	+1.6
15	15.31	+2.1
20	20.46	+2.3

metal ions in the same water samples. Comparison of the results obtained by the described SW-AS voltammetry method with those obtained by FAAS (Table 5) revealed the capability of the described stripping voltammetry method for simultaneous determination of Cd(II), Pb(II) and Cu(II) at the constructed 10% MMT-Ca modified CPE in nano-concentration levels. Since the analysed water samples were found free from mercury (II), tap water samples spiked with different concentrations of Hg(II) was analysed by the described SW-AS voltammetry method at the 10% MMT-Ca modified CPE and the obtained results (Table 6) indicated the reliability of the method for determination of Hg(II) in water samples when present.

4. Conclusion

A simple and efficient montmorillonite calcium modified carbon paste electrode (10% (w/w) MMT-Ca modified CPE) was constructed for simultaneous trace determination of Cd(II), Pb(II), Cu(II) and Hg(II) in various water samples. The constructed MMT-Ca

modified CPE significantly enhances the stripping peak current magnitudes of the investigated metal ions, compared to the bare CPE, due to the large cation-exchange capacity and the strong adsorptive property of montmorillonite-Ca clay. Therefore, a fully validated simple, sensitive, selective and precise square-wave anodic stripping voltammetric method was developed for the simultaneous trace determination of Cd(II), Pb(II), Cu(II) and Hg(II) in tap water, bottled natural water and seawater samples using the constructed 10% MMT-Ca modified CPE.

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