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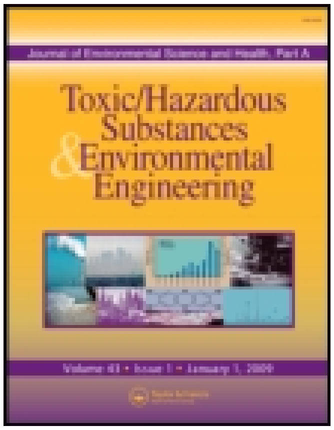

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Optimization of simultaneous electrochemical determination of Cd(II), Pb(II), Cu(II) and Hg(II) at carbon nanotube-modified graphite electrodes

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Optimization of simultaneous electrochemical determination of Cd(II), Pb(II), Cu(II) and Hg(II) at carbon nanotube-modified graphite electrodes

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The health of the environment is worsening every day. Monitoring of potentially toxic elements and remediation of environmental pollution are necessary. Therefore, the research and development of simple, inexpensive, portable and effective sensors is important. Electrochemistry is a useful component of the field of environment monitoring. The present study focuses on evaluating and comparing three types of electrodes (PIGE, PIGE/MWCNT/HNO_3 and PIGE/MWCNT/EDTA/HNO_3) employed for the simultaneous electrochemical determination of four potentially toxic elements: Cd(II), Pb(II), Cu(II) and Hg(II). Cyclic voltammograms were measured in an acetate buffer. The LOD, LOQ, the standard and relative precisions of the method and a prediction intervals were calculated (according to the technical procedure DIN 32 645) for the three electrodes and for each measured element. The LOD for PIGE/CNT/HNO_3 (the electrode with narrowest calculated prediction intervals) was 2.98×10^{-7} mol L^{-1} for Cd(II), 4.83×10^{-7} mol L^{-1} for Pb(II), 3.81×10^{-7} mol L^{-1} for Cu(II), 6.79×10^{-7} mol L^{-1} for Hg(II). One of the benefits of this study was the determination of the amount of Hg(II) in the mixture of other elements.

Keywords: Paraffin impregnated graphite electrode, carbon nanotubes, potentially toxic elements.

Introduction

The rapid development of industry increases environmental pollution through the introduction of potentially toxic elements (PTE), among which Cu, Cd, Hg and Pb still hold unpopular primacy. These elements affect humans and the environment in different ways. Copper concentrations in vegetation tend to be relatively constant regardless of the amount of copper in soil, as copper is an essential element in plant nutrition. The same observation is true for most animals,[1] in which copper is essential for the development and activity of the central nervous system (CNS) and many other biochemical processes. Absorption of excess copper by humans results in Wilson´s Disease, in which excess copper is deposited in the brain, skin, liver, pancreas and myocardium.[1]

Inhalation is the primary source of cadmium intoxication. It accumulates mainly in the kidneys, liver, lungs and pancreas. Chronic cadmium poisoning produces proteinuria and causes the formation of kidney stones.[1] Compared to other metals, cadmium is relatively water soluble and, therefore, also more mobile; it tends to bioaccumulate. Lead occurs in both organic and inorganic forms, namely as lead salts with varying water solubility. Although organometallic lead species, due to their solubility, are highly neurotoxic in situations of acute exposure, chronic low-level exposure to inorganic lead constitutes a more serious occupational and public health risk. A broad spectrum of biomedical effects has been associated with lead, the more critical of which are related to heme biosynthesis, erythropoiesis and nervous system function [1]

The classic symptoms of exposure to metallic mercury vapor result from the effect on the CNS, while Hg(I) and Hg(II) salts target the kidneys. There is general agreement that the differences in toxicity among inorganic mercury compounds are largely determined by their physical properties and redox potentials. The ability of mercury to form stable organic compounds with alkyl groups, which are commonly called methyl mercury, poses a significant public health risk.[1] Methyl mercury is particularly toxic to animals because it can readily pass the blood-brain barrier, causing injury to the cerebellum and cortex; the clinical symptoms of this damage are numbness, uncoordinated movements and blurred vision.[2]

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Most instrumental multi-elemental detection methods are very expensive and sometimes do not offer sufficient sensitivity for the accurate determination of elements at the ultra-trace concentrations often encountered in environmental samples.[3] Flame atomic absorption spectrometry (FAAS),[4,5] graphite furnace atomic absorption spectrometry (GFAAS),[6] inductively coupled plasma optical emission spectrometry (ICP-OES)[7–9] and inductively coupled plasma mass spectrometry (ICP-MS)[10,11] are often used to measure trace elements. Data reported in the literature[12] give a detailed comparison of the limit of detection, precision, interferences, analysis time, sample preparation, operation skills and operation costs of the individual techniques.

Electrochemical techniques, especially voltammetry, are also applicable to trace element determinations, and the widespread use of these techniques is attributed to their sensitivity, speciation capability and low cost.[13] The use of electrochemical methods in combination with a suitable working electrode appears to be a promising, fast and reliable approach to evaluating metal concentrations in environmental samples. Increased attention has been paid to the development of nanomaterials. Their prominent feature is a large specific surface area, allowing analyte detection at a greater number of binding sites than their bulk counterparts. A wide range of nanoscale materials is currently used in the development of electrochemical sensors.

Among these materials, carbon nanotubes (CNT) are very common due to their unique electronic, chemical and mechanical properties.[14] The application of CNT in electrochemical sensors benefits from their modifications that make them specific for detection of selected molecules through electron transfer reactions.[15,16] The production of specific functional groups on the surface (mainly oxygen-containing groups) can greatly increase the electron transfer rate.[17] Modified nanoelectrodes exhibit relevant properties such as high activity, high selectivity and strong adsorption capability, and they have become one of the top research focuses in modern electrochemistry. These nanoelectrodes allow rapid analysis speeds, exhibit good selectivity and offer high sensitivity in the detection of metal ions.[18]

A number of recent publications refer to heavy metal detection using carbon nanostructured materials as electrodes or electrode modifiers. A review involving the use of nanomaterials for the electrochemical detection of heavy metals was recently published by Aragay and Merkoci.[19] Literature on voltammetric studies provides information on the determination of individual metals[20-22] and the simultaneous determination of a metal pair[23-26] or a metal trinity[27,28] and, less commonly, of four metals.[29] The selection of the working electrode plays a key role in the effectiveness of the detection technique. Replacement of the conventional mercury electrode, despite its advantages, is now a common practice in electrochemical laboratories worldwide. The most commonly used alternative material is carbon, which forms the matrix of chemically modified electrodes (CME). Carbon is used for electrochemical applications in a variety of forms exhibiting different chemical and electrochemical properties.

The vast majority of voltammetric studies in the literature used nanomaterials based on glassy carbon (GCE).[30-33] Wang et al. described the modification of a GCE using polyaniline film[23] and polyaniline/multiwalled carbon nanotubes[33] for the detection of Cd(II) and Pb(II) ions using square wave anodic stripping voltammetry (SWASV); the coated electrodes performed better than bare GCEs. Afkhami et al.[26] constructed modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and 3-(4-methoxybenzylideneamino)-2-thioxothiazolodin-4-one for the simultaneous determination of trace amounts of Hg(II) and Pb(II) also using SWASV.

Under optimal conditions, the detection limits, calculated as three times the background noise, were 9.0×10^{-4} and 6.0×10^{-4} μmol L^{-1} for Hg(II) and Pb(II) with a 90 s preconcentration, respectively. A simple and economical approach for mass-producing graphene nanosheets (GNSs) is based on the thermal expansion of graphite oxide powder developed by Wang et al.,[34] and the use of GNSs for the detection of different trace heavy metal ions was discussed. A remarkably low detection limit of 10^{-11} mol L^{-1} for Pb(II) was achieved. Gong et al.[35] demonstrated a new highly sensitive and selective Hg(II) sensor with a graphene-based nanocomposite film as the enhanced sensing platform.

The detection limit of such a nanostructured composite film platform was found to be as low as 6 ppt ($S/N = 3$), which is well below the limits set by the World Health Organization. One advantage to screen-printed electrodes (SPEs) is that they do not need to be polished; they are also well known for their low-cost, availability, miniaturized size and ability to connect to portable instrumentation.[36] A method was developed for the simultaneous determination of Pb(II), Cd(II), and Zn(II) at low g L^{-1} concentration levels using sequential injection analysis-anodic stripping voltammetry (SIA-ASV) and screen-printed carbon nanotubes electrodes (SPCNTE).[37] A bismuth film was prepared by in situ plating of bismuth on the screen-printed carbon nanotube electrodes. The detection limits (S_{bl} /S = 3) were 0.2 g L^{-1} for Pb(II), 0.8 g L^{-1} for Cd(II) and 11 g L^{-1} for Zn(II). The application of SPEs was also described by Arduini et al.[38] and Aragay et al.[39] with a focus on Hg(II) and heavy metals determination, respectively. Recently, several metals have been tested for their capacity to replace mercury as an electrode (e.g., bismuth, gold, silver, antimony). Arduni et al.[40] described the use of electrochemical sensors for lead detection focusing on sensors modified with bismuth. In our previous study,[41] several binders were compared for the modification of paraffin impregnated graphite electrodes (PIGEs) using carbon nanotubes. Based on the excellent chemometric characteristics, three electrodes were chosen for use in this study. The aim of this study is to evaluate the simultaneous voltammetric determination of four PTE at a relatively abundant electrode material: the PIGE electrode. The results from the PIGE electrodes were satisfactory in terms of signal quality, detection limit and costs, thus increasing the popularity of PIGEs for routine voltammetric PTE determination.

Material and methods

All of the electrochemical experiments were performed using an Autolab Potentiostat/Galvanostat, Model 302 N (Metrohm Autolab B.V., Netherlands). A conventional three-electrode system was used with unmodified and modified PIGEs (diameter: 4 mm) as the working electrode, a saturated Ag/AgCl (3 mol L^{-1} KCl) as the reference electrode and a Pt wire as the counterelectrode. A standard solution containing a mixture of Cu(II), Pb(II), Cd(II) and Hg(II) with concentrations of 1×10^{-4} mol L^{-1} for each element was freshly prepared before each measurement. Cyclic voltammetry experiments were performed in a potential range from 1.0 V to −1.0 V vs. Ag/AgCl. The scan rate was 50 mV s^{-1}. The voltammetric behavior was studied in 0.2 and 1 mol L^{-1} acetic buffer. After each measurement, potentiostatic treatment of the electrode was performed at a potential of 300 mV vs. Ag/AgCl for 60 sec to dissolve potential traces of elements undissolved in voltammetric mode. All of the reagents used were analytically pure, and all of the solutions were prepared with twice-distilled water. Electrolytes were deoxygenated using nitrogen gas passing through a solution of pyrogallol. During the measurements, a gentle gas flow was kept above the electrolyte solution.

Multi-walled carbon nanotubes (MWCNT) (Sigma-Aldrich, St. Louis, MO, USA, outer diameter: 40–60 nm, inner diameter: 5–10 nm, length: 0.5–500 µm, purity: 95+%) were functionalized with –COOH groups (carboxylated under reflux in a mixture of concentrated sulphuric and nitric acid) and subsequently used to modify the PIGE surface. One suspension for modification of the electrode (marked as PIGE/MWCNT/HNO_3 throughout the text) was prepared by dispersing CNTs in concentrated hydrochloric acid (1:1) and sonicating for 20 min. The second type of suspension for modification of the electrode (marked as PIGE/MWCNT/EDTA/HNO_3) was made by dispersing CNTs in EDTA (1 mmol L^{-1}), followed by filtering out the CNTs, rinsing in distilled water and re-dispersion in concentrated nitric acid and sonicating for 20 min.

PIGEs were modified by drop-casting the CNT suspension on the prepared surface. A total suspension volume of 40 µl on the electrode surface was added by pipetting sequential 20 µl volumes; after each addition, the sample was left to dry at room temperature. The modification of the PIGEs consisted of the addition of a CNT dispersion in nitric acid (PIGE/MWCNT/HNO_3). Figure 1 shows the surface of modified electrode, where disarranged carbon nanotubes could be seen.

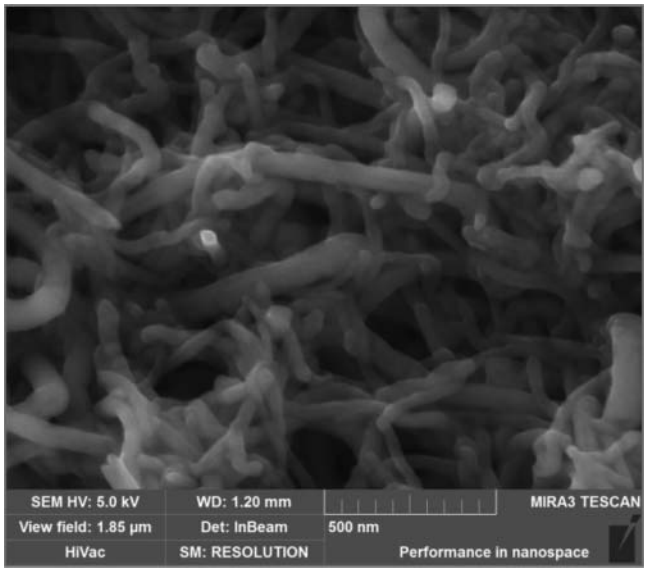

Fig. 1. SEM image of PIGE surface modified with a 40-µl MWCNT/HNO_3 suspension.

The chemometric characteristics of data measurements were calculated according to the technical procedure DIN 32 645. The calibration line "y = bx + a" was used. The standard precision of the method, s_{x0}, was expressed according to Eq. 1:

$$s_x = \frac{s_y}{b} \tag{1}$$

where s_y is the residual standard deviation and b is the slope of the regression line.

The relative accuracy of the method, V_{x0}, was defined as a ratio of the standard precision of the method, s_{x0}, and the mean of the concentration region (the coordinates of the regression line x) according to Eqs. 2 and 3:

$$V_{x_0} = \frac{s_{x_0}}{\bar{x}} 100\% \tag{2}$$

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N} \tag{3}$$

in which N designates the number of calibration points.

The detection limit (LOD) and the limit of quantification (LOQ) were calculated according to Equations 4 and

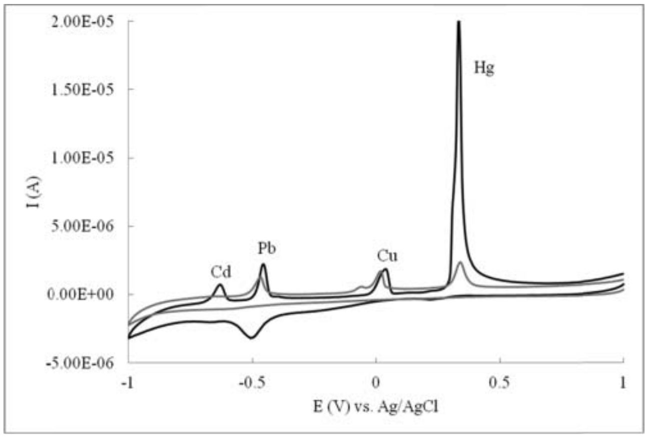

Fig. 2. Cyclic voltammogram of the simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) concentrations (c = 5.66 × 10^{-6} mol L^{-1}) at a PIGE in 0.2 mol L^{-1} (black line) and 1 mol L^{-1} (grey line) acetate buffer.

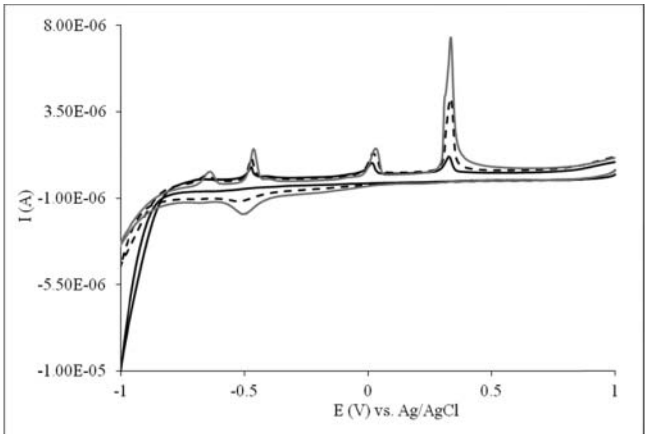

Fig. 3. Cyclic voltammogram of simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) concentrations at a PIGE electrode in 0.2 mol L^{-1}, c = 1.96 × 10^{-6} mol L^{-1} (black line), c = 2.91 ×10^{-6} mol L^{-1} (dashed line) and c = 3.85×10^{-6} mol L^{-1} (grey line).

5, respectively:

$$LOD = \frac{s_y}{b} t_{f,\alpha} \sqrt{\frac{1}{\hat{N}} + \frac{1}{N} + \frac{\bar{x}^2}{Q_{xx}}} \tag{4}$$

$$LOQ = k\frac{s_y}{b} t_{f,\alpha} \sqrt{\frac{1}{\hat{N}} + \frac{1}{N} + \frac{(kLOD - \bar{x})^2}{Q_{xx}}} \tag{5}$$

where N is the number of calibration points, $\hat{N}$ is the number of repetitions for one calibration point, k is equal to 3, and $t_{f,\alpha}$ is the critical value of the Student distribution and depends on the degrees of freedom (f = N-2) and the significance level, α (0.05). The residual standard deviation, s_y, and parameter Q_{xx} were obtained according to Eqs. 6 and 7, respectively:

$$s_y = \sqrt{\frac{\sum [y_i - (bx_i + a)]^2}{N-2}} \tag{6}$$

$$Q_{xx} = \sum_{i=1}^{N} x_i^2 - \frac{\left(\sum_{i=1}^{N} x_i\right)^2}{N}. \tag{7}$$

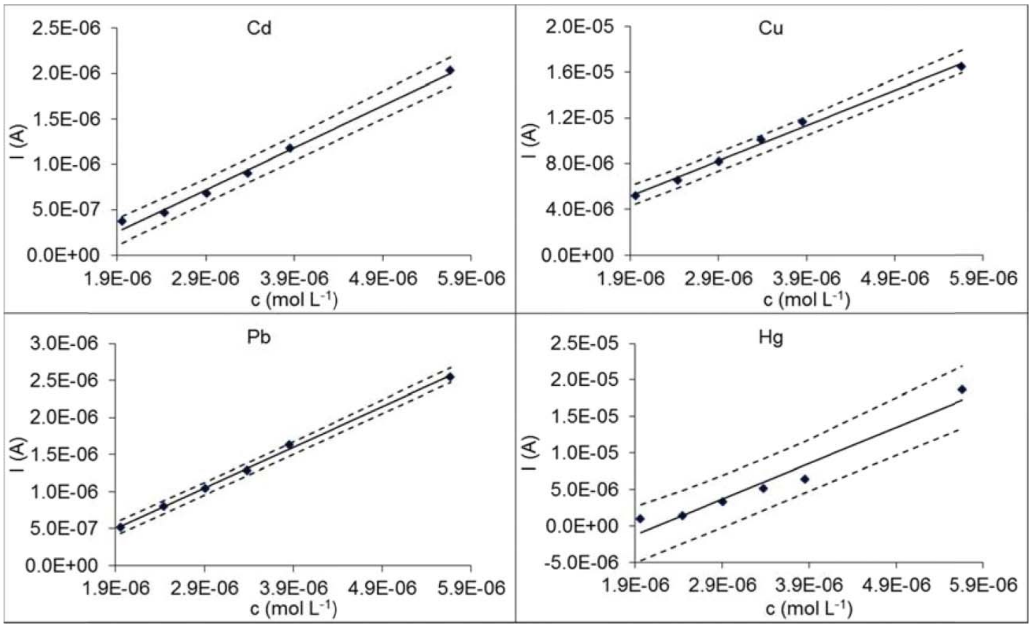

Fig. 4. Prediction intervals for unmodified PIGE for Cd(II), Cu(II), Pb(II) and Hg(II).

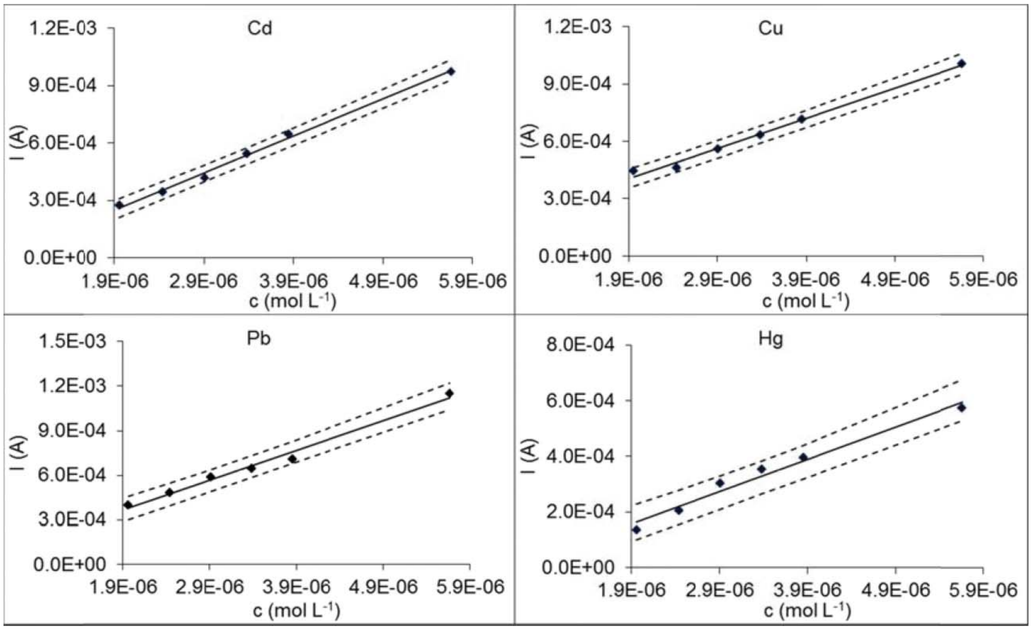

Fig. 5. Prediction intervals for modified PIGE/MWCNT/HNO_3 for Cd(II), Cu(II), Pb(II) and Hg(II).

The equation for calculation of the prediction intervals was published in our previous study[41] and is given as Eq. 8:

$$y_{1,2} = (bx + a) \pm s_y t_{f,\alpha} \sqrt{\frac{1}{N} + \frac{1}{\hat{N}} + \frac{(x - \bar{x})^2}{Q_{xx}}}. \qquad (8)$$

Results and discussion

To select the appropriate supporting electrolyte, acetate buffer solutions with two concentrations (0.2 and 1 mol L^{-1}) were tested. A supporting electrolyte must satisfy two conditions: (1) it must have a sufficient buffering capacity, and (2) it must produce a recognizable signal for each of the four studied elements. As seen in the cyclic voltammograms measured using unmodified PIGEs (Fig. 2), the

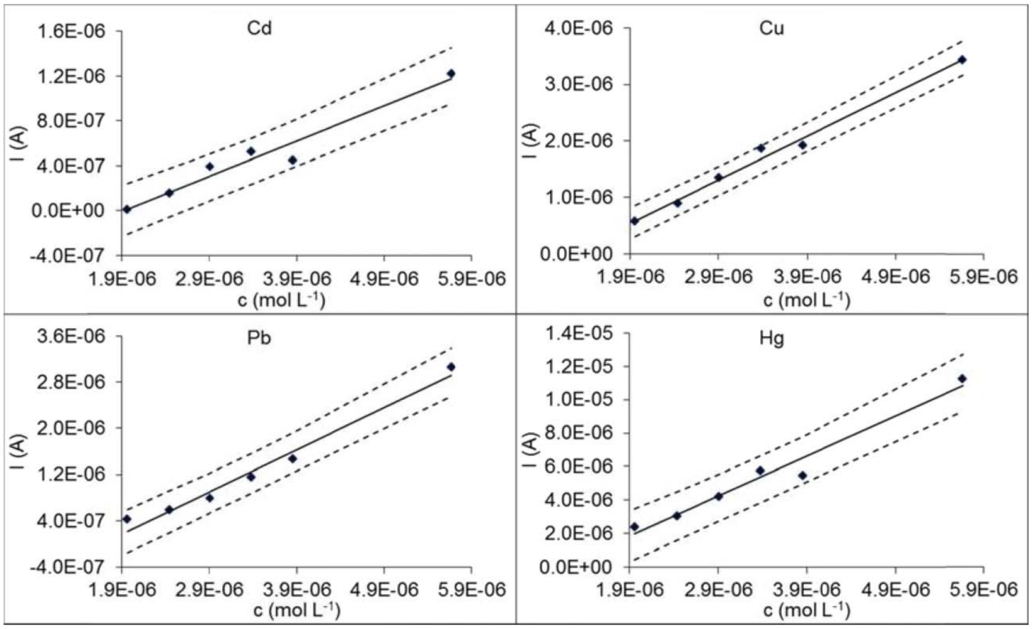

Fig. 6. Prediction intervals for modified PIGE/MWCNT/EDTA/HNO_3 for Cd(II), Cu(II), Pb(II) and Hg(II).

second condition was not met in the electrolyte with a higher acetate concentration.

Therefore, a 0.2 mol L^{-1} acetate buffer solution was used for both unmodified and CNT-modified PIGEs. The typical oxidation peaks for Cd, Pb, Cu and Hg could be seen at the potentials −636, −479, 30 and 307 mV vs. Ag/AgCl, respectively. The current response of Hg oxidation at the bare PIGE overshadowed other elements. Calibration lines in a concentration range from 1.96×10^{-6} mol L^{-1} to 5.66×10^{-6} mol L^{-1} were obtained by the standard addition method. Figure 3 shows that current responses increase with increasing element concentrations.

Modification of PIGEs using CNTs suspended in nitric acid increased the current responses (by approximately two orders of magnitude, to the milliamp scale) for all of the elements, as observed from the comparison of Figure 4 and Figure 5. The use of EDTA in the PIGE modification process did not yield the expected improvement of current responses compared to the responses observed for the PIGE/CNT/HNO_3 electrode, and voltammograms measured at this electrode exhibited similar peak heights to those recorded at the bare PIGE (Fig. 6).

In the CNT-modified sensor preparation process, the current response peak height was only one of six monitored parameters. Other measured or calculated chemometric characteristics are used for describing the quality and/or improvement of basic electrode materials. The LOD, LOQ, standard and relative precision of the method as a prediction intervals were calculated for these three electrodes and for each measured element. It is evident from the results in Table 1 that the above-mentioned characteristics varied from case to case.

The LOD values ranged from 1.98×10^{-7} mol L^{-1} to 8.23×10^{-7} mol L^{-1}. Modification of PIGE using the carbon nanotubes suspension produced notable improvements in the current responses and in the validation characteristics such as the relative precision of the method, V_{x0}. For PIGE/MWCNT/HNO_3, the V_{x0} ranged from 3.07% to 7.00%. In some cases, the value of V_{x0} was smaller for unmodified PIGEs compared to modified electrodes. On a larger scale, the modified PIGE/MWCNT/HNO_3 appears to be optimal for the simultaneous detection of PTEs.

All of the electrodes exhibited narrow prediction intervals, with small deviations from element to element

Table 1. Validation characteristics for unmodified and modified PIGE for Cd(II), Pb(II), Cu(II) and Hg(II).

Element	*Type of electrode*	*Limit of detection (LOD) mol L^{-1}*	*Limit of quantification (LOQ) mol L^{-1}*	*Standard method precision (s_{x0}) mol L^{-1}*	*Relative method precision (V_{x0})*
Cd(II)	PIGE	3.97×10^{-7}	1.14×10^{-6}	1.32×10^{-7}	3.91%
	PIGE/MWCNT/HNO_3	2.98×10^{-7}	9.50×10^{-7}	1.03×10^{-7}	3.07%
	PIGE/MWCNT/EDTA/HNO_3	8.23×10^{-7}	1.90×10^{-6}	3.03×10^{-7}	9.00%
Pb(II)	PIGE	1.98×10^{-7}	6.79×10^{-7}	6.89×10^{-8}	2.05%
	PIGE/MWCNT/HNO_3	4.83×10^{-7}	1.35×10^{-6}	1.67×10^{-7}	4.98%
	PIGE/MWCNT/EDTA/HNO_3	6.26×10^{-7}	1.58×10^{-6}	2.17×10^{-7}	6.46%
Cu(II)	PIGE	7.96×10^{-7}	1.80×10^{-6}	2.76×10^{-7}	8.21%
	PIGE/MWCNT/HNO_3	3.81×10^{-7}	1.14×10^{-6}	1.32×10^{-7}	3.92%
	PIGE/MWCNT/EDTA/HNO_3	2.60×10^{-7}	8.25×10^{-7}	9.03×10^{-8}	2.68%
Hg(II)	PIGE	6.48×10^{-7}	1.61×10^{-6}	2.25×10^{-7}	6.68%
	PIGE/MWCNT/HNO_3	6.79×10^{-7}	1.65×10^{-6}	2.36×10^{-7}	7.00%
	PIGE/MWCNT/EDTA/HNO_3	7.68×10^{-7}	1.76×10^{-6}	2.66×10^{-7}	7.91%

(Figs. 4–6). The differences among the current responses using the same analyte concentration favor the electrodes modified with carbon nanotubes suspended in concentrated nitric acid (PIGE/MWCNT/HNO_3) for applications in electroanalysis.

Conclusions

The paraffin impregnated graphite electrode (PIGE) represents a novel alternative to various types of solid electrodes employing carbon nanotubes at the electrode surface. In recent years, PIGEs were discovered and used as an abrasive electrode for the direct study of immobilized solid microparticles. In this article, simultaneous electrochemical detection of Cd(II), Pb(II), Cu (II) and Hg(II) was studied at bare PIGEs and two CNT-modified PIGEs. The peak height, prediction intervals and four validation characteristics were evaluated and compared. The PIGE/MWCNT/HNO_3 electrode set-up provides the optimal validation characteristics and highest current response. Further research is planned using this electrode for the construction of other electrochemical sensors, namely reproducible CNT-modified PIGEs for the determination of palladium and platinum in the environmental samples.

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References

[1] Duffus, J.H.; Worth, H.G.J. Metals. In *Fundamental Toxicology for Chemists*; Duffus, J.H.; Worth, H.G.J., Eds.; The Royal Society of Chemistry: Cambridge, UK, 1996; 175–176.

[2] Bockris, J.O'M. Mercury in the environment. In *Environmental Chemistry*; Bockris J.O′M., Ed.; Plenum Press: New York, NY, 1977; 452–460.

[3] Wasiak, W.; Ciszewska, W.; Ciszewskib, A. Hair analysis. Part 1: Differential pulse anodic stripping voltammetric determination of lead, cadmium, zinc and copper in human hair samples of persons in permanent contact with a polluted workplace environment. Anal. Chim. Acta **1996**, *335*, 201–207.

[4] Durana, C.; Gundogdua, A.; Bulutb, V.N.; Soylakc, M.; Elcid, L.; Sentürka, H.B.; Tüfekcia, M. Solid-phase extraction of Mn(II), Co (II), Ni(II), Cu(II), Cd(II) and Pb(II) ions from environmental samples by flame atomic absorption spectrometry (FAAS). J. Hazard. Mater. **2007**, *146*, 347–355.

[5] Chen, J.; Teo, K.Ch. Determination of cadmium, copper, lead and zinc in water samples by flame atomic absorption spectrometry after cloud point extraction. Anal. Chim. Acta **2001**, *450*, 215–222.

[6] Nowka, R.; Marr, I.L.; Ansari, T.M.; Müller, H. Direct analysis of solid samples by GFAAS – determination of trace heavy metals in barytes. Fresen. J. Anal. Chem. **1999**, *364*, 533–540.

[7] Sen, I.; Shandil, A.; Shrivastava, V.S. Study for determination of heavy metals in fish species of the River Yamuna (Delhi) by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Adv. Appl. Sci. Res. **2011**, *2*, 161–166.

[8] Uysala, K.; Emreb, Y.; Kösea, E. The determination of heavy metal accumulation ratios in muscle, skin and gills of some migratory fish species by inductively coupled plasma-optical emission spectrometry (ICP-OES) in Beymelek Lagoon (Antalya/Turkey). Microchem. J. **2008**, *90*, 67–70.

[9] Gomeza, M.R.; Ceruttia, S.; Sombraa, L.L.; Silvaa, M.F.; Martíneza, L.D. Determination of heavy metals for the quality control in argentinian herbal medicines by ETAAS and ICP-OES. Food Chem. Toxicol. **2007**, *45*, 1060–1064.

[10] Goullé, J.P.; Mahieu, L.; Castermant, J.; Neveu, N.; Bonneau, L.; Lainé, G.; Bouige, D.; Lacroix, Ch. Metal and metalloid multi-elementary ICP-MS validation in whole blood, plasma, urine and hair: Reference values. Forens. Sci. Int. **2005**, *153*, 39–44.

[11] Pereiraa, J.S.F.; Moraesa, D.P.; Antesa, F.G.; Diehla, L.O.; Santosb, M.F.P.; Guimarãesc, R.C.L.; Fonsecac, T.C.O.; Dresslera, V.D.; Floresa, E.M.M. Determination of metals and metalloids in light and heavy crude oil by ICP-MS after digestion by microwave-induced combustion. Microchem. J. **2010**, *96*, 4–11.

[12] Baysal, A.; Ozbek, N.; Akman, S. Determination of trace metals in waste water and their removal processes. In *In Waste Water—Treatment Technologies and Recent Analytical Developments*; Einschlag, F.S.G.; Carlos, L., Eds.; InTech: Rijeka, Croatia; 2013; 145–171.

[13] Scholz, F. Electroanalytical techniques. In: *Electroanalytical Methods, Stripping Analysis: Principles, Instrumentation and Applications*; Scholz, F., Eds.; Springer Berlin Heidelberg, New York, Germany, 2002; 49–240.

[14] Ahammad, A.J.; Lee, J.J.; Rahman, M.A. Electrochemical sensors based on carbon nanotubes. Sensors **2009**, *9*, 2289–2319.

[15] Dai, L. Electrochemical properties of carbon nanotubes. In *Carbon Nanotechnology: Recent Developments in Chemistry, Physics, Materials Science and Device Applications*; Dai, L., Eds.; Elsevier: Amsterdam, The Netherlands, 2006; 297–323.

[16] Kavan, L.; Dunsch, L.J. Electrochemistry of carbon nanotubes. In: *Carbon Nanotubes, Advanced Topics in the Synthesis, Structure, Properties and Application;* Jorio, A.; Dresselhaus, G.; Mildred S.; Dresselhaus, M.S., Eds.; Springer Berlin Heidelberg, New York, Germany, 2008; 567–603.

[17] McCreery, R.L. Carbon electrodes: structural effects on electron transfer kinetics. In: *Electroanalytical Chemistry*; Bard, A.J., Eds.; Marcel Dekker, Inc.: New York, 1991; 221–374.

[18] Zhang, L.; Fang, M. Nanomaterials in pollution trace detection and environmental improvement. Nano Today **2010**, *5*, 128–142.

[19] Aragay, G.; Merkoci, A. Nanomaterials applications in electrochemical detection of heavy metals. Electrochim. Acta **2012**, *84*, 49–61.

[20] Vicentini, F.C.; Silva, T.A.; Pellatieri, A.; Janegitz, B.C.; Fatibello-Filho, O.; Faria, R.C. Pb(II) determination in natural water using a carbon nanotubes paste electode modified with crosslinked chitosan. Microchem. J. **2014**, *116*, 191–196.

[21] Arduini, F.; Calvo, J.Q.; Amine, A.; Palleschi, G.; Moscone, D. Bismuth-modified electrodes for lead detection. Trends Anal. Chem. **2010**, *29*, 1295–1304.

[22] Wang, Z.; Liu, E. Graphene ultrathin film electrode for detection of lead ions in acetate buffer solution. Talanta **2013**, *103*, 47–55.

[23] Wang, Z.; Liu, E.; Zhao, X. Glassy carbon electrode modified by conductive polyaniline coating for determination of trace lead and cadmium ions in acetate buffer solution. Thin Solid Films **2011**, *519*, 5285–5289.

[24] Kokkinos, Ch.; Economou, A. Disposable Nafion-modified microfabricated bismuth-film sensors for voltammetric stripping analysis of trace metals in the presence of surfactants. Talanta **2011**, *84*, 696–701.

[25] Prabakar, S.J.R.; Sakthivel, C.; Narayanan, S.S. Hg(II) immobilized MWCNT graphite electrode for the anodic stripping voltammetric determination of lead and cadmium. Talanta **2011**, *85*, 290–297.

[26] Afkhami, A.; Bagheri, H.; Khoshsafar, H.; Saber-Tehrani, M.; Tabatabaee, M.; Shirzadmehr, A. Simultaneous trace-levels determination of Hg(II) and Pb(II) ions in various samples using a modified carbon paste electrode based on multi-walled carbon nanotubes and a new synthesized Schiff base. Anal. Chim. Acta **2012**, *746*, 98–106.

[27] Hwang, G.H.; Han, W.K.; Park, J.S.; Kang, S.G. Determination of trace metals by anodic stripping voltammetry using a bismuth-modified carbon nanotube electrode. Talanta **2008**, *76*, 301–308.

[28] Injang, U.; Noyrod, P.; Siangproh, W.; Dungchai, W.; Motomizu, S.; Chailapakul, O. Determination of trace heavy metals in herbs by sequential injection analysis-anodic stripping voltammetry using screen-printed carbon nanotubes electrodes. Anal. Chim. Acta **2010**, *668*, 54–60.

[29] Alves, G.M.S.; Magalhaes, J.M.C.S.; Salaun, P.; van der Berg, C. M.G.; Soares, H.M.V.M. Simultaneous electrochemical determination of arsenic, copper, lead and mercury in unpolluted fresh waters using a vibrating gold microwire electrode. Anal. Chim. Acta **2011**, *703*, 1–7.

[30] Chen, L.; Su, Z.; He, X.; Liu, Y.; Qin, C.; Zhou, Y.; Li, Z.; Wang, L.; Xie, Q.; Yao, S. Square wave anodic stripping voltammetric determination of Cd and Pb ions at a Bi/Nafion/thiolated polyaniline/glassy carbon electrode. Electrochem. Commun. **2012**, *15*, 34–37.

[31] Morton, J.; Havens, N.; Mugweru, A.; Wanekaya, A.K. Detection of Trace Heavy Metal Ions Using Carbon Nanotube-Modified Electrodes. Electroanalysis **2009**, *21*, 1597–1603.

[32] Guo, X.; Yun, Y.; Shanov, V.N.; Halsall, H.B.; Heineman, W.R. Determination of Trace Metals by Anodic Stripping Voltammetry Using a Carbon Nanotube Tower Electrode. Electroanalysis **2011**, *23*, 1252–1259.

[33] Wang, Z.; Liu, E.; Gu, D.; Wang, Y. Glassy carbon electrode coated with polyaniline-functionalized carbon nanotubes for detection of trace lead in acetate solution. Thin Solid Films **2011**, *519*, 5280–5284.

[34] Wang, B.; Chang, Y.; Zhi, L. High yield production of graphene and its improved property in detecting heavy metal ions. New Carbon Mater. **2011**, *26*, 31–35.

[35] Gong, J.; Zhou, T.; Song, D.; Zhang, L. Monodispersed Au nanoparticles decorated graphene as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II). Sens. Actuators B **2010**, *150*, 491–497.

[36] Sosa, V.; Barceló, C.; Serrano, N.; Arino, C.; Díaz-Cruz, J.M.; Esteban, M. Antimony film screen-printed carbon electrode for stripping analysis of Cd(II), Pb(II), and Cu(II) in natural samples. Anal. Chim. Acta **2015**, *855*, 34–40.

[37] Injang, U.; Noyrod, P.; Siangproh, W.; Dungchai, W.; Motomizu, S.; Chailapakul, O. Determination of trace heavy metals in herbs by sequential injection nalysis-anodic stripping voltammetry using screen-printed carbon anotubes electrodes. Anal. Chim. Acta **2010**, *668*, 54–60.

[38] Arduini, F.; Majorani, C.; Amine, A.; Moscone, D.; Palleschi, G. Hg2+ detection by measuring thiol groups with a highly sensitive screen-printed electrode modified with a nanostructured carbon black film. Electrochim. Acta **2011**, *56*, 4209–4215.

[39] Aragay, G.; Pons, J.; Merkoc, A. Enhanced electrochemical detection of heavy metals at heated graphite nanoparticle-based screen-printed electrodes. J. Mater. Chem. **2011**, *21*, 4326–4331.

[40] Arduini, F.; Calvo, J.Q.; Amine, A.; Palleschi, G.; Moscone, D. Bismuth-modified electrodes for lead detection. Trends in Anal. Chem. **2010**, *29*, 1295–1304.

[41] Pikna, L'.; Kovačová, Z.; Heželová, M. Performance Characteristics of Modified Paraffin Impregnated Graphite Electrodes-Testing of Different Carbon Nanotubes Binders. Part. Sci. Technol. **2014**, *32*, 602–607.