

Screen-printed electrodes modified with functionalized mesoporous silica for voltammetric analysis of toxic metal ions

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Abstract

Mercury-free sensors for lead (Pb^{2+}) assay based on chemical modification of screen-printed carbon electrodes (SPCEs) with acetamide phosphonic acid self-assembled monolayer on mesoporous silica (Ac-Phos SAMMS) have been developed. The analysis of Pb using SPCEs-based adsorptive stripping voltammetry (AdSV) includes two steps. Pb^{2+} ions are firstly adsorbed on electrode surface in a Pb^{2+} solution (15 ml) during a preconcentration step, followed by a measurement step using one drop of acidic solution (50 μl) as medium for stripping voltammetry. The preconcentration of Pb^{2+} at SAMMS-based sensors utilize the binding affinity of the acetamide phosphonic acid and Pb^{2+} , which can be accomplished at open circuit potential without electrolyte and solution degassing. Due to the strong covalent bonding of the functional groups on mesoporous silica, the SAMMS-based sensors with a built-in three electrode system can be reused for tens of measurements with minimal degradation, enabling the establishment of the calibration curve and lowering the costs. Linear calibration curve was found in the range of 0 to at least 100 ppb Pb^{2+} after 5 min of preconcentration. The detection limit was calculated from 3S/N to be 0.91 ppb of Pb^{2+} . Reproducibility (%RSD) was found to be 5% for a single sensor (six measurements) and 10% for five sensors. The reproducibility can be improved through the precision of manufacturing of the sensors, in which SAMMS modification can be done in situ, increasing the user-friendliness of the sensors. Cadmium, lead, and copper can also be detected simultaneously at the SAMMS modified screen-printed sensors.

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1. Introduction

Disposable sensors for the assay of toxic metal ions are gaining popularity because of their ease-of-use, simplicity and, low costs [1–8]. Of all the disposable sensors, screen-printed carbon electrodes (SPCEs) coupled with adsorptive stripping voltammetry (AdSV) techniques have been increasingly investigated due to their measurement sensitivity and their potential to be mass-produced at very low costs [9]. Most screen-printed electrodes for the sensitive assay of metal ions have been based on mercury film [10–13], or mercury oxide particles [9] as the modifier for

the working electrodes. Disposal and use of electrodes containing mercury leads to occupational and environmental health concerns which may result in future regulation of the mercury-based electrodes. Mercury-free screen printed electrodes have been developed by employing gold [14], silver [15], bismuth [16], or bare carbon electrodes by applying suitable reduction potential to reduce the target metals (e.g., Cu and Pb) [4,17]. However, the sensitivity, reliability, and cost competitiveness of such electrodes are yet to reach those of the mercury-based electrodes. Although chemically modified screen-printed electrodes have been developed using ligands such as 1-(2-pyridylazo)-2-naphthol [5] or calixarene [6], the ligand modification has been done ex situ by drop coating technique with the complexation of Pb^{2+} and ligands being accomplished in ammonia buffer. The ex situ film or ligand deposition by pre-plating

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of the metal from the metal ion solution or by drop coating of the ligands from the ligand containing solution prior to the assay of the target metal ions increases the operating step for the end-users and thus decreases the user-friendliness of the disposable sensors.

Self-assembled monolayer on mesoporous silica (SAMMS) is a new class of nanostructured sorbent materials developed at the Pacific Northwest National Laboratory (PNNL) through the marriage of nanoporous ceramic materials (MCM-41) with self-assembly chemistry [18–23], which provides a simple and direct method of chemically derivatizing ceramic oxide surfaces. These hybrid materials with particle sizes of 5–200 μm are highly efficient sorbents because of their large adsorption capacity, multi-ligand chelation ability that enhances the binding affinity and stability, their pore structure that allows easy facial diffusion of analytes into the nanoporous matrix and the rigid ceramic backbone that prevents pore closure due to solvent swelling resulting in fast sorption kinetics. The interfacial chemistry of SAMMS has been fine-tuned to selectively sequester a specific target species, including lanthanides [31], actinides [18,21], heavy and transition metal ions [19,22,23], and oxometallate anions [20].

This paper reports the development of mercury-free sensors for lead (Pb^{2+}) assay based on chemical modification of screen-printed carbon electrodes with self-assembled acetamide phosphonic acid on mesoporous silica (Ac-Phos SAMMS). The Ac-Phos SAMMS material has been tested in batch adsorption experiments to be excellent for Pb uptake in term of capacity, selectivity, and rate [23]. Pb is one of our most concerned metals due to its high toxicity and common occurrence of Pb poisoning from environmental and occupational exposures especially in children [24,25]. With Ac-Phos SAMMS modified electrodes, the preconcentration of Pb^{2+} at the electrode surface utilizes the binding affinity of the acetamide phosphonic acid and Pb^{2+} , thus it can be done at open circuit potential and with no electrolyte needed. Ultimately, the electrode modification with SAMMS can be easily achieved in situ during the manufacturing for mass production of the sensors.

2. Experimental

2.1. Electrodes and apparatus

Differential pulse voltammetry (DPV) experiments were performed on a hand-held potentiostat, model CHI1232 (CH Instruments, Inc., Austin, TX), equipped with the sensor connector (model SC-01P, AndCare, Durham, NC) for connecting the screen-printed sensors (Fig. 1(a)) electronically to the potentiostat. Fig. 1(a) shows a screen-printed sensor (AndCare, Durham, NC) consisting of three built-in electrodes on a 0.5-mm plastic substrate: screen-printed carbon as working electrode and counter electrode, and Ag|AgCl electrode as the reference electrode. To modify an as-received screen-printed sensor with SAMMS, a mask was used to cover all the elements of the electrode system

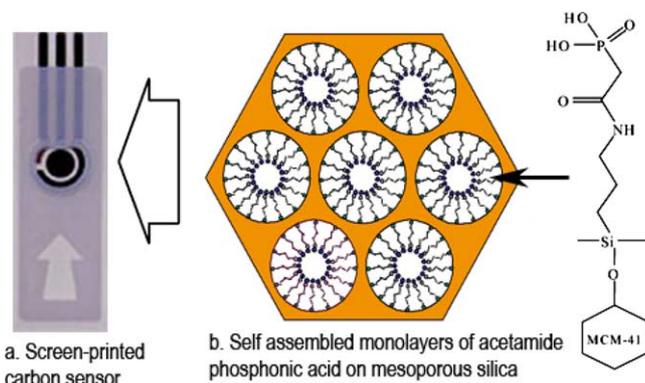


Fig. 1. Schematic of a screen-printed sensor (a) with Ag|AgCl as reference electrode, carbon as counter electrode, and carbon modified with self-assembled monolayers of acetamide phosphonic acid on mesoporous silica (b) as working electrode.

leaving the working electrodes (the black circle portion with a diameter of 4 mm, Fig. 1) uncovered. Then a known quantity of Ac-Phos SAMMS was mixed thoroughly with a known quantity of graphite ink (Ercon, Inc., Wareham, MA) to achieve 5% or 10% by weight of Ac-Phos SAMMS. The mixture was then printed onto the electrode surface as a thin layer. The surface was left to dry overnight. Once dried, the mask was removed and the screen-printed sensor was stored at room temperature prior to use. Synthesis protocol of Ac-Phos SAMMS was published elsewhere [23]. The silica substrate (MCM-41) of Ac-Phos SAMMS had a BET surface area of 989 m^2/g and a nominal pore size of 5.0 nm. The Ac-Phos SAMMS had a functional group content of 2.0 mmol Ac-Phos/g.

2.2. Voltammetric measurements

The analysis of Pb using SPCEs-based AdSV includes two steps. Pb^{2+} ions are firstly adsorbed on electrode surface in a Pb^{2+} solution (15 ml) during a preconcentration step, following by a measurement step using one drop of acidic solution (50 μl) as medium for stripping voltammetry. Prior to the metal ion preconcentration, the electrode activation may be achieved (but not required) by performing cyclic voltammetry technique at scan rate of 100 mV/s from -1.0 to 0 V in a dilute acid until the background was stable [26]. Table 1 summarizes the typical operating parameters of the voltammetric measurements. In a preconcentration step, the sensing portion of SAMMS-modified sensor was immersed in a stirred Pb^{2+} solution (15 ml) for a desired period of time. The immersed part was then rinsed with DI water and the sensor was connected to the potentiostat via the sensor connector. The negative potential of -1 V was applied to the sensor as soon as 50 μl of an acid solution was dropped onto the sensor surface covering all three electrodes. The DPV parameters were: pulse amplitude of 0.05 V, pulse width 0.05 s, and pulse period of 0.2 s. All Pb voltammetric measurements were performed at room temperature and under an

Table 1
Typical operating parameters for Pb detection at a SAMMS modified screen-printed sensor

Parameter	Preconcentration	Electrolysis	Stripping
Solution/electrolyte	1–500 ppb Pb ²⁺ in DI water	0.3–0.5 M HCl	0.3–0.5 M HCl
Immersion time	3–5 min	70–120 s	–
Solution volume	10–15 ml (stirred)	50 μ l	50 μ l
Applied potential	Open circuit	–1.0 V	–0.7 to –0.49 V

atmospheric environment. All acid solutions were of highest purity grade and all metal ion solutions were ICP standards consisting of 1000–10,000 ppm of metal ions in 1–3% HNO₃ (Aldrich Co.). Dilution was prepared daily. No degassing of any solutions was required. Only for the detection of multi-component metal ions, square-wave voltammetry was performed on a desk-top potentiostat (CHI660A, CH Instruments, Inc., Austin, TX) at a frequency of 100 Hz with a pulse amplitude of 50 mV and a potential step height of 5 mV.

3. Results and discussion

The voltammetric detection of metal ions on SAMMS modified sensors is based on AdSV which involves a preconcentration step in a sample solution followed by a detection step (electrolysis/stripping) in a new medium. Optimization of the operating parameters in both steps were performed to achieve the most accurate and sensitive Pb measurements.

3.1. Factors affecting the detection step

Factors affecting the detection step include the type and concentration of the electrolyte and stripping solution, the potential and duration of the cathodic electrolysis, and the stripping potential.

3.1.1. Electrolyte/stripping solution

Because SAMMS is an electronic insulator, for the voltammetric detection to be accomplished, desorption of previously accumulated Pb²⁺ from the surface of SAMMS to the conductive carbon must occur, usually by immersing the electrode in an acidic solution. Concurrent to the desorption process in acid solution, a thorough cathodic electrolysis was performed by applying a negative potential to reduce the desorbed metal ion (Pb²⁺) to elemental metal (Pb(0)). This was followed by the quantification of metal ions via stripping voltammetry, which oxidizes the previously reduced Pb(0) to Pb²⁺ and yields the peak current for Pb (at about –0.6 V) as a function of Pb solution concentration.

Table 2 shows the effects of electrolyte type and concentration on the peak current of Pb at a 10% (w/w) Ac-Phos SAMMS screen-printed sensor. The most effective Pb detection by a SAMMS-modified sensor was accomplished by performing both electrolysis and stripping in acid solution [27,28]. In comparison, HCl performed better than HNO₃

Table 2
Effect of electrolyte/stripping solution on the peak current of 500 ppb Pb²⁺, measured at a 10% Ac-Phos SAMMS screen-printed sensor, 3 min preconcentration time, electrolysis at –1 V for 120 s

Electrolysis/stripping solution	Pb peak current (μ A)	Means \pm SD (μ A)
0.3 M HCl	26.7	26.4 \pm 0.9
	25.3	
	27.1	
0.5 M HCl	29.3	31.0 \pm 9.9
	22.0	
	41.6	
0.3 M HNO ₃	6.1	11.1 \pm 4.5
	14.5	
	12.8	

as the electrolysis and stripping solution since it provided Cl[–] ion for a proper function of the built-in Ag|AgCl electrode [29] in addition to proton to elute the bound Pb²⁺. As the concentration of HCl increased from 0.3 to 0.5 M, the peak current of Pb increased since higher electric current was achieved at higher electrolyte concentration. However, the standard deviation of the duplicates were also larger at 0.5 M than at 0.3 M HCl due to the larger extent of hydrogen evolution in 0.5 M HCl. Under both concentrations, there was no need for regeneration of the electrode since Pb was completely removed from the surface after the stripping. The SAMMS-sensor was rinsed with DI water to remove the acid prior to a subsequent run.

3.1.2. Cathodic electrolysis and stripping

A potentials of –1.0 V was found to be more effective than –0.80 V in reducing Pb²⁺ to elemental Pb(0). With higher potential than –1.0 V, hydrogen gas may occur at the electrode surface leading to high background current. Fig. 2 shows the effect of electrolysis time on the peak current of Pb²⁺ at a 10% SAMMS screen-printed sensor. At the applied potential of –1.0 V, the peak currents increased as the electrolysis time increased from 0 to 90 s and leveled off after 90–150 s. However, for the electrolysis at 90 s, larger standard deviation for three replicates (Y-error bar) was obtained than at 120 and 150 s, thus a 120-s period was chosen as the optimal electrolysis period. Following the electrolysis, the stripping or detection step was performed by scanning the potential from –0.70 to –0.49 V; at this range, the high background at below –0.70 V was avoided and the second Pb peak at above –0.49 V, caused by multilayered lead depositions which are common on screen-printed carbon surface [4] was not seen.

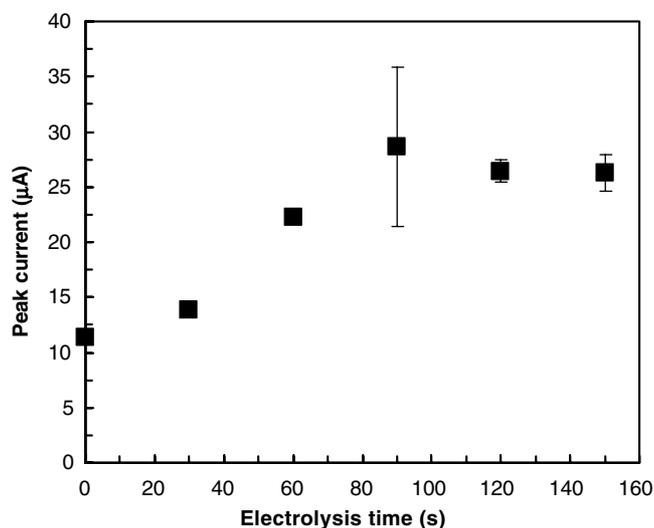


Fig. 2. Effect of electrolysis time on the peak current of 500 ppb Pb^{2+} , measured at a 10% Ac-Phos SAMMS screen-printed sensor, after 3 min preconcentration time, electrolysis at -1 V in 0.3 M HCl. Y-error bars represent the standard deviation of three replicates.

3.2. Factors affecting the preconcentration process

Factors affecting the preconcentration of metal ions onto the electrode surface, which in turn affect the voltammetric responses in the detection step, include electrode composition, preconcentration time, and metal ion concentration and pH of the samples.

3.2.1. Electrode composition

Modification of the working electrode with Ac-Phos SAMMS was achieved by mixing the powder SAMMS with graphite ink. Table 3 demonstrates the effect of SAMMS content of the screen-printed sensors on the peak current of 500 ppb Pb^{2+} after 3 min preconcentration time. At bare carbon electrode (A), very small peak of Pb was observed. As the SAMMS content was increased from 5% (electrode B) to 10% (electrodes C to G), the Pb peak current increased by about two-fold because more functional group were available for the preconcentration of Pb^{2+} . Higher content of SAMMS than 10% resulted in the graphite ink-SAMMS mixture becoming too thick and dry, thereby preventing creation of a uniform surface of the working electrode.

3.2.2. Preconcentration time

Fig. 3 shows the effect of preconcentration time on the voltammetric response of 100 ppb Pb^{2+} solution. The peak currents of Pb increased linearly with time from 0 to 10 min. The large linear response range (from 0 to at least 10 min) suggests that the SAMMS-modified sensors having high functional group content would not be saturated easily by Pb ions. For a rapid analysis of Pb, a 2–3 min-preconcentration period at the modified sensor was found to be sufficient for this concentration range of Pb (i.e., 100 ppb Pb^{2+}) but longer time (5 min) may be required

Table 3
Effect of SAMMS content of the screen-printed sensors on the peak current of 500 ppb Pb^{2+} , 3 min preconcentration time, electrolysis at -1 V for 120 s

Electrode #	% (w/w) Ac-Phos	Pb peak current (μA)	Means \pm SD (μA)
A	0	0.3 0.3	0.3 ± 0.0
B	5	9.2 11.9 13.6	11.6 ± 2.2
C	10	20.4 19.9 19.5	20.0 ± 0.5
D	10	19.2 17.6 18.4	18.4 ± 0.8
E	10	20.0 20.7 18.2	19.6 ± 1.3
F	10	23.8 24.3 23.2	23.8 ± 0.6
G	10	22.0 23.0 21.9	22.3 ± 0.6

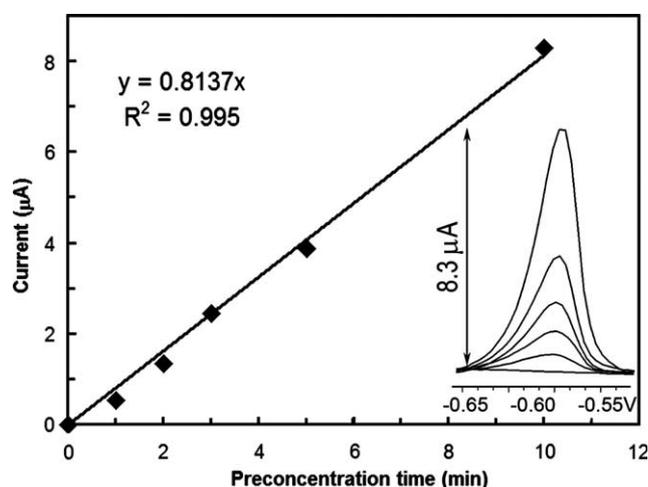


Fig. 3. Effect of preconcentration time on the peak current of 100 ppb Pb^{2+} , measured at a 10% Ac-Phos SAMMS screen-printed sensor, electrolysis at -1 V for 70 s in 0.5 M HCl. Inset shows the voltammograms of the corresponding data points.

for lower Pb-content samples. Even when being mixed with graphite ink, SAMMS on the screen-printed sensors still adsorbed Pb well within a short period, which is attributed to the rigid, open-parallel mesopores and the suitable interfacial chemistry of SAMMS that allow easy access to hydrated metal ions [23].

3.2.3. Metal ion concentrations and solution pH

The pH of the preconcentration solution was found to exert a significant effect on the preconcentration process

since the binding affinity of acetamide phosphonic acid and Pb^{2+} is a function of pH [23]. The Ac-Phos SAMMS has optimal working window from pH 4.5 to 6.5 in which the Pb distribution coefficients from batch adsorption experiments (initial concentration of 5 ppm of Pb^{2+} , solution per solid ratio of 200 ml/g, and ionic strength of 0.1 M) was over 11,000 [23]. As a result, the best solution pH that resulted in highest peak current for Pb at an Ac-Phos SAMMS carbon paste electrode was found to be between 4.5 and 6 [27]. At too low pH, protons may compete for the binding sites. Above pH 7, the peak currents decrease due to the formation of metal hydroxide complexes, causing a significant decrease in the number of solution phase metal ions that may reach and adsorb on the electrode surface. At ppb level of Pb binding on Ac-Phos SAMMS, the pH drop caused by hydrogen ion being displaced by Pb^{2+} was negligible, therefore buffer solution was not needed to regulate the sample pH. For analysis of waste water and groundwater with a pH near neutral using this technique, it is not needed to add electrolytes or buffers to the water samples. This will minimize the potential sample contamination.

Fig. 4 shows the voltammetric responses of Pb^{2+} measured after a 5-min preconcentration period in Pb^{2+} solutions with concentration ranging from 2.5 to 100 ppb of Pb^{2+} . The response of Pb^{2+} (peak current) was linear to the solution concentration with the slope of 0.0336 (in $\mu\text{A/ppb Pb}^{2+}$) and R^2 of 0.999. Note that Fig. 4 only shows the linearity up to 100 ppb of Pb^{2+} , which is a useful range in the real world applications, but the linearity was found to be up to at least 500 ppb of Pb^{2+} (not shown). The large working linear calibration curve can be attributed to the large number of the functional group of the SAMMS on the electrode surface.

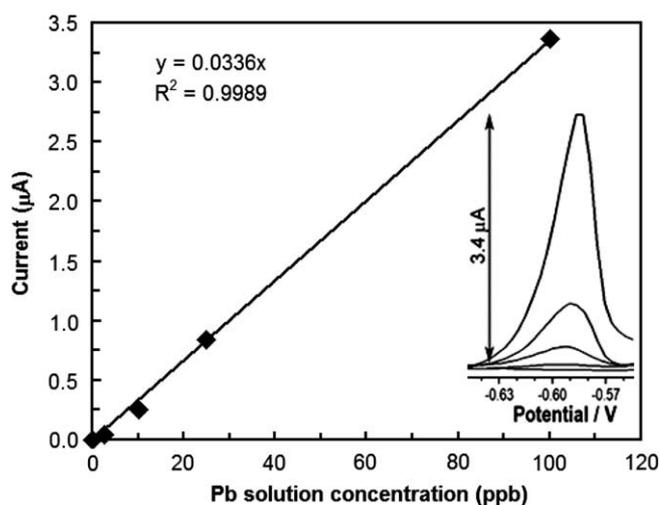


Fig. 4. A calibration curve measured at a 10% Ac-Phos SAMMS screen-printed sensor after 5 min of preconcentration, electrolysis at -1 V for 120 s in 0.3 M HCl. Inset shows the voltammograms of the corresponding data points.

3.2.4. Detection of multicomponent metal ions and interferences

With SAMMS modified sensors, the preconcentration of Pb^{2+} involves the adsorption of Pb^{2+} at open circuit potential followed by the stripping/detection step which is performed in a clean medium. This is advantageous in eliminating the interferences during the stripping step because many interference species can be left in the sample solutions. However, during the preconcentration step, interference may be caused by competitive adsorption of the metal ions to the binding sites. The Ac-Phos SAMMS was tested to have high affinity for Pb^{2+} with the decreasing order of affinity as $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} \sim \text{Ca}^{2+} \ll \text{Na}^+$ [23]. Based on the affinity series, Ca, Zn, Ni, Co, and Mn could not compete with Pb for the binding sites. This was proven to be true at a SAMMS modified carbon paste electrode; at much higher molar concentrations of interferences (e.g., 100-fold for Ca, 70-fold for Zn, Ni, Co, and 10-fold of Mn), Pb peak currents were not affected [30].

The Ac-Phos SAMMS modified screen-printed sensor was also tested for simultaneous detection of multi-component metal ions. Fig. 5 shows the representative voltammograms of Cd, Pb, and Cu at a 10% SAMMS screen-printed electrode. The high functional density of Ac-Phos SAMMS, resulting from the combined effect of an extremely large surface area of MCM-41 and the self-assemble chemistry used for functional group installation, enables high sensitivity for the sensors as well as minimizes the competition among metal ions, allowing them to be detected simultaneously without sacrificing the response intensity [27]. However, Cu when present at high concentration could increase the sensitivity of Pb detection. This has been attributed to the ability of Cu to possess intermetallic and underpotential deposition properties [15]. On the other hand, cadmium was not found to interfere with the Pb signal.

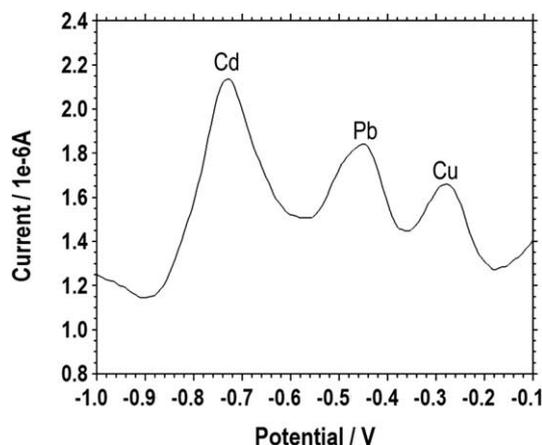


Fig. 5. Representative square-wave voltammograms of 90 ppb Cd^{2+} , 18 ppb Pb^{2+} , and 18 ppb Cu^{2+} , measured at a 10% Ac-Phos SAMMS screen-printed sensor after 5 min preconcentration time, electrolysis at -1.1 V for 120 s in 0.3 M HCl.

3.3. Evaluation of electrode performances

Three criteria that set a good sensor apart from the rest are the low detection limit, the excellent measurement reproducibility, and the long sensor life time.

3.3.1. Detection limits

The detection limit was determined as the concentration of Pb^{2+} that would give a signal three times the background noise. The background noise was measured using the optimal conditions previously described (10% Ac-Phos SAMMS sensor, electrolysis at -1 V for 120 s in 0.3 M HCl) but the preconcentration was done for 5 min in DI water without Pb^{2+} . Three times of the background noise was measured to be $0.03 \mu\text{A}$, which corresponded to a detection limit of 0.91 ppb Pb^{2+} .

3.3.2. Reproducibility

The 10% SAMMS screen-printed sensors had good reproducibility for the metal ion detections both at a single and various electrode surfaces. For example, for a single electrode surface the RSD% for the detections of 500 ppb Pb^{2+} after 3 min of preconcentration (number of samples = 6) was 5%. Lower the Pb^{2+} concentration may decrease the reproducibility, while increased the preconcentration time may increase the reproducibility. For best five electrodes with 10% SAMMS (electrodes C to G, Table 3), the RSD% for the current responses of 500 ppb Pb^{2+} after 3 min of preconcentration was 10%. The measurement reproducibility at different sensors can be increased with increased precision of SAMMS in situ coating during a manufacturing process.

3.3.3. Sensor life time

Due to the strong covalent bonding of the functional groups on the mesoporous silica support of SAMMS before being embedded onto the screen-printed sensors, SAMMS-based sensors can be reused for tens of measurements with minimal degradation [28]. For example, each data set in Figs. 2–4 was collected using a single screen-printed sensor. Being able to reuse the same screen-printed sensor many times makes the establishment of the calibration curve possible and the costs more competitive when compared with most disposable sensors allowing a single-use.

4. Conclusion

The SAMMS modified screen-printed sensors has advantages of being mercury-free, reusable, and low cost, yet as sensitive as Hg-based SPCEs. The voltammetric detection procedure consisted of preconcentration by utilizing the affinity of the functional group to the target metal ions, cathodic electrolysis, and stripping steps. The self-assembled monolayer chemistry of SAMMS enables ready installation of a wide variety of functional interfaces on mesoporous MCM-41 silica, leading to excellent specificity

and selectivity for many desired metal ions when the materials are used as modifiers in electrochemical sensors. The SAMMS modification can be done in situ during the manufacturing process which will increase the measurement precision from one sensor to another. The strong covalent bonding between the functional group and the mesoporous silica on SAMMS resulted in reusability of sensors, making the establishment of the calibration curve easier and the costs more competitive compared to single-use electrodes. In addition to its simplicity, low-cost, low reagent consumption, and reusability, the SAMMS-based screen-printed sensors can also detect analytes that cannot be easily reduced to elemental species $\text{M}(0)$, such as many actinides, lanthanides, and iron. The SPCEs required only one drop of acid on the electrode surface during the stripping step. Therefore, desorbed species from SAMMS that is not reduced to zero oxidation state will not be swept away in bulk acid solution but remained in the acid droplet on the sensor surface at sufficiently high concentration to be detected voltammetrically. The results will be reported in due course.

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