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Detection of Cd, Pb, and Cu in non-pretreated natural waters and urine with thiol functionalized mesoporous silica and Nafion composite electrodes

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ABSTRACT

Electrochemical sensors have great potential for environmental monitoring of toxic metal ions in waters due to their portability, field-deployability and excellent detection limits. However, electrochemical sensors employing mercury-free approaches typically suffer from binding competition for metal ions and fouling by organic substances and surfactants in natural waters, making sample pretreatments such as wet ashing necessary. In this work, we have developed mercury-free sensors by coating a composite of thiol self-assembled monolayers on mesoporous supports (SH-SAMMSTM) and Nafion on glassy-carbon electrodes. With the combined benefit of SH-SAMMSTM as an outstanding metal preconcentrator and Nafion as an antifouling binder, the sensors could detect 0.5 ppb of Pb and 2.5 ppb of Cd in river water, Hanford groundwater, and seawater with a minimal amount of preconcentration time (few minutes) and without any sample pretreatment. The sensor could also detect 2.5 ppb of Cd, Pb, and Cu simultaneously. The electrodes have long service times and excellent single and inter-electrode reproducibility (5% R.S.D. after 8 consecutive measurements). Unlike SAMMSTM-carbon paste electrodes, the SAMMSTM-Nafion electrodes were not fouled in samples containing albumin and successfully detected Cd in human urine. Other potentially confounding factors affecting metal detection at SAMMSTM-Nafion electrodes were studied, including pH effect, transport resistance of metal ions, and detection interference. With the ability to reliably detect low metal concentration ranges without sample pretreatment and fouling, SAMMSTM-Nafion composite sensors have the potential to become the next-generation metal analyzers for environmental and bio-monitoring of toxic metals.

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1. Introduction

Electrochemical sensors have great potential for environmental and biological monitoring of toxic metal ions in water and biological samples (blood, urine) due to their portability and field-deployability, excellent sensitivity (in low ppb levels), automation, short analysis time, low power consumption, and inexpensive equipment. However, a problem preventing the wide application of electrochemical sensors for monitoring of

metal ions is the use and disposal of toxic mercury conventionally used as the metal preconcentrator. To avoid the use of toxic mercury in the detection of Cd and Pb, researchers have focused on silver electrode [1], gold electrode [2], glassy-carbon disk [3], silver-coated [4] and bismuth-coated [5] carbon electrodes. Other class of mercury-free electrodes relies on chemical modifications for metal preconcentrations. Ligands may be immobilized on the electrode surfaces using conductive binders (e.g., carbon paste)[6–9]. However, these ligands

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are in loose association with the binders, thus degradation of the sensors due to depletion of the ligands during measurements can occur. Most importantly, surfactants and organic molecules in real samples often prevent successful use of the electrochemical sensors because they can competitively bind to the metal ions and they can foul the electrodes [10–13]. For mercury-based electrodes, pretreatment by acidifying the samples to release metals from the proteins followed by protein removal via ultrafiltration has been used to reduce the negative affect of proteins in blood, saliva, urine [10,11]. For mercury-free electrodes, these organic complexants and organic surfactants in the samples must be using methods such as UV digestion (which can take many hours unless it is done in-line) [14] and wet ashing (which requires high acid and high temperature up to 650 °C) [12,15]. Even for a relatively clean matrix such as drinking water (e.g., water from cooler and tap water), wet ashing was necessary prior to Pb and Cd analysis using a silver electrode [12,15]. These pretreatment methods are time- and labor-consuming, inappropriate for field monitoring, and may risk adding metals to the samples (e.g., from metal contamination in the reagents and equipments).

In this work, mercury-free electrodes based on a composite of thiol self-assembled monolayers on mesoporous supports (SH-SAMMSTM) [16] and a Nafion binder have been developed and optimized for successful detection of metal ions in natural waters (river, ground, sea waters) and human urine without sample pretreatment. SAMMSTM materials have been developed at the Pacific Northwest National Laboratory (PNNL) originally for environmental cleanups. They are created by self-assembly of organic functional groups on mesoporous silica substrate. The interfacial chemistry of SAMMSTM have been fine-tuned to selectively capture heavy metals [17–19], actinides [20,21], lanthanides [22,23], oxometallate anions [24], cesium [25], and radioiodide [26]. For Cd, Pb, and Cu, SH-SAMMSTM have shown outstanding selectivity in aqueous solutions. For preconcentration of metal ions at electrochemical sensors, SAMMSTM have many advantageous characteristics because they have (1) high selectivity for target metals, (2) high loading capacity, (3) fast sorption kinetics, (4) excellent material stability analogous to a plastic and sand composite, and (5) the ability to be easily regenerated in acid solutions. SAMMSTM materials have recently been investigated for this purpose by our research group using carbon paste or graphite ink as the binders [27,28]. However, this is the first report on SAMMSTM-Nafion composite electrodes for metal analysis that is aimed at “real world” complex samples instead of lab-simulated samples (e.g., metal spiked buffered solutions) as in our previous work. Although Cd is the focus of this work, we also extend the SAMMSTM-Nafion sensors for sensitive detection of Pb and Cu.

2. Experimental

2.1. Samples and reagents

Natural waters were obtained from the Columbia River (Richland, WA), Hanford groundwater (Richland, WA), and Sequim

Table 1 – Typical operating conditions of SH-SAMMSTM-Nafion sensors

Parameters	Conditions
Electrode	GC coated with 10 (w/v%) SH-SAMMS TM -Nafion solution
Sample	8 mL of samples containing Cd, Pb, and Cu
Preconcentration	3 min in stirred sample at open circuit
Electrolysis	–0.95 V, 60 s in 8 mL of 0.1 M HCl
Detection	Scan from –0.95 to –0.30 V in same acid
SWV parameters	Amplitude: 25 mV, increment: 5 mV, frequency: 50 Hz

Bay seawater (WA). They were either filtered with 0.45- μ m cellulose acetate membranes to remove particulates or used as-received without filtration to show the versatility of the sensors. In the pH effect study only, the pH of river water was adjusted with 0.1 M HNO₃ and 0.1 M NaOH, otherwise the three waters were used without pH adjustment. Human urine sample (pH 5.8) was purchased from Innovative Research, Inc. (Novi, MI) and was used after 50% dilution with DI water and without any other pretreatment. Bovine serum albumin (BSA) was purchased from Aldrich Co. Cadmium, Pb, and Cu ions were from ICP standard solutions (consisting of 1000 ppm metal ion in 1–2% HNO₃, Aldrich Co.) and diluted with DI water to 1 ppm prior to spiking to the solutions. All reagents are of highest purity grade.

2.2. Binding affinity (K_d) measurements

For measuring K_d , filtered natural waters and 0.01 M CH₃COONa were spiked with Cd, Pb, and Cu ion solutions to obtain 100 μ g L⁻¹. After 30 min of incubation, it was aliquoted into 5 mL volumes in a 20 mL polypropylene vial containing 0.001 g of solid sorbent (liquid per solid (L/S) ratio of 5000 mL g⁻¹). The sample was then shaken for 2 h at 160 rpm on an orbital shaker. The solution was then removed by filtering through 0.20- μ m Nylon-membrane syringe filters and the filtrate was kept in 1 vol.% HNO₃ prior to metal analysis. The concentrations of metal ions in solutions before and after being contacted with a sorbent material were analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies, CA). All batch experiments were performed in triplicates and the averaged values were reported. Similar experiment was performed with human urine, except that the initial concentration of Cd was 50 ppb and L/S was 1000 mL g⁻¹.

2.3. Voltammetric detection

Square wave voltammetry (SWV) experiments were performed with a handheld electrochemical detector, model CHI1232A (CH Instruments, Inc., Austin, TX), equipped with a three electrode system: a custom-made working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl in 3 M NaCl electrode as the reference electrode. Typical operating conditions are summarized in Table 1. The working electrode was prepared by dip-coating a clean glassy-carbon electrode (3 mm dia., Bioanalytical Systems, Inc., IN) in a mixture of 0.01 g SH-SAMMSTM and 0.1 mL of Nafion solution (consisted

of 5 wt.% of 1100 equivalent weight (EW) Nafion solid in a mixture of water and alcohols from Ion Power, Inc., DE), which was sonicated for 1 min prior to the coating. The film was then air-dried at room temperature for about 1 h prior to using the electrode. The preparation and surface characterization of SH-SAMMSTM were described elsewhere [17]. All measurements were made at room temperature and in an ambient atmospheric environment. All solutions were used without degassing. The SWV was operated at a frequency of 50 Hz with a pulse amplitude of 25 mV and a potential step height of 5 mV. Electrolysis was performed at -0.95 V for 60 s in 0.1 M HCl. After 5 s quiet period, the potential was scanned from -0.95 to -0.3 V and the peak of Cd, Pb, and Cu appeared at about -0.75 , -0.50 , and -0.21 V, respectively. If needed, regeneration of the electrode was performed by applying 0.6 V for 60 s to the working electrode immersed in the stirred acid solution (same as the stripping solution).

3. Results and discussion

3.1. Detection principle

Stripping voltammetric detection of metal ions at the SAMMSTM-based electrodes is a 3-step process; (1) preconcentration of metals in sample solutions at open circuit by exploiting the binding affinity between the thiol functional groups and the target metals, (2) simultaneous desorption and cathodic electrolysis in an acid solution, and (3) subsequent detection by an anodic stripping voltammetry technique in the same acid solution. Cleaning is also performed in the same acid solution and in some cases (in which metal concentrations are lower than ~ 30 ppb and are completely stripped out) is not required. This is because the stripped metal ions do not re-adsorb on the SH-SAMMSTM in acid solutions due to the low affinity of SH-SAMMSTM for Cd, Pb, and Cu in acid solutions ($K_d \sim 0$, not shown). The optimal parameters such as electrolysis time and potential as well as type and concentration of electrolyte solutions obtained from other SAMMSTM-based electrodes [29] were found to be applicable to the SAMMSTM-Nafion electrodes.

3.2. Nafion electrode versus SAMMSTM-Nafion electrode

Having negative charges of sulfonic acid, Nafion is known to have some sorption affinity for metal cations and has been studied for metal preconcentration at electrode sur-

Table 2 – The distribution coefficients^a (mL g^{-1}) of Cd, Pb, and Cu in various matrices

Matrices ^b	pH	Cd	Pb	Cu
Columbia river water	7.84	8700000	3100000	1300000
Hanford ground water	8.13	16000000	6000000	1400000
Sequim Bay seawater	7.65	1100000	1400000	1700000
0.01 M CH_3COONa	6.64	4000000	1800000	1300000
Human urine	5.80	5100	NA	NA

^a The distribution coefficients were measured at L/S of 5000 mL g^{-1} and initial metal ions of 100 ppb (each) with triplicates, except for human urine, L/S of 1000 mL g^{-1} , initial Cd of 50 ppb.

^b The natural waters were filtered through 0.45 μm filter before use.

faces [30,31]. However, the interaction between metal cations and Nafion are relatively weak, easily competed by other non-target cations [30,31], and highly pH dependent [32], thus limiting its effectiveness as a metal preconcentrator. In contrast, the SH-SAMMSTM has shown superior sorption properties for soft metal ions compared to commercial resins having similar thiol groups (e.g., GT-73) [17,33]. The distribution coefficients (K_d in mL g^{-1}) of SH-SAMMSTM to Cd, Pb, and Cu in acetate solution, natural waters, and human urine are summarized in Table 2. K_d is a measurement of the binding affinity and is simply a mass-weighted partition coefficient between the SAMMSTM and the supernatant. The higher the K_d value, the more effective the sorbent material is at capturing and holding the target species. In general, sorbents with K_d values of 10^2 – 10^3 mL g^{-1} are good and those with K_d above 10^4 mL g^{-1} are outstanding [20]. From the K_d values, the SH-SAMMSTM is an outstanding sorbent for Cd, Pb, and Cu in the four matrices ($K_d \sim 10^6$ – 10^7) and a good sorbent for Cd in human urine ($K_d \sim 5000$). This is owed to the suitable interfacial chemistry and large surface area of SH-SAMMSTM (>800 $\text{m}^2 \text{g}^{-1}$), which results in large binding site density (2.8 mmol SH g^{-1}) and hence large metal binding (2.5 mmol Hg g^{-1}) [17]. As a result, Table 3 shows that after 3 min of preconcentration, the SAMMSTM-Nafion sensor could detect 25 ppb of Cd in acetate solution and natural waters, while the Nafion sensor (without SH-SAMMSTM) could detect 25 ppb Cd sensitively in acetate solution but poorly in natural waters, where Cd ions may be bound to the various constituents of natural waters. SH-SAMMSTM also increases the detection sensitivity; the SAMMSTM-Nafion sensor could simultaneously detect 2.5 ppb of Cd, Pb, and Cu in acetate solution after 3 min of preconcentration, while the Nafion sensor (without SAMMSTM) could detect only 10 ppb of Pb, but not

Table 3 – Comparison of signals of Cd, Pb, and Cu, detected at a Nafion sensor and a SH-SAMMSTM-Nafion sensor

Matrix	Metal	Signal (μA)	
		Nafion sensor	SAMMS TM -Nafion sensor
0.01 M NaAC	25 ppb Cd	12.81	18.40
Ground water	25 ppb Cd	0.03	16.83
River water	25 ppb Cd	0.20	14.28
Sea water	25 ppb Cd	0.09	5.92
0.01 M NaAC	2.5 ppb Cd/Pb/Cu	NA	0.04 (Cd), 0.24 (Pb), 0.08 (Cu)
0.01 M NaAC	10 ppb Cd/Pb/Cu	0 (Cd), 0.07 (Pb), 0 (Cu)	0.36 (Cd), 1.20 (Pb), 0.35 (Cu)

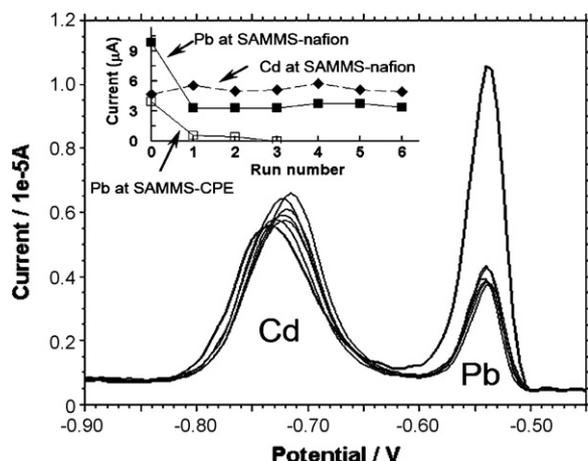


Fig. 1 – Responses to 25 ppb of Cd and Pb in 0.01 M CH_3COONa (thick line) and for 6 consecutive runs with the addition of 20 mg L^{-1} of BSA at SAMMSTM-Nafion electrode. Inset shows the responses at the SAMMSTM-Nafion electrode and at the SAMMSTM-CPE.

10 ppb of Cd and Cu. These results clearly show the advantage of SH-SAMMSTM for metal preconcentration at electrochemical sensors.

3.3. Antifouling properties of Nafion in protein rich samples

Nafion has been claimed to have antifouling properties [34] owing to its ability to exclude molecules of large size (e.g., $\text{MW} > 200$). Fig. 1 shows the responses of the SH-SAMMSTM-Nafion electrode to 25 ppb of Cd and Pb in 0.01 M CH_3COONa without bovine serum albumin, BSA, (thick line) and for 6 consecutive runs after the addition of 20 mg L^{-1} of BSA (thin line) after 3 min of preconcentration. The addition of BSA did not affect the Cd signals but reduced the Pb signals by 65%, suggesting some competition between BSA and SH-SAMMSTM for Pb. Nevertheless, Pb and Cd peaks remained stable after 6 consecutive measurements in samples containing the BSA, indicating the antifouling at the SAMMSTM-Nafion composite electrode. On the other hand, a carbon paste electrode (CPE) modified with 10 wt.% SH-SAMMSTM was fouled after the first measurement in the same solution. It also yielded six-fold smaller signals for 25 ppb Pb and no signal for 25 ppb Cd even after 5 min of preconcentration (inset of Fig. 1); relative to the Pb and Cd at the SH-SAMMSTM-Nafion electrode, respectively. The results clearly reveal the benefit of Nafion as an antifouling binder.

The following sections describe the use of SH-SAMMSTM-Nafion sensors for metal detections in natural waters and human urine by taking advantage of the combined benefit of SH-SAMMSTM and Nafion materials.

3.4. Effect of solution pH

Solution pH has profound effects on the preconcentration of metal ions at the SH-SAMMSTM-Nafion electrodes, which relies on the binding affinity between the metal ions and the

thiol groups on SAMMSTM. Fig. 2 shows the effect of solution pH on the signals of 25 ppb Cd measured at a SH-SAMMSTM-Nafion electrode in pH-adjusted filtered river. Fig. 2 also shows the distribution coefficients (K_d) of Cd on SH-SAMMSTM, also measured in pH adjusted river water (initial Cd^{2+} concentration of 100 ppb, L/S of 5000 mL g^{-1}). The voltammetric signals of Cd depend on the affinity of SH-SAMMSTM that is immobilized on the electrode surface in capturing Cd, which in turn is a function of pH. For pH ranges from 0 to 4, the K_d values were small, corresponding to small Cd signal in that pH range. As pH increased from about 4 to 8, the K_d values increased significantly, and dropped off at pH above 8. This corresponds to a substantial increase in Cd signal from pH 4 to 6.5, which then remained constant from pH 6.5 to 8.2. Thus the optimal pH for Cd measurements was found in the range of 6–8, which is relevant to the pH of natural waters and urine. The shift in the effect of pH on Cd sensor signals compared to that the observed K_d may be primarily a local pH issue [35] (e.g., SH ligands buried in Nafion matrix may experience pH higher than pH of the bulk solution recorded as the K_d values were measured).

3.5. Cd responses versus metal concentrations

Fig. 3 shows the voltammograms of 0–50 ppb of Cd, measured in matrices including 0.01M sodium acetate, filtered river water, ground water, and seawater. Insets of Fig. 3 show the plot of signals versus metal concentration from 0 to 100 ppb Cd in the solutions. Note that the voltammograms at 100 ppb was omitted from the figure for the clarification of those at low Cd concentrations. In all four matrices, Cd could be detected at 2.5 ppb after only 3 min of preconcentration, indicating excellent detection sensitivity. In acetate solution, a linear response was obtained for the whole concentration range. In natural waters, negative deviation from linear response at low concentration of Cd (e.g., 0–25 ppb) is likely attributed to the slow transport of metal ions (that may bind with anions or organic molecules in natural water) into the Nafion matrix [36] since

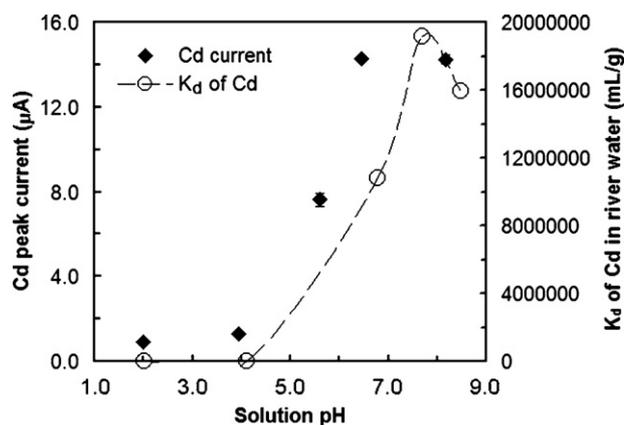


Fig. 2 – Responses to 25 ppb Cd at a SH-SAMMSTM-Nafion electrode in pH-adjusted filtered river water, other operating conditions as in Table 1. Second Y-axis shows the distribution coefficient (K_d) of Cd on SH-SAMMSTM, measured in pH-adjusted filtered river water with L/S of 5000 mL g^{-1} and initial Cd concentration of 100 ppb.

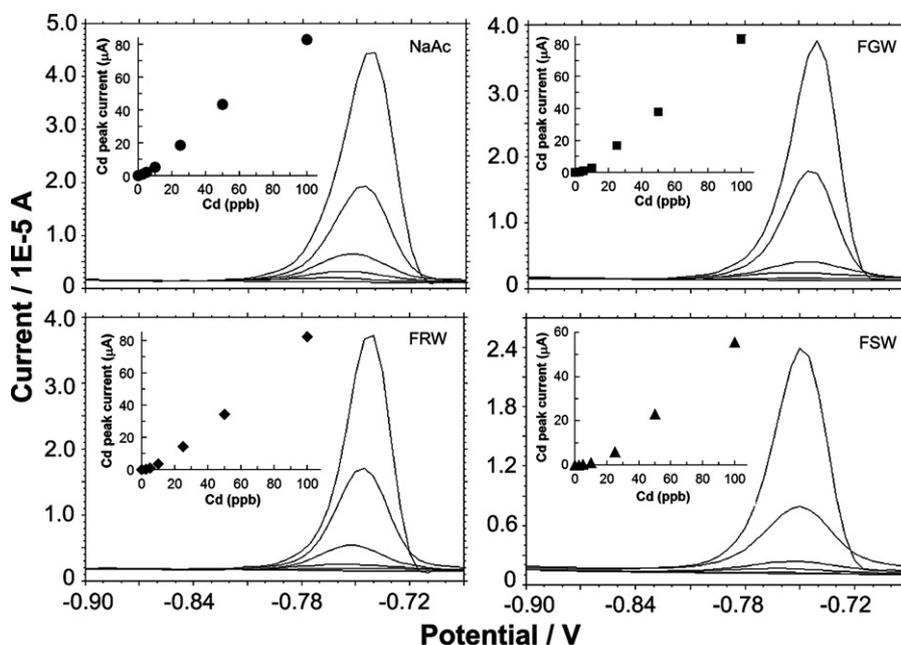


Fig. 3 – Voltammograms of 0–50 ppb of Cd measured in 0.01 M CH_3COONa (NaAc), filtered ground water (FGW), filtered river water (FRW), and filtered seawater water (FSW) at a SH-SAMMSTM-Nafion electrode. Insets show Cd responses from 0 to 100 ppb.

the resistance to the transport of metal ions into the pores of SH-SAMMSTM in natural water was found to be negligible [33]. When the Cd concentration increases to above 25 ppb, a linear response was achieved, which may be due to the higher concentration gradient of free Cd ions between the bulk solution and the interior of the Nafion matrix. The deviation from linear response at low metal concentrations in natural waters has also been found at mercury film electrodes for the detection of nickel in river water (from 0 to 0.35 ppm of Ni) and uranium in ground water (from 0 to 1.5 ppm of U) [37]. Therefore, we propose using log–log plot of the data in order to obtain linear relationship for the whole data range ($R^2 > 0.99$). The linear parameters are summarized in Table 4.

3.6. Cd responses versus preconcentration time

Owing to the rigid silica supports and appropriate pore structure (parallel, hexagonal) and pore size (5 nm) [17], SH-SAMMSTM allows rapid metal sorption rate: it could remove over 99 wt.% of 1 mg L^{-1} Pb from groundwater after 1 min of contact time, while it took over 10 and 120 min for Chelex-100 (EDTA based resins) and GT-73 (thiol based resins) to remove over 96% of Pb [33]. This fast sorption rate makes it possible

to have a short preconcentration time with an electrochemical sensor. Fig. 4 shows the response versus preconcentration time of (a) 10 ppb Cd in acetate solution and (b) 10 and 50 ppb of Cd in filtered river water. In all systems, 10 ppb of Cd could be detected after only 1 min of preconcentration. It is worth noting that with mL of solution and 1 min of assay this systems can detect Cd near the EPA drinking water standard (5 ppb) [38]. In acetate solution, the linear response of 10 ppb Cd was obtained from 0 to 10 min of preconcentration. In filtered river water, the linear response was obtained from 0 to 10 min of preconcentration for 50 ppb Cd, while it took over 5 min for 10 ppb Cd to achieve linear response. Again this deviation from the linear responses is thought to be due to the resistance to the transport of Cd that is bound to organic molecules into the Nafion matrix. Thus, for the detection in the low concentration range (e.g., below 25 ppb) in natural waters, a preconcentration time of 5 min or higher is recommended if a linear calibration curve is desired.

3.7. Detection of Pb, Cd, and Cu

In addition to Cd, the SH-SAMMSTM also has high affinity for Pb and Cu as shown in Table 2 and can be used for pre-

Table 4 – Linear parameters of Cd analytical curves measured at SH-SAMMSTM-Nafion electrodes in various matrices

Matrix	log (current in μA) versus log (Cd concentration in ppb)		Data range (ppb)	R^2
	Slope	Intercept		
0.01 M CH_3COONa	0.76	0.48	2.5–100	0.996
Ground water	0.63	0.72	2.5–100	0.991
River water	0.65	0.69	2.5–100	0.994
Sea water	0.56	0.97	2.5–100	0.994

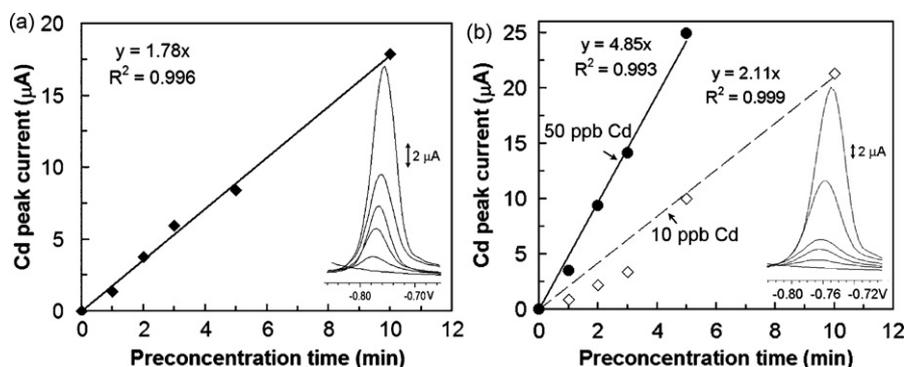


Fig. 4 – Responses of (a) 10 ppb Cd in 0.01 M CH_3COONa and (b) 10 ppb Cd and 50 ppb Cd in filtered river water, measured at a SH-SAMMS[™]-Nafion electrode with varied preconcentration time. Inset shows the corresponding voltammograms of 10 ppb Cd, other operating conditions as in Table 1.

concentration of such metals at electrochemical sensors. The same principle found with Cd can be applied to other metal cations such as Pb, which suggests that the counter ions and organic molecules, and not the type of target metal cations, are responsible for restricting the transport of metal ions inside the Nafion matrix. Fig. 5 shows the linear responses of Pb in the range of 0–1.5 ppb in unfiltered river water, seawater, and groundwater, which were obtained after 6 min of preconcentration. For the same Pb concentration, the signals were larger in seawater than in river water and smallest in groundwater. This suggests that the organic substances (present at relatively high levels in river water) more than electrolytes (present at high levels in seawater) that negatively affect the detection of Pb. Nonetheless, the SH-SAMMS[™]-Nafion sensors were exceptionally sensitive for Pb and Cd detection, considering that the EPA's action level of the metals in public drinking water supplies is 15 ppb of Pb [39] and 5 ppb of Cd [38]. Until the SH-SAMMS[™]-Nafion sensors, this low concentration range of metal ions in un-pretreated natural waters has been extremely difficult to detect using mercury-free electrodes. Although others have reported the detection limits of

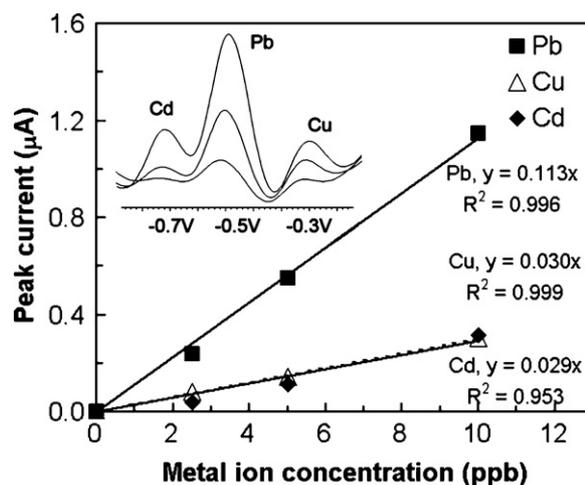


Fig. 6 – Simultaneous detection of multiple metals in 0.01 M CH_3COOH (pH 7.12) at a SH-SAMMS[™]-Nafion electrode after 3 min preconcentration. Inset shows voltammograms of (in the increasing order) of 2.5, 5, and 10 ppb (each) of Cd, Pb, and Cu.

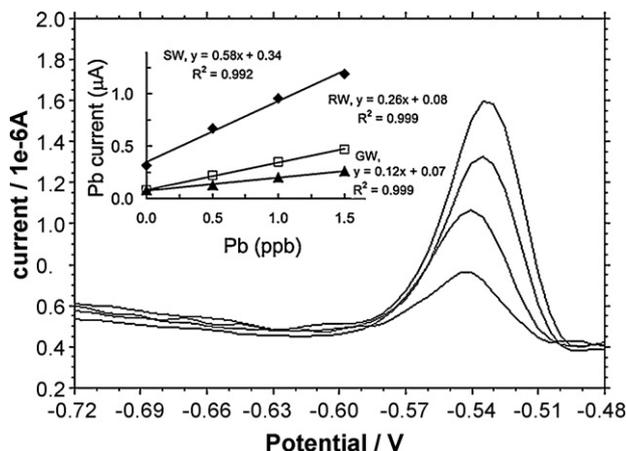


Fig. 5 – Responses of 0–1.5 ppb of Pb in unfiltered seawater (SW) at a SH-SAMMS[™]-Nafion electrode after 6 min preconcentration and the corresponding linear curve in the inset. Inset also shows the linear curve measured in unfiltered river water (RW) and groundwater (GW).

Cd, Pb, and Cu to be in low ppb levels at either mercury based electrodes or mercury-free electrodes, the values were based on 3S/N and were measured in metal spiked buffered solutions rather than in real samples [40–43]. Simultaneous detection of Cd, Pb, and Cu in 0.01 M CH_3COONa after 3 min of preconcentration in a very low concentration range (0–10 ppb), relevant to trace level assay of the metal ions was also demonstrated in Fig. 6.

3.8. Urinary Cd detection

Urine is recognized as one of the best non-invasive matrices for biomonitoring of exposure to a broad range of xenobiotics, including toxic metals [44]. Urine is a more complex matrix than natural waters since it contains proteins/peptides, electrolytes, and metabolic byproducts such as urea, uric acid, and creatinine. Detection of metal ions in urine has been problematic due to protein competition and electrode fouling [10].

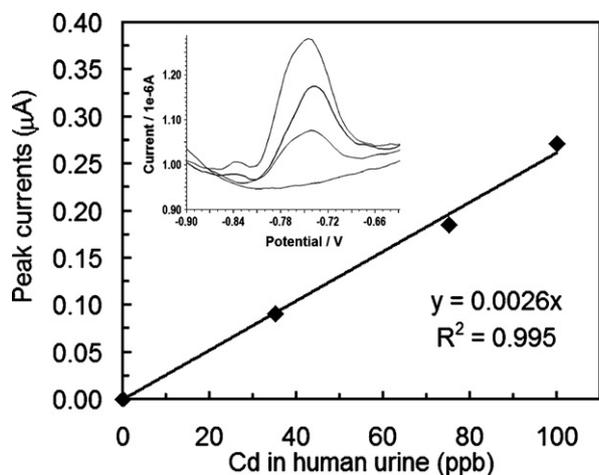


Fig. 7 – Response of Cd in human urine (pH 5.8) at SH-SAMMSTM-Nafion electrode after 3 min of preconcentration time. Inset shows the corresponding voltammograms.

Fig. 7 shows that Cd spiked in human urine could be detected at concentrations of 35, 75, 100 ppb, with 99, 95, 104% recovery, respectively, a result we attribute to the good affinity of SH-SAMMSTM to Cd and the antifouling properties of Nafion.

3.9. Reliability and reproducibility

The perfluorinated backbone chains of Nafion are noted for their chemical and physical stability [45]. With a completely calcined silica support structure and surface functionalized with covalent crosslinked ligands, SAMMSTM materials are also very stable. As a result, the composite of Nafion and SAMMSTM provides a porous film with good mechanical and chemical stability resulting in robust and stable electrodes. While the SAMMSTM-carbon paste electrode counterparts need daily surface renewal (even when used with metal spiked buffered solutions), the SH-SAMMSTM-Nafion composite electrodes have a long service life. For example, two electrodes were in service for 4 operational days with the total of 120 measurements for one electrode and 70 measurements for the other. The SAMMSTM-Nafion sensors are reliable and robust; for instance, Figs. 2–4 were measured with just a single electrode surface without renewal. Although 0.1 M HCl was used as the electrolyte, the electrode was also stable in higher acid concentrations. After immersing an electrode in 0.25 M HCl for 30, 60, and 120 min, the ratio of 25 ppb Cd signals in 0.01 M sodium acetate measured with the same electrode was 0.99, 1.00, and 0.91 (normalized with the average signal after 30 min of immersion). Reproducibility on a single electrode surface was determined, as a relative standard deviation of 8 consecutive measurements of 25 ppb Cd in 0.05 M sodium acetate after 3 min of preconcentration, to be 5% (signals were 15.9, 15.3, 14.2, 15.9, 14.2, 15.8, 14.4, and 15.0 μ A, respectively). Good inter-electrode reproducibility was demonstrated by measuring the ratios of signals at 25 ppb Cd in 0.05 M sodium acetate from four electrode surfaces, yielding 1.0, 1.0, 1.1, and 1.2 (normalized with an average sig-

nal from the first electrode surface). Higher inter-electrode reproducibility can be easily achieved through precise manufacturing of the electrode surface (e.g., through spin-coating of SAMMSTM-Nafion composite instead of manually dip-coating).

3.10. Detection interferences

Unlike other sensors that preconcentrate a target metal and detect it in a sample solution, SAMMSTM based sensors preconcentrate a target metal in a sample solution, but detects it in a clean medium. Thus, an active species will only interfere with the analysis of the target metal if (1) it can out-compete the target metals for the binding sites on SAMMSTM and (2) once it adsorbs on SAMMSTM yields a signal that overlaps with that of the target metal in the stripping (detection) step [27]. Natural waters and urine contain a number of confounding components including: proteins, organic substances, surfactants, anions, which all may compete with SH-SAMMSTM for the target metals. They also contain other cations that may compete with the target metals for the binding sites on SAMMSTM. The K_d values of Cd, Pb, and Cu are about 10^6 – 10^7 in natural waters (Table 2), suggesting that the SAMMSTM is outstanding for selective preconcentration of these metals in these waters. With high content of proteins and metabolic wastes in urine, K_d of Cd in urine is still as high as 5000. From previous competitive sorption studies [17], background ions, such as Na, Ba, and Zn, although present at high concentrations (i.e., 350 times higher concentrations than Pb), did not bind to the SH-SAMMSTM. The presence of other anions (i.e., CN^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-}) did not significantly interfere either with the adsorption of Pb onto the SH-SAMMSTM [18]. In summary, successful detection of low ppb Cd and Pb in natural waters and Cd in human urine, indicates that SAMMSTM-Nafion sensors can overcome these interferences during the preconcentration.

Once a species adsorbs on SH-SAMMSTM during the preconcentration step, it can interfere with the detection of the target metal if its signal overlaps with that of the target metal. Unlike at gold-based electrodes where overlapping of Cd and Pb signals is severe [2], at SAMMSTM-Nafion electrodes Cd and Pb signals do not overlap (see inset of Fig. 6). Tl tends to be found in trace levels in the same mineral formations that contain the more common heavy metals of concern (e.g., Cd, Pb, etc.) and can leach (e.g., from mines) to natural waters that have been exposed to these minerals. Tl has been reported to interfere with the detection of Cd due to its close proximity to the Cd peak (e.g., at slightly more negative potential than Cd) [12,46]. To study the effect of Tl on Cd detection at SH-SAMMSTM-Nafion sensors, Tl was added to 25 ppb Cd in 0.01 M CH_3COONa to obtain concentrations of 0, 25, 50, 100, and 200 ppb of Tl. The interference of Tl to Cd signals was not observed until the Tl:Cd mass ratio is larger than 2, while previous work observed the Tl interference starting from a Tl:Cd mass ratio of 0.08 at a silver electrode [46]. This improved selectivity is a result of the much higher selectivity of SH-SAMMSTM for Cd over Tl; in this regard SH-SAMMSTM has a K_d of 10^7 for Cd versus 10^2 for Tl (as measured in river water, pH 6.8–8.1) and consequently captures Cd far more preferentially than Tl.

4. Conclusions

This work reports for the first time the utility of functionalized silica and Nafion composite as an electrode modifier in the development of Hg-free electrodes. The sensor has the combined advantage of Nafion as an antifouling binder and the SH-SAMMSTM as an efficient metal preconcentrator. As low as 2.5 ppb of Cd and 0.5 ppb of Pb can be detected in natural waters after only 3 and 6 min of preconcentration time. Also, Cd, Pb, and Cu could be detected simultaneously. The use of a Nafion binder can potentially make conventional carbon paste and graphite ink obsolete because (1) it offers better accessibility to the binding sites on SAMMSTM than SAMMSTM that is embedded in carbon paste or graphite ink matrix, resulting in higher detection sensitivity, (2) it offers antifouling properties while the other two binders do not, and (3) the electrode preparation is simpler, yields a more reproducible surface, and can be mass-produced by a spin-coating technique. The resulting SAMMSTM-Nafion composite electrode is proven to be robust, reliable, and reproducible, thus has a great potential to be used in the development of the next-generation of portable and field-deployable metal analyzers.

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