

# Voltammetric analysis of europium at screen-printed electrodes modified with salicylamide self-assembled on mesoporous silica

Wassana Yantasee, Glen E. Fryxell and Yuehe Lin\*

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Mercury-free sensors for europium ( $\text{Eu}^{3+}$ ) assay based on the chemical modification of screen-printed carbon electrodes (SPCEs) with self-assembled salicylamide on mesoporous silica (Sal-SAMMS) have been developed. The preconcentration of  $\text{Eu}^{3+}$  at SAMMS-based sensors utilizes the binding affinity of the salicylamide and  $\text{Eu}^{3+}$ , accomplished at open circuit potential without electrolyte and solution de-gassing. Optimal Eu detection was obtained after 3–5 min preconcentration in Eu solution (pH 2–6), electrolysis at  $-0.9$  V for 60 s in a new medium (0.1–0.2 M  $\text{NH}_4\text{Cl}$ , pH 3.5), followed by a square-wave voltammetric detection of Eu in the same electrolyte. Attributed to the strong covalent bonding of the functional groups on mesoporous silica and silane cross-linking, the SAMMS-modified SPCEs with a built-in 3-electrode system can be re-used for tens of measurements with minimal degradation, enabling the establishment of the calibration curve and lowering the costs. A linear calibration curve was found in the range of 75 to at least 500 ppb  $\text{Eu}^{3+}$  after 5 min preconcentration. The experimental detection limit was 10 ppb after 10 min preconcentration, which can be improved with increased preconcentration time. Reproducibility (% RSD) of 100 ppb  $\text{Eu}^{2+}$  was 10% for a single sensor and 10% for 5 sensors, which can be improved through the precision of sensor manufacturing, in which SAMMS modification can be made *in-situ*.

## Introduction

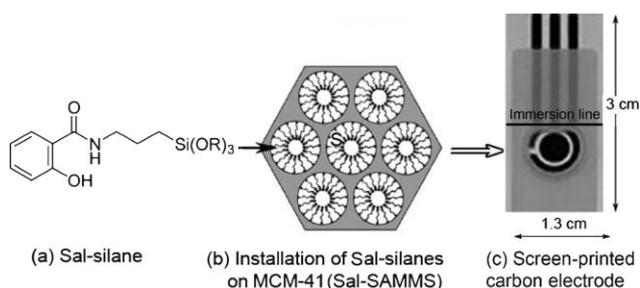
Disposable sensors for the assay of toxic metal ions are gaining popularity because of their ease-of-use, simplicity and low costs.<sup>1–6</sup> Of all the disposable sensors, screen-printed carbon electrodes (SPCEs) coupled with an adsorptive stripping voltammetry (AdSV) technique have been increasingly investigated due to their measurement sensitivity, simplicity during field applications, and ability to be mass-produced at very low costs.<sup>7</sup> Most screen-printed electrodes for trace metal ion analysis have been based on mercury film,<sup>8–11</sup> or mercury oxide particles.<sup>7</sup> Disposal of electrodes containing mercury leads to occupational and environmental health concerns. Mercury-free SPEs have been developed by employing gold,<sup>12</sup> silver,<sup>13</sup> or bare carbon electrodes.<sup>2</sup> However, the sensitivity, reliability, and cost competitiveness of such electrodes have yet to reach those of the mercury based electrodes. Chemically modified screen-printed electrodes have been developed by drop coating of solutions containing 1-(2-pyridylazo)-2-naphthol<sup>3</sup> or a calixarene<sup>4</sup> on electrode surfaces. In this work, mercury-free screen-printed electrodes have been developed by *in situ* modification of the carbon electrodes with a highly efficient solid sorbent, the self-assembled salicylamide on mesoporous silica (Sal-SAMMS).

Successful preconcentration of trace metal ions (in  $\mu\text{g L}^{-1}$  or ppb) present in a complex matrix at an electrode surface requires that the sorbent meet a number of important criteria, including (a) high selectivity for target metals, (b) high loading

capacity, (c) fast sorption kinetics, (d) excellent stability, and (e) ability to be easily regenerated. Pacific Northwest National Laboratory (PNNL) has been a leader in developing a new class of nanostructured sorbents, the self-assembled monolayer on mesoporous silica (SAMMS), by installation of differing well-designed organofunctional moieties on high surface area ( $\sim 1000 \text{ m}^2 \text{ g}^{-1}$ ) silica. Initially aimed at facilitating environmental cleanup of the complex nuclear/chemical waste, SAMMS interfacial chemistry has been tailored for selective sequestering of lanthanides,<sup>14,15</sup> actinides,<sup>16–18</sup> heavy and transition metal ions,<sup>19–23</sup> radiocaesium,<sup>24</sup> radioiodide,<sup>25</sup> and oxometallate anions.<sup>26</sup> The use of this class of materials in electrochemical sensors is relatively new, yet attractive, since they enable the development of solid-state and mercury-free electrodes.

Rare earth cations like lanthanides are difficult to electrochemically reduce to elemental forms. In order to detect Eu at the nanomolar level, researchers have electrolytically accumulated Eu in the presence of thenoyltrifluoroacetone<sup>27</sup> or salicylic acid<sup>28</sup> in aqueous solution at the mercury drop electrode. However, sensors employing non-electrolytic methods and without mercury use are preferable.<sup>29,30</sup> Nafion-coated electrodes have been used to preconcentrate  $\text{Eu}^{3+}$  at open circuit potential, but the Eu detection limits by normal voltammetric methods are still in the micromolar level since  $\text{Eu}^{3+}$  is only weakly incorporated *via* ion-exchange with Nafion binding sites<sup>31,32</sup> and is competed with by other cations such as  $\text{NH}_4^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Li}^+$ .<sup>31,33</sup> Europium ( $\text{Eu}^{3+}$ ) is often present in nuclear wastes and used as an Am(III) mimic. It is also very similar in size to U(IV), Np(IV) and Pu(IV).<sup>15</sup> Having considered its significance, we have recently developed

Pacific Northwest National Laboratory, Richland, WA 99352, USA.  
E-mail: Yuehe.Lin@pnl.gov



**Fig. 1** Sal-SAMMS modified screen-printed carbon sensor with built-in three-electrode system.

sensors for Eu based on SPCEs modified with salicylamide-SAMMS. The results are report herein.

## Experimental

### Electrodes and apparatus

Square wave voltammetry (SWV) experiments were performed on a potentiostat, Model  $\mu$ Autolab III (Eco Chemie, Utrecht, Netherlands), equipped with the sensor connector (Model SC-01P, AndCare, Durham, NC) for connecting the screen-printed carbon sensors (Fig. 1(c), AndCare) electronically to the potentiostat. The as-received sensor consists of three built-in electrodes on a 1.3 cm  $\times$  3 cm  $\times$  0.05 cm plastic substrate, screen-printed carbon (SPC) as the counter and working electrodes, and silver 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, leaving the working electrodes (the black circle portion with a diameter of 4 mm, Fig. 1(c)) uncovered. Then Sal-SAMMS powder (Fig. 1 (a,b)) was mixed thoroughly with graphite ink (Ercon Inc., Wareham, MA) to achieve 10% by weight of the 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 and characterizations of Sal-SAMMS were published elsewhere.<sup>14</sup> BET analysis revealed a surface area of 886 m<sup>2</sup> g<sup>-1</sup> and an average pore diameter of 6.0–6.5 nm of the mesoporous silica substrate (MCM-41) prior to the installation of Sal-silanes. Analysis of the <sup>29</sup>Si integrals revealed a surface population density of 0.88 silanes per nm<sup>2</sup>.

### Voltammetric measurements

Prior to the metal ion preconcentration, the electrode was cleaned by immersion in 0.5 M HCl for 1 min, follow by 0.05 M

acetate buffer (pH 4.6 or 6.5) for 30 s to 1 min. Table 1 summarizes the typical operating parameters for Eu<sup>3+</sup> voltammetric measurements. In a preconcentration step, the electrode was immersed in a stirred solution of Eu<sup>3+</sup> in 0.05 M acetate buffer up to the immersion line (Fig. 1(c)) 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  $-0.9$  V was applied to the sensor as soon as 20  $\mu$ L of NH<sub>4</sub>Cl solution, used as the electrolyte, was dropped onto the sensor surface covering all three electrodes. All solutions were of highest purity grade and Eu<sup>3+</sup> stock solution was the ICP standard consisting of 10 300 ppm Eu<sup>3+</sup> in 3% HNO<sub>3</sub> (Aldrich Co.). Dilution of Eu<sup>3+</sup> solution was done just prior to use. De-gassing of all solutions was not required. All measurements were performed using square-wave voltammetry at room temperature and under an atmospheric environment with the parameters as specified in Table 1. Two to four electrodes were used to repeat a given set of experiments to confirm the trend of the Eu voltammetric responses as parameters were varied. For a given data set, the results from the same electrode were normally reported.

## Results and discussion

The voltammetric detection of europium (Eu<sup>3+</sup>) involves preconcentration of Eu<sup>3+</sup> at Sal-SAMMS, immobilized on the SPCE surface, in a sample solution at open circuit, followed by a detection step in an electrolyte solution. From batch sorption experiments, Sal-SAMMS sorbent had the distribution coefficients ( $K_d$ ) for Eu of 0, 129, 17 000 and 48 000 mL g<sup>-1</sup> at pH 1, 2.5, 4.5 and 6.5, respectively.<sup>14</sup>  $K_d$  is a mass-weighted partition coefficient between the liquid supernatant phase and SAMMS solid phase: sorbents having  $K_d$  above 10<sup>4</sup> mL g<sup>-1</sup> are considered outstanding.<sup>17</sup> Without SAMMS, the graphite-ink modified sensors could not detect below 500 ppb of Eu after 5 min preconcentration (not shown). Optimization of the operating parameters in both preconcentration and detection steps was performed to achieve the most accurate and sensitive Eu measurements as follows.

### Factors affecting the detection step

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

**Electrolyte.** With SAMMS modified sensors, the preconcentration of Eu<sup>3+</sup> involves the adsorption of Eu<sup>3+</sup> at open circuit

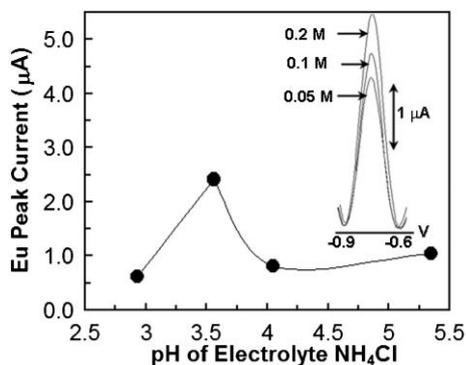
**Table 1** Typical operating conditions for Eu<sup>3+</sup> voltammetric measurements

Parameter	Preconcentration	Electrolysis	Detection
Solution/electrolyte	Stirred in 10–500 ppb Eu <sup>3+</sup> in 0.05 M acetate buffer	0.1 M–0.2 M NH <sub>4</sub> Cl	0.1 M–0.2 M NH <sub>4</sub> Cl
Solution pH	4.6–6.5	3.3–3.6	3.3–3.6
Solution volume	8 mL	20 $\mu$ L	20 $\mu$ L
Preconcentration time	3–5 min	—	—
Applied potential	Open circuit	$-0.9$ V, 60 s	$-0.95$ V to $-0.4$ V
SWV conditions:	step potential = 2.5 mV, amplitude = 50 mV, frequency = 50 Hz, quiet time = 5 s		

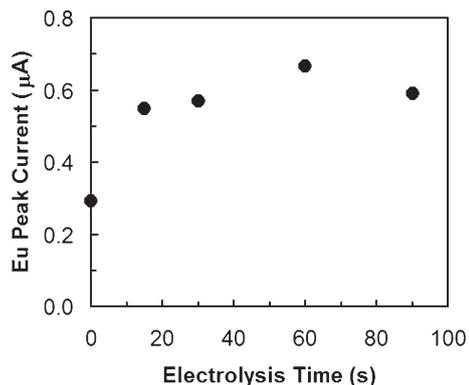
potential followed by the electrolysis/detection step, which is performed in a clean medium. This is advantageous in eliminating the interferences during the detection step because many interference species can be left in the sample solutions. Redox reaction of Eu by cyclic voltammetry has been studied in various electrolytes like  $\text{NH}_4\text{ClO}_4$ ,<sup>31</sup>  $\text{NaClO}_4$ ,<sup>34</sup>  $\text{NaClO}_4/\text{HClO}_4$  mixture,<sup>35</sup> and  $\text{LiClO}_4$ .<sup>36</sup> Ugo *et al.*<sup>31</sup> and Moretto *et al.*<sup>33</sup> found that  $\text{NH}_4\text{Cl}$  improved the reversibility of the reduction of rare earth metals at Nafion-modified glassy carbon electrodes. However,  $\text{NH}_4^+$  that was spiked to Eu solution (pH 4) competed with Eu for the Nafion sites, thus voltammetric Eu signals (measured in the same solution) decreased as the  $\text{NH}_4^+$  concentration increased.<sup>33</sup> At the Sal-SAMMS modified SPCEs, Eu also underwent a reversible one-electron reduction process in  $\text{NH}_4\text{Cl}$ , but because of the selectivity of the salicylamide ligands for Eu, it was not subject to competition with  $\text{NH}_4^+$  for the binding sites. Evidence is shown in Fig. 2 that at the same pH (3.56), a higher molarity of  $\text{NH}_4\text{Cl}$  yielded higher Eu peak response (*e.g.*, 0.2 M > 0.1 M > 0.05 M).  $\text{Cl}^-$  ions in  $\text{NH}_4\text{Cl}$  were also needed to provide the proper function of Ag/AgCl reference electrode.

In our previous work using carbon paste electrodes<sup>37</sup> we found that higher detection sensitivity was obtained in acidic electrolytes than in the neutral ones because the hydrogen ions eluted more metal ions out from the non-conductive silica to the conductive carbon paste, leading to higher voltammetric metal signals. For Eu detection in this work,  $\text{NH}_4^+$  and not acidic electrolyte was our choice for the reasons mentioned above. Fig. 2 also shows that the optimal pH of the electrolyte was about 3.5. Not using highly acidic electrolyte was beneficial since the detection of Eu in acidic electrolytes could be affected by the onset of hydrogen evolution at  $-0.9$  V on these specific SPCEs (not shown).

**Electrolysis time.** After the preconcentration,  $\text{Eu}^{3+}$  could be detected directly by reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ , but the signals were not as sensitive as when  $\text{Eu}^{2+}$  was oxidized to  $\text{Eu}^{3+}$ . Therefore,  $\text{Eu}^{3+}$  was first reduced to  $\text{Eu}^{2+}$  in 0.1 to 0.2 M  $\text{NH}_4\text{Cl}$  (pH 3.3–3.6) by applying  $-0.9$  V for a period ranging from 0 to 90 s, as shown in Fig. 3, followed by detection in the same solution yielding an  $\text{Eu}^{2+}/\text{Eu}^{3+}$  anodic peak at  $-0.72$  V.



**Fig. 2** Voltammetric responses of 500 ppb  $\text{Eu}^{3+}$  (3 min preconcentration) as a function of pH of electrolyte (0.1 M  $\text{NH}_4\text{Cl}$ ); inset shows the increased Eu responses with increasing concentration of the electrolyte (pH 3.56); other conditions as in Table 1.

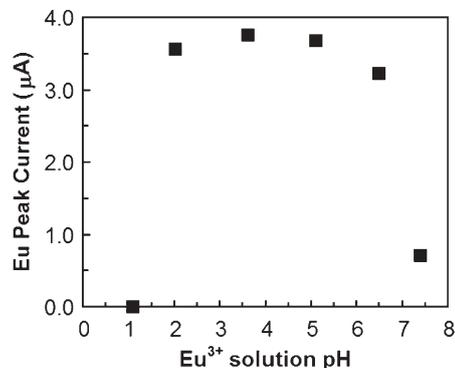


**Fig. 3** Voltammetric responses of 100 ppb  $\text{Eu}^{3+}$  (3 min preconcentration) with differing electrolysis period: other conditions as in Table 1.

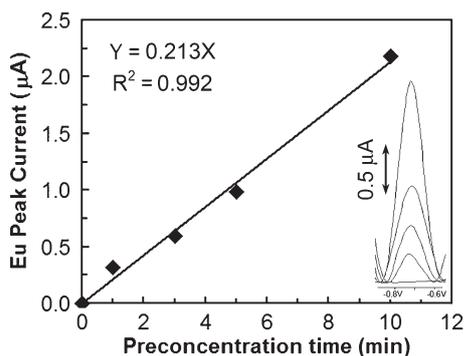
The reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  appeared to be a fairly fast process. The optimal Eu detection was found at 60 s of electrolysis time.

#### Factors affecting the preconcentration step

**pH of Eu samples.** Fig. 4 shows the effect of pH of the  $\text{Eu}^{3+}$  samples on the Eu voltammetric response at a Sal-SAMMS-SPCE. The Eu voltammetric responses were comparable from pH 2 to 6.5. At pH 1.0, deprotonation of salicylamide ligand to permit the Eu preconcentration did not occur, thus Eu was not detected. Above pH 7, the peak currents dropped significantly perhaps due to the formation of Eu-complexes which were sparingly soluble, causing a significant decrease in the amount of solution phase  $\text{Eu}^{3+}$  reaching the electrode surface. Interestingly, the Eu voltammetric response was still high at pH 2 while the  $K_d$  value was noticeably low. This may have been contributed to primarily by a local pH issue. In the sorption experiment that generated the  $K_d$  values, the Sal-SAMMS was in equilibrium with the solution both in terms of the metal binding equilibrium and various proton transfer equilibria. In such a system, the  $\text{p}K_a$  of the metal/ligand adduct presumably plays a role in determining the stability of the complex as a function of pH which would be reflected in the  $K_d$  values. However, at the Sal-SAMMS-SPCEs, the ligand



**Fig. 4** Voltammetric responses of 500 ppb  $\text{Eu}^{3+}$  after 5 min preconcentration as a function of pH of  $\text{Eu}^{3+}$  solution: other conditions as in Table 1.

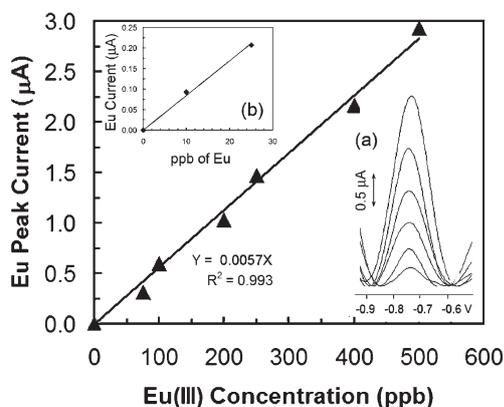


**Fig. 5** Linear voltammetric responses of 100 ppb  $\text{Eu}^{3+}$  as a function of preconcentration period: other conditions as in Table 1.

field is buried in a graphite ink matrix which may restrict the transport of  $\text{H}^+$  into the matrix, causing the effective pH at the Sal–ligand interface to be more moderate than it is out in the bulk solution.

**Preconcentration time.** Fig. 5 shows the effect of preconcentration time on the voltammetric response of 100 ppb  $\text{Eu}^{3+}$  solution. The peak currents of Eu increased linearly with time from 0 to 10 min (a longer time was not preferable from the application stand point). For a rapid analysis of Eu, a 3–5 min preconcentration was found to be sufficient for the concentration range above 75 ppm  $\text{Eu}^{3+}$ , but a longer time (10 min) was required for lower Eu-content samples (*e.g.*, 10 ppb  $\text{Eu}^{3+}$ ).

**Eu concentrations.** Fig. 6 shows a linear voltammetric response of Eu measured after a 5-min preconcentration period in 0.05 M acetate solutions containing  $\text{Eu}^{3+}$  ranging from 75–500 ppb (higher concentrations were not studied since they are often not applicable in real waste). The large working linear calibration curves in Figs. 5 and 6 were attributed to the large number of the functional groups of the Sal-SAMMS on the electrode surface. The preconcentration of Eu at Sal-SAMMS was not affected by 0.05 M sodium acetate buffer. Sal-SAMMS was designed to have high affinity for  $\text{Eu}^{2+}$ , even with a large excess of alkaline and alkaline earth metals; for



**Fig. 6** Linear voltammetric responses of  $\text{Eu}^{3+}$  after 5 min preconcentration. Inset obtained after 10 min preconcentration, other conditions as in Table 1.

example, in solutions having 10 000-fold molar excess of  $\text{NaNO}_3$ , the  $K_d$  for Eu was still in the order of  $10^4 \text{ mL g}^{-1}$ ,<sup>14</sup> suggesting that the sensors can be used effectively in complex matrices (*e.g.*, real world samples). Other lanthanides and actinides are less likely to interfere with Eu sorption on Sal-SAMMS at this Eu concentration range because the large capacity of SAMMS will minimize the competitive binding.<sup>38</sup>

### Evaluation of electrode performances

Three criteria that set a good disposable screen-printed sensor apart from the rest are the low detection limit, good measurement reproducibility, ability to be regenerated, and long sensor life time.

**Detection limits.** The lower detection limits of electrochemical sensors employing electrolytic deposition are often estimated from the signal-to-noise ratio (*e.g.*, 3 S/N). For SAMMS-based electrodes that preconcentrate metal ions at open-circuit, detection limits are obtained experimentally because they are governed by the ability of the sorbent materials to preconcentrate metal ions. The detection limits depend highly on preconcentration time. For example, the experimental detection limits for  $\text{Eu}^{3+}$  were 75 ppb after 5 min preconcentration and improved to 10 ppb after 10 min preconcentration. Longer preconcentration time would improve the lower detection limits.<sup>37,38</sup>

**Reproducibility.** The Sal-SAMMS screen-printed sensors had good reproducibility for the  $\text{Eu}^{3+}$  detections both at a single and various multiple electrode surfaces. For a single electrode surface the % RSD for five measurements of 100 ppb  $\text{Pb}^{2+}$  (5 min preconcentration) was 10%. For five electrodes (all having 10 wt% of Sal-SAMMS), the % RSD was 10%. The reproducibility can be improved with increased precision of *in situ* SAMMS modification in the manufacturing process.

**Regeneration.** The  $K_d$  value of zero at pH 1 suggests that Eu adsorption on Sal-SAMMS was negligible. Thus, the regeneration can be carried out in acidic solution. In fact, after each measurement, immersing the Sal-SAMMS-SPCEs in a stirred 0.5 M HCl solution for one minute was sufficient to remove residual Eu and other metal impurity from the electrode surface. Prior to a new measurement, the electrode was immersed in 0.05 M acetate buffer in order to equilibrate the electrodes prior to Eu preconcentration.

**Sensor life time.** Owing to the strong covalent bonding of the salicylamide–silanes on a silica substrate as well as the strong cross-linking of the silanes, SAMMS based sensors can be re-used for many measurements with minimal degradation. For example, all data in Figs. 3 and 5 were collected using a single screen-printed sensor while those in Figs. 2 and 4 were from another sensor.

### Conclusion

Screen-printed sensors modified with self-assembled monolayers on mesoporous silica (SAMMS) have the advantages of being mercury-free, simple, re-usable, low cost, with low

reagent consumption, yet as sensitive as Hg-based SPCEs. The measurement procedure consists of preconcentration of an analyte at open circuit by utilizing its affinity to the functional group, cathodic electrolysis, and voltammetric detection. 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 detection specificity for the desired metal ions. The screen-printed carbon sensors that were modified with salicylamide-SAMMS could detect a ppb level of Eu. To increase the sensitivity of lanthanide detections, other SAMMS that have known high affinity for lanthanides may also be investigated. These include SAMMS that are modified with acetamide phosphonate,<sup>14</sup> propionamide phosphate,<sup>14</sup> glycyl urea,<sup>14</sup> and hydroxypyridonates.<sup>15</sup> The strong covalent bonding of the functional groups and silane cross-linking of SAMMS minimizes depletion of the ligands, leading to re-usability of sensors. This will make the establishment of the calibration curve easier and the costs more competitive compared with single-use electrodes. With all these advantages, SAMMS-modified screen-printed sensors are highly promising as metal ion analyzers for screening- and field-applications.

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