

## Short Communication

# Carbon Paste Electrode Modified with Carbamoylphosphonic Acid Functionalized Mesoporous Silica: A New Mercury-Free Sensor for Uranium Detection

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## Abstract

This study reports a new approach for developing a uranium electrochemical sensor that is mercury-free, solid-state, and has less chance for ligand depletion than existing sensors. A carbon-paste electrode modified with carbamoylphosphonic acid self-assembled monolayer on mesoporous silica was developed for uranium detection based on an adsorptive square-wave stripping voltammetry technique. Voltammetric responses for uranium detection are reported as a function of pH, preconcentration time, and aqueous phase uranium concentration. The uranium detection limit is 25 ppb after 5 minutes preconcentration and improved to 1 ppb after 20 minutes preconcentration. The relative standard deviations are normally less than 5%.

**Keywords:** Uranium, Sensor, Modified electrode, Mesoporous silica

Uranium is both radiologically and chemically toxic. Uranium and its salts can cause kidney damage and acute arterial lesions [1]. Concentrations of uranium compounds in contaminated groundwater are typically at very low levels, increasing the difficulty of accurate analysis. Adsorptive stripping voltammetry assay techniques that preconcentrate uranium chelates on an electrode surface prior to the detection step have been shown to be highly sensitive for detection of trace uranium concentrations. Sensors based on voltammetric techniques are also well suited for portability (with respect to size, power consumption, and cost to manufacture), making them a good choice for on-site characterization of uranium [2–3].

During the last few decades, adsorptive cathodic stripping voltammetry has been used to identify and characterize uranyl species in the absence [4] and in the presence [3, 5–12] of organic ligands. These approaches utilize mercury drop electrodes [3–11] or iridium-based mercury [12] electrodes, which is a drawback because of issues related to use and disposal of toxic mercury [2]. Mercury drop electrodes also have the disadvantage of being mechanically unstable during various steps of the assay procedure, thus they are less desirable than solid-state sensors in routine field applications [2, 12]. Solid-state carbon paste electrodes modified with functional ligands for uranium detection have been reported previously [2]. However, the ligands in these sensors are in loose association with the conductive carbon matrix, thus the sensors may easily degrade over time from depletion of ligand-bearing material. This is especially noticeable in solvents where the ligands have a high degree of solubility. In this study, an acetamide phosphonic acid ligand (a carbamoylphosphine oxide, CMPO, analog), was

immobilized via covalent bonding onto a high surface area mesoporous silica substrate (MCM-41), depicted in Figure 1. The ligand-bearing mesoporous silica was then embedded in a carbon graphite matrix. Thus the chemical functionality of the sensor is retained despite diffusion or abrasive wear.

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 mesoporous ceramic science with self-assembly chemistry [13–16]. The acetamide phosphonic acid (Ac-Phos) SAMMS material was designed to be highly selective for actinide ions by pairing a “hard” anionic Lewis base with a suitable synergistic ligand. The Ac-Phos SAMMS material displays excellent selectivity for actinide ions with virtually no competition from a wide variety of transition metal cations [16]. One issue for stripping voltammetric detection of uranium is the potential interferences from heavy metal ions. The proven superior selectivity for uranium binding over heavy metal ions of the Ac-Phos SAMMS will greatly improve the selectivity for uranium sensing. Self-assembly chemistry on the extremely high surface area of MCM-41 silica allows the Ac-Phos SAMMS material to have a high surface density of functional groups (e.g., 2 mmol phosphonic acid/g Ac-Phos SAMMS), resulting in high sensitivity of the sensors. Compared with propyl gallate (PG) [2] and trioctylphosphine oxide (TOPO) [11], CMPO is a more notable class of ligands in which a carbonyl amide and a P=O double bond are arranged in a suitable fashion to chelate actinide cations [16–19]. The characteristic of the C=O methyl P=O moiety in the Ac-Phos SAMMS plays an important role just like

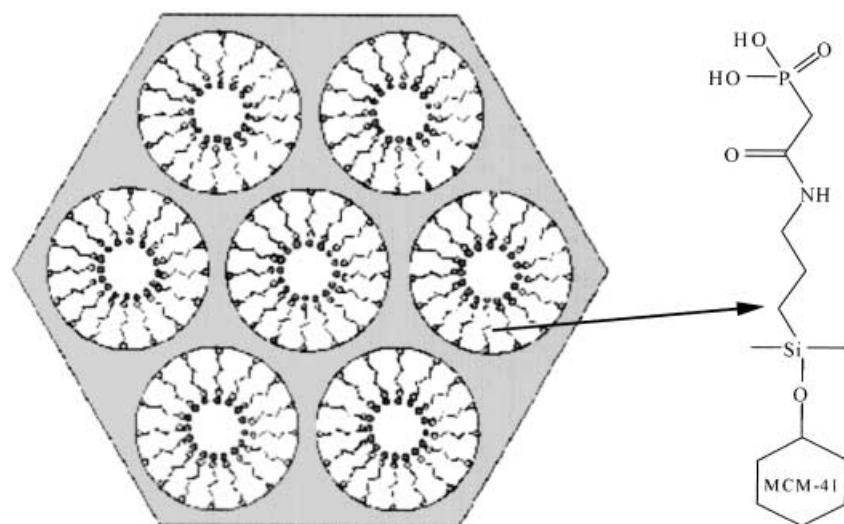
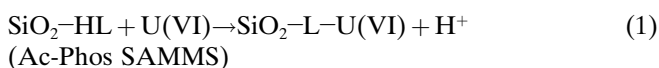


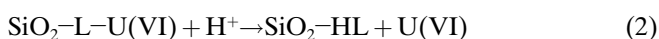
Fig. 1. Depiction of acetamide phosphonic acid self-assembled monolayer on mesoporous silica (Ac-Phos SAMMS).

CMPO, which leads to high selectivity for actinide binding.

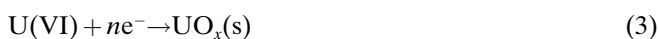
The Ac-Phos SAMMS modified carbon paste electrode was demonstrated to be effective for detecting U(VI) in aqueous solutions using adsorptive stripping voltammetry (AdSV). The process of U(VI) detection involves several steps. U(VI) in 0.05 M sodium acetate ( $\text{CH}_3\text{COONa}$ ) was first accumulated on the electrode surface during an open circuit preconcentration step:



Since the Ac-Phos SAMMS is an electrical insulator, desorption of the preconcentrated uranium ions from the Ac-Phos SAMMS to the conductive matrix was performed in 0.2 M nitric acid ( $\text{HNO}_3$ ) solution:



Concurrent with the desorption process, cathodic electrolysis was performed to reduce U(VI) to insoluble, lower oxidation-state uranium species:



Because the electrolysis was performed in an acidic solution, the potential used for the electrolysis process was limited to  $-0.80$  V to prevent generation of hydrogen ions, which typically occurs at around  $-1.0$  V. A 60 second period was used for desorption and reduction of the U(VI). In the detection step, the anodic stripping was performed in the same acidic solution by scanning the potential from  $-0.80$  V to  $0.40$  V.

The detection of 500 ppb ( $\mu\text{g/L}$ ) U(VI) in 0.05 M  $\text{CH}_3\text{COONa}$  at pH 5 using an unmodified carbon paste elec-

trode did not yield any voltammetric response (current) for uranium, indicating that the conductive matrix was inert with respect to uranium adsorption. For the Ac-Phos SAMMS modified carbon paste electrode, the anodic peak of uranium appeared at  $-0.37$  V, which is likely associated with the oxidation of U(V) to U(VI) [20]. A series of experiments at different aqueous U(VI) concentrations showed that the current of this  $-0.37$  V peak was proportional to the U(VI) concentration. The current was therefore selected as the measured response for U(VI) detection.

Uranium in aqueous solution will form complexes with ligands that may vary as a function of solution pH. Speciation can greatly affect the voltammetric responses of uranium (matrix effect). The type and concentration of anions, the concentration of uranium, and the pH of the solution are factors that determine which uranium complex will be preferentially formed in the solution. Sensors based on cathodic stripping voltammetry techniques rely on electrodeposition of metal-ligand complexes on electrode surfaces before detecting the metal within the same solution, hence the presence of ligands in the sample matrix can affect both deposition and detection steps. Using SAMMS-based electrodes with medium exchange in the detection step after uranium preconcentration can overcome the matrix effect and ligand interference.

Figure 2a shows the effect of pH on uranium speciation of 500 ppb U(VI) in 0.05 M  $\text{CH}_3\text{COONa}$  and open to atmosphere, as simulated using version 4.5 of the MINEQL+ software (Environmental Research Software, Hallowell, ME). The pH of the solution was predicted to affect the distribution of uranyl complexes with acetate, hydroxyl, and carbonate ligands.

Figure 2b shows the effect of pH on the voltammetric responses of 500 ppb U(VI) in 0.05 M  $\text{CH}_3\text{COONa}$ . In the pH range of 2–5, uranyl species with positive or neutral charge (e.g.,  $\text{UO}_2^{2+}$ ,  $\text{UO}_2(\text{Ac})^+$ ) were predicted to be dominant in the solution. In this pH range, the binding

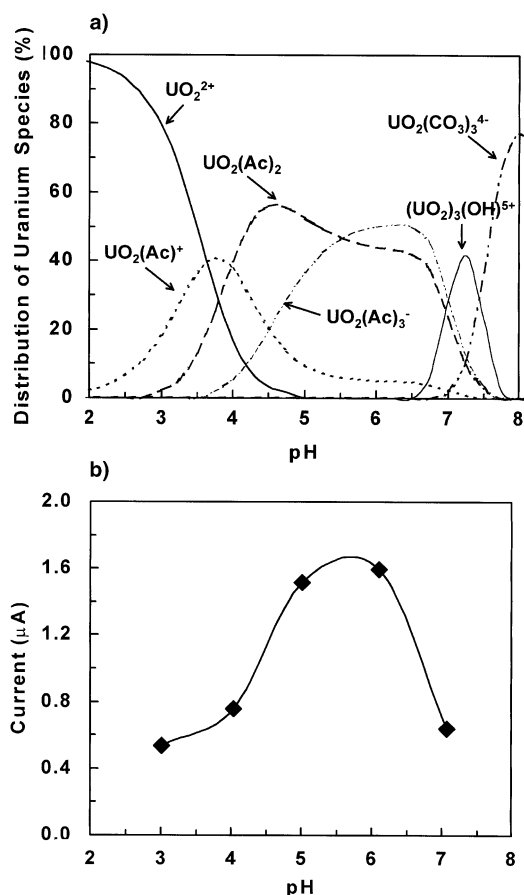


Fig. 2. The effects of pH on a) uranium speciation, as predicted by MINEQL+ for conditions of 500 ppb U(VI) in 0.05 M  $\text{CH}_3\text{COONa}$  and open to atmosphere ( $\text{Ac} = -\text{COOCH}_3$ ), and b) uranium voltammetric responses, measured after 5 minutes pre-concentration with 500 ppb U(VI) in 0.05 M  $\text{CH}_3\text{COONa}$ .

strength between uranium species and phosphonic acid on Ac-Phos SAMMS increased with increasing pH, leading to increasing amount of uranium being preconcentrated, and hence increasing voltammetric responses with increasing pH. Above pH 6, uranyl species with negative charge appear to cause repulsive forces, resulting in low uranium adsorption onto binding sites and correspondingly low voltammetric responses. The optimal current peak response was obtained at around pH 5–6. Therefore, a 0.05 M  $\text{CH}_3\text{COONa}$  solution having a pH 5 was chosen as the preconcentration medium for subsequent experiments.

Figure 3 shows that the voltammetric response to 500 ppb U(VI) in 0.05 M  $\text{CH}_3\text{COONa}$  solution (pH 5) was a linear function of the preconcentration time, which ranged from 1 to 10 minutes. As the preconcentration period was increased to 20 minutes, the uranium detection limit improved significantly, reaching 1 ppb (data not shown). Figure 4 shows that, for a 5-minute preconcentration period, the uranium voltammetric response was a function of U(VI) concentration, which ranged from 25–500 ppb.

In addition to being a mercury-free approach, the SAMMS-based electrochemical sensors have many advan-

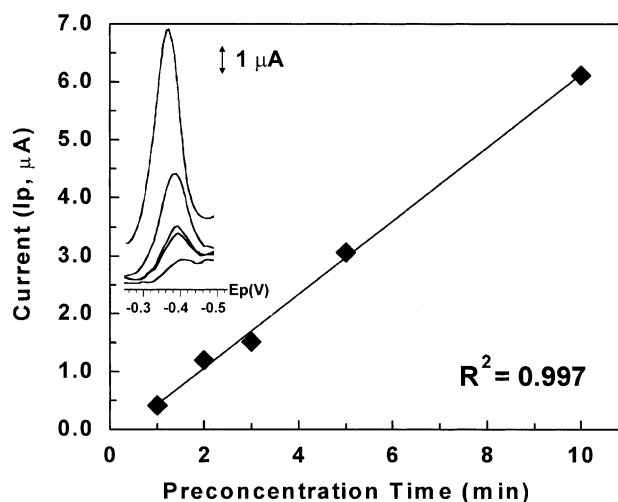


Fig. 3. Uranium voltammetric responses as a function of preconcentration time, measured for 500 ppb U(VI) in 0.05 M  $\text{CH}_3\text{COONa}$  (pH 5). Inset shows the voltammograms with varied preconcentration time (in the ascending order) from 1, 2, 3, 5, to 10 minutes.

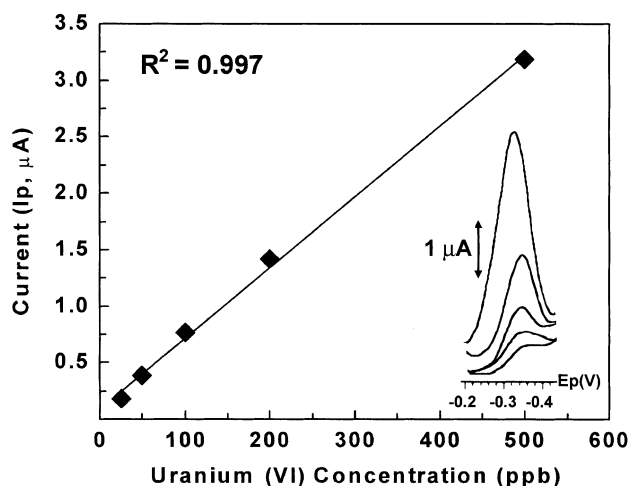


Fig. 4. Uranium voltammetric responses as a function of U(VI) concentration in 0.05 M  $\text{CH}_3\text{COONa}$  (pH 5), measured after 5 minutes of preconcentration. Inset shows the voltammograms with varied U(VI) concentration (in the ascending order) from 25, 50, 100, 200, to 500 ppb.

tages. They have good stability (i.e., the surface renewal was normally not required even after 80 consecutive runs) because the ligands are immobilized via covalent bonding onto silica substrates before being embedded in the carbon-graphite matrix. They have low maintenance; no regeneration of the electrode was required because the stripping step was performed in acid solution. No deaeration of the samples is needed, making the electrode suitable for use in field situations. Further investigation of redox reactions of uranium species involved in each AdSV step will be performed using electrochemical and surface characterization spectroscopic methods and the results will be reported in due course.

### Experimental

A stock solution of 350  $\mu\text{M}$  U(VI) was made by dissolution of analytical-grade  $\text{UO}_2(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O}$  (Fluka) in a 0.1 M perchloric acid solution. Uranium solutions of concentrations ranging from 1 to 500 ppb ( $\mu\text{g/L}$ ) were prepared daily by diluting the stock solution in 0.05 M  $\text{CH}_3\text{COONa}$  buffer solution. Before adding the metal ion solution, the pH of the acetate solution was adjusted to a nominal value of 3, 4, 5, 6, or 7 with 1.0 M  $\text{HNO}_3$  and/or 0.1 M  $\text{NaOH}$ . All solutions were made with ultrapure Millipore water (18 M $\Omega$  cm).

The modified carbon paste electrode was prepared by thoroughly mixing a 0.05 g quantity of Ac-Phos SAMMS with a 0.15 g quantity of CPO carbon paste (Bioanalytical Systems, Inc.). The preparation and characterization of Ac-Phos SAMMS are described elsewhere [16]. A 0.05 g quantity of mineral oil (Aldrich Co.) was added to the carbon paste/Ac-Phos SAMMS mixture and mixed until obtaining a uniformly wetted paste. Unmodified carbon paste, prepared in the same fashion, but without adding Ac-Phos SAMMS, was packed into an 8-cm long cylindrical PTFE tube (inside cross sectional area of 0.08 cm<sup>2</sup>) with a copper piston providing an inner electrical contact. Then the carbon paste/Ac-Phos SAMMS mixture was packed into the end of the same tube. The electrode surface was polished on a weighing paper. When necessary, a new electrode surface was obtained by removing about 2–3 mm of electrode material from the exposed end, adding freshly-made Ac-Phos SAMMS/carbon paste mixture, and polishing it.

Square-wave voltammetry (SWV) experiments were performed on an electrochemical detector, Model CHI 660A (CH Instruments, Inc.) equipped with a three electrode system: a self-made carbon paste electrode modified with Ac-Phos SAMMS as the working electrode, a platinum wire as the auxiliary electrode, and a KCl saturated Ag/AgCl electrode as the reference electrode. All measurements were made at room temperature and under an atmospheric environment. Square-wave voltammetry was operated at a frequency of 100 Hz with a pulse-amplitude of 50 mV and a potential step height of 5 mV.

The voltammetric detection procedure consisted of preconcentration, cathodic electrolysis, and stripping steps. During preconcentration step, the electrode was immersed (at 2 cm from the solution surface) in a 20-mL cell (2-cm inside diameter) containing 15 mL of metal ion solution at open circuit for a specified period of time (typically 3–5 minutes, but varied from 1 to 10 minutes in the preconcentration time study). During preconcentration, the solution was stirred at over 300 rpm using a magnetic stirring bar. The electrode was then removed, rinsed with DI water, and transferred to another 20-mL cell containing 15 mL of 0.2 M  $\text{HNO}_3$  as the supporting electrolyte solution. A negative potential (–0.80 V) was applied to the electrode immediately after immersing it in the acid solution to initiate cathodic electrolysis. The stripping voltammetry was per-

formed in the same cell by sweeping square-wave potential toward positive direction (i.e., from –0.80 V to 0.40 V). Both cathodic electrolysis and stripping steps were done under quiescent conditions. No regeneration of the electrode was required. Each measurement was performed in duplicate, and the average values were reported. The percent relative standard deviations (%RSD) were normally less than 5%.

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### References

- [1] R. J. Lewis, Sr., *SAX's Dangerous Properties of Industrial Materials*, 10th ed., Wiley, New York **2000**.
- [2] J. Wang, J. Lu, D. D. Larson, K. Olsen, *Electroanalysis* **1995**, *7*, 247.
- [3] J. Wang, J. Wang, J. Lu, K. Olsen, *Anal. Chim. Acta* **1994**, *292*, 91.
- [4] R. Djogic, M. Branica, *Anal. Chim. Acta* **1995**, *305*, 159.
- [5] M. Mlkar, M. Branica, *Croat. Chem. Acta* **1987**, *60*, 325.
- [6] M. Mlkar, *Anal. Chim. Acta* **1993**, *276*, 367.
- [7] K. Cha, C. Park, S. Park, *Talanta* **2000**, *52*, 983.
- [8] J. Wang, J. Lu, J. Wang, D. Luo, B. Tian, *Anal. Chim. Acta* **1997**, *354*, 275.
- [9] C. M. G. van den Berg, Z. Q. Huang, *Anal. Chim. Acta* **1984**, *164*, 209.
- [10] C. M. G. van den Berg, M. Nimmo, *Anal. Chem.* **1987**, *59*, 924.
- [11] K. H. Lubert, M. Schnurrbusch, A. Thomas, *Anal. Chim. Acta* **1982**, *144*, 123.
- [12] J. Wang, J. Wang, B. Tian, M. Jiang, *Anal. Chem.* **1997**, *69*, 1657.
- [13] X. D. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu, K. Kemner, *Science* **1997**, *276*, 923.
- [14] X. B. Chen, X. D. Feng, J. Liu, G. E. Fryxell, M. Gong, *Sep. Sci. Technol.* **1999**, *34*, 1121.
- [15] Y. Lin, G. E. Fryxell, H. Wu, M. Engelhard, *Environ. Sci. Technol.* **2001**, *35*, 3962.
- [16] J. C. Birnbaum, B. Busche, Y. Lin, W. Shaw, G. E. Fryxell, *Chem. Commun.* **2002**, 1374.
- [17] K. M. Michael, G. H. Rizvi, J. N. Mathur, S. C. Kapoor, A. Ramanujam, R. H. Iyer, *Talanta* **1997**, *44*, 2095; and references cited therein.
- [18] E. P. Horwitz, R. Chiarzia, in *Separation Techniques in Nuclear Waste Management* (Eds: T. E. Carleson, N. A. Chipman, C. M. Wai), CRC Press, Boca Raton **1995**, ch. 2, pp. 3–33.
- [19] E. P. Horwitz, W. W. Schulz, in *Metal Ion Separation and Preconcentration: Progress and Opportunities*, ACS Symposium Series 716 (Eds: A. H. Bond, M. L. Dietz, R. D. Rogers), ACS, Washington, DC **1999**, ch. 23, pp. 390–400.
- [20] M. Paneli, H. Ouguenoune, F. David, A. Bolyos, *Anal. Chim. Acta* **1995**, *304*, 177.