Final Report: Technical

Portable Hand-Held Electrochemical Sensor for the Transuranics

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1. Final Report Summary: Technical Report

This final report covers the period of October 1, 2001– September 30, 2005. Research accomplishments are presented in the following sections, which parallel the objectives of the original proposal and also reflect new directions that were developed along the way.

Table of Contents:	Page Number
1. Summary of accomplishments.....	3
2. Synthesis and optimization of the actinyl ion selective co-polymer film.	
a. original design.....	4
b. the <i>in situ</i> derivatization process.....	5
c. regioregular polymerizing monomer for the surface layer.....	6
d. deposition of polymer on metals; metals suitable for integrated circuit fabrication.....	7
e. the polymer bilayer design.....	35
f. full factorial experiment for optimization of the primary polymer layer.....	36
g. the current “best” design.....	39
h. Suggestions for the immediate future.....	40
3. Laboratory demonstration of UO_2^{2+} detection using millimeter scale electrodes	
a. detection limit of 10 part-per-trillion uranium and thorium.....	40
b. differentiation of uranium, thorium and plutonium in mixtures.....	42
4. Operating limits and chemical interferences of the lab-scale sensor.	
a. response time of sensor.....	43
b. pH.....	44
c. presence of various chemical species.....	45
d. Temperature.....	46
e. impact of microorganisms on the carbon-based polymer.....	47
f. shelf life of sensing element.....	48
5. Incorporation of actinyl-ion selective film into chem-FET device, and demonstration.....	48
6. Assembly and demonstration of hand-held voltammetric instrument.....	50
7. The battery-powered portable potentiostat for voltammetric operation.....	52
8. Patents, publications and presentations.....	54
9. Student involvement.....	56
10. Continued work.....	57
11. Conclusions.....	58
12. References.....	59
13. Appendix: List of students who worked on the project.....	60

1. Summary of accomplishments

During the four-year period of the grant all of the goals of the originally proposed work were achieved, and some additional accomplishments are here reported. Two types of sensors were designed and built in the lab, capable of detecting uranium, plutonium and thorium at the 10 part-per-trillion level. The basis of both sensor types is a specially designed polymer having selective binding sites for actinyl ions of the form $\text{MO}_2^{2+}(\text{aq})$, where M is any actinide in the +6 oxidation state. This binding site also traps ions of the form $\text{MO}_2^{+}(\text{aq})$, where M is any actinide in the +4 oxidation state. In this way, the polymer is responsive to the two most common water-soluble ions of the actinide series. The chelating ring responsible for binding the actinyl ions was identified from the literature, calix[n]arene where $n = 6$. Several versions of this sensing polymer were coated on conductive substrates and demonstrated for actinide sensing. An optimized sensor was developed and is fully described in this report. It has a polymer bilayer, fabricated under the particular conditions given below. Two different operating modes were demonstrated having different capabilities. One is the chemFET mode (a FET is a field effect transistor) and the other is the voltammetric mode. These two sensors give complementary information regarding the actinide species in a sample. Therefore our recommendation is that both be used together in a probe. A detailed design for such a probe has been filed as a patent application with the United States Patent Office, and is patent pending.

The sensing polymer incorporating this actinyl-chelating ring was tested under a variety of conditions and the operating limits were determined. A full factorial experiment testing the polymerization method was conducted to optimize performance and characteristics of this polymer. The actinyl-sensing polymer was also deposited on the gate of a field effect transistor (FET) and demonstrated as a sensitive detector for uranium. Millimeter scale electrodes, operated by a hand-held instrument assembled in this lab and operated in the voltammetric mode, were transported to the DOE-Nevada test site (Las Vegas, NV) where field detection and quantitation of plutonium, uranium, and a mixture of these two elements was also demonstrated. Several probe designs were prepared, built and tested including probes with movable protective windows. A miniature, battery powered potentiostat was designed, built and demonstrated for use in a hand-held field portable instrument.

This work was performed largely by undergraduates who gained valuable research experience, and many of them have continued on to graduate schools. In addition, they all gained exposure to and appreciation for national security research, in particular non-proliferation research. Four graduate students participated and one earned the MS degree on this project.

2. Synthesis and optimization of the actinyl ion selective co-polymer film.

(a) Original Design:

First attempts to demonstrate uranium detection in aqueous media relied on electrodeposition of a co-polymer consisting of (1) thiophene monomer, and (2) thiophene derivatized to have a calix[6]arene functional group attached in the 3-position. This chelating ring was identified from the literature¹ for its exceptionally high affinity for uranyl ion, $K_f = 10^{26}$. This process is illustrated in Figure 1, but the illustration shows only a monolayer. In fact, the sensing element consisted of many monolayers to a depth of about 1 micron.

The thiophene was chosen as the basic polymer for a number of chemical and electronic reasons. It is readily polymerized by electrooxidation onto a conductive substrate. The bulk polymer is electronically speaking, a semiconductor. If poised with a bias potential it is electrically conductive. The injection of charge carrying electrons by an electrode, or conversely their removal to create “holes” is an electrochemical form of semiconductor doping. The polymer conductivity also increases with temperature, according to Fig. 2, as electrons are moved into the conduction level by thermal energy. Another reason for choosing a thiophene based polymer backbone is that this monomer contains a sulfur atom that forms donor attachment to the metal surface, rather than a nitrogen atom common to many other conductive polymers. The nitrogen is a strong hydrogen-bonding element but sulfur does not form hydrogen bonds. The consequence of this is that nitrogen-heterocyclic monomers swell in the presence of humidity or moisture and can in the extreme case delaminate from the substrate. Sulfur-containing heterocyclic monomers such as the thiophene family do not exhibit this problem. Finally, the thiophene family of monomers is readily derivatized to have the desired binding site for the actinide target species.

This first type of polymer tested proved to be less robust than one developed later, because it contained the large chelating rings in the bulk. These rings disrupt both mechanical integrity and electrical conductivity of the bulk polymer. Many early results, previously reported, were obtained using this polymer. A second problem with this particular polymer was the deep entrapment of analyte species in the bulk polymer and the difficulty of removal for re-use. A third problem also arising from having the bulky chelating groups interior to the bulk polymer was a decrease in conductivity of the polymer. Finally, the inclusion of chelating rings not involved in actinide sensing added needless, additional expense to the cost of preparing the

sensor. Calix[6]arene is an expensive reagent and groups trapped deep within the bulk polymer contributed nothing to actinide sensing, while simultaneously degrading polymer performance. This polymer design was abandoned in favor of a fabrication method that put the chelating rings only on the solution-accessible surface of the sensing polymer.

Figure 1. Illustration of the first type of uranium sensing polymer, used in the early experiments. Bulky calix[6]arene groups are trapped in the interior of the polymer as multilayers are formed.

Figure 2. Semiconductor behavior of a polythiophene prepared in this lab. Note temperature dependence of the conductivity. Conductivity changes slowly in the temperature regime where water is a liquid.

(b) Development of the in situ derivatization process

Having the expensive calix[6]arene only where needed would reduce cost, and increase robustness and response of the sensor. Therefore a method of surface derivatization of the bulk

polymer was developed. In this method, the polymer is first prepared from a mixture of thiophene and 3-thiophenemethanol monomers. The polymer is then subjected to the synthetic protocol for attaching the calix[6]arene chelating ring, as shown in Figure 3. The advantage of this method is that the expensive chelating ring is attached only at solution accessible, surface sites, and is not trapped deep in the bulk polymer. It was hoped that the polymer surface could then be refreshed for re-use by removal of surface bound actinide species. However this proved not feasible because the calix[6]arene had such a high affinity for the actinides, with a formation constant reported in the literature¹ on the order of 10^{26} .

Figure 3. Surface derivatization scheme. A thiophene polymer is created first and chelating rings are attached after polymerization, *in situ* and only at solution accessible sites on the surface of the polymer.

(c) *The regioregular polymerizing monomer for the surface layer.*

The literature indicates that polymer could be formed regioregular as opposed to regiorandom, and that such a polymer would have desirable properties of mechanical integrity and enhanced electrical conductivity.² Therefore a monomer capable of forming only regioregular polymer was identified. This monomer is cyclopentadithiophene (CPDT). This monomer has a derivatizable site at the bridging carbon atom. However attempts to use it exclusively failed as its oxidation potential is relatively high, resulting in degradative over-oxidation of the backbone polythiophene units. This overoxidation was observed as physical

charring of the polymer to elemental carbon. A bilayer deposition (poly-CPDT over poly(bithiophene)) is described below which overcame this problem.

Figure 4. Cyclopentadithiophene (CPDT) which forms regioregular polymers.

(d) Deposition of polymer on metals, especially those suitable for integrated circuit fabrication.

Platinum is the metal of choice for lab scale experiments and demonstrations. It may also be the metal of choice for the millimeter scale voltammetric mode sensors. However it is expensive and its deposition on silicon substrates is more difficult than for many other metals. It is not a metal of choice for the integrated circuit devices or FETs based on this actinide sensing polymer. A set of experiments was performed to determine the best polymer deposition method, as well as the most polymer-compatible metals. Several monomers including thiophene, bithiophene, terthiophene, 3-thiophene methanol and CPDT were compared in their deposition characteristics and mechanical integrity, once deposited. Adhesion to the metal, internal cohesion of the polymer, and conductivity of the polymer coating were measured. In addition to the monomers being tested, several solvents, several electrolyte salts and several deposition techniques were also studied.

All of the monomers tested were found to deposit readily on platinum which is a metal of choice for the millimeter scale application. It is chemically inert and can be shaped into suitable electrodes without weld joints. The presence of weld joints introduces grain boundaries and other defects into the metal surface and subsequently into the polymer surface formed by electrooxidative polymerization of monomers onto the metal. A hardened steel press was designed and built for preparing weld-free platinum paddle-shaped electrodes, and these are what is used in all of the work reported here on the millimeter scale electrodes. Figure 5 shows the wire before and after pressing, and Figure 6 shows the coated paddle electrodes. The wire is cut to length, de-burred, polished, pressed at 10,000 psi in the press, polished a second time and then plated by electrodeposition from solution.

Figure 5. Platinum wire before and after pressing at 10,000 psi in hardened steel press. There are no weld joints.

Figure 6. Platinum paddle electrodes coated with polybithiophene.

It was important to find more IC compatible metals for use as substrates and demonstrate electrodeposition of the polymer on them. Figure 7 shows the results of the first 8 cycles of a cyclic voltammetric method of electrodeposition on several metals commonly used in fabrication of IC devices. The polybithiophene was found to be the most favorable overall, and is now used as the first step of the two-layer fabrication process, discussed in greater detail below. Deposition of polybithiophene prepares the sensor surface for the deposition of the poly-CPDT which is then surface-derivatized to have the actinide binding sites. It gives good coverage at a deposition potential below the oxidation potential of the polymer, which is not true for all of the other

monomers tested with the exception of terthiophene. Terthiophene also deposits readily below the oxidation potential of the monomer, however it is more expensive than bithiophene and the small decrease in polymerization potential below that of bithiophene was not deemed enough of an advantage to offset the added expense in its use.

Figure 7. IC compatible metals coated with polybithiophene via cyclic voltammetric method of deposition. 8 consecutive cycles are shown.

The results of these experiments showed clearly that bithiophene could be deposited on all of the metals at lower potentials than either thiophene, or the chelate-derivatized thiophene. It is desirable to deposit at lower potentials for two reasons: (1) lower deposition potentials minimize oxidation of the thiophene polymer while it is forming, and (2) lower deposition potentials minimize oxidation of the metal surface, and that in turn improves polymer adhesion to the surface as well as electron transport across the interface.

Testing of the electrolyte salts:

Aluminum was tested in the presence of various electrolytes to determine their effects on the red/ox processes. The electrolytes tested were 0.1M concentrations of TBAHFP, TBATFB, TBAClO₄, NaClO₄, and LiClO₄ in acetonitrile. Figure 8 shows the cyclic voltammetric evaluation of aluminum in the presence of various electrolytes with no monomers present.

Figure 8: Effects of various salts in acetonitrile on the cyclic voltammograms of aluminum. Scan rate equals 200 mV/s. (A) 0.1M TBATFB (B) 0.1M TBAClO₄ (C) 0.1M TBAHFP (D) 0.1M LiClO₄ (E) 0.1M NaClO₄ (F) Overlay of the fourth cycles for all the electrolytes

This data shows that the anion has the most striking influence on the red/ox activity of the metal. Figure 8(A) and (C) show that, with repeated scans, a passivation of the electrode is taking place. This is seen by the obvious decrease in current densities between the 1st and 4th scans. The anions used in both of these scans contain fluorine, and can thus contribute to passivation of the electrode surface. Decomposition chemistry of this anion releases F⁻ ion which can coordinate relatively strongly with the bare metal at the surface. Figure 8 (B), (D), and (E), on the contrary show an increase in current with progressive scans. This suggests oxidation of the aluminum surface as is observed from a white discoloration of the substrate. The anion present in those three scans is ClO₄⁻, a commonly used anion in the literature for the polymerization of thiophene. It should be noted that although perchlorates are often used as supporting electrolytes, the substrate is most often platinum. This study suggests that when less noble metals such as aluminum are used as the substrate, perchlorates are not an acceptable choice.

The cation of the supporting salt appears to have less effect, as can be seen in Figure 8(F). The greatest current intensity is observed with the smallest cation. Thus the order of current intensity is as follows: Na⁺ > Li⁺ > TBA⁺. One can presume that the smaller the size of the cation, the more easily it can make contact with the substrate. Therefore, an electrolyte with a large cation accompanied by a multiple fluorine containing anion, appears to be a good choice when attempting electro-polymerization on less noble metals.

TBAHFP, TBATFB, and TBAClO₄ were also tested for their effects on the polymerization of thiophene on both aluminum and platinum. Figure 9 shows the effects of these different electrolytes on the cyclic voltammetric polymerization process. The 6th scan for each respective electrolyte and substrate combination are shown.

As shown in the figure, the greatest current density is observed in the presence of TBAHFP, followed by TBATFB and then TBAClO₄. Under these conditions, the amount of polymer produced can not accurately be judged by the cyclic voltammograms. The greater current density observed with TBAHFP, however, shows that more electrons are mobile in the polymer, and therefore a higher degree of conductivity and/or polymer formation is likely. In the case of an aluminum substrate, in the presence of TBAClO₄, k_1 is larger than k_2 . Thus, the formation of aluminum oxide is the dominant mechanism. This is evidenced by the lack of the characteristic quasi-reversible polythiophene wave, and the lack of any visible polymer on the

substrate. In fact, only a white discoloration was observed on the aluminum substrate, characteristic of aluminum oxide formation.

Figure 9: Effects of various salts on the cyclic voltammetric polymerization of thiophene on (A) aluminum and (B) platinum. 0.1M electrolytes in acetonitrile with 0.1M thiophene concentration. Scan rate = 200mV/sec

These results further show that, all other conditions being equal, perchlorate anions are not suitable for the formation of polythiophene on more highly red/ox active metals. Therefore, due to TBAHFP's ability to form a passivating layer on more electroactive metals, and the observations that more polythiophene and/or more highly conductive polythiophene is formed when it is used as a supporting electrolyte, it has been chosen as the main electrolyte for the study of polythiophene formation on various metals.

Deposition of polymer on various metals from various solvents.

With the sensor applications envisioned^{8, 11} specifically with a view toward integration of the sensors into micro-circuitry, cost effective metals compatible with both integrated circuit fabrication and thiophene-type polymers are of great interest. Several metals have been tested for their suitability for the electrosynthesis of polythiophenes, these include, Al, Au, Cu, Fe, Mo, Ni, Pd, Pt, Sn, Ta, Ti, W, and Zn. Some of these metals are commonly used in IC fabrication. Fe and Zn are not usually used in this capacity as they are readily oxidized under ambient conditions. These two metals were chosen specifically as difficult test cases, in which we tested

our hypotheses about the *in situ* passivation of conductive substrate during the electropolymerization process.

Solvent is expected to have a significant impact on deposition potential, according to Marcus' Theory. The inner and outer sphere reorganization processes of the solvated monomer contribute to redox potentials unless these processes are faster than the electron transfer process. Therefore several solvents were examined to determine the most favorable for polymer deposition.

Figure 10 shows the first eight cyclic voltammograms of thiophene electro-oxidatively polymerized from acetonitrile. In the nine metals shown below, polythiophene is formed in all cases. This is evidenced by the growth of the quasi-reversible oxidation and reduction waves between approximately 0.25 V and 1.5 V. With each successive cycle, the oxidation and reduction waves grow in intensity, indicative of increased polymer formation.

Figure 10: The first eight cyclic voltammograms of 0.1M thiophene electro-polymerized on various metals in acetonitrile. Scan rate = 100 mV/sec

An interesting feature of each voltammogram is a lowering of the plating potential after the initial cycle. A possible explanation for this is that in the first scans, the thiophene monomer

is undergoing an oxidative breakdown. In ensuing cycles, nucleation sites have formed, and the thiophene radicals have a more facile ability to join the polymer chain. The lowering of the potential decreases to a finite point at which no further nucleation sites are created, and polymerization occurs only at the sites already formed. The oxidative thiophene breakdown potentials for the first and second cycles for each metal are listed in Table 1.

Cycle	Thiophene Breakdown Potentials in Acetonitrile (V)								
	Al	Au	Mo	Ni	Pd	Pt	Ta	Ti	W
1	1.65	1.57	1.68	1.64	1.60	1.51	1.69	1.68	1.68
2	1.59	1.46	1.59	1.52	1.45	1.43	1.58	1.56	1.58
ΔV	0.06	0.11	0.09	0.12	0.15	0.08	0.11	0.12	0.10

Table 1: The oxidative thiophene breakdown potentials for the first and second cycles of the CVs shown in Figure 10.

From Table 1, it can be seen that the thiophene oxidation potentials have the lowest values for Pt, Pd, and Au. This result is not surprising since these are the most noble of the metals studied. The k_1 values for these metals is expected to be much lower than the k_2 value. Substrate oxidation would be expected to show the least interference with the polymerization process, and, therefore, the potential required to initiate nucleation sites is lowered. The other metals tested all show the same general thiophene breakdown potentials (1.58-1.59 V) after the second scan, with the exception of Ti and Ni, which settle into the slightly lower voltages of 1.56 V and 1.52 V respectively.

The change in current intensity per cycle for the reduction peaks of each metal is plotted in Figure 11. This analysis can give a general comparison of the degree of polymer growth and conductivity. With each successive cycle, an increase in current intensity occurs. The increase is dependent on the substrate employed, as is evident from the slopes of the plots. The lowest slopes are observed with tantalum and aluminum, suggesting less polymer formation on those substrates. Tungsten and molybdenum show a higher degree of current increase, but not as significant as that observed with platinum, palladium, gold, titanium, and nickel.

Figure 11: Dependence of the metal substrate on the change in current intensity per cycle of the reduction peaks during polythiophene synthesis in acetonitrile.

An interesting result is shown with gold and palladium. Although these metals start with a large increase in current intensity, with gold being the highest in the group, a decrease is observed after their eleventh cycles. This is a likely result of loss of available monomers and an over-oxidation of the polymer. The consequence of this is an irreversible breakdown of the polymer conjugation and a decrease in the overall conductivity of the polymer. It is well known that polythiophene is not stable at the potentials used for its synthesis⁵, and that if thiophene monomers are unavailable, over-oxidation of the polymer will result.

As a comparative study to that shown in Figure 10, polythiophene was polymerized on several metals using nitromethane as the solvent. The results of these experiments are shown in Figure 12.

Figure 12: The first eight cyclic voltammograms of 0.1M thiophene electro-polymerized on various metals in nitromethane. Scan rate = 100mV/sec

The results of thiophene polymerization in nitromethane, is similar to that observed for polymerization in acetonitrile. The current increases with succeeding scans, characteristic of polythiophene formation. Some major differences are observed, however. The increase in the overall current is approximately an order of magnitude for all substrates when compared to acetonitrile. Another major difference is the number of cycles necessary for the “breakdown region” to reach a defined and repeatable slope. Compared to acetonitrile, it takes several more cycles for this to occur when nitromethane is used as the electro-polymerization solvent. This is particularly evident in the case of aluminum and tantalum. A magnified view of the thiophene “breakdown region” for aluminum is shown in Figure 13.

Figure 13: The thiophene “breakdown region” for aluminum in (A) acetonitrile and (B) nitromethane

The slope of the “breakdown region” in acetonitrile reaches a set and repeatable value after only two cycles. Nitromethane in contrast, shows a slower increase in the slope, and after eight cycles, it still has not reached a set and repeatable value. Although, this phenomenon is not fully understood, it is possible that the slower increase in the slope of the “breakdown region” observed with nitromethane is a result of an increase in the formation of nucleation sites on the substrate. This would result in greater overall coverage, as is evident from visual inspection of the resultant polymers. An example of the dramatic difference observed in the overall coverage when using nitromethane in place of acetonitrile is shown in Figure 14.

Figure 14: Polythiophene grown on gold using (A) acetonitrile and (B) nitromethane

The oxidative breakdown potential of thiophene in nitromethane generally reaches a set position after the second cycle. This is true regardless of substrate and regardless of the slope of the “breakdown region.” The polymerization potentials from the first and second cycles for substrates tested in nitromethane are listed in Table 2.

	Thiophene Breakdown Potentials in Nitromethane (V)								
Cycle	Al	Au	Mo	Ni	Pd	Pt	Ta	Ti	W
1	1.64	1.53	1.68	1.61	1.51	1.51	1.51	1.61	1.62
2	1.50	1.40	1.47	1.43	1.36	1.37	1.37	1.50	1.50
ΔV	0.14	0.13	0.21	0.18	0.15	0.14	0.14	0.11	0.12

Table 2: The oxidative thiophene breakdown potentials for the first and second cycles of the CVs shown in Figure 12.

In all cases, the potentials for thiophene polymerization in nitromethane are lower than those observed for acetonitrile. In addition, the ΔV s are greater. The lower polymerization potentials, along with the slower increase in the slopes at the breakdown region point to a lower possibility of over-oxidation of the polymer.

Plots of the increase in current intensity of the reduction waves for thiophene polymerization in nitromethane are shown in Figure 15.

Figure 15: Dependence of the metal substrate on the change in current intensity per cycle of the reduction peaks during polythiophene synthesis in nitromethane.

The increase in current intensity when nitromethane is used as a solvent follows the same general trend as is seen with acetonitrile. Aluminum and tantalum show the lowest increase in current intensity, while tungsten and molybdenum are in the midrange. The remainder of the substrates tested, show a larger increase in current intensity. Breakdown of the current intensity due to over-oxidation is slower when nitromethane is used. In fact no breakdown is observed until the twentieth cycle, and then only in the case of molybdenum. This is difficult to explain, however, since following the slight plateauing effect, it agains shows an increase in current at the twenty third cycle. Aluminum and tantalum begin to show a leveling off of the current intensity at approximately the twenty fourth cycle.

When compared to the cyclic voltammetric polymerizations using acetonitrile, the current intensity of the CVs in nitromethane are at least an order of magnitude greater. Corresponding to this, the initial slopes of the plots of current intensity versus cycle number are several times greater when nitromethane is used in place of acetonitrile. Table 3 shows the slopes taken from the cathodic peaks of the first seven cycles on each substrate tested. The larger slope reveals the

possibility that more electrons are being transferred per cycle when nitromethane is used as the solvent and corresponds to an increase in the total amount and/or conductivity of the resultant polymer.

	Slopes								
Slope	Al	Au	Mo	Ni	Pd	Pt	Ta	Ti	W
MeCN	1E-5	5E-5	2E-05	4E-05	4E-05	5E-05	9E-06	4E-05	2E-05
NM	3E-05	0.000 1	9E-05	0.000 1	0.000 1	1E-04	3E-05	0.000 1	6E-05

Table 3: The slopes from the cathodic peaks of the first seven cycles.

Under the conditions employed above, polythiophene was not successfully formed on copper, iron, tin, or zinc. Aeiya et al.⁶ have been successful in electro-polymerizing thiophene on iron and zinc in dichloromethane. This, however, was performed galvanostatically at high current densities and corresponding potentials (approx. 2.5 V to 4 V).

In this study, it has been determined that polymerization through the methods employed is only possible on substrates that are stable in the region where thiophene breakdown occurs. Aided by the correct choice of electrolyte (Figure 8), the metals tested in Figures 10 and 12 are all stable at the potentials needed for thiophene polymerization. However, as Figure 15, shows, this is not the case for Cu, Fe, Sn, and Zn.

Figure 15: Cyclic voltammetry of Cu, Sn, Fe, and Zn in 0.1 M TBAHFP in acetonitrile with 0.1 M thiophene.

The metals shown in Figure 15, all show a significant breakdown in the region where thiophene polymerization occurs, suggesting that k_I is quite large and that metal dissolution will be the dominant mechanism when attempting to polymerize thiophene. Upon repeated cycles, iron begins to show passivation, which is a likely result of the formation of insoluble FeF_3 . When compared to the metals tested in Figures 10 and 12, the passivation of iron proceeds relatively slowly, which may explain why Aciyach et al. were able to form polythiophene on iron only at relatively high potentials⁶.

Copper is well known as not being a suitable substrate for thiophene polymerization⁷. Copper oxide, however, has been successfully employed⁸. This, again, is a result of the passivation of the metal surface.

Figure 16: Cyclic voltammetry of copper and copper oxide in 0.1M TBAHFP in acetonitrile

Figure 16 illustrates the electrode passivation obtained when copper is converted to its oxide. Bare copper, in this region, undergoes a breakdown in the test solution, as is verified by a yellowing of the acetonitrile electrolyte solution. Acetonitrile is known to complex with copper resulting in the observed yellow solution⁹. The oxidized copper in contrast shows a passivation of the surface, making a more capable site for thiophene polymerization.

Electro-polymerization of Bithiophene on Various Substrates:

Bithiophene was polymerized cyclic voltammetrically on all of the metals tested in Figures 10 and 12. Polymerization of bithiophene in 0.1M TBAHFP in acetonitrile is shown in Figure 17.

Figure 17: The first eight cyclic voltammograms of 0.1M bithiophene electro-polymerized on various metals in acetonitrile. Scan rate = 100mV/sec

As expected, bithiophene polymerizes oxidatively in the same fashion as thiophene. The polymerization of bithiophene, however, is obtainable at lower potentials than is needed for the polymerization of thiophene. As the potential proceeds toward the oxidative breakdown region,

a dark bluish gray / black polymer layer is formed. When the potential is cycled back toward the reduction region, the polymer changes to a reddish color. This well documented chromic shift¹⁰ is a likely result of a change in the bandgap of the semi-conducting polymer, as it shifts from an oxidized to a neutral form. As was seen with thiophene, the increase in peak current with each successive cycle is indicative of a greater amount of polymer coverage.

Due to bithiophene's lower polymerization potential, poly(bithiophene) is more easily formed under conditions that do not support polymerization from thiophene monomers. An example of this is the formation of poly(bithiophene) on iron. As seen in Figure 15, the breakdown of iron surpasses the formation of polythiophene, due to its instability in the thiophene breakdown region. However, it is relatively stable in the region where bithiophene undergoes breakdown into its radical cation intermediates. This is especially true after several cycles and the formation of an FeF_3 passivation layer. Figure 18 shows poly(bithiophene) formation on iron in the presence of 0.1 M TBAHFP in acetonitrile.

Figure 18: The first eight cyclic voltammograms of 0.1 M bithiophene electro-polymerized on iron in acetonitrile. Scan rate = 100 mV/sec

The first two polymerization potentials for bithiophene on all the of the metals tested are shown listed in Table 4.

Bithiophene Breakdown Potentials in Acetonitrile (V)										
Cycle	Al	Au	Fe	Mo	Ni	Pd	Pt	Ta	Ti	W
1	1.12 6	0.93 4	1.10 8	1.02	1.01 6	0.934	0.933	1.126	1.06	1.052
2	0.99 3	0.93 4	1.00 4	0.96 4	0.93 6	0.934	0.933	0.974	0.99 4	0.931
ΔV	0.13 3		0.10 4	0.05 6	0.08		0		0.06 6	0.121

Table 4: The oxidative bithiophene breakdown potentials for the first and second cycles of the CVs shown in Figure 18.

The polymerization potential on all except the most noble metals (Pt, Pd, Au) drops significantly after the first cycle. This, again, is the likely result of the formation of nucleation sites on the substrate surface. Pt, Pd, and Au show no such decrease in the polymerization potentials. This suggests that there is little or no competition between the polymerization and the dissolution of the metal on these substrates.

The increase in the cathodic current with each successive cycle for bithiophene in 0.1M TBAHFP in acetonitrile is plotted in Figure 19.

Figure 19: Dependence of the metal substrate on the change in current intensity per cycle of the reduction peaks during poly(bithiophene) synthesis in acetonitrile.

The results obtained above behave similarly to those observed when thiophene was used as a monomer. The lowest increase in peak intensity is observed with Al, Ta, and Fe. The rest of the metals show an increase in current that is as much as 3×10^{-4} A higher than that observed for Al, Ta, and Fe. The notable exception, in this data, is the low current increase observed with titanium, compared to the results obtained while using thiophene as a monomer. These results are certainly unexpected and stand as a point where further investigation is warranted.

Polymerization of bithiophene using nitromethane shows the same general relationships as observed with acetonitrile. The cyclic voltammetric polymerization of bithiophene in nitromethane is shown in Figure 20.

Figure 20: The first eight cyclic voltammograms of 0.1M bithiophene electro-polymerized on various metals in nitromethane. Scan rate = 100mV/sec

The oxidation potentials for each metal are shown in Table 5.

Cycle	Bithiophene Breakdown Potentials in Nitromethane (V)								
	Al	Au	Mo	Ni	Pd	Pt	Ta	Ti	W
1	1.01 3	0.83 1	0.85 4	0.96 9	0.84	0.838	1.028	0.95 4	0.862
2	0.90 7	0.83 1	0.85 4	0.87 5	0.84	0.838	0.922	0.86 1	0.862
ΔV	0.10 6	0 0	0 0	0.09 4	0 0	0 0	0.106	0.09 3	0 0

Table 5: The oxidative bithiophene breakdown potentials for the first and second cycles of the CVs shown in Figure 20.

Nitromethane allows for lower polymerization potentials overall than those observed with acetonitrile. This is a difference of approximately 100 mV, regardless of the substrate employed. Another interesting result is the lack of a significant polymerization potential change between the first and second cycles for not only Pt, Pd, and Au, as was the case with acetonitrile, but also with Mo and W. This again suggests ease in the formation of nucleation sites and a lack of competition between metal dissolution and polymer formation.

Observation of the consecutive cyclic voltammograms (Figures 17 and 20), also shows that regardless of substrate or solvent, the resulting reduction wave undergoes a downward shift in potential upon increased polymer deposition. This is especially noticeable in the more noble metals and conversely less apparent in the more readily oxidized metals, Al and Ta. Indeed this happens when thiophene is used as a monomer as well, but is more apparent when bithiophene is employed due to the lone, comparatively narrower reduction wave that results upon polymerization. This shift in potential is indicative of an increase in the electrical resistance of the polymer film¹¹, and is a result of the increasing amount polymer formed on the substrates.

Figure 21 shows the increase in reduction peak current with the first twenty-five cycles of bithiophene polymerized in 0.1M TBAHFP in nitromethane.

Figure 21: Dependence of the metal substrate on the change in current intensity per cycle of the reduction peaks during poly(bithiophene) synthesis in nitromethane.

The number of cycles performed with nitromethane was greater than the number of cycles performed when acetonitrile was used as a solvent. This was done based on the observation that thiophene began to show over-oxidation much sooner in acetonitrile than in nitromethane. Interestingly, when bithiophene is tested the current intensities are very similar regardless of the solvent. Review of the current intensities from cycles 2-12 reveal that they are far closer in intensity when bithiophene is used as a monomer than when thiophene is used.

Figure 21 shows the same plateau effect that was observed with thiophene polymerization (Figures 10 and 12) as a result of monomer depletion and over oxidation effects. Interestingly, this effect is not observed with Al and Ta. These two substrates continue to show slow growth even after twenty-five cycles. One can presume that this is a result of the competition between polymer formation and metal breakdown. Since polymer growth is slowed by the oxidative breakdown of these two metals it is logical to assume that bithiophene monomers remain in solution even after twenty-five cycles. As the surface is slowly passivated with insoluble MF_x layers, more nucleation sites become available, and polymerization continues.

In general, bithiophene gives fuller and more homogenous coverage than does thiophene when it is polymerized under these conditions. This is particularly true when acetonitrile is used as the electro-synthesis solvent. In addition there is a clear difference in the color of the final polymer. Poly(bithiophene) is generally a reddish color (Figure 22) while the polythiophene

formed under these methods (Figure 14) tends to be a darker color ranging from dark green and blue to black. The difference in the color of the polymers is a result of the level of oxidation, as can be seen during the polymerization process. During polymerization, when the cyclic voltammograms enter into the oxidizing region, a shift in the color is seen from the red observed in Figure 22 to a dark blue/black. As the potential proceeds to the reduction region, another chromic shift is observed and the polymer returns to a reddish color.

Figure 22: Polybithiophene synthesized in (A) acetonitrile and (B) nitromethane on gold.

The difference in the oxidation levels of polythiophene and poly(bithiophene), as observed from the color of the resultant polymers, is due to the different potentials required to electro-synthesize the respective polymers. Literature sources have been inconclusive as to why polythiophene is primarily reported to have a greater overall conductivity than poly(bithiophene)⁴. Since thiophene requires higher potentials to reach its “breakdown” region, it makes sense that the final polymer will be more highly oxidized. This higher oxidation level will result in an overall narrowing of the polythiophene band gap and consequentially a greater conductivity.

In Figure 22 (B), the poly(bithiophene) formed in nitromethane appears darker in color than does the poly(bithiophene) formed in acetonitrile (Figure 22 (A)). A conclusive explanation cannot be obtained for this result. However, since the number of electro-synthesis cycles was fewer during polymerization with acetonitrile than with nitromethane, an increase in the amount of polymer formed and an increase in the polymer oxidation is probable.

FTIR spectral analysis of polythiophene and poly(bithiophene)

The properties of the polythiophene films vary dramatically depending upon preparation conditions. By using FTIR methods in conjunction with the electrochemistry it is possible to learn a great deal about the properties of the polymers. Figure 23 shows a typical FTIR spectrum for polythiophene, and is followed by table 10 with the peak interpretations.

Figure 23: Reflectance FTIR spectra of thiophene polymerized on nickel in nitromethane

Wavenumbers (cm ⁻¹)	Assignment
3063	C-H stretch (olefenic)
2965	C-H asymmetric stretch
2879	C-H symmetric stretch
1472.8	C=C stretch (ring)
1347.5	C=C stretch (ring)
1110.5	C-C vibration
1035.6	C-H deformation
833.8	PF ₆ ⁻ stretch (electrolyte)
788.9	C-H out-of-plane bend (a,a' di-substituted)
694.9	C-H out-of-plane bend (a,a' mono-substituted)

Table 10: FTIR peak interpretation of polythiophene from Figure 23.

Using the methods of Furukuwa et al.¹², it is possible to determine the general degree of polymerization through the ratio of the IR peaks resultant from the C-H out-of-plane bending of mono- and di-substituted thiophenes. These peaks are found in the general area of 690 cm^{-1} and 790 cm^{-1} respectively, and are indicative of a,a' -bonding. As the number of monomer units in the chain increases, the intensity of the di-substituted C-H out-of-plane(d-OOP) bending peaks increases (790 cm^{-1}) and the intensity of the mono-substituted C-H out-of-plane(m-OOP) bending peaks decreases (690 cm^{-1}). Figure 24 shows an example of mono- and di-substituted polythiophenes, along with an example of the labeling method used for the carbons on the thiophene ring.

Figure 24: Illustrations of mono- and di-substituted thiophene and the thiophene carbon labeling conventions.

To further illustrate the dependence of the intensity of the OOP-bending on the number of monomer units in the polymer, semi-empirical AM1 calculations were performed on polymer chains ranging in size from two monomer units to seven (Figure 25). Doing so allows for calculation of the vibration modes and their respective intensities.

Figure 25: AM1 vibration calculations showing the dependence of C-H OOP peak intensity on the number of monomer units.

Calculation of the vibration modes results in the inclusion of every possible peak obtainable from the specific molecule being studied. For the purpose of clarity, only the peaks of interest were included in Figure 25. It is apparent that as the size of the polymer chain increases, the ratio of d-OOP to m-OOP also increases. Bithiophene has only mono-substituted thiophenes and therefore only shows the lone peak corresponding to C-H m-OOP bending.

A comparison of this region of the spectra, of thiophene polymerized on platinum and aluminum are shown as Figure 26.

Figure 26: FTIR spectra of the C-H m-OOP and d-OOP bending peaks of thiophene polymerized in nitromethane (NM) and acetonitrile (MeCN) on platinum and aluminum.

In each case shown in Figure 26 the intensity of the peak associated with C-H d-OOP bending (approx. 790 cm^{-1}) is greater than the intensity of the peak associated with C-H m-OOP bending (approx. 690 cm^{-1}). It is clear, however, that there is a distinct difference between the polymers synthesized in acetonitrile (MeCN) and nitromethane (NM). Based on the intensity of the peaks, polymerization in NM appears to have resulted in the formation of polymers with a higher degree of polymerization through a,a' bonding. In addition, the polymers obtained with acetonitrile both show a strong peak located between the m-OOP bend and d-OOP bend, this

peak usually located at approximately 730 cm^{-1} is indicative of polymerization through *a,B*-coupling, particularly when accompanied by a peak at approximately 820 cm^{-1} ⁽¹²⁾. A peak at 820 cm^{-1} is not readily noticeable in any of the spectra, however, it is possible that it is being masked by the presence of the strong PF_6^- dopant peak at $830\text{--}845\text{ cm}^{-1}$. *a,B*-bonding would explain the lack of homogeneity and the spotty coverage obtained when thiophene was polymerized with acetonitrile (Figure 14(A)).

Figure 27 shows the same experiment as shown in Figure 26 using bithiophene as the electro-synthesis monomer.

Figure 27: FTIR spectra of the C-H m-OOP and d-OOP bending peaks of bithiophene polymerized in nitromethane(NM) and acetonitrile (MeCN) on platinum and aluminum.

Interestingly, when bithiophene is used as the starting monomer the degree of polymerization of the polythiophene formed with NM is much lower than that formed with MeCN. This is certainly an unexpected result, considering that the degree of polymerization using thiophene was greater in all cases when using NM. The exact reason for this result is uncertain, but suggests that polymerization using MeCN offers better overall results when the applied potentials are lower than the 1.7 to 1.5V range generally used for the synthesis of polythiophene. In contrast, synthesis in NM is well suited for higher potentials, but the drive

toward “fuller” polymerization is stunted at the lower potentials used for polymerizing bithiophene.

Figures 27 and 28 show the degree of polymerization results obtained for the remainder of the metals tested with thiophene in NM and bithiophene in MeCN respectively.

Figure 28: FTIR spectra of the C-H m-OOP and d-OOP bending peaks of thiophene polymerized in nitromethane(NM).

Figure 29: FTIR spectra of the C-H m-OOP and d-OOP bending peaks of bithiophene polymerized in acetonitrile(MeCN).

In all of the cases, shown in Figures 27 and 28 the intensity of the d-00P bend is significantly greater than the m-OOP bend. In the case of poly(bithiophene) in acetonitrile, the ratio of intensities is lower than what is observed with polythiophene in nitromethane, suggesting a lower overall degree of polymerization. The lower degree of polymerization is a likely result of the lower potentials used during the electro-synthesis.

Furukuwa et al.¹², developed the following equation to give a numerical value to the degree of polymerization (N_{dp}),

$$N_{dp} = \frac{2R_o}{R} + 2$$

Where, R is the ratio of the of the experimental d-OOP and m-OOP peak intensities and R_o has a value of 1.07, taken from the ratio of peak intensities obtained from 6-thiophene. Figures 29 and 30 show the results obtained by using this equation on the peak intensities observed with polythiophene from nitromethane and poly(bithiophene) from acetonitrile.

Figure 30: The degree of polymerization of polythiophene synthesized in nitromethane, on several different metals.

Figure 31: The degree of polymerization of poly(bithiophene) synthesized in acetonitrile, on several different metals.

Overall, the degree of polymerization follows the same trend as is observed with the change in peak intensity per cycle (Figures 12 and 17), the most noble metals show the highest degree of polymerization which is one reason platinum continues to be the metal of choice when IC compatibility is not a design requirement. In both cases represented, tantalum and aluminum show the lowest degree of polymerization, this result is expected, since visually and electrochemically, the amount of polymer obtained on these metals was minimal compared to the other substrates tested.

The observation that polythiophene shows a larger degree of polymerization than poly(bithiophene), also aids in showing why it has been reported as having a greater level of conductivity⁴. In general, as the number of monomers in the chain increase, so does the amount of overall conjugation. A higher level of conjugation allows for a greater likelihood for charge transfer and therefore increased conduction.

(e) Polymer bilayer design

A third iteration on sensing polymer improvement, developed only in the past year, was to prepare a bilayer of two separate polymers. This concept grew out of the work described

above, in which the conductive polymer was plated on about 20 different metal substrates, in order to determine the best metals, solvent, electrolyte and deposition methods to use on the gate electrode for the FET sensors.

The new sensing polymer design thus became a bi-layer: a primary layer of polybithiophene to ensure best possible coverage of the metal and adhesion of the polymer to the metal followed by deposition of the thiophene like monomer cyclopentanedithiophene-one (CPDT-one). This monomer constrains the polymer to form as a regioregular polymer, as opposed to a regiorandom deposition. This improves polymer conductivity and minimizes surface roughness. This surface is then derivitized *in situ*, according to the scheme in Figure 4, to attach the actinyl chelating group. Figure 32 illustrates the bilayer polymer coating on a conductive substrate.

Figure 32. Bilayer polymer sensor. The first poly(bithiophene) layer is electro-oxidatively polymerized onto the conductive substrate. A second polymer layer of poly-CPDT adheres well to the poly(bithiophene). The CPDT is derivitized to have the calix[6]arene rings attached at only the solution accessible sites.

f. Factorial experiment for optimization of the primary polymer layer:

Based on the preliminary work, nitromethane appeared to be the best solvent, and TBAHFP the best supporting electrolyte for the deposition process. There remained several questions about how the polymer could be improved, based on literature survey.

In March of this year, a full factorial experiment was undertaken to optimize the mechanical and electrical properties of the sensing polymer. This work is partially funded by, and continuing under a DOE grant to SUNY-Binghamton with Dr. Harold Ackler as PI. The parameters tested are itemized in the table below and include, importantly, temperature of deposition.

Experimental design is used to evaluate the polymer deposition variables which might have significant effects on the magnitude of the current that measures the presence of the trapped uranium in the sensing polymer. In the experiment, the variables (factors) and levels of factors are listed in Table 7. In mixed experimental design, three-level variables could be partitioned into linear and quadratic components and two two-level factors could be used to represent the linear component. Performing the full factorial means 36 experiments are performed. Repetitive runs are performed for the purpose of determining reproducibility. Overall, 108 experiments are performed.

Table 7.

Variable	Level of variable			Levels
Solvent	Acetonitrile	Nitrobenzene	Benzonitrile	3
Temperature of deposition	0 °C	5 °C		2
Electrodeposition mode	Galvanostatic	Cyclic voltammetric	Short high pulse/ long low pulse	3
Monomer concentration	0.01 M	0.05 M		2

Three solvents are chosen to represent the most commonly reported solvent in the literature (acetonitrile), the solvent that appeared the best in our preliminary work (nitrobenzene) and a “wild card” solvent reported very favorably by some workers in the literature. A quick set of experiments showed immediately that low temperature deposition was clearly preferred to ambient temperature, so both temperatures chosen for the factorial study are below ambient. Tetrabutyl ammonium hexafluorophosphate electrolyte gave best polymer coverage of a set of four electrolytes soluble in all solvents at 0.1 M level, and the best passivation of the metallic substrate. Therefore all electrodes are prepared using this electrolyte.

Best electrodeposition mode needs to be determined and the three apparently workable methods were chosen for the study.

- (i) a potential step-and-hold method, to deposit polymer at 1.0 v (± 0.5 v) vs. silver/silver chloride reference electrode.
- (ii) a cyclic voltammetric method wherein the potential of the electrode to be coated is swept from about 0.5 v. to about 1.1 v, vs a Ag/AgCl reference electrode.
- (iii) a controlled current method, where a constant anodic current is imposed at the electrode to be coated.

Finally, monomer concentration is reported in the literature as having a significant impact on polymer quality so we chose two concentrations, one being a 5-fold increase over the other. In this factorial experiment, only bithiophene is coated on the metal substrate. This is the primer layer which passivates the metal and provides a surface for formation of the second, sensing polymer on the electrode. The response variables for this set of experiments include film thickness, conductivity of the polymer, passivation range and characteristics of the metal substrate, FTIR of the polymer coating, adhesion of the polymer to the substrate, and visual microscopic examination of the polymer surface. Not all of this data is ready to report. Results of this factorial are still being worked up at SUNY-Binghamton by Dr. Susan Lu, under funding provided by DOE under a grant through the NNSA. Film thickness has been determined by AFM method with typical results shown in Figure 33. Measured roughness varies considerably with the deposition conditions, and is one parameter being used to determine “best” method.

Figure 33. Typical AFM data for polymer coatings prepared in the factorial experiment. Surface roughness is about 6 nm. Surface defects are minimal.

g. Current Best Design for the actinide sensor.

The current best design is as follows:

1. Deposit a thin layer of poly(bithiophene) on the prepared metal substrate under the conditions determined to be optimal in the statistically designed factorial described above. Probably those conditions will be nitromethane solvent, TBAHFP electrolyte, low temperature and low monomer concentration. However that is conjecture based on a preliminary reading of the factorial experiment and is subject to change as the response variables in the full factorial are measured and interpreted.
2. Deposit a second polymer layer consisting of poly(CPDT) having a derivatizable site in the bridging carbon position. The same polymer deposition conditions as in part 1 are used, or it is possible that the CPDT deposition conditions will be slightly different.
3. *In situ* derivatization to attach the chelating ring, according to the scheme in Figure 34.

Figure 34. In situ derivatization scheme for poly-CPDT.

h. Suggestions for the immediate future.

1. One possible improvement to the current design would be to attach the chelating ring in a manner that continues the polymer backbone conjugation up to the ring. We are investigating synthetic pathways to accomplish this.
2. Vary the polymer film thickness. Thinner will probably be better provided complete coverage of the metal substrate is achieved.
3. Determine the amount of chelating ring to put on the polymer surface. More may not necessarily be better. An electrode with full coverage of surface-derivatizable sites with the calix[6]arene was prepared. When tested for response to uranium(VI) ion in solution, this electrode gave a current corresponding to uranium binding that continued to increase for several hours without saturating. This is not a necessarily desirable condition for a trace uranium sensor. It may be desirable to have an electrode with only about 5 % derivatized sites and a quicker time to steady state signal. On the other hand, such a sensor surface would have a limited dynamic range. The intended application of the sensor will determine the optimum density of calix[6]arene on the surface.

3. Laboratory demonstration of UO_2^{2+} detection using microelectrodes

(a) Detection limit of 10 part-per-trillion uranium and thorium

Using millimeter scale electrode described in section (d) above, uranium and thorium concentrations were measured in our lab, and plutonium concentrations were measured at the DOE-Nevada test site, under the supervision of Dr. Richard Venedam. Standard solutions of uranium acetate, uranium nitrate and thorium nitrate were prepared, including mixtures of the uranium and thorium salts. Cyclic voltammetry was performed and the peaks analyzed for each metal. Current corresponds to concentration, all other parameters held constant, and the data for peak current vs. actinide standard concentration are shown in Figures 35 and 36 below. The data below shows 100 part per trillion measurement of standard. Based on 3σ analysis of the noise on the current, 10 part per trillion detection should be achievable, and possibly even lower.

Figure 35(A). Standard calibration curve for uranium(VI) ion in water. Cyclic voltammetric reduction peak current vs. uranium ion concentration. The shape of the curve follows an adsorption isotherm, according to theory. The function can be approximated by a logarithmic relationship. (B) Linearization of the curve by plotting current vs. log of concentration. Lowest measured standard concentration is 0.1 part per billion for both plots.

Figure 35. Standard calibration curve for thorium(IV) ion in water. Cyclic voltammetric oxidation peak current vs. log thorium ion concentration. The relationship has been linearized by the log plot but actually follows an adsorption isotherm relationship, as predicted by theory. Lowest measured standard concentration in this experiment is 0.1 part per billion.

(b) differentiation of actinide mixtures:

It is important to note that the room temperature, neutral pH favored ion of uranium is the +6 oxidation state, and its irreversible cyclic voltammetric wave appears as a reduction (probably to the +5 state). The thorium ion is initially +4 oxidation state, and its cyclic voltammetric wave is an oxidation, probably to the +5 oxidation state. This is shown in the cyclic voltammogram for a mixture of the two ions in equal molar concentrations. (Figure 36) They have different redox potentials and their cyclic voltammetric peaks occur not only at different potentials but across the x-axis from each other, one being an oxidation and the other process a reduction. It is clearly possible to determine each of these actinides in the presence of the other, on this polymer in cyclic voltammetric mode.

Figure 36. Cyclic voltammogram for a 1:1 mixture of uranium(VI) ion and thorium (IV) ions. The pink trace is the baseline of an electrolyte solution with no actinide ions present. The blue trace is the mixed sample, 50 ppb of each, uranyl and thoranyl ions. The reduction peak (at the lower left of the plot) is uranium and the oxidation peak (upper right) is thorium.

4. Operating limits and chemical interferences of the lab-scale sensor.

Some limits on operation have been determined. These include response time, pH, temperature, and sensor lifetime.

(a) response time of the probe.

We have demonstrated detectable response within 1 second, provided the uranium concentration is in the range of 1 ppb. The calix[6]arene forms two different complexes with the actinide ions in water. These are identified as the exo- and endo-complexes. The exo complex is kinetically favored and forms rapidly on contact. This form gives rise to the signal observed the instant the probe is inserted into a sample containing actinide ion species. A current can be recorded for the electron transfer from the exo complex within 0.1 sec. Over time, however, the endo complex forms as the actinide ions punch through the cup-shaped ligand molecules. This form is thermodynamically favored. Once formed, it does not revert to the exo complex. The kinetics of this process are much slower and the time to steady state signal for the probe is about 90 minutes, as the endo-complex slowly forms and gives rise to the steady state signal. Figure 37

shows results of this experiment. The baseline current is included, and shows sensor response in the absence of uranyl ion. The first trace is taken immediately upon insertion of the probe into a uranyl ion solution (1 ppm). The time of the trace is about 0.1 sec. The second trace is after 15 minutes and the third trace is the steady state curve at 90 minutes. Traces taken after 90 minutes were identical to the 90 minute trace. The conclusion is that at 1 ppm uranyl ion concentration, an acceptable signal is obtained within a second of exposure to the sample.

Figure 37. Time response of uranium probe in a solution of 1 ppm uranyl ion.

(b) Response of actinide sensor with change in pH.

The response of the sensor was tested in various pH regimes from pH 4 to pH 9, representing the most probable range of naturally occurring surface and ground waters. At pH 4, phenolic sites in the calix[6]arene are partially deprotonated. Published pKa's for the first 4 acid dissociations are in the range of 3 to 5. (ref. 13). This means that binding competition at pH 4 is favorable for the uranyl ion versus the H⁺ ion. Detection of uranium improves with increasing

pH as the donor atoms are increasingly deprotonated and binding competition continues to favor the uranyl ion.

(c) Presence of various chemical species as possible interferences.

OTHER ACTINIDE SPECIES: It is clear that the calix[6]arene functionalized polymer will bind not only uranium but also thorium and plutonium. It is expected to also bind any other water soluble actinide ion of the form MO_2^{2+} or MO_2^+ . If only one species is targeted for analysis then technically the others are interferences. This is why both sensors should be combined in the same probe. The FET probe cannot distinguish either the chemical identity of the bound species or the oxidation of them. However the FET will bind all water soluble actinide species and give a signal that shows the presence of any and all. The voltammetric probe is able to distinguish different elements based on differences in redox potential, as shown in the data above. The voltammetric probe can also yield quantitative information because the current of each wave is a function of concentration.

LANTHANIDES: It is expected that lanthanide species may also be bound by the polymer. They also form metal-ligand complexes using their f-orbitals which means 7 and higher coordination numbers are available to them. They are not significantly different in diameter from the actinides. The coordination sphere of the calix[6]arene is expected to provide a favorable coordination sphere for lanthanide species. A set of experiments designed to test this hypothesis is in progress using neodymium, lanthanum and dysprosium as the test elements. This work is not completed.

OTHER HEAVY METALS: The calix[6]arene is not a good ligand for smaller ions for several reasons, and these ions are not strongly coordinated. They do not compete successfully for the binding site. The binding site is 5-coordinate and is conformationally constrained such that tetrahedral and square planar coordination spheres cannot be accommodated. The ring is fairly rigid and cannot collapse around smaller ions to form a good fit. The distance across the ring is too great for all of the donors to be simultaneously active for metals smaller than the lanthanides. Therefore, coordination of smaller-diameter ions is unfavorable. The donor atoms in

the ring are all oxygen and this type of donation is not favored by some metals. Selectivity coefficients of the calix[6]arene for uranyl ion versus a number of other metals have been published. They are orders of magnitude smaller for monoatomic metal ions than for any actinide. The very high formation constant of calix[6]arene for uranyl and other actinyl ions makes it a “hyperchelator” for these species.

SOLUTION PHASE ANIONS: We are not concerned with anions that precipitate the actinide as these remove the actinide from solution where it is not accessible to the probe. Our probe is not a total actinide sensor, but rather a solution-phase sensor. Several anions coordinate in solution with actinide oxycations and could compete with the calix[6]arene binding site for the actinide species. Carbonate, acetate and a few others form solution phase complexes with actinides. It was a consideration, that carbonate could conceivably compete for uranyl binding against the calix[6]arene and thus act as an interference in detection. However the pH 7 solution showed the best response to uranyl (and also to thorium), and this solution was prepared as a carbonate buffer. Carbonate concentration was about 0.1 M. Uranium concentrations of measured standards ranged down to 0.1 part-per-billion without any observed interference from the carbonate buffer. Therefore carbonate is apparently not an interference to uranium detection with this probe. Acetate and nitrate are also dismissed as solution phase interferences because these are the counterions of the uranyl and thoranyl used in preparing all of the standard solutions. They are also present in the buffer solutions in far greater concentrations. Because a 0.1 ppb uranium or thorium ion solution is measurable even in the presence of 0.1 M nitrate and 0.1 M acetate, it is concluded that these ions do not compete successfully for the uranyl ion.

(d) Temperature response of polymer conductivity.

The thiophenic polymer is a semiconductor, as shown in Figure 2, above. Increasing temperature provides sufficient energy to promote electrons from the valence band into the conduction band, according to the band gap model. It should be noted that the shallow slope in the temperature range of liquid water (0 to 100 °C) means the sensor conductivity is not rapidly changing under the conditions of use. It is only near the normal boiling point of water that the knee of the conductivity curve is reached and conductivity of the polymer rapidly increases. Use

of the sensor in this temperature regime would require some compensation for the change in conductivity of the polymer, possibly by a look-up table and a calculation in the software.

(e) Polymer availability to microorganisms:

If the probe is to be used for long term deployment, it must not be degraded by microorganisms. Microbiological tests were performed on the monomers used for the polymer. Nutrient agar was prepared with varying amounts of the monomers incorporated at various levels as a weight percent. The agars were inoculated with known soil bacteria. A thiobacillus was used because it has a high tolerance for sulfur containing compounds and also because it is known to be present in the soil at the Idaho National Laboratories near Idaho Falls, ID. The plates were incubated for several days, and colony counts performed at 12, 24, 48 and 72 hours. At 0.6 % monomer concentration, the number of colonies is near zero for all counts, and at all concentrations higher than 0.6% monomer, no colonies were ever observed. The monomer is toxic to this organism. Polymer compounds are in general less available than monomers. Therefore, we concluded that this particular compound does not serve as a carbon source for this thiobacillus. It may be desirable in the future examine the availability of the polymer, or of the CPDT monomer to other soil organisms. Figure 38 is a plot of one of these tests, showing the number of bacterial colonies to be near zero for the 0.6% wt/wt monomer in agar for thiobacillus.

Figure 38. Thiobacillus growth at 48 hours on various levels of monomer (wt/wt) in nutrient growth medium. Growth is almost completely inhibited at 0.6% monomer concentration.

(f) Sensor Lifetime:

Only one test of sensor lifetime has been performed, and it was essentially a “shelf life” test, not an operating life test. This test needs to be repeated and an average lifetime determined. In the one test performed, a polymer coated electrode was kept for two years in a soaking solution in the lab. The sensor response was measured at the beginning and at the end of the two years, and the two measurements were within 2 % of each other. The conclusion is that a hydrated sensing polymer can detect the analyte reproducibly after two years of disuse.

5. Incorporation of actinyl-ion selective film into chem-FET device, and demonstration.

Anticipating applications of the actinide sensing polymer in IC devices, we have fabricated and demonstrated a field effect transistor (FET) sensor. In order to coat the polymer onto the gate of a working FET, we invented a nanoliter deposition method. A patent application has been filed with the United States Patent Office for this invention. In this method, a droplet of plating solution with volume of about 400 nL or less, is placed on the gate and gate contact pad of the FET. A chemically inert electrode is placed in electrical contact with the contact pad and a second chemically inert electrode is placed in physical contact with the droplet. When current is passed between the two electrodes such that the electrode on the contact pad serves as the anode, the monomer is electro-oxidatively polymerized onto the gate metal, and also on any other surface in both physical contact with the deposition solution, and in electrical contact with the anode. This method of nanoliter deposition eliminates the need for photolithography, masking or etching to achieve precision placement of a functional polymer on the device. In principle, multiple different polymers could be deposited on multiple devices on the same wafer without any masking, photolithography or etching. Figure 39 shows a photomicrograph of an actual working FET in process of nanoliter deposition of polymer. Figure 40 shows the FET with polymer coating on the gate, only. Figure 41 shows a typical family of I_D vs. V_D curves generated for this FET at various values of applied gate and source voltages. As applied gate voltage increases, the source drain current increases as the current pathway has more charge carriers in it. The middle curve in each group is the bare (uncoated) FET, and shows characteristic operation of the device. The lower curve in each group is the operation of the FET with the polymer coating on the gate. Current is reduced. The upper curve in each group is the response characteristic of the FET at the indicated applied potentials after exposure to a solution

containing uranyl ion. The analytical signal for the device is the difference in current between the upper and lower curves in each group. This data shows that the probe sensitivity increases as applied gate potential increases because the current difference between upper and lower curves increases at all values of bias voltage across source and drain. This relationship will hold true until the breakdown voltage of the device is reached.

Figure 39. FET in process of being coated with sensing polymer, using nanoliter deposition method. Tungsten microprobe on the right is in contact with the gate contact pad. Tungsten microprobe on left is in contact with plating solution on the gate electrode. It is not in focus because it is not touching the gate.

Figure 40. FET showing sensing polymer coating on gate only. The contact pad has defects in the polymer from placement of the tungsten microprobe however the functional part of the device has a flawless coating. (In the red rectangle)

Figure 41 Characteristic I_D vs. V_D curves for uranium sensing FET. Middle curve in each group of three is the uncoated, bare FET. (Red trace) Lower curve is the coated FET before exposure to uranyl ion. (green trace) Upper curve is FET response after 1 hour exposure to uranyl ion solution. (blue trace)

The conclusion drawn from this set of experiments is that source drain current increases measurably upon coordination of uranyl ion into the chelating ring. This is because the binding of the uranyl ion changes the effective gate potential. The extremely small size of the FET sensor, the potential for automated fabrication and the extremely low cost on a per-device basis makes this an attractive option for uranium and other actinide sensing capability. Robust solid state function, inexpensive fabrication and rapid response capability makes this device suitable for incorporation into a single use instrument, including clandestinely deployed instrumentation.

6. Assembly and demonstration of hand-held voltammetric instrument

The work on this phase of the project used the millimeter scale sensors for several reasons. First, we have far more experience with this size of electrode and for field demonstration wanted to use a well characterized electrode. Secondly, if the entire instrument, including housing, power supply and data system, is several centimeters in dimension, it is not a design requirement that the sensing element be microns in dimension. A commercially available PalmSens™ potentiostat was purchased. This instrument is small in size and has a battery pack option for the power supply. It is field portable in a small carrying case. Experiment control and data acquisition were provided by a Compaq™ “Pocket PC” computer interfaced to the potentiostat. Data acquired on-site was downloaded to an Excel spreadsheet and processed later. Figure 42 shows this field portable system with the voltammetric type of uranium probe in a Teflon housing with a sliding protective window. Three electrode are inserted into the Teflon housing, the uranium sensor, the reference electrode and an auxiliary electrode to complete the circuit. Potential is controlled between the uranium probe and the reference electrode. Current

resulting from electron transfer at the uranium probe is measured between it and the auxiliary electrode. Figure 43 shows a close up of the probe itself. Several different models of this probe have been designed, having various types of windows for protection of the electrode and remote removal to permit sample measurement.

Figure 42. Field portable sensor for uranium and other actinide species. Potentiostat and computer components are commercially available. The probe is the one designed and implemented in this project.

Figure 43. Close up of the uranium probe. Teflon™ housing with uranium sensing polymer coated on platinum substrate (the visible wire).

This field portable instrument was taken to the DOE-Nevada test site north of Las Vegas, NV where uranium and plutonium contaminated waste waters were measured. Figure LLL shows cyclic voltammetric data for a typical sample having plutonium concentration approximately 10 times uranium concentration. Two samples and a 0.1 M LiClO₄ salt solution baseline were run. One sample was a 1:1 dilution of the other, with the KCl salt solution as diluent. Actual concentration information was not available at that time. The data show an

approximately 2:1 current level for the more concentrated plutonium solution versus the less concentrated solution, according to theory. The plutonium ion is in the form MO_2^+ (+4 oxidation state) and the electron transfer process occurring is an oxidation (anodic current.) In contrast, the much smaller uranium concentration appears as a small wave at about -0.4 V for the UO_2^{2+} species (+6 oxidation state) and the electron process is a reduction. These curves show the 2:1 relationship for both elements arising from the dilution of the original sample, as well as the approximately 10-fold greater plutonium current corresponding to the same relationship in relative concentration.

This data is proof of concept that both plutonium and uranium ions can be simultaneously detected with this voltammetric probe. The two elements have different redox potentials, occur naturally in different oxidation states, and their voltammetric traces readily distinguish these features.

7. The battery-powered portable potentiostat for voltammetric operation

A review of the literature did not yield any simple, inexpensive and low power consumption designs for construction of a potentiostat. Therefore, an inexpensive, battery powered potentiostat was designed, implemented and demonstrated. This potentiostat addresses inadequacies of the commercially available model used in the field portable instrument demonstrated above. First, the new potentiostat is much smaller. The breadboard dimensions are 3 cm x 13 cm, making it suitable for use in a direct push cone penetrometer for insertion in the shallow geologic subsurface. It could easily be made even smaller if necessary. A number of functionalities are built into this potentiostat which are not presently offered in a commercially available instrument. The potentiostat accepts a trigger pulse to initiate the data cycle. Then it temporarily records the full cyclic voltammogram in a data buffer, applies noise filters and smoothing algorithms, detects peaks, extrapolates a baseline and finds the faradaic current for the analyte, compares the current to a look-up table for concentration determination, compresses the concentration data and transmits only the compressed data, for very low power transmission requirement. A full paper on this design and implementation has been published. Figure 44 is the circuit schematic for the potentiostat and Figure 45 is a photograph of the working potentiostat.

Figure 44. Schematic of the breadboard potentiostat.

Figure 45. Photograph of the working potentiostat. Breadboard dimensions were designed for incorporation into a small bore direct push cone penetrometer, approximately 2.5 inches ID.

This all-solid state potentiostat is also rugged enough to incorporate into an instrument intended for clandestine deployment such as being dropped from a drone aircraft into a waste pond.

8. *Patents, publications and presentations*

(a) Patents: two patents have been filed with the United States Patent Office from this work.

1. A nanoliter deposition method for polymer layers in silicon based devices. Filed 2005.
2. A combined sensor probe for uranium and other actinide species in aqueous samples. Filed 2005.

(b) Publications (* indicates student co-author):

1. *T.Vamsi Krishna, J. Jessing, D. Russell, *J. Scaggs, *L. Warner, J. Hartman, "Modeling and design of polythiophene gate electrode chemFET for environmental pollutant sensing", IEEE 803-7972-1/03 2003
2. *Ashwini Vittal Gopinath, Dale Russell, "An inexpensive, field-portable programmable potentiostat", *The Chemical Educator*, in press, December, 2005.

(c) Presentations (* indicates student co-author):

1. Michael Hill, *Jonathan Scaggs, Dale Russell, "Electrochemical Sensors for Heavy Metals" 9th International Meeting on Chemical Sensors, Boston MA July 7-10, 2002.
2. *Jon Scaggs, Dale Russell, *Ryan Meyer, William Knowlton, Michael Hill, William Bauer, Tedd Lister. "Field Portable Electrochemical Sensors for Heavy Metals" American Chemical Society National Meeting, August 18, 2002, Boston MA.

3. Dale Russell, *Jon Scaggs, *Ryan Meyer, William Knowlton, Michael Hill, William Bauer, Tedd Lister, "Electrochemical Sensors for the Transuranics" American Chemical Society National Meeting, August 18, 2002, Boston MA.
4. *Jon Scaggs, Dale Russell, *Ryan Meyer, William Knowlton, Michael Hill, William Bauer, Tedd Lister. "Field Portable Electrochemical Sensors for Heavy Metals" , Subsurface Science Symposium, October 13-16, 2002. Boise ID.
5. Invited Paper: Russell, Dale, D. "Electrochemical Sensor for Uranium and the Actinides" Washington State University, Analytical, Environmental and Radiochemistry (AER) Seminar, February 28, 2003.
6. *Wilson, T.; Russell, Dale; Warner, D. L. "Synthesis of a Cyclopentadithiophene: Monomer Unit in the Semi-Conductive Film of an Electrochemical Sensor" Poster presentation at the 45th Annual Meeting of the Idaho Academy of Sciences; Lewiston, ID; April, 2003.
7. *Scaggs, JM, Russell, DD, Knowlton, WB, Bauer, Wm. "Chem-Fet sensors for heavy metals", American Chemical Society Nat'l Meeting, New Orleans, LA. March 23-27, 2003, (Poster, in Analytical Section)
8. *Meyer, RL; Russell, DD; *Scaggs, JM; Knowlton, WB; Hill, MW; Bauer, Wm. "Design and development of heavy metal selective chem.-FET sensors using conductive, chelating polymers" American Chemical Society Nat'l Meeting, New Orleans, LA. March 23-27, 2003 (Poster, in Analytical Section)
9. *Meyer, RL; Russell, DD; Knowlton, WB; *Scaggs, JM; *Warner, LR; *Kiri, D; Bauer, Wm. "Design and development of heavy metal selective chem.-FET sensors using semi-conductive, chelating polymers" American Chemical Society Nat'l Meeting, New Orleans, LA. March 23-27, 2003 (Oral, in Materials Science Section)
10. *J. Scaggs, D. Russell, *L. Warner, *R. Meyer, W. Knowlton, *D. Kiri, *Z. Clark, W. Bauer, T. Lister, "Design and Development of Heavy Metal Sensors", INRA Subsurface Science Symposium, Salt Lake City, UT, Oct. 6-8, 2003.
11. Knowlton, William B., Dale D. Russell, *Dorian Kiri, *Jonathan M. Scaggs, *Lisa Warner and *Ryan Meyer, *Fabrication of ChemFETs for uranium detection in geological subsurface groundwater*, invited talk (& extened abstract) at the 2003 Subsurface Science Symposium (5-8 October 2003).
12. *T. Vamsi Krishna, J. Jessing, D.D. Russell, *J. Scaggs, *L. Warner, J. Hartman, "Modeling and design of polythiophene gate electrode chemFETs for environmental pollution sensing" , IEEE UGIM (University/Government/Industry Microelectronic) Symposium, Boise, ID. June 29-July 2, 2003.
13. *Kiri, Dorian, William B. Knowlton, Dale Russell, *John Scaggs, and *Lisa Warner, *Reliability of Molecular Electronic Chemical FET Sensors*, poster presentation at the 2003 IEEE International Integrated Reliability Workshop, Oct, 20-23, 2003.
14. *Ryan Meyer, Dale D. Russell, William B. Knowlton, *Dorian Kiri, *Lisa Warner, *Jonathan M. Scaggs, "Design and development of heavy metal sensors using conductive chelating polymers." PittCon, Chicago, Il. March 7-12, 2004

15. *Dorian Kiri, William B. Knowlton, Dale D. Russell, *Lisa Warner, *Jonathan M. Scaggs, and *Ryan Meyer, "Heavy Metal Chem-Fet Sensors Fabricated Using Nanoliter Electrochemical Deposition Of Polymer " PittCon, Chicago, Il. March 7-12, 2004
16. Dale Russell, *Jonathan Scaggs, *Ryan Meyer, William Knowlton, *Dorian Kiri, *Lisa Warner, "Field Portable Sensor For Uranium And Plutonium", PittCon, Chicago, Il. March 7-12, 2004
17. *Dorian Kiri, W.B.Knowlton, Dale D. Russell, *Lisa Warner and *Jon Scaggs, "Molecular Electronic Chemical FET sensor for Uranyl Cation (UO_2^{2+}) Detection", 2004 IEEE Electron Device Society Second Regional Meeting, a Workshop on Microelectronics and Electron Devices, Boise, ID. April 16, 2004
18. "Field portable electrochemical sensor for uranium and other actinides in aqueous samples", D.D. Russell, *B.M.Cawrse, *N. Minskoff. 230th American Chemical Society National Meeting, Washington, D.C., August 28-Sept. 1, 2005. (paper 382, Analytical Division, Symposium on Sensors and Instrumentation for Counterterrorism: Detection of NUC/RAD materials)
19. Invited paper: "Field portable electrochemical sensor for uranium and other actinides in aqueous samples", D.D. Russell, the Federal Remediation Technologies Roundtable, Dec.7, 2005. Arlington VA.

9. Student involvement

A number of students worked on this project and gained appreciation for national security and non-proliferation related research. 17 undergraduate students, four graduate students, one post doctoral fellow and one post-MS research associate worked at least one semester for university credit, for pay or for both, on the development and demonstration of the actinide sensors. In a predominately undergraduate environment, which Boise State University is, students often work on a project for only a semester or two prior to graduation. That was the case for about half of these undergraduates. The other half, started with the project more than a year prior to their graduation, and stayed with (or are still staying with) the project until graduation. These undergraduate and graduate students performed most of the work reported herein.

Many of the students, both undergraduates and graduates, made presentations at national and international meetings on this work which are listed in the previous section.

This particular project required an interdisciplinary approach such that expertise outside of chemistry or engineering was often needed. We were able to identify and attract students for short term, self-contained projects, who brought some particular expertise. One example of this was Joeli Adriany, a student who majored in microbiology, and who performed the tests of bioavailability of the polymer coating, reported here. Another example is Brian Stokes, a skilled machinist who designed and made the Teflon probe housings, including 5 different

configurations having sliding windows and multiple electrically insulated compartments for the electrodes.

Several **women and underrepresented minorities** worked on this project. These included Joeli Adrian, Lisa Warner, Kathy Freeman, Chris Pentico.

Several of the project personnel are particularly interested in **national security and non-proliferation** work. These include Noah Minskoff, US Army veteran who is presently working on his undergraduate degree in chemistry and plans to continue with this project; 1Lt. Benjamin Smith, presently with the US Army Rangers, 1Lt. Jonathan Scaggs, presently with the Idaho Air National Guard; Jason Roethig, presently employed at Micron Technology, and Brian Cawrse, presently with the Peace Corps.

A list of all students and other technical staff, and their current positions, is included as an appendix.

10. Continued work

This project continues to be funded by the DOE under two separate sources. First, a DOE-NNSA grant to SUNY-Binghamton (PI is Dr. Harold Ackler) includes a pass-through contract to Boise State University to continue work on this actinide sensor. Secondly, Dr. Richard Venedam of the Advanced Monitoring Systems Initiative (AMSI) has committed funding for testing the probes at the DOE-Nevada test site in 2006.

A “Phase 1” proposal has been submitted to the DOE STTR type of grant in cooperation with Burge Environmental, specifically to bring this sensor to the point of commercialization.

With continued funding, this work progresses in the following areas:

- (a) Optimization of the actinide sensing polymer. This is the full factorial experiment outlined above in section 2(f). Optimization will be based on sensor response to uranyl ion and minimization of response to any known, possible interference.
- (b) Characterization of lanthanide interference, as discussed in section 4 (d).
- (c) Determining the best method to remove the uranium or other actinide species from the surface, in order to re-use the sensor. We are looking into opening the calix[6]arene, or derivatizing it in some way that reduces its binding coefficient and permits removal of the target analyte. If successful, this will reduce the thermodynamic constant for actinide coordination

possibly permitting removal and re-use. The disadvantage of this would be loss of selectivity for the actinides, but it needs to be examined.

(d) Investigating multiple identical sensing elements on a re-usable probe, such that only one polymer sensor is exposed for each measurement. If this route is chosen, then each sensing element will be single-use only, but the advantages of the calix[6]arene's chemical selectivity for actinide species will be retained and chemical interferences would remain minimal.

(e) Field deployment down-hole at Idaho National Laboratories and at DOE-Nevada test site north of Las Vegas, NV. The plan is to incorporate the uranium sensor into a cone penetrometer for insertion down hole at the INL. This is being done in collaboration with Dr. Molly Gribb, Department of Civil Engineering, BSU, and is being funded by the US EPA. The other deployment is planned for mid-spring at DOE-NV test site and is being funded by AMSI.

11. Conclusions

We have designed and demonstrated working models of two types of sensors for uranium and other actinide species in water. These sensors have detection limits in the range of 10 parts-per-trillion, with response time under 1 second at concentration of 1 ppb. The sensors also exhibit several characteristics making them field portable and suitable for clandestine deployment. These characteristics include all-solid-state components, mechanical and electronic ruggedness, low cost, simplicity of design, resistance to chemical interferences, and broad dynamic range in concentration response. The combined probe, consisting of both the FET and the voltammetric modes of operation is capable of detecting total actinide as well as differentiating and quantifying the actinides separately. We are moving toward optimization of design and commercialization of the probe in collaboration with an industrial partner.

This sensor addresses the original purpose of an instrument capable of detecting uranium for the purpose of nuclear non-proliferation treaty verification. It addresses the desired goal of a sensor suitable for clandestine deployment. It also addressed very successfully the additional stated purpose of giving students hands-on experience in national security and non-proliferation research.

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Appendix. Students who worked on the uranium sensor from October 2001 to September 2005

Student Name	Student Status while on project	Present position
Michael W. Hill	post-doctoral fellow	owner and CEO, Boise Technology, Inc.
Jonathan Scaggs	undergrad and grad	Ph.D. candidate at Washington State, also an officer in ID Air National Guard.
Ryan L. Meyer	graduate (MS)	Micron Technology, Boise, ID
Ashwini Vittal Gopinath	post-MS res. assoc.	Texas Instruments, Bangalore, India
Chris Pentico	graduate (undeclared)	graduate student at BSU
Lisa Warner	graduate (MS)	graduate student at BSU
Thomas Owen	undergraduate	graduate student at UC-Riverside
Benjamin Smith	undergraduate	1Lt. in US Army Rangers (deployed)
Devin Erickson	undergraduate	undergraduate at BSU
Jason Roethig	undergraduate	Micron Technology, Boise, ID
Tyler Wilson	undergraduate	graduate student at Univ. Illinois, Champaign-Urbana
Joeli Adrian	undergraduate	employed at St. Luke's Medical Center awarded BSU Top 10 Scholar 2004
Brian Stokes	undergraduate	undergraduate
Roy Davis	undergraduate	undergraduate
Markus Degirmenci	undergraduate	undergraduate
Craig Johnson	undergraduate	undergraduate
Scott Schlegel	undergraduate	graduate student
Brian Cawrse	undergraduate	Peace Corps in Malawi
Taylor Dixon	undergraduate	undergraduate
Dorian Kiri	undergraduate	Micron Technology, Boise ID awarded BSU Top 10 Scholar 2004
David Jenkins	undergraduate	undergraduate
Zak Clark	undergraduate	undergraduate