DEVELOPMENT OF A SELECTIVE CALIXARENE SENSOR FOR URANIUM

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ABSTRACT
Traditionally, measurements of uranium in wastewater have been obtained by laboratory based instrumentation, such as inductively coupled plasma spectroscopy, ion-chromatography and radiochemical methods. However, such methods and equipment, whilst offering excellent sensitivity and reproducibility, are far too large and heavy to be portable. Therefore, there has been a lot of interest in developing a portable sensor to carry out uranium measurements.
This work describes how a class of molecule called calixarenes have been used to develop a sensing methodology for measuring uranium concentration at low levels. This has been achieved by taking the established co-ordinating properties of the calixarene molecule for uranium and then adding functionalities to the molecule to make it adhere to metal surfaces. This way, a layer of the uranophilic molecule has been prepared on electrode surfaces, one molecule thick. These electrodes have been shown to be sensitive to uranium between 5 and 300 parts per billion.
Using these modified electrodes, a portable device has been developed, which potentially allows for measurement of uranium in the field.
This sensor therefore presents a very significant advantage in that it allows for rapid determination of low levels of uranium in wastewater, whilst offering portability.

INTRODUCTION
The development of chemical sensors for monitoring contaminants in the environment is a topical and exciting area of research (1). Inevitably, in and around nuclear establishments, there is a need to measure and monitor levels of potentially toxic and radioactive contaminants which result as part of a process, or as part of the continuing environmental monitoring of sites, as levels deemed acceptable by regulatory bodies decrease. One such contaminant of interest is uranium.
Routine analysis of contaminated wastes may be accomplished by classical techniques such as inductively coupled plasma atomic emission or mass spectroscopy and radiochemical counting techniques for low levels of radioactive samples. Also, laser spectroscopic techniques, such as laser induced fluorescence have been shown to be able to detect uranium at very low levels (2). These methods are extremely good at providing accurate measurements of metal cations in aqueous samples and they offer, in many cases, incomparably good detection limits. Unfortunately, although these methods offer excellent accuracy and reproducibility, they are expensive, usually very large, and often require long analysis times and highly trained staff to interpret the data. On the other hand, sensors offer the possibility of providing a small device, which can be easily deployed to the site of contamination and require little maintenance or operator skill and time.
This paper describes how a uranophilic calixarene has been developed to make a small uranium sensing apparatus, which has great potential to be developed as a uranium sensor.

RESULTS AND DISCUSSION

In typical aqueous environmental samples, uranium exists as the uranyl cation (UO_2^{2+}). There are very many inorganic and organic molecules that readily bond to uranyl, for example, sulphate, carbonate, acetate, carboxylic acids (3), catechols (4), crown ethers (5), humic acids, citrate (6) and calixarenes (7) This fact can be used to the chemists advantage or disadvantage; it can make uranium more soluble in aqueous samples, or it can be used to isolate uranium from aqueous samples. Interest in using calixarenes to isolate uranium from water began with the discovery that certain calixarenes bonded to uranyl extremely well (7,8,9,10). Calixarenes are a type of cup shaped molecule that can be readily chemically manipulated and to this end can be used to complex many chemical species, including metal cations. By attaching different chemical functionalities to the molecule, its resulting properties can be changed, indeed, studies showed that solvent extraction of uranium with a specific calixarene, the acid-amide calixarene (11)(Figure 1a), was very efficient and this opened up the possibility of using calixarenes as extractants for uranium (12). Then by chemically attaching the calixarene to polymer supports (13), quantitative extraction of uranium was demonstrated.

Our success with using calixarenes to extract uranium led to investigations of the use of calixarenes as sensors. The calixarene molecule may also be functionalised with molecules that may give it sensor properties, for example, by chemically attaching chromophores or fluorescent groups (14,15,16,17), the resulting calixarene has the potential to be used as an optical sensor, or by adding groups that respond electrochemically (18,19,20), such as ferrocene, an electrochemically sensing calixarene can be prepared.

Initially the acid-amide calixarene was incorporated into an ion-selective membrane and it was demonstrated that this could be used to measure uranium in part per million level wastes (21). However, in order to develop calixarenes as sensors for detecting very low levels (part per billion) of uranium, sensor functionality needed to be added to the molecule. In addition to the methods of converting calixarenes into sensing molecules as already described, it is well established that organic molecules may be adhered to metal surfaces by the use of sulphur functionalities (22). Workers have used this technique to measure low levels of metals at electrode surfaces, for example, crown ethers (23) and calixarenes (24) have been adhered to electrode surfaces for the selective measurement of metals.

Therefore, firstly, a calixarene was required that would (a) bind to uranyl and (b) would adhere or anchor itself to an electrode surface. With this in mind, through considerable synthetic manipulation, a calixarene molecule as shown in Figure 1b was prepared. The calixarene molecule was designed in two essential parts; it contained chemical functionality on the lower rim (acid and amide groups) that complex uranium and then a linker to sulphur atoms which provides the anchor to the metal surface (25).

Secondly, in order to prepare electrodes modified with the calixarene, gold wire electrodes were chemically polished, then immersed in a solution of the calixarene. This process allowed a single monolayer of the calixarene to adhere to the gold surface to give the uranium sensing electrodes.

ELECTRODE RESPONSE TO WASTE

There were a number of waste streams available for analysis: these varied from samples containing medium levels of uranium (*ca*. 100 ppm or 10^6 Bqm^{-3}), often as a sludge, to samples prepared in the laboratory containing only depleted uranium [ca. 1-100ppb or 10^2 Bqm^{-3} (α)]. These samples potentially contained a number of possible interferents. Previous work had shown that the calixarene also exhibited good take up of the lanthanides, cadmium, lead and strontium (12), therefore there was a strong possibility that these metals might cause

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interference depending on the pH of the matrix. Similarly, the anions such as carbonate were known to exhibit high stability constants with uranium, therefore these also presented a potential for interference by competing with the calixarene for uranium when using real wastes.

For the purpose of this work, two different uranium containing wastes were studied. These were (i) uranium only standard solutions, (ii) a real waste solution. Table 1 shows the composition of the uranium containing wastes. All solutions were adjusted to pH 2 using dilute sulphuric acid. As can be seen from Table 1, the uranium concentrations were very low. The compositions of the waste were determined by ICP MS/AES and ion-chromatography prior to testing in these experiments.

The wastes were then analysed using the calixarene modified electrodes connected to standard cyclic voltammetry apparatus, either using the benchtop instrument or a portable mini-potentiostat connected to a lap-top. The portable instrumentation has the potential to be further reduced in size.

It was found that the response varied greatly with the type of electrode used and the method of electrode preparation also had an influence on the response. The electrodes were prepared using a number of cleaning steps including abrasion with alumina and sonification. Commercially available polychlorotrifluoroethylene (CTFE) coated gold electrodes were used for the results reported here.

It was found that all the wastes required a certain induction period before an electrochemical response was found, then following this, both oxidation and reduction peaks corresponding to a chemical change due to the presence of uranyl appeared which grew as a function of uranyl concentration and time. Both the solutions (laboratory and real waste) provided similar results and are shown in Figures 2a and 2b as a plot of peak area against uranium concentration. From this plot it was clear that the electrode response increased with concentration for both solutions: peak heights were recorded in each instance following a pre-set time of immersion in the particular waste solutions. Current infrared studies (26) have provided information on the mechanism by which this response is obtained and additional work is in progress to further understand the underlying chemistry.

The variation in response between different wastes currently precludes the use of this apparatus in unknown uranium containing matrices: current indications suggest that each waste stream behaviour must be firstly well studied and characterised before the electrochemical apparatus can be used "blind."

Therefore, current work is focussed on determining the response of the electrodes to a range of other wastes and then to obtain a profile of response against concentration in a uniform matrix.

CONCLUSIONS

By preparing calixarene monolayers on gold electrodes a sensing mechanism for uranium has been developed. The methodology has shown excellent response to laboratory generated uranium solutions and with real uranium containing wastes. Currently, the mechanism of the response is not fully understood, however, future work will address this issue. The sensing methodology has also been developed for use in the field using portable equipment.

EXPERIMENTAL

Metal ion concentrations were determined from ICP measurements performed on either an ARL 3410+ ICP-AES or a Fisons VG PlasmaQuad ICP-MS. ICP measurements were recorded with an error of two relative standard deviations. Matrix anions were determined by ion chromatography using a Dionex 2010i instrument and CN analysis was obtained using the pyridine pyrazalone method, using a HACH DR2000 spectrophotometer and values are quoted to within ±5%. All chemicals were obtained from Aldrich. Laboratory prepared solutions used depleted uranium (DU) in 1% nitric acid and distilled water was used throughout the experiments. The real waste was prepared by 10-fold dilution of well-characterised waste samples, then these were spiked with standard uranium solution to produce the uranium containing real waste solutions. Cyclic Voltammagrams were recorded using a BAS 1000 Electrochemical Analyser and a silver/ silver chloride reference electrode was used throughout the experiments.

Table I. Analysis of Three Wastes Used in Experiments (Figures in ppb unless stated)

	Real Waste*							Uranium Only							
Uranium	0	2.0	8.0	15	20	40	52	5	10	15	25	50	100	200	300
Beryllium	<1														
Chromium	2														
Iron	850														
Nickel	13														
Copper	11														
Zinc	75														
Cadmium	<1														
Lead	4														
Mercury	<1														
Chloride	380														
Nitrate	<200														

* Wastes were diluted 10 fold. Concentrations quoted are for undiluted wastes.

a.

b.

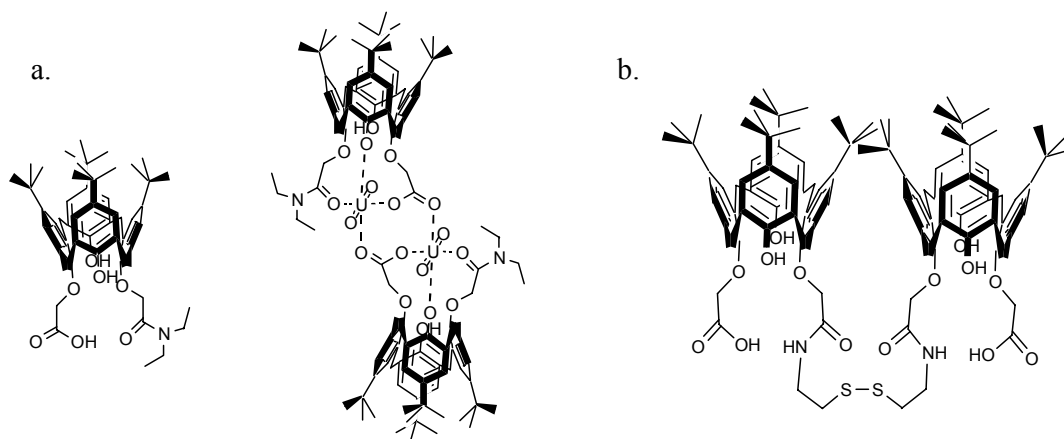Fig. 1a. Acid-amide Calixarene and its Uranyl Complex.

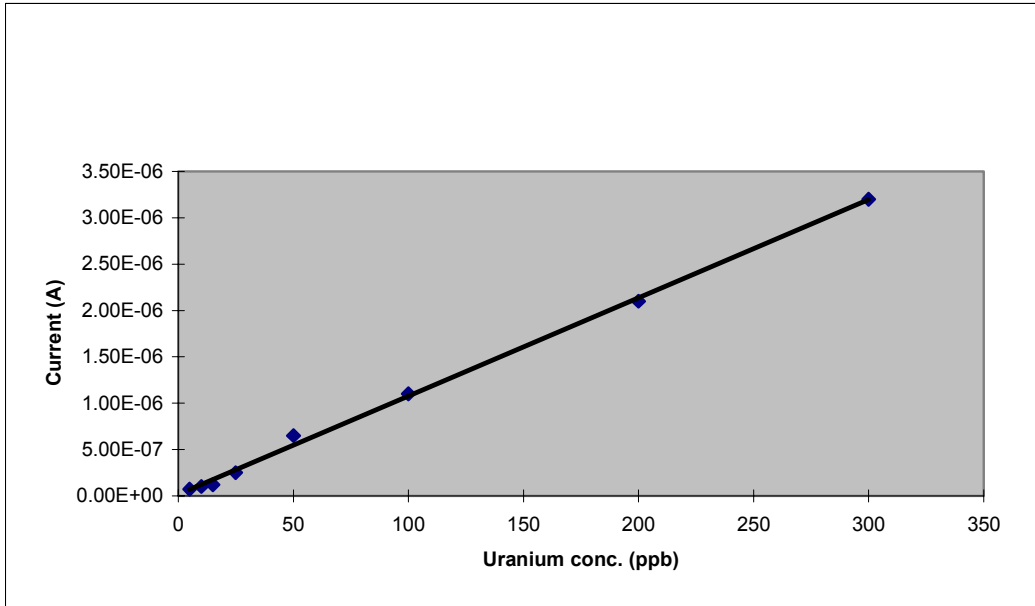Fig. 1b. Structure of Calixarene Used to Coat Electrodes.

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Fig. 2a, Relationship between Ip (anodic) for the voltammetric peak at 200mV and concentration of Uranium in Laboratory Prepared Solutions.
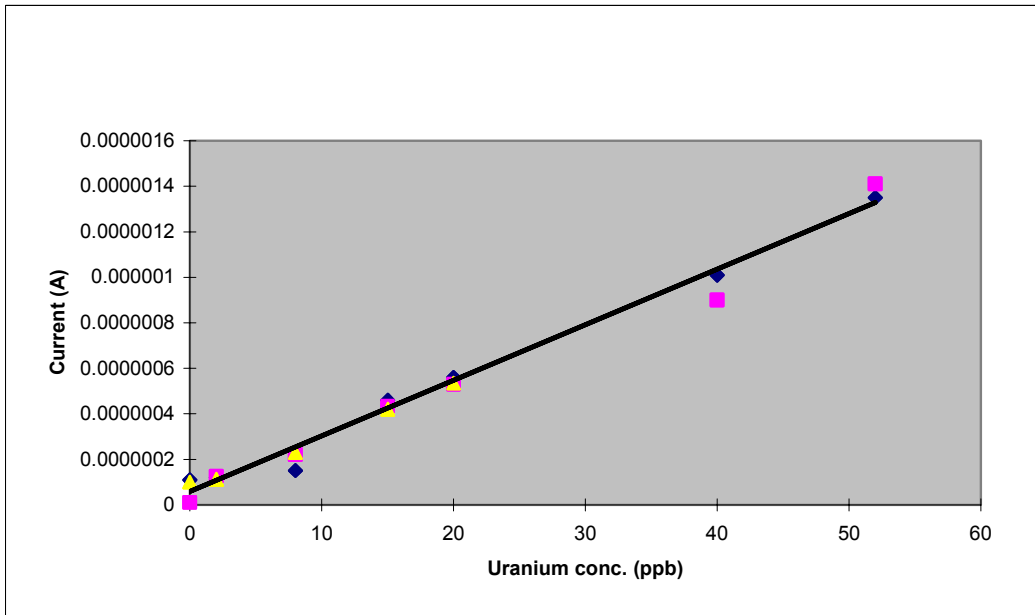

Fig. 2b, Relationship between Ip (anodic) for the voltammetric peak at 200mV and concentration of Uranium in Real Waste Effluent.

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