

The Micro-Optical Ring Electrode: A Sensor for Multiple Actinide Ions Monitoring-17586

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ABSTRACT

We present on the development of the Micro-Optical Ring Electrode (MORE) for the analysis of trans-uranium elements in aqueous mixtures. The MORE is a photo-electrochemical device based on a ring microelectrode that uses the insulator interior to the ring as a light guide. This single device exploits the unique photophysical and electrochemical properties of multiple analytes present in mixtures to quantify them. Our study aims to develop a protocol for the analysis of ions of uranium, neptunium and plutonium, which are most relevant to the nuclear industry, especially in the areas of decommissioning and fuel reprocessing, where speedy and safe identification of radioactive contaminants is essential.

The technique offers a number of advantages over traditional methods in the area of radiochemical analysis such as real time monitoring *in-situ*, reduced radiation dose impact to the analyst as a result of greatly reduced sample handling and preparation, improved analysis times allowing quick decision making, at a much reduced cost (e.g. compared to ICP-MS and Scintillation counting).

Here we present results of our study on non-radioactive surrogates for the target elements and discuss the advantages the technique can deliver to the nuclear industry.

INTRODUCTION

The Micro Optical Ring Electrode (MORE, fig. 1) is a microelectrode that consists of a central cylindrical fibre optic support (inner insulator), surrounded by a concentric gold ring (conducting layer). The fibre optic facilitates the delivery of monochromated light to a solution containing the analyte of interest and initiate a series of photochemical reactions whose products can be detected electrochemically at the gold ring. Careful selection of the illumination wavelength and operating electrode potential, offers a dual means of determining the concentration of the target analyte in the solution of interest.

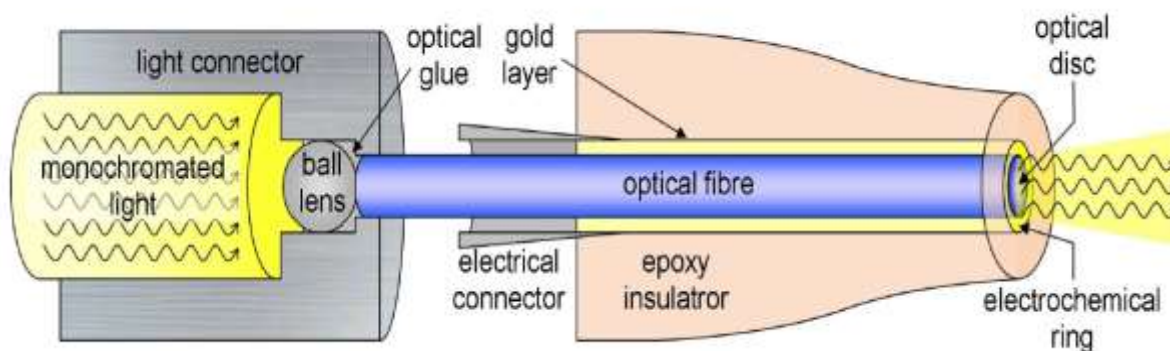


Fig. 1. Diagram showing components of the MORE [1]

Mechanism of Detection

The MORE is capable of detecting photocurrents via two types of photoelectrochemical interactions. In a photophysical – electrochemical (PE) system, the photoexcited analyte of interest, which is referred to as the sensitizer (S), can be detected directly by the MORE.

If the photoexcited species is very short lived it may relax into its ground state prior to being detected at the ring. An acceptor (A) can then be added to the system to react with the photo-excited species producing a more stable compound which may more easily be detected at the ring (photophysical – chemical electrochemical (PCE) system).

This forms the basis on how the MORE will operate, with either uranium, neptunium or plutonium ions acting as the sensitizer. The necessity of adding an electron scavenger (acceptor) will be investigated and will depend on the lifetime of the photoexcited analyte.

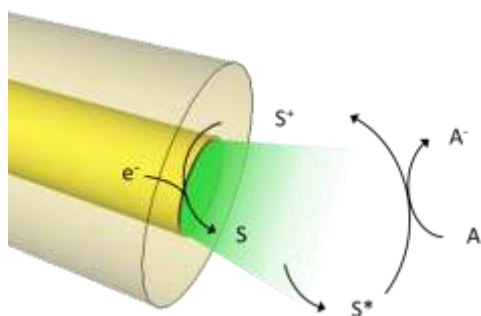


Fig. 2. Diagram showing the sensitizer and acceptor system.

This process has been modelled mathematically [2] and, as can be seen in equation (1), the photocurrent (i_{ph}) is dependent on both the concentration of the sensitizer [S] and acceptor [A]. Other symbols in the equation are either constants or parameters due to the dimensions of the MORE. One parameter of particular importance is the diffusion coefficient (D_s), this is a measure of the velocity that a sensitizer moves through a solution.

$$i_{ph} = nFD_s\pi \frac{\phi I_{ph}\epsilon[S]}{1.2k_2} \left[\frac{k_1[A]}{k_0+k_1[A]} \right] \sqrt{\frac{a}{x_k}} \sqrt{b^2 - a^2} \frac{3}{2\Gamma(2/3)} \int_0^{(k_2t)^{2/3}} e^{-z^{3/2}} dz \quad (\text{Eq. 1})$$

n- number of electrons exchanged, F- Faradays constant, D_s – Diffusion coefficient species S ($\text{m}^2 \text{s}^{-1}$), [S] – concentration of sensitizer (mol m^{-3}), [A] – concentration of acceptor (mol m^{-3}), Ψ – quantum yield, I_{ph} – Flux of light at electrode surface ($(\text{mol photons}) \text{m}^{-2} \text{s}^{-1}$), k_0, k_2 – pseudo-first-order rate constants (s^{-1}), k_1 – second- order rate constant ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$), x – distance into the solution from and normal to the plane of the electrode surface (m), t time(s), ϵ – extinction coefficient at wavelength λ .

Target Analytes

Uranium (VI), neptunium (IV), plutonium (III) and (IV) ions all have maximum absorbance peaks at different wavelengths of the electromagnetic spectrum (fig.3).

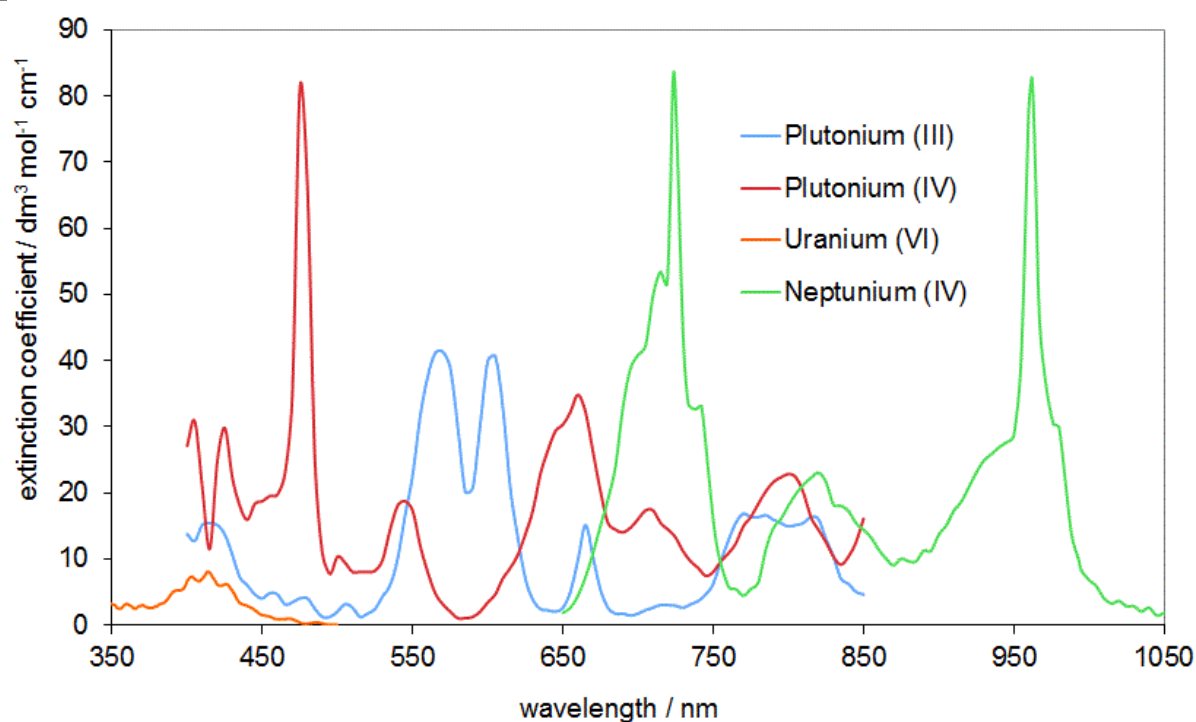


Fig. 2. Comparison of absorbance spectra for uranium (VI), neptunium (IV), plutonium (III) and plutonium (IV) [3][4][5].

There are a number of absorption peaks for uranium (VI) between 338nm and 500nm. There is a clear absorption maximum with an extinction coefficient of $9.7 \text{ l mol}^{-1} \text{ cm}^{-1}$ at a wavelength of 413.8nm. The absorption spectrum between 400 and 500 nm is due to transitions from the ground state to sublevels of the first excited state. A higher bonding molecular orbital which is located

predominately on the oxygen atom is transferred to the non-bonding uranium 5f orbital [4]. This type of excitation is known as charge transfer because a fraction of the electronic charge is transferred between molecules. The absorbance band at 490nm is due to an electronic transition to the zero vibrational sublevel of the first electronically excited state [3].

Relatively speaking, there has been little research concerning the spectrum of the remaining three ions of interest. Their absorbance spectrum will be as a result of both electron excitation and molecular vibrations. For wavelengths less than 800nm absorbance will most likely be due to electron excitation. Molecular vibrations become a possibility above 800nm.

Neptunium (IV) has a number of absorption peaks between 650nm and 1050nm. The spectrum is dominated by two large peaks; both have an extinction coefficient of $83 \text{ L mol}^{-1} \text{ cm}^{-1}$ at wavelengths of 723nm 964nm [4].

Plutonium (III) has a number of absorbance peaks between 400nm and 850nm. As with neptunium (IV), the spectrum contains two absorbance peaks which are significantly larger than the rest. These peaks both have an extinction coefficient of $41 \text{ L mol}^{-1} \text{ cm}^{-1}$ at a wavelength of 570nm and 605nm [5].

Plutonium (IV) has a range of absorption peaks between 400nm and 850nm. There is an absorption peak with an extinction coefficient of $81 \text{ L mol}^{-1} \text{ cm}^{-1}$ at a wavelength of 477nm [5].

Monochromated light may be used to independently promote each analyte to an excited state and the resulting products monitored at the MORE. This can be achieved due to the MORE's ability to deliver light of desired wavelengths. For example, if light of wavelength 725nm is shone into a mixture containing all four ions, the target analyte neptunium (IV), will enter an excited state creating a photocurrent, resulting in its detection. This process can then be repeated altering the illumination wavelength each time to match that of a desired target analyte.

The possibility of interference between the different analytes will be investigated. This will be done by measuring the photocurrents at various wavelengths for solutions containing a single analyte. Close attention will be given to wavelengths in the range of the maximum absorbance of other target analytes. The results generated from this will determine if signal-deconvolution techniques will be required and will also establish the limits of detection for each analyte.

Surrogates and the MORE

Experiments were designed using inactive surrogates thus allowing for the developing experimental procedure and to maximise the limited time to be spent working with uranium, neptunium and plutonium at the National Nuclear Laboratory (NNL). The surrogates were chosen due to having similar thermodynamic properties to their corresponding actinides and have been used by the NNL for some time.

TABLE I. Showing actinides of interest and corresponding surrogates.

Actinide	Surrogate
Uranium (VI)	Depleted Uranium
Neptunium (IV)	Vanadium (IV)
Plutonium (III), (IV)	Cerium (III), (IV)

Before photoexcitation experiments of V(IV) could be performed, both the photophysical and electrochemical parameters needed to be determined. This was achieved by collecting the absorbance spectrum using a spectrophotometer and performing cyclic voltammetry.

MATERIALS AND METHODS

Manufacturing the MORE

The fabrication of the MORE was carried out at Lancaster University and consisted of 5 steps which are outlined below. Commercially available 200 μ m diameter fibre optic was used (model HO200/220). This was purchased from Horiba scientific and will form the optical disc of the MORE. It was chosen due to its transmittance which does not attenuate light at wavelengths corresponding to the absorbance spectrum range for the target analytes. All chemicals used were purchased from Sigma Aldrich UK.

Firstly, the outer cladding surrounding the fibre optic must be removed; this was achieved by placing the fibres in Piranha Solution (3 parts sulfuric acid and 1 part hydrogen peroxide). Following this, the fibres were cleaned by ultra-sonication in nitric acid, then submerged overnight in potassium hydroxide and finally the fibres underwent ultra-sonication in nitric acid again. Next, the fibres were treated with silane to prepare them for the third stage in which a sputter coater was used to coat the fibres in gold. Next, an electrical contact was secured to the fibre which was then placed into a pipette and plotted in araldite. Finally, the tip of the electrode was sawn off and the pipette removed. The tip of the electrode was then polished with decreasing grades of silicon-carbide papers.

Electrolyte

A 50ml solution consisting of 10mM of Vanadium (IV) oxide sulfate hydrate (sensitizer), 5mM of iron(III) chloride (acceptor) and 0.1M of potassium chloride (supporting electrolyte) was dissolved in distilled water. Sulfuric acid was then added to the solution to adjust the pH to between 1 and 2. The solution was then purged with nitrogen for at least 15 minutes to remove dissolved oxygen.

RESULTS

Photophysical Results for Vanadium (IV)

As can be seen from fig 2, vanadium (IV) has an absorbance maximum at 770nm with a calculated extinction coefficient of 13.28 L mol⁻¹ cm⁻¹.

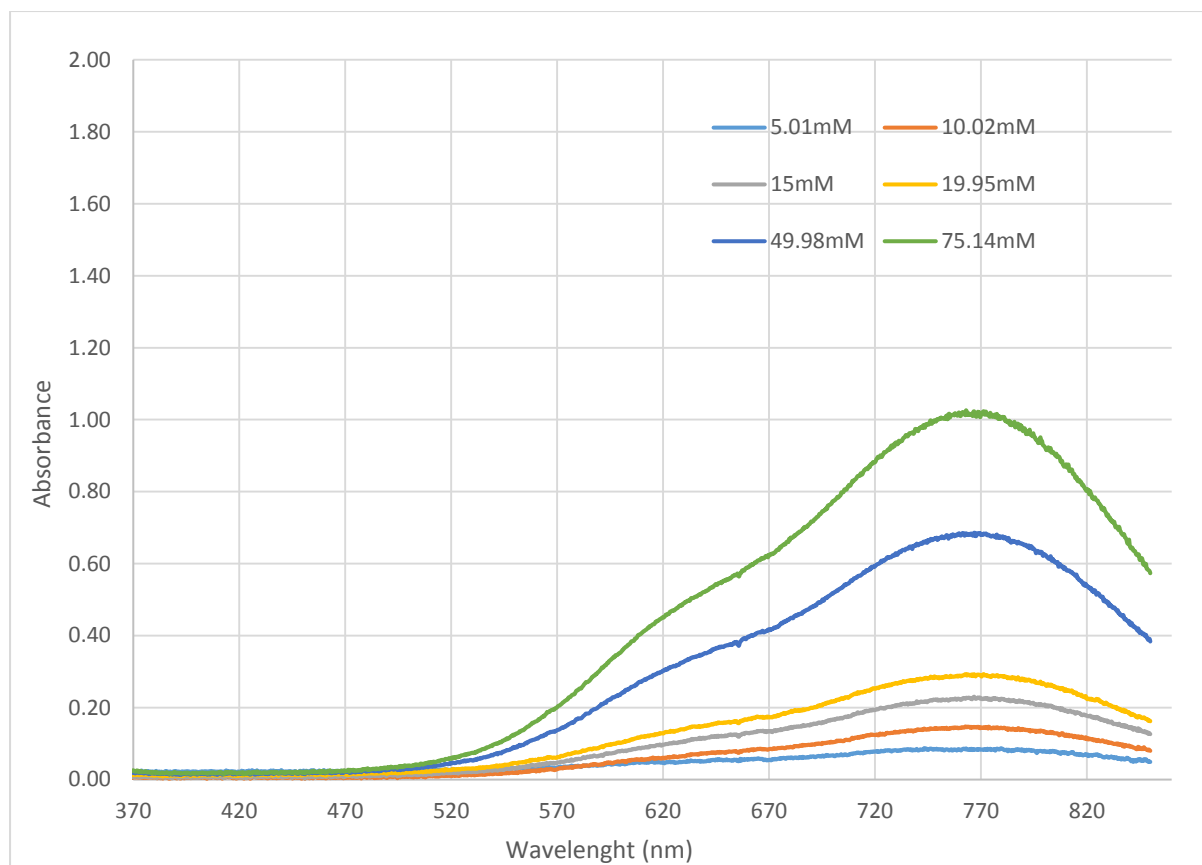


Figure. 2. Absorbance spectrum for various concentrations of vanadium (IV).

Electrochemical Results for Vanadium (IV)

Fig.3 shows a reduction process at $E = -200\text{mV}$ corresponding to the reduction of V(IV) to V(III).

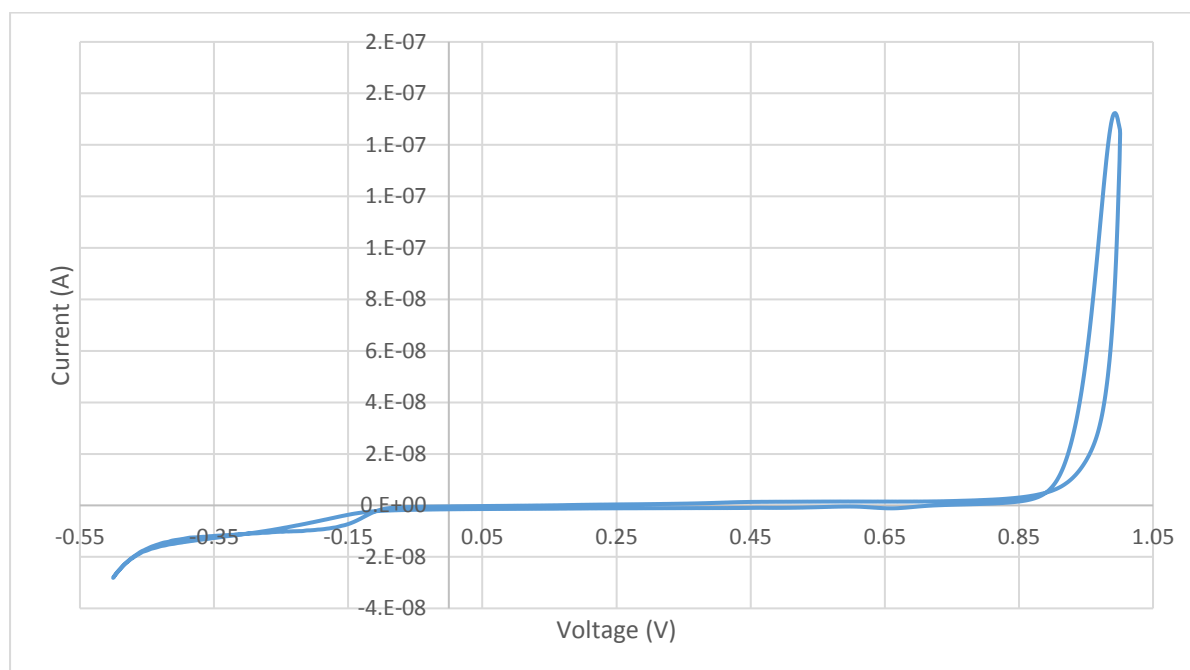


Figure. 3. Cyclic Voltammetry for 10mM V(IV) +0.1M of KCL at 1mvs⁻¹ pH 1.77 using disc electrode.

Diffusion Coefficient Result for Vanadium (IV).

The diffusion coefficient was determined by recording the diffusion limited current at a rotating disk electrode, in accordance to the Levich equation (equation 2).

$$i_{diff} = 1.55nFACD^{2/3}v^{-1/6}\omega^{1/2} \quad (\text{Eq. 2})$$

The diffusion limited current is then plotted as a function of the square root of roatation speed (ω), the slope of the line of best fit then gives access to the diffusion coefficient ($\frac{i_{diff}}{1.55nFACv^{-1/6}} VS \omega^{1/2}$)

The graph below shows the result of the RDE experiment for the data collected for V(IV) (fig.4), a value of 3.30E-8 cm²s⁻¹ is obtained.

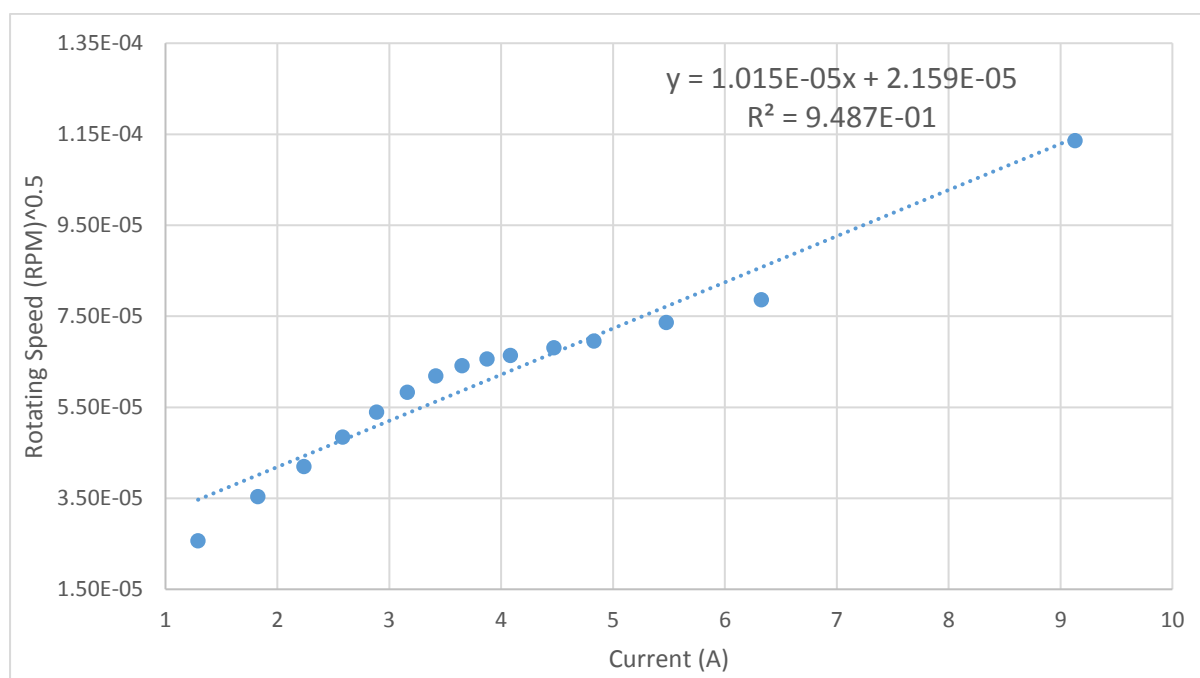


Figure. 4. Results used to calculate diffusion coefficient of V(IV).

CONCLUSION

Results thus far have given a value to the maximum absorbance spectrum and diffusion coefficient of V(IV), a redox process has also been identified from cyclic voltammetry.

The next stage is to generate a photocurrent from V(IV). A literature search will aim to find the redox potential for V(IV) allowing an appropriate electron acceptor to be identified. Once this has been established the experiment will be repeated, if a photocurrent is seen the concentrations of both the V(IV) and

acceptor will be changed and the resulting photocurrent recorded. This will be used to verify the mathematical model (equation 1) for the V(IV) / acceptor system.

A new radioactive research facility (UTGARD – U/Th/beta-Gamma Active process chemistry R&D) has been built by the engineering department at Lancaster University. This will allow for active work to be carried out on campus, without time limitations. Therefore the decision has been made to design experiments using only vanadium (IV) and depleted uranium as surrogates before proceeding to active work.

Once vanadium (IV) work has been complete, experiments will be repeated for depleted uranium before progressing to active samples. Once a photocurrent has been identified for uranium, neptunium and plutonium ions the MORE will be used in solutions containing mixtures of these analytes confirming the MORE as a single probe-multi analyte tool.

REFERENCES

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