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Rare Elements Electrochemistry: The Development of a Novel Electrochemical Sensor for the Rapid Detection of Europium in Environmental Samples Using Gold Electrode Modified with 2-pyridinol-1-oxide

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This work presents for the first time the electrochemical determination of europium using cyclic voltammetry at gold electrodes modified with 2-pyridinol-1-oxide. A well-defined oxidation peak was observed in cyclic voltammetry as a result of the oxidation of the europium at ~1100 mV in phosphate buffer at pH 7.0. The peak current increased linearly with the increase of concentration of the europium over the range from 1 to 80 μM and detection limit (based on 3-sigma) and quantification were found to be 0.3 and 0.549 μM, respectively. The analytical utility of the developed protocol was evaluated by performing the detection of the europium in river water. Europium is also linear over the concentration range 10 to 150 μM. (I_p/μA = 0.7239x + 108.19, R^2 = 0.9981 and n = 9) with a detection limit of 6.5 μM (based on 3-sigma). This simple and effective protocol exhibited good sensitivity, precision and reliability towards the detected analyte.

Keywords Lanthanides, electrochemical sensor, enviromental, water and gold electrode

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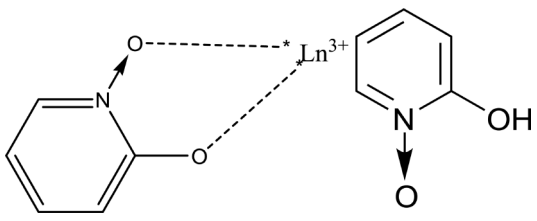
Introduction

The lanthanide group, containing stable elements from lanthanum to lutetium (Z from 57 to 71),[1] is strongly electropositive and mostly trivalent under a wide range of oxygen fugacity. Europium, samarium and ytterbium also have a valence of +2 and cerium, terbium and praseodymium have a valence of +4. Europium and cerium are the most reactive elements of the rare earth elements (REE). In lanthanide atoms, the configuration of the valence electrons of the outermost shell is the same for all the species while the 4f orbitals are progressively filled with increasing atomic number.[2] Screening of the 4f orbitals leads to the extremely similar physical and chemical properties.[1-4]

The structure of the 2-pyridinol-1-oxide (2-PO) and the predicted lanthanide complex is depicted in Scheme 1.

The current analytical methods employed to analyze the lanthanides are generally: inter alia,[1,5] flame or graphite furnace atomic absorption spectrometry,[5-7] atomic absorption with chemical vapour generation,[5,7-8] X-ray fluorescence spectrometry,[5,7-8] inductively coupled plasma optical emission spectrometry,[5,9-11] inductively coupled plasma mass spectrometry[5,10,12] and neutron activation analysis.[5,10,13] However, many of these methods require several time-consuming manipulation steps, sophisticated instruments and special training.[4-5] These methods are also subject to serious interferences from the main elements, and from the long irradiation time used in determination of lanthanides, and matrix effects from major constituents, such as organic compounds and inorganic salts.[1,4,14] Therefore the development of a sensor that is fast, portable, reproducible and reliable is needed.



Scheme 1 Structure of (a) the lanthanide chelate to 2-pyridinol-1-oxide and (b) the 2-pyridinol-1-oxide.

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Electrochemistry is an advantageous analytical tool that is cost effective, portable and fast. It has been widely employed in biological matrixes,[15-16] pharmaceutical[17] and some drugs containing tertiary amine functional group[15,18-20] due to its continuance, sensitivity, reproducibility and selectivity towards many target analytes.[15,19,21-22]

Electrochemical determination has been carried out at gold electrodes owing to its wide potential window, strong adsorption tendency, low background current and easy maintenance. In coordination chemistry 2-pyridinol-1-oxide has been extensively employed as a ligand.[23-24] Muller *et al.*[24] employed lanthanide(III) complexes of a pyridine N-oxide to form a six-membered chelate ring.

To the best of our knowledge, there is no report based on electrochemical determination of lanthanides in river water. The present paper reports the application of modified electrode with chelates as a sensor for the determination of europium. The electrochemical behaviors of europium using gold electrode modified with chelates in river water samples was also investigated and discussed in this manuscript.

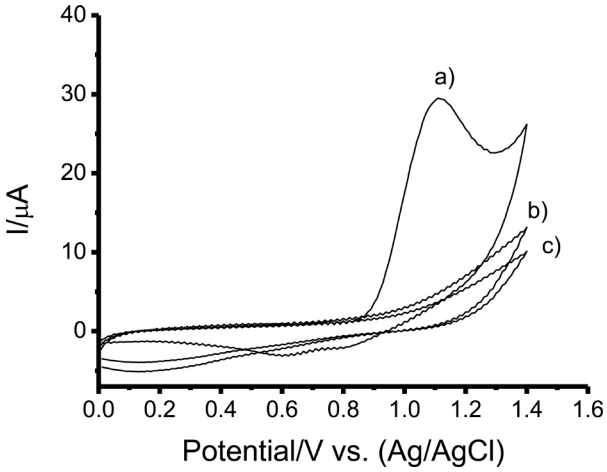


Fig. 1 Cyclic voltammogram responses at gold electrode (a) modified electrode with chelate in 1 μM europium buffer phosphate solution at pH 7.0 (b) modified electrode with chelate in phosphate buffer solution at pH 7.0 and (c) unmodified electrode in 1 μM europium phosphate buffer solution at pH 7.0. Scan rate: 100 mV/s.

Experimental

Reagents

All chemical reagents used to prepare solutions were purchased in their purest commercially available forms from Aldrich. All aqueous solutions were made up with water (of resistivity of not less than 18 MΩ cm) taken from an Elgastat filter system (Vivendi, Bucks., UK). All experiments were undertaken at 23 ± 2°C.

All chemicals were obtained from Sigma-Aldrich and used without further purification. Europium was obtained as europium chloride hexahydrates, 99.9% purity and 2-pyridinol-1-oxide was 99% purity. Buffer solutions were adjusted using a Hanna instruments PHM2254 pH meter (Hanna Instruments, Kings Langley, UK) which was calibrated prior to use. We prepared 0.1 M phosphate buffer solution by mixing potassium phosphate monobasic anhydrous and sodium phosphate dibasic and the pH was adjusted by adding either a solution of sodium hydroxide or a solution of hydrochloric acid. 2-pyridinol-1-oxide was dissolved in methanol.

Voltammetric settings

Cyclic voltammetry was employed to carry out all the experiments (unless stated otherwise). The scan rate utilized was 100 mV/s. The parameters started at potential 0.0 V and ended at potential 1.4 V.

Apparatus

Voltammetric measurements were carried out using a PG 580 (Uniscan Instruments Ltd., UK) potentiostat/galvanostat and controlled by UiEchem software with a conventional three-electrode system comprised of a platinum wire as auxiliary electrode, Ag/AgCl (saturated. KCl) as reference, and gold electrode as a working electrode (AuE, 2 mm i.d.).

Preparation of the modified electrode

Before modification, the gold electrode was polished to a mirror finish using finer emery-paper and 0.5 μm alumina slurry followed by rinsing thoroughly with water. After successive sonication in 1:1 nitric acid, acetone, and doubly distilled water, the electrode was rinsed with doubly distilled water. The cleaned gold electrode was dried under nitrogen steam for the next modification. The gold modified electrode was prepared by casting 5 μL of chelate solution on the gold surface. After the solvent evaporated, the electrode surface was thoroughly rinsed with redistilled water and air dried. The obtained electrode was noted as Au/chelate.

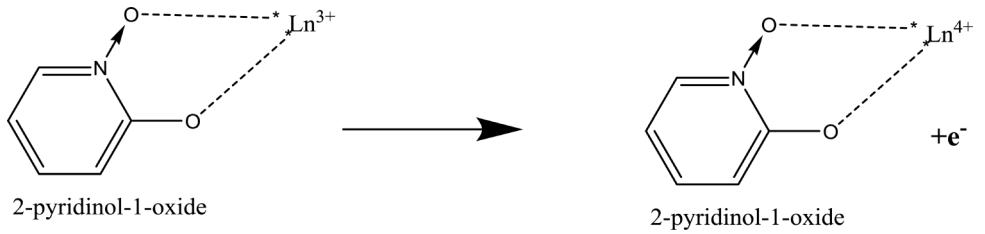
This sensor was coated with 2-pyridinol-1-oxide, which is partially soluble in water; the coating was applied each time that the electrode was immersed in the solution. The coating is stable in water for 5 min (with standard deviation 95% n = 10); after this time the coating started to dissolve.

Results and Discussion

Cyclic voltammetry

Cyclic voltammetry (CV) provides considerable information about the redox process of a reaction. CV was used to investigate the electrochemical behavior of europium on the surface of the gold electrode in pH 7.0 phosphate buffer solution. The cyclic voltammograms of blank, the chelate modified electrode and europiumin pH 7.0 phosphate buffer solution at scan rate: 100 mV/s were recorded and are shown in Fig. 1. The oxidation of the lanthanides is depicted in Scheme 2.

As can be seen from Fig. 1(a) a well-defined oxidation peak at 1.10 V due to the oxidation of the europium in the complex, which is depicted in Scheme 2, was observed when the sweep was initiated in the positive direction from 0 to 1.5 V. The current is also higher when is compared to Figs. 1(b) and 1(c). Figure 1(b) shows a voltammogram of the chelate modified on the surface of the electrode without europium in which oxidation/reduction peaks were not observed. Figure 1(c) shows the unmodified electrode in 1 μM europium phosphate buffer solution at pH 7.0 and, as expected, no oxidation/reduction peaks were found. When Figs. 1(b) and 1(c) are compared, there is a slight increase in the current; this is due to the modification of the surface of the electrode. When the surface of the electrode is modified with the chelate the surface area increases as well as affects the electrode kinetics compared to the unmodified electrode. These two factors therefore generate an enhancement in the current.



Scheme 2 Reaction of lanthanides with chelates 2-PO.

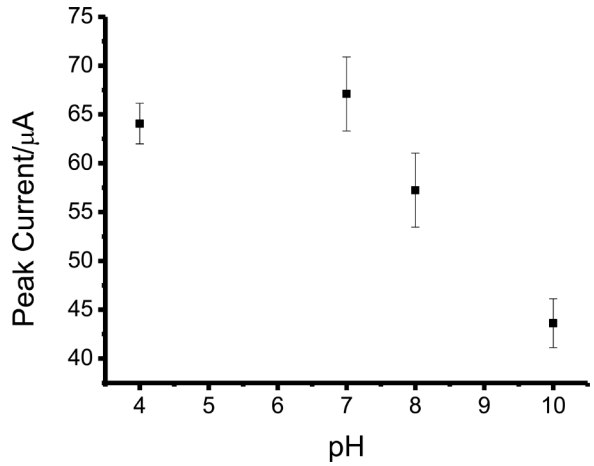


Fig. 2 A plot of peak height as a function of pH for the electrochemical oxidation of europium using gold electrode modified with chelate at scan rate: 100 mV/s.

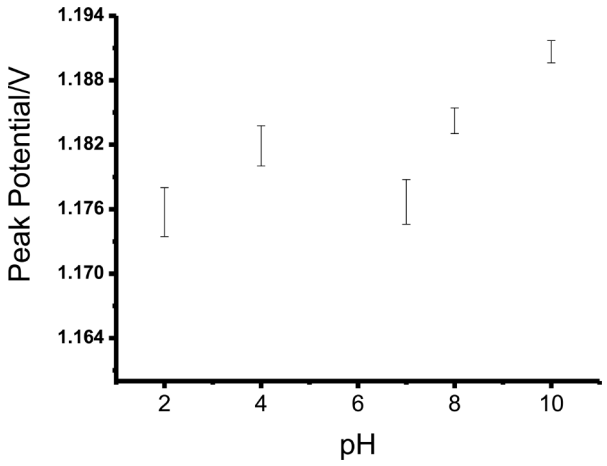


Fig. 3 A plot of peak potential (E_p) as a function of pH for the electrochemical oxidation of europium using gold electrode modified with chelate at scan rate: 100 mV/s.

Optimization of the experimental conditions

The effect of pH

The pH of the supporting electrolyte is an important factor that affects the redox behavior of biomolecules and drugs. Next, the effect of peak height current *vs.* pH and peak potential *vs.* pH were investigated. In order to investigate the effect of peak height current versus pH, the peak height current of 1 μM of europium complex at the gold electrode modified with chelate in phosphate buffer was measured over a solution range of pHs from 4 to 10 (Fig. 2). Figure 2 illustrates that the maximum peak height current value for the complex was observed at pH 7. This high value of peak height current indicates that the electro-oxidation process of the europium complex is more favorable at pH 7 compared to others pHs. The lowest peak height value can be observed at basic pH 10 indicating that the electro-oxidation process of the europium complex is less favorable. Figure 2 also illustrates a linear response over pH 6 to pH 10 and the linear equation for that is showed to be: I_p/μA (pH 6 – 10) = –11.5x + 196.798 *versus* Ag/AgCl for europium complex with correlation coefficients of 0.99.

Next, the effect of peak potential and pH were investigated as it is illustrated in Fig. 3. Figure 3 shows that at pH 7 there is a slight drop of the potential indicating that pH 7 is the optimum pH for the electro-oxidation of the europium complex. At higher pHs the electro-oxidation process of the europium complex is less favorable.

The above results indicated that the peak current (I_{pa}) and peak potential (E_{pa}) were affected by the pH of the solution. For the subsequent analytical experiments pH 7 was chosen to be the most favourable condition for the electro-oxidation of the europium complex.

Effect of concentration

After determining that the optimum experimental pH was 7.0 for the oxidation of europium using the modified gold electrode with a chelate, a range of different europium concentrations were explored. The oxidation of europium occurs at a high positive potential as is illustrated in Fig. 4 where the oxidation peak observed at +1100 mV increases in magnitude with the concentration of europium. Peak current (I_p) depends on the concentration of analytes hence the dependence of the oxidation I_p of europium on its concentration was investigated in phosphate buffer solutions of pH 7.0 by CV. By increasing the concentration of europium, a linear increase in the oxidation peak current was observed. A plot of oxidation peak current versus concentration of europium showed a good linearity between 1 – 80 μM as depicted in Fig. 4.

The linear regression equation was (I_p/μA = 1.3129x + 17.915 with n = 6, R^2 = 0.9915) over the analytical range studied 1 – 80 μM into a pH 7.0 phosphate buffer solution (n = 6) with a detection limit of 0.3 μM (based on 3-sigma).

In a blank solution (curve a), no redox peak was observed in the potential range from 0 to 1.5 V using the gold electrode, indicating that phosphate pH 7.0 was non-electroactive in the scanned potential window. A very sensitive anodic peak with current of 1100 mV was observed when europium was used to modify the gold electrode in pH 7.0 phosphate buffer solution.

Electroanalytical applications of the proposed method to detect europium in river water

Following confirmation that successful determination of

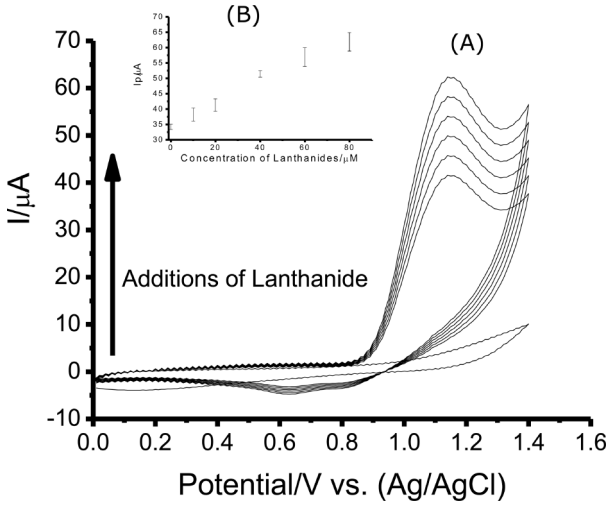


Fig. 4 (A) Cyclic voltammogram response observed for phosphate buffer solution pH 7.0 at gold electrode modified with chelate over a range of europium concentrations from 1 to 100 μM, scan rate: 100 mV/s. (B) A plot of peak height (I_p) as a function of europium concentrations using gold electrode modified with a chelate at a scan rate: 100 mV/s.

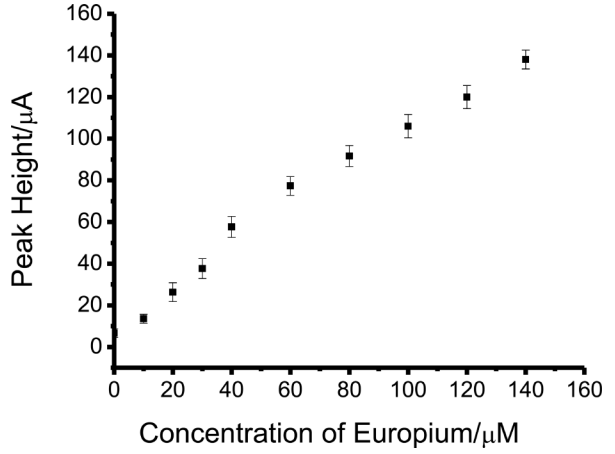


Fig. 5 A calibration plot of peak height (I_p), as a function of europium concentration corresponding to the addition of europium into river water solution over the concentration range 10 to 150 μM. Scan rate: 100 mV/s.

europium was possible in ideal conditions utilizing a standard pH 7.0 phosphate buffer, the viability of the analytical protocol was tested in relation to detection within analytically relevant media.

Europium is extensively used in industry such as in the manufacture of TVs, therefore could be a cause of environmental pollution. It is also clinically employed for analgesic and antipyretic effects and it is taken orally. We thus considered it worthwhile to determine the concentration of europium in river water from the river Dee in Aberdeen (Scotland). First, attention was turned to exploring the analytical sensing of europium in river water. Additions of europium were made into river water solution over the concentration range of 10 to 150 μM (Fig. 5).

As is shown in Fig. 5, the calibration plot resulting from the addition of europium is linear over the concentration range 10 to 150 μM. (I_p/μA = 0.7239x + 108.19, R^2 = 0.9981 and n = 10)

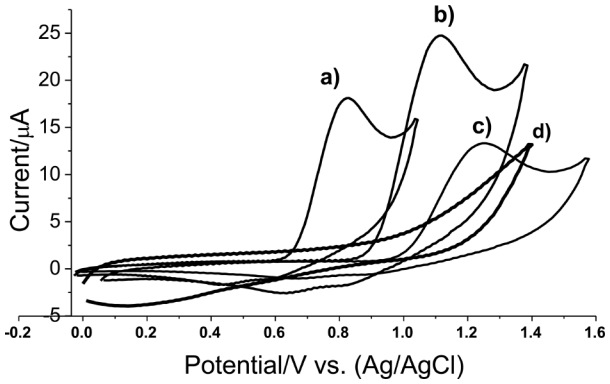


Fig. 6 Cyclic voltammogram responses at gold electrode in river water for: (a) Modified electrode with 2-pyridinol-1-oxide with 10 μM of cerium, (b) modified electrode with 2-pyridinol-1-oxide in presence of 10 μM europium, (c) modified electrode with 2-pyridinol-1-oxide in presence of 10 μM arsenic and (d) modified electrode with 2-pyridinol-1-oxide. Scan rate: 100 mV/s.

with a detection limit of 6.5 μM (based on 3-sigma). Returning to the observed analytical response, critically the river water solution employed was not modified in any way prior to use. The lack of sample pretreatment highlights the truly useful nature of the analytical protocol when utilized for real-world applications. Another important factor is lack of interferences from other trivalent ions (*e.g.* Al and Fe) which are more prevalent and could also complex with 2-PO. Our proposed analytical protocol provides sensing over a magnitude of 6.5 μM which is in the dosage range expected to be hazardous for humans.

The reproducibility of the 2-PO modification on the gold electrode was studied by repeating the determination of 10 μM europium in river water. After each determination, the used modified electrode undergoes 10 successive CV sweeps between 0.0 and 1.5 V at 100 m/Vs in the phosphate buffer to remove any adsorbents before cleaning the electrode. The six measurements achieved good reproducibility with a relative standard deviation (RSD) of 4.8%. The electrode was used 10 times without obvious performance deterioration a refreshed electrode surface can be used for successive determinations with an RSD of 5.0%, which shows that the sensor has good stability.

Last, it is useful to question the role of selectivity over and interference with similar lanthanides such as cerium and metals such as arsenic that might be present in the river water. In this particular case, as Fig. 6 shows each analyte gives a different peak potential and peak height that it can be used as a tool to differentiate different analytes. In our approach, we are proposing a screening tool and if present, all analytes will give rise to an electrochemical signal.

Conclusions

The proposed protocol demonstrates for the first time the selective determination of europium in river water samples with excellent sensitivity and selectivity using a gold modified electrode with 2-PO chelates. Long term stability and excellent reproducibility of the proposed sensor with essentially no pretreatment or maintenance offers a good possibility for extending the method for routine analysis of europium and potentially other lanthanides in other environments. A linear response is observed for a buffered solution (I_p/μA = 1.3129x +

17.915, R^2 = 0.9915 and n = 6) over the range 1 to 80 µM into a pH 7.0 buffer solution with a detection limit of 0.3 µM (based on 3-sigma). Europium is also linear over the concentration range 10 to 150 µM. (I_p/µA = 0.7239x + 108.19, R^2 = 0.9981 and n = 9) with a detection limit of 6.5 µM (based on 3-sigma) studied for river water. The additional advantage of the approach is that no sample pretreatment is required and rapid testing times with on-site determination are possible.

Acknowledgements

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