SQUARE WAVE VOLTAMMETRIC DETERMINATION OF TRACE AMOUNTS OF EUROPIUM(III) AT MONTMORILLONITE-MODIFIED CARBON PASTE ELECTRODES

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A carbon paste electrode modified with montmorillonite for the determination of Eu(III) was developed. This chemically modified electrode exhibits strong and stable electroactivity for Eu(III). Square wave voltammetry (SWV) of Eu(III) was evaluated with respect to the quantity of modifier, pH of electrolyte solution, accumulation potential and time. The stripping peak currents increase linearly with concentrations of Eu(III) from 1.0×10^{-7} to 2.0×10^{-5} mol l^{-1}. The detection limit is estimated to be 4×10^{-8} mol l^{-1} (S/N = 3). The recommended method has been applied to the quantitation of Eu(III) in stream sediment samples; the results obtained by the SWV approach are in good agreement with reference values.

Keywords: Europium(III); Square wave voltammetry; Montmorillonite; Chemically modified electrodes; Electrochemistry.

In recent years, quantitative determination of rare earth elements[1–6], such as Eu^{3+}, has gained in importance[7–14]. Besides increasing relevance to geological and environmental studies, it has been applied in nutritional studies as inert markers of the solid phase to determine the passage rates of nutrients through the digestive tract of ruminants[15]. Thus, it is necessary to develop a sensitive method for the detection of Eu^{3+}. A number of qualitative and quantitative techniques for the determination of Eu^{3+} have been reported. These include polarography, inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma optical emission spectrometry (ICP-OES), spectrophotometry[16–20], etc. However, all these procedures are troublesome or the instruments are not readily available. Therefore, there is a need for a suitable method to carry out a fast detection of Eu^{3+}.

Electrochemical stripping techniques have received much attention for trace metal analysis in recent years because of their inherent sensitivity and, especially they are suitable for decentralised analysis due to the rela-

tively compact and low-cost instrumentation needed and the possibility of employing inexpensive, disposable electrochemical cells. Due to a relatively large amount of electrochemical research devoted to the development and applications of different types of chemically modified electrodes (CMEs), they have continued to be of major concern. A few numbers of CMEs have been demonstrated for europium determination. Ugo et al.[21] used the Nafion-coated thin mercury film electrodes for determining trace amounts of Eu^{3+}. Ion-exchange preconcentration of submicromolar levels of rare earth elements was achieved efficiently with a rotating modified electrode. At the modified electrode, the rare earth cation undergoes quasi-reversible one-electron reduction and the analytical performance of the ion-exchange voltammetric determination of Eu^{3+} is improved by using differential pulse detection of the preconcentrated analyte. A detection limit of 8×10^{-8} mol l^{-1} was obtained. Moretto et al.[22] described the ion-exchange voltammetric determination of europium(III) at polymer-coated electrodes. Eu^{3+} determinations by multiple square wave techniques at Nafion-coated electrodes are characterised by detection limits 2–3 orders of magnitude lower than those obtained with differential pulse voltammetry and the rare earth cation can be analysed at nano- and subnanomolar levels.

The objective of this work is to establish a SWV method for the determination of Eu^{3+} at trace levels in real samples by using a montmorillonite-modified carbon paste electrode. Its major advantage compared with other pulse techniques lies in its ability to achieve highly effective sweep, which greatly reduces the time to measure voltammograms over a wide potential range. The modifier, montmorillonite (Fig. 1), can accumulate Eu^{3+} from

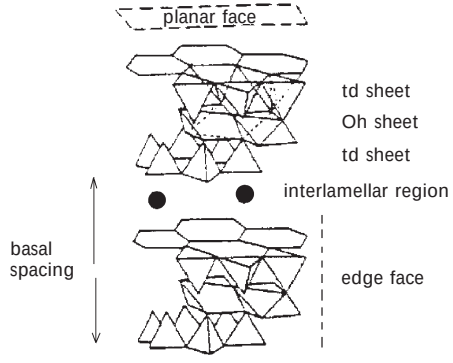

FIG. 1
Structure of montmorillonite

aqueous solution at the electrode surface. Advantages of the new procedure are high sensitivity, good reproducibility, and a low detection limit. It has been verified that the sensors is quite selective in determination of Eu^{3+}. When the proposed modified electrode was used as a sensor for the determination of Eu^{3+} in stream sediment material, the results have been in good agreement with the reference values.

EXPERIMENTAL

Reagents

All chemicals were of analytical-reagent grade. A standard stock solution of Europium(III) (1.0×10^{-2} mol l^{-1}) was prepared from Eu_2O_3, purchased from Aldrich (Milwaukee (WI), U.S.A.). Further dilutions with water gave for appropriate concentrations. Montmorillonite was obtained from the University of Missouri. The stream sediment reference material (GBW07301) was obtained from the Perambulation Institute of Physical Geography and Geochemistry of the Geological and Mineral Ministry, Langfang, China. 0.2 M NaOAc–AcOH buffer (pH 4.4) was selected as the supporting electrolyte. All the solutions were prepared with doubly distilled water.

Apparatus

Voltammetric measurements were performed with a CHI 830A Electrochemical Analyzer (CH Instrument, U.S.A.). A typical three-electrode system consisting of a montmorillonite-modified carbon paste working electrode, a platinum wire auxiliary electrode and a reference saturated calomel electrode (SCE) was used.

Preparation of Modified Electrode

The modified electrode was fabricated as follows: 5 mg of montmorillonite, 50 mg of graphite powder were mixed to form a uniform mixture. Then homogeneous carbon pastes were made by hand-mixing the montmorillonite-graphite mixture and 20 μl of paraffin oil. Finally a portion of the modified carbon paste was packed into the tip of a piston glass tube electrode (3 mm in diameter). Prior to every measurement, the modified electrode was smoothed out with a paper to gain a fresh electrode surface. Whenever regeneration of the electrode was required, a thin layer of the surface was removed with a spatula and replaced by fresh paste.

Analytical Procedure

The working electrode was immersed for a given time in 10 ml of the above buffer containing Eu^{3+}, the accumulation potential (–1.00 V) was applied to the working electrode for a selected time while the solution was stirred. After 10 s at rest, a square wave stripping voltammogram was recorded by an anodic potential scan from –1.0 to –0.40 V. The peak current was measured at –0.650 V.

RESULTS and DISCUSSION

Figure 2 shows typical cyclic voltammograms of Eu^{3+} solution with bare carbon paste electrode (*1*) and the montmorillonite-modified carbon paste electrode (*2*). It can be seen that no voltammetric peak is observed with the unmodified electrode in buffer solution containing 0.1 mM Eu^{3+}. Compared with the bare carbon paste electrode, a remarkable current response, corresponding to the redox Eu^{3+}/Eu^{2+}, well-defined anodic peak at –0.65 V and cathodic peak at –0.750 V were obtained. The peak separation (ΔE_p) is nearly 100 mV. The formal potential, $E^0 = (E_{p,a} + E_{p,c})/2$, was –0.70 V. This result is nearly consistent with the formal potential of Eu^{3+} reported by Ugo et al.[23] Figure 3 shows a square wave voltammogram obtained from 5-min preconcentration in 1×10^{-5} M Eu^{3+} solution. The result demonstrated that the modified CPE accumulated Eu^{3+} from solution and greatly increased the current response.

A difficulty associated with the determination of Eu^{3+} is the solution conditions. For the purpose, it was necessary to find suitable electrolytes. The voltammetric response of the proposed modified carbon paste electrode was examined in different supporting electrolytes as Na_2HPO_4, $Na_4P_2O_7$ and NaOAc–AcOH solution with pH adjusted to 2.0, 3.0, 4.0, 5.0 and 6.0. Voltammetric peaks were observed in all these electrolytes; however, a well-defined and sensitive peak was observed in NaOAc-AcOH buffer.

The effect of pH on the voltammetric response of Eu^{3+} at the modified electrode was examined over a pH range between 2.0 and 6.0 in 0.2 M

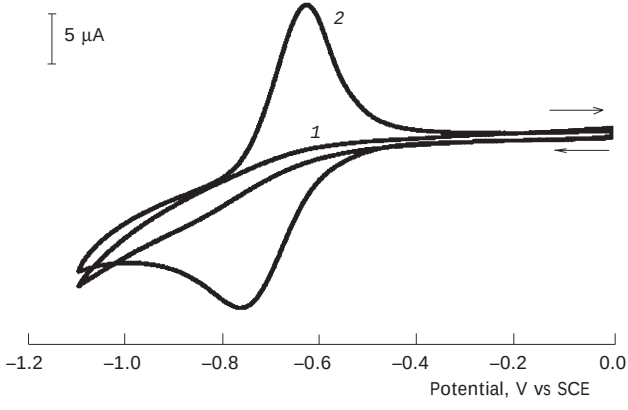

FIG. 2
Cyclic voltammogram for 1×10^{-4} M Eu^{3+} using different carbon paste electrodes: *1* bare carbon paste electrode, *2* montmorillonite-modified carbon paste electrode; supporting electrolyte acetate buffer (pH 3.4)

NaOAc–AcOH containing 5×10^{-6} M Eu^{3+}. Figure 4 shows the effect of solution pH on the anodic peak current. When the solution pH is changed from 3.0 to 4.0, the peak height increased and reached a maximum value at pH 3.4. Above pH 3.8, the peak height decreased rapidly, this is due to the hydrolysis of Eu^{3+} in the buffer solution. The determination was performed at

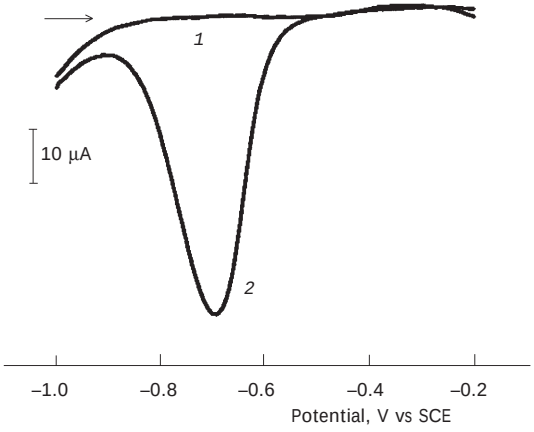

FIG. 3

Square wave voltammograms of 1×10^{-5} M Eu^{3+} with different carbon paste electrodes: *1* bare carbon paste electrode, *2* montmorillonite-modified carbon paste electrode; supporting electrolyte acetate buffer (pH 3.4), accumulation time 5 min, accumulation potential –1.0 V, pulse amplitude 50 mV, scan rate 20 mV s^{-1}, pulse width 50 ms

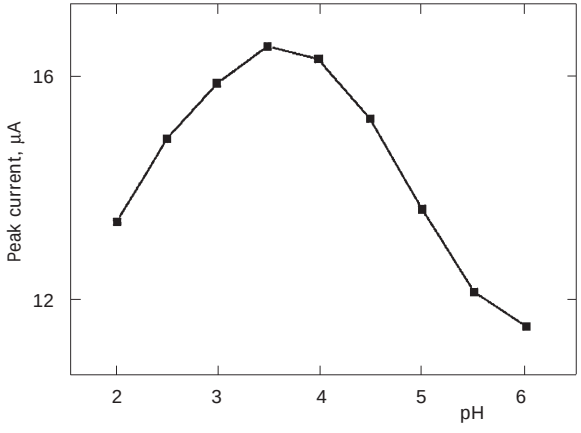

FIG. 4

Effect of pH on stripping peak currents of 5×10^{-6} M Eu^{3+}. Other conditions, see Fig. 3

pH 3.4 to obtain best response. Therefore, only a 0.20 M acetate buffer (pH 3.4) was used in further studies.

As the accumulation of Eu^{3+} at the montmorillonite CPE was based on the complex formation of montmorillonite and Eu^{3+} ion, the loading of the former on the CPE can influence the voltammetric response of Eu^{3+} at the modified electrode. Therefore, an investigation was made to establish the relationship between the SWV current and the montmorillonite loading. Figure 5 shows the voltammetric responses at different montmorillonite loadings with a fixed concentration of Eu^{3+}. The stripping currents reach the maximum values at a montmorillonite/carbon powder weight ratio of 5%. This behaviour may correlate with the maximum number of montmorillonite–Eu^{3+} binding sites, which can subsequently permit the electron transfer to the metal ion. However, a higher montmorillonite loading could cause a decrease in the peak current. This may be explained by the fact that fewer of these ions reach the inner binding sites for subsequent reduction to Eu^{2+}. Another explanation for the signal decrease is related to the decrease in conductivity of the modified electrode. As a result of the observation, the montmorillonite/carbon powder weight ratio was considered as optimum and used in our study.

Having established that the optimum conditions for accumulation of Eu^{3+} at the montmorillonite-modified carbon paste electrodes were 0.2 M NaOAc–AcOH buffer (pH 3.4), these conditions were employed to deduce the optimum deposition potential. The dependence of the preconcen-

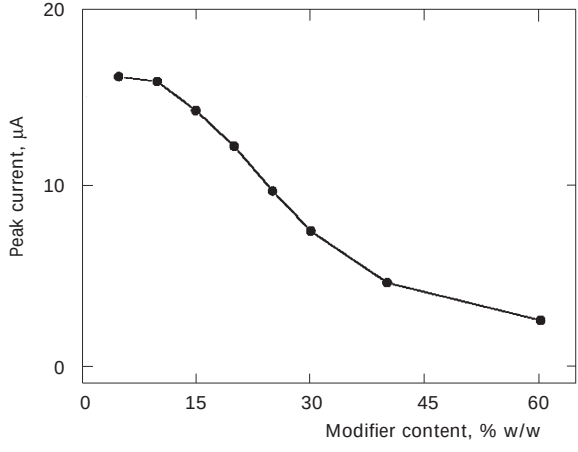

FIG. 5
Effects of the montmorillonite content (% w/w) in carbon paste mixture on stripping peak currents of 5×10^{-6} M Eu^{3+}. Other conditions, see Fig. 3

tration potential on the stripping peak current was examined over the range from –0.3 to –1.1 V. The results are presented in Fig. 6. The figure clearly shows that the peak rises rapidly as the preconcentration potential becomes more negative. When this preconcentration potential is close to –1.0 V, the peak tends to be steady. Thus, we consider that the potential –1.0 V would be appropriate for further studies.

For the method developed here, under the chosen set of conditions, the calibration plot for Eu(III) was linear over the range from 1×10^{-7} to 2×10^{-5} mol l^{-1} for a 5-min accumulation. For this range, the linear plot gave a regression equation of $I_p = 0.21104 \times C + 1.69055$ (correlation coefficient 0.99561). The estimated detection limit was 4×10^{-8} mol l^{-1} ($S/N = 3$). In addition, Fig. 7 shows a voltammogram of 4×10^{-7} M Eu(III), which is 10 times of concentration of detection limit.

The relative standard deviations (r.s.d.) of six measurements of 1×10^{-5} M Eu^{3+}, which was carried out with a single modified electrode, is 4.9%. When the modified electrode was remade after each measurement, the r.s.d. of 2×10^{-7} M Eu^{3+} is 5.3% ($n = 8$).

The influence of other ions, including some rare earth ions, present in the analyte solution on the current response of Eu^{3+} was tested. The experiment data are listed in Table I. The investigated maximum weigh ratio of foreign ions to Eu^{3+} was 100:1. As can be seen from Table I, it is evident that SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-, ClO_4^- have a small effect on the determination of Eu^{3+}. However, the most serious interferences are caused by Pb^{2+} and

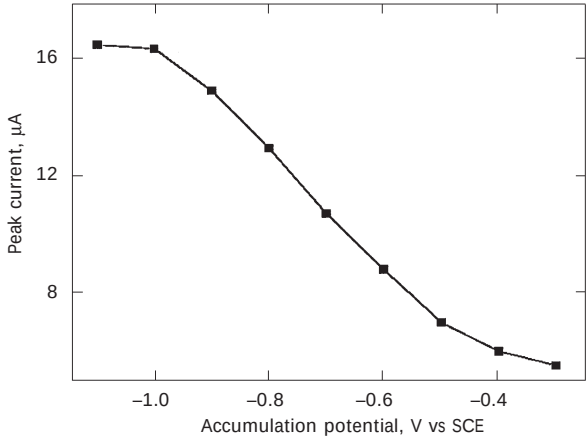

FIG. 6
Effects of accumulation potential on stripping peak currents of 5×10^{-6} M Eu^{3+}. Other conditions, see Fig. 3

TABLE I
Interferences of other ions on the SWV peak currents of 5×10^{-6} M Eu^{3+}

Interfering ion	Concentration, mol l^{-1}	Peak current change, %
In^{3+}	5×10^{-5}	+4.5
Tl^{+}	5×10^{-5}	+5.3
Na^{+}	5×10^{-4}	+0.5
K^{+}	5×10^{-4}	+1.2
Ca^{2+}	5×10^{-4}	–1.8
Zn^{2+}	5×10^{-4}	+1.2
Cu^{2+}	5×10^{-4}	–4.1
Pb^{2+}	5×10^{-4}	–12.6
Cd^{2+}	5×10^{-4}	–8.4
La^{3+}	5×10^{-4}	+1.2
Y^{3+}	5×10^{-4}	–3.2
Yb^{3+}	5×10^{-4}	–1.5
Dy^{3+}	5×10^{-4}	–1.9
Nd^{3+}	5×10^{-4}	+2.9
Ho^{3+}	5×10^{-4}	–4.7
Cl^{-}	1×10^{-3}	–0.7
SO_4^{2-}	1×10^{-3}	–0.5
NO_3^{-}	1×10^{-3}	–0.9
PO_4^{3-}	1×10^{-3}	+0.3

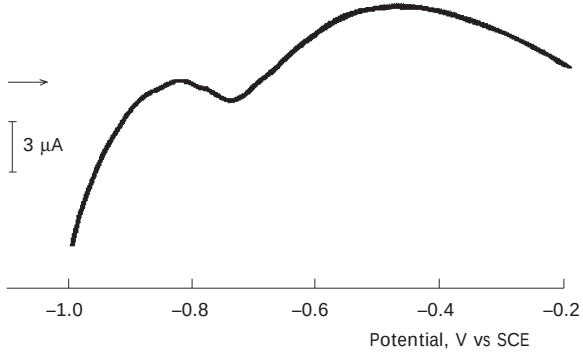

FIG. 7
Square wave voltammograms of 4×10^{-7} M Eu^{3+} using montmorillonite-modified carbon paste electrode. Other conditions, see Fig. 3

Cd^{2+} due to strong competition of Pb^{2+} and Cd^{2+} with Eu^{3+} for the reduction on the surface of the modified electrode.

A samples (0.5000 g) of a stream sediment reference material were transferred into PTFE beakers, then 5 ml of concentrated HNO_3, 3 ml of concentrated $HClO_4$ and 6 ml of concentrated HF were added successively. The solution was heated until became transparent, further heated almost to dryness and the residue was dissolved in 0.1 M HCl. After adjustment of pH to 3.4, the solution was made up with water to 20 ml.

The development of an easily prepared modified electrode is of high importance for both on-site and industrial applications. Analytical characteristics of the modified CPE applied to sample solutions were performed. An amount of 5 ml of a sample solution was added to 5 ml of 0.2 M NaOAc–AcOH buffer and the determination of Eu^{3+} was carried out as described above. The concentration of europium was determined by the standard addition method. As can be seen in Table II, the results obtained by the proposed method obtained are in good agreement with reference values and the recoveries of the standard addition experiment for sample solutions are satisfactory (average recovery 97.5%).

TABLE II
Analytical results for Eu^{3+} in standard reference material

Referense material	Reference value, μg g^{-1}	Found, μg g^{-1}	r.s.d., %
GBW07301	1.7 ± 0.2	1.6 ± 0.4	3.1

Determination of Eu^{3+} in a stream sediment reference material by the proposed method.

CONCLUSION

The main results from this experimental study can be summarised as follows: detailed analysis of the experimental parameters that determine voltammetric responses obtained by SWV with montmorillonite-modified carbon paste electrode allowed optimisation of the determination of Eu(III) at trace concentration levels. The method developed has been applied to determination of europium traces in real samples.

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