

## Multiple square wave voltammetry of nanomolar and subnanomolar concentrations of europium(III) at polymer-coated electrodes

Ligia M. Moretto<sup>a</sup>, Barbara Brunetti<sup>a</sup>, Jean Chevalet<sup>b</sup>, Paolo Ugo<sup>a,\*</sup>

<sup>a</sup> Department of Physical Chemistry, University of Venice, S. Marta 2137, I-30123 Venice, Italy

<sup>b</sup> LI2C, Laboratoire d'Electrochimie, Université P. et M. Curie, UMR 7612 CNRS, Boite 51.4, place Jussieu, 75252 Paris Cedex 05, France

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### Abstract

The ion-exchange voltammetric determination of europium(III) at polymer-coated electrodes is examined. The comparison between the ion-exchange cyclic voltammetric behaviour at glassy carbon electrodes, modified with the poly(estersulfonate) Kodak AQ55 and Nafion, indicates a better suitability of the latter. The use of multiple square wave voltammetry (MSWV) results in a dramatic improvement of the signal-to-noise ratios of the voltammograms recorded at the modified electrodes. Eu(III) determinations by MSWV 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, depending on the experimental conditions adopted. ©2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Poly(estersulfonate); Nafion; Europium; Multiple pulse; Ion-exchange; Voltammetry

### 1. Introduction

The development of electrochemical methods of analysis which employ non-faradaic preconcentration steps allows the determination of low concentration levels of electroactive species for which the use of classical stripping methods is prevented. Among the other non-faradaic preconcentration methods, ion-exchange voltammetry at polymer-coated electrodes is rapidly increasing its popularity thanks to the easy preparation of the modified electrodes as well as the great sensitivity and interference rejection which can be achieved with this method [1].

Cations of f-elements, belonging both to the lanthanide and actinide groups, are typical species for which successful preconcentration can be achieved using Nafion-coated glassy carbon electrodes [2,3]. By employing classical voltammetric pulsed techniques, such as differential pulse voltammetry, Nafion-coated electrodes allow the determination of  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  concentrations with detection limits in the 20–30 nM range [4]. The increase in sensitivity achieved with the modified electrode is significant with respect to the use of unmodified electrodes; however, detection limits are not low enough for analysis in some natural samples, such as surface

waters or sediments and soils, where determinations of concentrations at subnanomolar levels can be required.

Progress in this direction may come from the application at the modified electrodes of a new pulsed technique named multiple square wave voltammetry (MSWV) [5].

MSWV is a multi-pulse technique which implies a combination of a square wave signal with a staircase waveform, this latter scanning the entire domain of electroactivity of the redox system [5,6]. This perturbation mode is similar to Barker's square wave voltammetry [7,8] with the difference that, onto each step of the staircase, more than one pair of square pulses of opposing sign is applied. Proper sampling of the charge during the pulse sequence allows the improvement of the signal-to-noise ratio so that it is possible to achieve detection limits lower than those obtained with conventional pulsed techniques.

It was recently shown that multiple square wave ion-exchange voltammetry at Nafion-coated electrodes allows one to determine the methylmercury cation in aqueous solutions at ultratrace concentration levels [9]. For this purpose, a new MSWV mode called double differential square wave (MSW-DD) has been implemented and successfully applied.

Recently, a new cation exchanger, i.e. the poly(estersulfonate) Eastman Kodak AQ55, has been proposed as an electrode coating alternative to Nafion [10–12]. After a preliminary comparison of the ion-exchange voltammetric

\* Corresponding author. Tel.: +39-041-2578-503; fax: +39-041-2578-594; e-mail: ugo@unive.it

properties of AQ55 and Nafion with respect to Eu(III) pre-concentration, we report in this communication the possibility of using MSW-DD at polymer-coated electrodes in order to push detection limits for electrochemical europium determinations into the nanomolar and subnanomolar concentration range.

## 2. Experimental

### 2.1. Chemicals

All chemicals used were of analytical grade. Europium solutions were prepared by dissolving the proper amount of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (Aldrich).

Milli-Q water was used throughout to prepare the solutions. The measurements were performed in a clean laboratory, under a Class 100 laminar flow hood. All electro-analytical measurements were carried out at room temperature ( $22 \pm 1^\circ\text{C}$ ) under a nitrogen atmosphere. A conventional single-compartment cell equipped with a platinum coil counter electrode and a KCl saturated Ag|AgCl reference electrode was employed. The working electrode was a PTFE shrouded glassy carbon (GC) disk (area  $0.2\text{ cm}^2$ ) polished to a mirror finish with graded alumina powder.

2.5% w/v Nafion solutions were prepared by 1:1 dilution with methanol of 5% w/v Nafion solutions (Aldrich). Nafion-coated electrodes (NCEs) were prepared by droplet evaporation of 3  $\mu\text{L}$  of the 2.5% w/v Nafion (film coating  $0.375\text{ mg cm}^{-2}$ ). Solvent evaporation was performed in a methanol atmosphere in order to achieve a slow evaporation rate.

The polymer Eastman Kodak AQ55 (supplied as irregularly shaped pellets) was kindly provided by Eastman Italia. Kodak AQ55-coated electrodes (AQCEs) were prepared by deposition of 2  $\mu\text{L}$  of an acetone/water dispersion obtained by 1:1 (v/v) acetone dilution of the AQ55 15% aqueous dispersion, following the procedure described elsewhere [13].

Preconcentration of Eu(III) was carried out for 15 min, under open circuit conditions in a stirred solution (200 rpm with a magnetic stirrer).

Regeneration of the modified electrode was achieved by transferring it into a 2 M KCl solution, as described previously [4].

### 2.2. Electrochemical instrumentation

MSWV experiments were carried out using a prototype instrument 'MPulse', controlled by its own software, which is currently under development for commercial production [14].

The principles and the waveform applied to the electrode in MSWV have been presented elsewhere [5,6]. As mentioned in Section 1, this differential method is an extension of the original concepts proposed by Barker and Gardner

[7,8] for DPP and SWV. However, MSWV differs from Barker's SWV by the means used to collect the transient information: instead of the double current sampling operated by Barker, in MSWV the response is built by multiple integration and combination of transient currents. It was shown that this technique enhances the signal-to-noise ratio and the sensitivity [4,15] and can be successfully applied for trace analysis even in complex samples [16–20].

In this work, the mode of perturbation named MSW-DD (DD for 'double differential') has been used; the principles of this method have been detailed elsewhere [9]. Briefly, MSW-DD performs combinations of summations and differences of the multiple integrals in correlation with the polarity of the transitions and with the inversion of the superimposed signal  $\Delta E$ . The response of this special mode MSW-DD has the shape of the first derivative of the usual mode (i.e. second derivative of the polarographic wave) and offers a better signal-to-noise ratio [15].

Under favourable conditions of concentration, the baseline of MSW-DD becomes (close to) zero, while in the worst cases — like ultratrace analysis far below the ppb range — the base line of the DD response is (close to) a sloping straight line. This is the result expected by operating the derivative of the baseline of the MSWV response which is (close to) a parabola (as well as for SWV, under similar conditions). In practice, the mode of formation of the measure of charge at each step of the potential scan in MSW-DD has, itself, an effect of minimisation on the 'noises' that are generated by all the elements of the system; it acts on the electrochemical components (the baseline) and performs an inherently fast, real-time filtering and averaging on each data point of the voltammogram, within the crucial time scale (between 10  $\mu\text{s}$  and 100 ms) where the main noises (electrochemical and mechanical fluctuations, electrical or electronic perturbations due to residual jitter in the signals and to the closed loop potentiostatic circuit, current conversion amplifiers, etc.) may appear.

## 3. Results and discussion

### 3.1. Cyclic voltammograms at AQCE and NCE

In order to test whether the use of electrodes modified with the cation exchanger AQ55 could improve the ion-exchange voltammetric determination of Eu(III), a cyclic voltammetric comparison between NCE and AQCE was first performed. Fig. 1 shows the cyclic voltammograms recorded at a NCE (b) and at a AQCE (a), dipped in 0.6 mM  $\text{Eu}^{3+}$ . Signals were recorded after ion-exchange equilibration of the modified electrodes with the europium solution, i.e. after obtaining stable voltammetric responses, which do not change with time. Typically, this equilibration process takes 10–15 min in stirred solutions. The reduction peak currents measured in these voltammograms show that higher peak currents are recorded at the NCE, while at the AQCE they

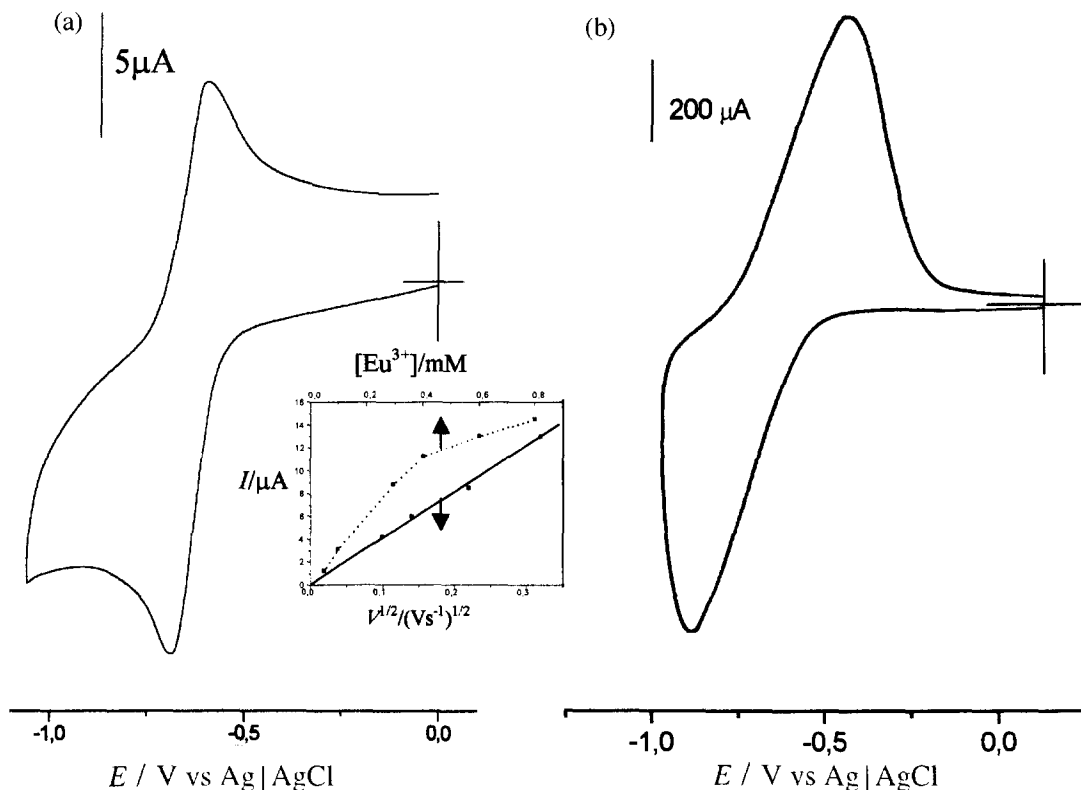


Fig. 1. Cyclic voltammograms recorded at an AQCE (a) and at a NCE (b) in 0.6 mM  $\text{Eu}^{3+}$ , 0.1 M  $\text{LiClO}_4$ . Scan rate  $50 \text{ mV s}^{-1}$ . Inset (refers to data recorded at the AQCE): full line, peak current dependence on scan rate, 0.6 mM  $\text{Eu}^{3+}$ ; broken line, calibration plot at  $100 \text{ mV s}^{-1}$ . Initial potential 0.00 V; vertex potential  $-1.00 \text{ V}$ ; final potential 0.00 V.

remain in the same range as signals recorded at a bare GC electrode. Both the AQCE and NCE, rinsed with water and transferred to pure supporting electrolyte solution, still show voltammetric signals related to the reversible one-electron reduction of  $\text{Eu}^{3+}$ , even if peak currents after the transfer become slightly lower than those recorded in the loading solution. On the contrary, no signal is observed, after transfer, at the bare GC electrode. A calibration plot obtained at an AQCE, equilibrated in solutions containing different  $\text{Eu}^{3+}$  concentrations, is reported in the inset in Fig. 1 (broken line); its shape parallels the shape of typical ion-exchange partition isotherms at polymer-coated electrodes [1].

This evidence indicates that  $\text{Eu}^{3+}$  cation is incorporated by ion exchange in both modified electrodes; however, the preconcentration effect displays a much higher influence on the voltammetric response observed at the NCE rather than at the AQCE. Note that signals recorded at the AQCE also display a different scan rate ( $\nu$ ) dependence than signals observed at the NCE. As shown by the full line plot in the inset of Fig. 1, at the AQCE a linear dependence on  $\nu^{1/2}$  (diffusive control) is observed even at scan rates as low as  $1 \text{ mV s}^{-1}$ , while at the NCE, for scan rates lower than  $50 \text{ mV s}^{-1}$ , voltammetric peak currents depend linearly on  $\nu$  (thin layer-like behaviour) [2]. Similar behaviour at the AQCE was also previously observed for other analytes [13,21]. The diffusion-controlled behaviour described above suggests that the apparent diffusion coefficient,  $D_{\text{app}}$ , for  $\text{Eu}^{3+}$  at the AQCE is so small that the thickness of the diffusion layer,

$(D_{\text{app}} \times t)^{1/2}$ , is always thinner than the thickness of the polymeric coating. Such a low value of  $D_{\text{app}}$  for  $\text{Eu}^{3+}$  within the AQ55 coating might be responsible for the low values of peak currents observed at the AQCE.

Considering that the preconcentration effect observed on Nafion gives a dramatically larger increase of the  $\text{Eu}^{3+}$  reduction peak with respect to AQ55, we decided to continue this research (aimed at improving the detection performances of the modified electrode for  $\text{Eu}(\text{III})$  determinations) by studying the use of multiple pulsed techniques at NCEs.

### 3.2. MSW-DD voltammograms at NCE

Fig. 2(a, full line) shows the MSW-DD cathodic pattern recorded at a NCE after equilibration in open circuit in 10 nM  $\text{EuCl}_3$  solution in 0.1 M NaCl, pH 4. The experimental parameters, not yet optimised, are: height of staircase steps,  $\Delta E_s = 5 \text{ mV}$ ; height of multiple square wave pulses,  $\Delta E = 50 \text{ mV}$ ; number of square wave pulses, of the same polarity, superimposed on each staircase step,  $N = 10$ ; integration time 20 ms. The MSW-DD voltammogram is characterised by a signal very well resolved from the background, here represented by the broken line which was recorded in pure supporting electrolyte. For reversible redox couples (as the  $\text{Eu}^{3+/2+}$  couple [2])  $E_{1/2}$  values can be obtained from MSW-DD curves by using the simple relationship:  $E_{1/2} = (E_{\text{pf}} + E_{\text{pb}})/2$  [5], where  $E_{\text{pf}}$  and  $E_{\text{pb}}$  are the potentials of MSW-DD peaks corresponding to the positive and negative

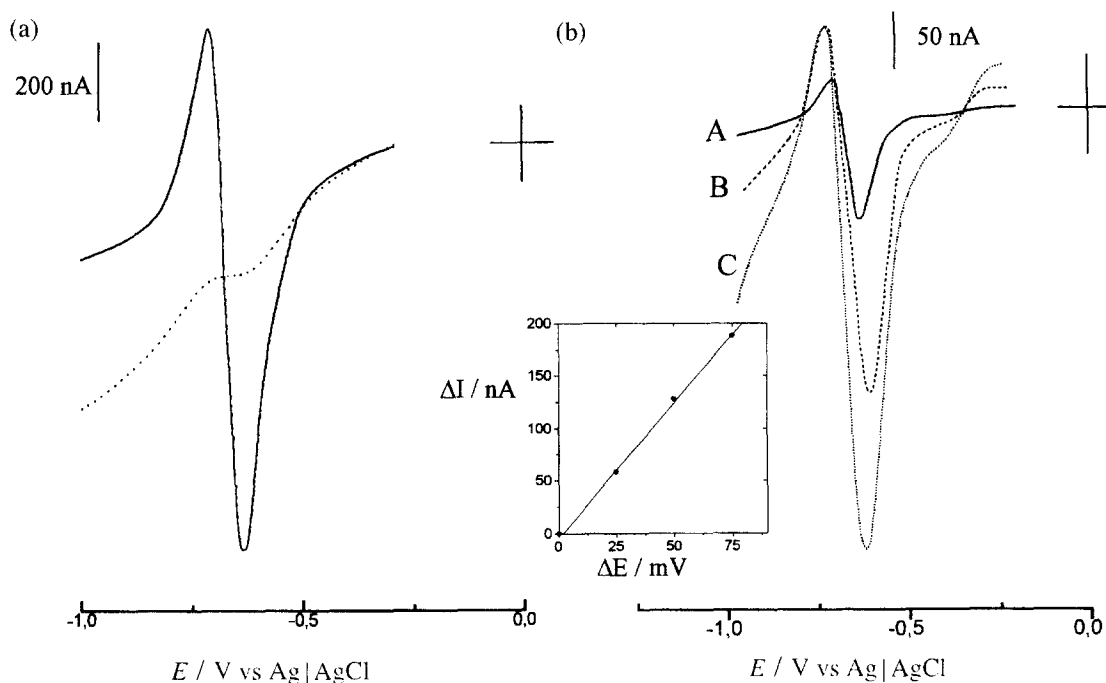


Fig. 2. (a) Direct reduction scan recorded in MSW-DD at a NCE in 10 nM  $\text{Eu}^{3+}$ , 0.1 M NaCl, pH 4.0 (full line) and in pure supporting electrolyte (dotted line). Experimental parameters:  $\Delta E_s = 5$  mV,  $\Delta E = 50$  mV,  $N = 10$ , integration time 20 ms. (b) MSW-DD curves recorded at a NCE equilibrated in 50 nM  $\text{Eu}^{3+}$ , 0.1 M  $\text{NaNO}_3$ .  $\Delta E$  values: (A) 25, (B) 50 and (C) 75 mV. Other experimental parameters:  $\Delta E_s = 5$  mV,  $N = 10$ , integration time 20 ms. Initial potential  $-0.28$  V; final potential  $-1.00$  V. Inset: dependence of peak heights (peak-to-peak amplitude) on  $\Delta E$ .

sequences of pulses, respectively [9]. From the pattern in Fig. 2(a), a value of  $-0.660$  V is obtained which agrees with the  $E_{1/2}$  obtained by cyclic voltammetry. Note that the  $\text{Eu}(\text{III})$  concentration used in the experiment shown in Fig. 2(a) is lower than the detection limit of 30 nM obtained by using 'classical' differential pulse voltammetry for determining  $\text{Eu}^{3+}$  at NCEs [4]; this proves the ability of MSWV to improve the voltammetric detection of redox cations at polymer-coated electrodes.

The choice of pulse height is particularly relevant for optimising MSW-DD analyses. Fig. 2(b) shows the cathodic patterns recorded using different  $\Delta E$  values in MSW-DD at a NCE in 50 nM  $\text{Eu}^{3+}$ . The inset in Fig. 2(b) shows a linear dependence of  $\Delta I$  (peak-to-peak amplitude on the Y-axis) on  $\Delta E$ . Such a trend agrees with previous literature findings obtained by applying MSWV in the normal mode at the HMDE for copper determinations [6,20], and by applying MSWV in DD mode at a NCE for methylmercury determination [9]. However, an increase of  $\Delta E$  produces more sloping baselines; therefore, a compromise should be found in order to optimise a good sensitivity with a good baseline and peak width; in our case, from a preliminary point of view, we estimate that a  $\Delta E = 50$  mV is close enough to the optimum value of this parameter.

Fig. 3(a) shows the cathodic pattern in MSW-DD recorded at the NCE in 4 nM  $\text{Eu}^{3+}$  solution. The inset in Fig. 3(a) indicates that  $\Delta I$  increases linearly with the europium concentration with a sensitivity (slope,  $m$ ) of  $59$  nA nM $^{-1}$ . Analytically useful signals are also obtained at lower concentrations, e.g. 1 nM. By measuring the background noise as

the standard deviation ( $\sigma_b$ ) of ten independent  $\Delta I$  measurements in blank solutions ( $\sigma_b = 9.65$  nA), a detection limit,  $\text{DL} = 3\sigma_b/m$  [22], of 0.5 nM is calculated. This value is about two orders of magnitude lower than the detection limit obtained at NCEs by differential pulse voltammetry.

A further improvement in this value is obtained using 0.1 M  $\text{NH}_4\text{Cl}$  as the supporting electrolyte. As shown in Fig. 3(b), a well-resolved MSW-DD signal is recorded under these experimental conditions even for  $\text{Eu}^{3+}$  concentrations as low as 0.2 nM. In this case, from the slope of the linear calibration plot (see inset) and background noise measurements, a detection limit of 0.1 nM is obtained. The improvement coming from the use of  $\text{NH}_4\text{Cl}$  can be attributed, in principle, to a buffering capability of  $\text{NH}_4^+$ , which somehow can prevent the precipitation of insoluble hydroxide products [2].

Further investigations on the role of the supporting electrolyte, on the presence of possible interference as well as on the optimisation of MSW-DD parameters for this analysis are presently in progress.

#### 4. Conclusions

Nafion-coated glassy carbon electrodes are superior to electrodes coated with AQ55 for determining trace concentrations of  $\text{Eu}^{3+}$ . The combined use of MSW-DD and Nafion-coated electrodes allows the achievement of detection limits for the ion-exchange determination of europium down to nano- and subnanomolar concentration levels.

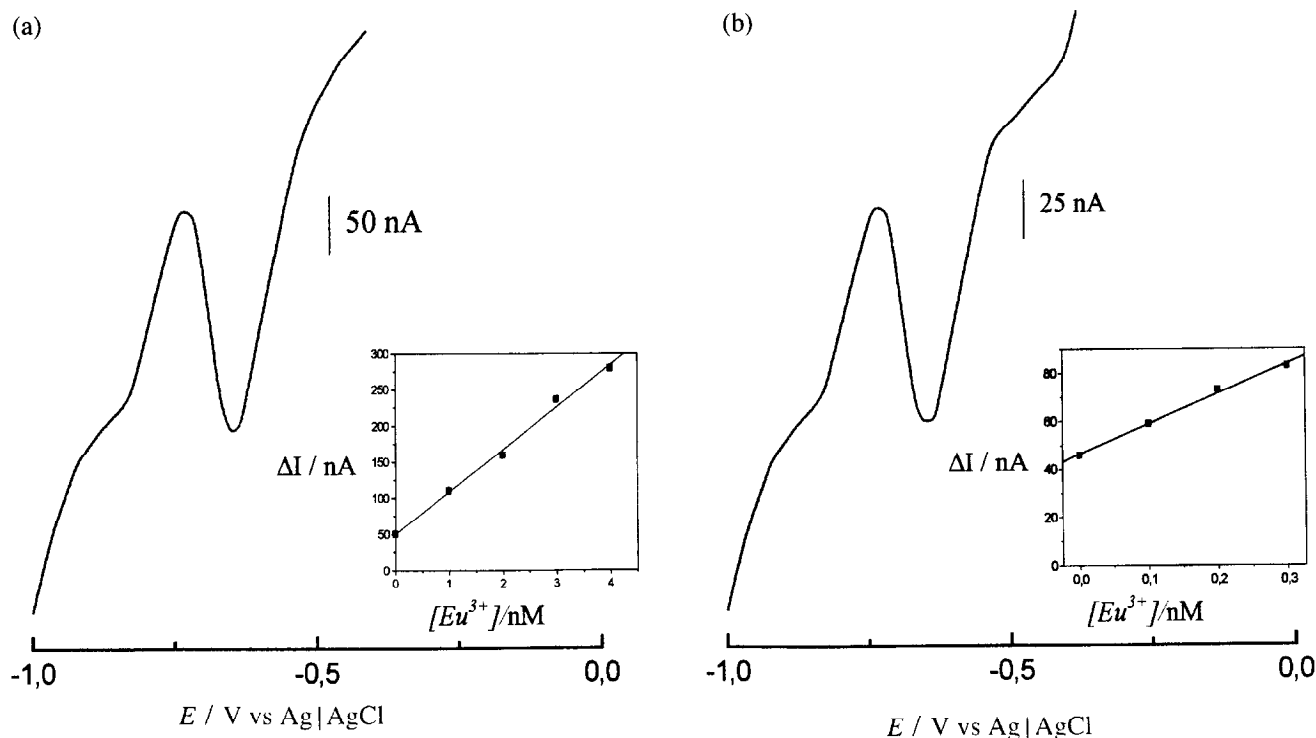


Fig. 3. MSW-DD voltammograms recorded at a NCE equilibrated (a) in 4 nM  $\text{Eu}^{3+}$ , 0.1 M NaCl, pH 4.0, and (b) 0.2 nM  $\text{Eu}^{3+}$ , 0.1 M  $\text{NH}_4\text{Cl}$ . Insets: relevant calibration plots. Experimental parameters:  $\Delta E_s = 5$  mV,  $\Delta E = 50$  mV,  $N = 10$ , integration time 20 ms. Initial potential  $-0.40$  V; final potential  $-1.00$  V.

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