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Differential pulse polarographic determination of europium in the presence of humic substances

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Abstract

Humic substances (HS) and other substance of similar nature ("building blocks" of HS, such as salicylates or phthalates) influence strongly a polarographic behaviour of europium at a mercury drop electrode. An addition of these substances into the supporting electrolyte causes an enhancement of the differential pulse polarographic (DPP) peak of Eu and an anodic shift of the maximum peak potential. It was deduced from the dependence of the peak height on the pulse time and from other experimental dependencies that an adsorption of the Eu–HS (salicylate, phthalate) complexes on the working electrode is the main mechanism responsible for the peak enhancement. Because no peak distortion or splitting were observed, the DPP determination of Eu can be realised readily in the presence of HS, e.g. in environmental samples. The sensitivity of the measurements increased in the presence of HS, whereas the limit of detection (LOD) decreased (LODs were 255 and 140 nmol/l in the absence and in the presence of HS, respectively). However, the calibration dependencies were non-linear in the presence of HS. It was found that the non-linear calibration dependencies may be approximated by the Langmuir-type equation. Special procedures, such as a method of (at least) two standard additions and numerical iterative calculations, are necessary for an evaluation of measurements.

Keywords: Determination of europium; Differential pulse polarography; Humic substances

1. Introduction

Safety assessments of radioactive waste disposal require a prediction of the migration behaviour of radionuclides in terrestrial systems. In laboratory as well as in field studies, the lanthanides are often used to simulate the behaviour of radioactive fission products, exploiting a well known analogy between the lanthanide and actinide cations. Especially, there is a strong correlation between the properties of elements in the pairs: Eu–Am, Gd–Cm, Tb–Bk [1]. Therefore, the interactions of europium with various minerals have been extensively studied [2–4]. The radioactive isotope ^{152}Eu has been often used in these studies and its concentration was determined by γ-spectroscopy [3]. This technique, however, is not commonly available in most laboratories.

Polarography, especially in its more advanced modes, offers possibility to determine europium at rather low concentration levels in the presence of other rare earths. The polarographic behaviour of europium has been studied for a long time [5–11], and several procedures have been proposed for the Eu determination mainly in ores and ore concentrates. Environmental studies, however require to determine europium in the presence of natural complexing substances that affect strongly the migration behaviour of polyvalent metal cations including lanthanides and actinides [2,3,12]. Humic substances (HS), subdivided usually into humic acids (HA) and fulvic acids (FA), represent the most important class of natural organic complexing substances.

In general, complexing agents influence the polarographic behaviour of Eu [13] in a similar way as is known for other metal ions [14]. Even more pronounced effect may be expected for those substances that induce an analyte adsorption onto working electrode [15,16]. It was observed in our older

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work [9] that a differential pulse polarographic (DPP) peak of Eu increased in the presence of potassium hydrogen phthalate (KHP), which was utilised for the Eu determination in rare earth concentrates.

More recently, we have observed a significant increase of the europium DPP peak in the presence of some other organic substances, such as salicylates, an also in the presence of natural organic matter, namely of HA. It is not very surprising that phthalates and salicylates exhibit similar effects as HA, because these substances are commonly called the "building blocks" of HA [17]. In this work, an inductive (adsorption) enhancement of the DPP peak of Eu in the presence of HA and similar substances was investigated in more details. Most important performance characteristics for the DPP determination of Eu, such as sensitivity, limit of detection, linearity and repeatability, were measured both in the presence as well as in the absence of HA.

2. Experimental

2.1. Apparatus and data evaluation

A 797 VA Computrace analyser (Metrohm, Herisau, Switzerland) was used for all voltammetric measurements. The analyser consists of a 787 VA Computrace Stand and is fully controlled with a 797 VA Computrace Software 1.0. The Metrohm Multimode Mercury electrode served as a working electrode, typically in a hanging mercury drop electrode (HMDE) mode, whereas a Pt-wire electrode was used as an auxiliary electrode and an Ag/AgCl (3 mol/l KCl) electrode with a ceramic diaphragm was used as a reference electrode. Dissolved oxygen was removed by nitrogen bubbling prior measurements. Polarographic mercury (99.9999%) was purchased from Fluka, Buchs, Switzerland. All measurements were carried out at laboratory temperature 22 ± 1 °C.

Computrance Software 1.0, DataFit 8.0 (Oakdale Engineering, USA) and MS-Excel were used for the data acquisition and evaluation. To approximate the calibration functions, the Langmuir-type (Eq. (1)) and Freundlich-type (Eq. (2)) equations were used in the following forms

$$i_{\mathrm{p}} = \frac{abc_{\mathrm{Eu}}}{1 + bc_{\mathrm{Eu}}} \tag{1}$$

$$i_{\mathrm{p}} = Kc_{\mathrm{Eu}}^{m} \tag{2}$$

where i_{p} is the maximum peak current intensity (peak height), c_{Eu} the analyte concentration and a, b, K, m are constants.

2.2. Chemicals and reagents

A stock solution of Eu (0.01 mol/l) was prepared by dissolving europium oxide (99.99%, REActon, Johnson Matthey, Widnes, UK) in a small excess of hot nitric acid (Suprapur, Merck, Darmstadt, Germany) and diluting with deionised water. Stock solutions of KCl (1 mol/l), KHP (0.01 mol/l) and sodium salicylate (0.01 mol/l) were prepared by dissolving analytical reagent-grade chemicals in deionised water. A stock solution of HA (1 g/l) was prepared by dissolving the sodium salt in deionised water. HA were prepared by alkaline extraction from young brown coal as described elsewhere [18]. Some characteristics of HA used in this work are listed in Table 1.

Table 1
Properties of HA [18]

Total content of acidic functional groups (mequiv./g)	8.42
Content of carboxylic functional groups (mequiv./g)	3.64
Weight-averaged molecular weight (M_{w})	19300
Number-averaged molecular weight (M_n)	10200

All solutions were prepared in deionised water from the system Demi Ultra 20 (Goro, Prague, Czech Republic) utilising reverse osmosis and mixed-bed ion-exchange for the water purification.

3. Results and discussion

3.1. Polarographic behaviour of Eu in the presence of HA

Europium gives a well developed DPP peak with a maximum peak potential (E_{p}) at ca. −660 mV in 0.25 mol/KCl as supporting electrolyte. An addition of HA caused an anodic shift of the E_{p} values and an increase of the peak height (Fig. 1). It should be pointed out that similar effects were observed also in the supporting electrolytes with a negligible complexing ability, such as in KNO_3 or $NaClO_4$. The presence of HA did not affect negatively the peak shape; none peak distorsions or splitting were observed at any HA concentration. The DPP peaks of common divalent metal cations were affected to considerably lesser extent by the presence of HA. Under comparable conditions, the Pb^{2+} peak was only slightly enhanced (by a factor of 1.41) and shifted towards the negative values ($\Delta E_{\mathrm{p}} = 66$ mV) in the presence of 5 mg/l HA, whereas the Cd^{2+} peak was decreased wery slightly (factor 1.14) without the E_{p} shift, and the Zn^{2+} peak remained almost unchanged. (Compare with a similar but not entirely identical behaviour of these ions in the presence of fulvic acids [19]).

The enhancement of the europium peak reached a plateau at the concentration of HA about 5 mg/l and the peak height increased only slightly with further increasing the HA concentration. The dependence of the peak increase on the HA concentration can be described by the Langmuir-type equation; the linearized forms of the Langmuir isotherms are plotted in Fig. 2. For all the straight lines in Fig. 2, coefficients of determination (R^2) were higher than 0.99 supporting an assumption that an adsorption of HA on the surface of the working electrode plays an important role in the overall electrode process.

Quite similar effects, i.e. the peak enhancement and anodic shift, were observed also in the presence of some aro-

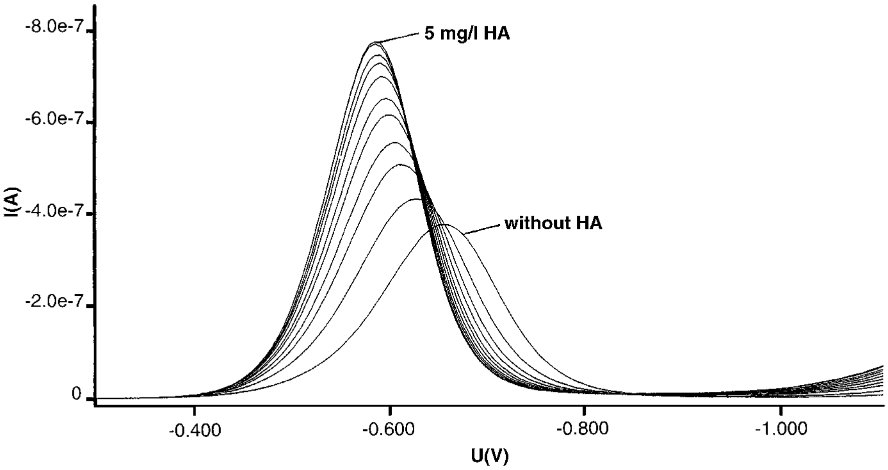

Fig. 1. DPP polarograms of Eu in the presence of HA. HMDE as a working electrode, drop size 4. Pulse amplitude, 50 mV; pulse time, 40 ms; sweep rate, 15 mV/s. Concentration of Eu 0.250 mmol/l. Supporting electrolyte 0.25 mol/l KCl with growing concentrations of HA from 0 to 5 mg/l.

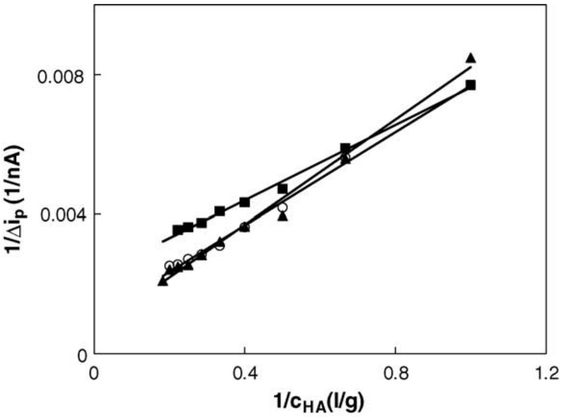

Fig. 2. Dependencies of the peak increase on the HA concentration plotted in the form of the linearized Langmuir isotherm ($1/\Delta i_p$ vs. $1/c_{HA}$) for various concentrations of Eu: 0.125 mmol/l (■), 0.250 mmol/l (○), 0.375 mmol/l (▲). Experimental conditions as in Fig. 1.

matic acids (or their salts), namely in the presence of KHP or sodium salicylate. The differential pulse polarograms of Eu recorded at growing concentrations of salicylate are shown in Fig. 3. The polarograms recorded in the presence of KHP were very similar and therefore, they are not presented here. An addition of salicylate or KHP caused an enhancement of the europium DPP peak that may be described by the Langmuir isotherm in a similar way as in the case of HA—see Fig. 4 (R^2 ranged from 0.95 to 0.98). Only very low ("substoichiometric") concentrations of salicylate or KHP caused a slight decrease of the Eu peak (see Fig. 3).

The above presented results suggested that an adsorption of Eu on the working electrode in the form of complexes with voluminous organic ligands (HA, salicylate, KHP) is the main mechanism responsible for the peak enhancement. It is well known that pulse polarographic techniques are very sensitive to the adsorption phenomena [15,16]. Therefore,

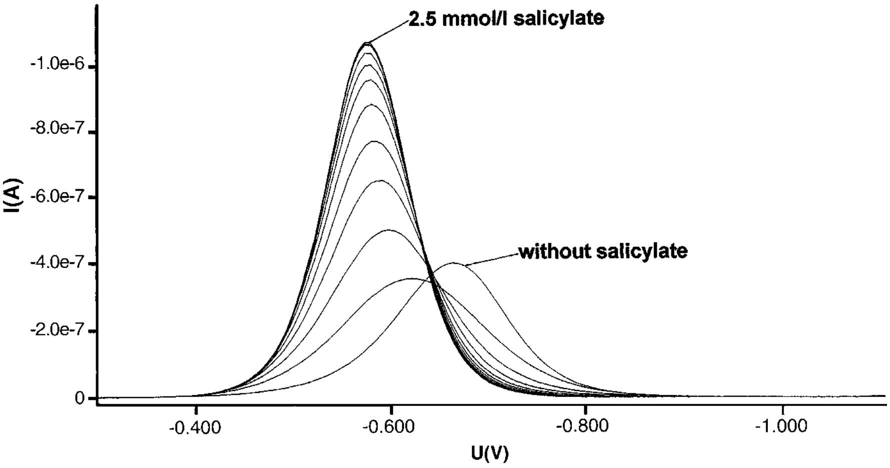

Fig. 3. DPP polarograms of Eu in the presence of salicylate. Instrumental conditions as in Fig. 1. Concentration of Eu 0.250 mmol/l. Supporting electrolyte 0.25 mol/l KCl with growing concentrations of salicylate from 0 to 2.5 mmol/l.

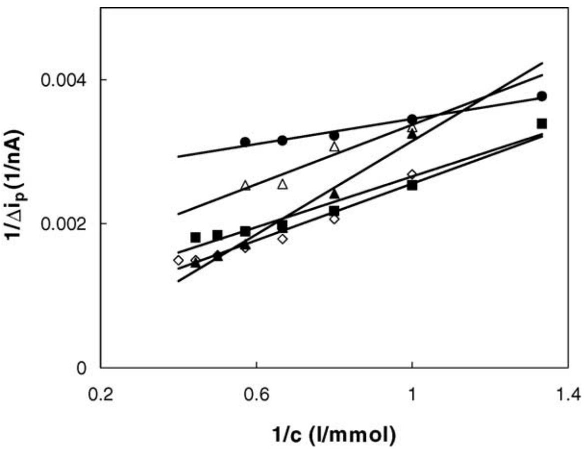

Fig. 4. Dependencies of the peak increase on the concentration of salicylate or KHP plotted in the form of the linearized Langmuir isotherm for various concentrations of Eu: 0.125 mmol/l Eu in the presence of KHP (●); 0.250 mmol/l in the presence of KHP (■); 0.375 mmol/l Eu in the presence of KHP (▲); 0.125 mmol/l Eu in the presence of salicylate (△); 0.250 mmol/l Eu in the presence of salicylate (◊). Experimental conditions as in Fig. 1.

effects of some operational parameters on the DPP peak of Eu were investigated in more details. It was found that the peak height changed, but not very dramatically, with an initial (starting) potential; the peak height decreased by ca. 20% with changing the initial potential from −100 to −350 mV in the presence of 5 mg/l HA. The equilibrating time period before the start of measurements did not affect the peak height. The peak height decreased significantly with increasing the pulse time, t_p. Variations of t_p provide a sensitive tool to inspect adsorption effects [16]. As can be seen from Fig. 5, the i_p–$t_p^{-0.5}$-dependence (Cottrell plot) exhibited a non-zero intercept in the supporting electrolyte containing HA, witnessing the presence of the reactant adsorption [16].

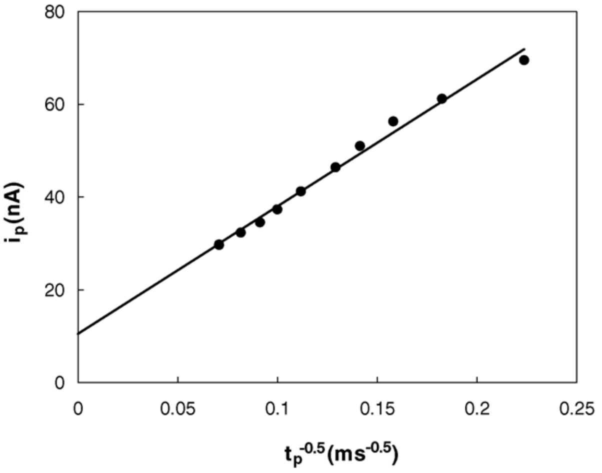

Fig. 5. Effect of the pulse time on the peak height–the i_p vs. $t_p^{-0.5}$-dependence. Concentration of Eu 0.015 mmol/l, concentration of HA 5 mg/l, other conditions as in Fig. 1.

Table 2
Performance characteristics for the DPP determination of Eu

Characteristic	Without HA	In the presence of HA (5 mg/l)
Limit of detection (nmol/l)[a]	255	140
Limit of quantification (nmol/l)[b]	850	470
Sensitivity (nA × l/mol)[c]	0.98	3.38
Repeatability (RSD) (%)[d]	3.39	1.87

Supporting electrolyte: 0.25 mol/l KCl. Instrumental parameters as in Fig. 1.

[a] 3*s* [20].

[b] 10*s* [20].

[c] Slope of the calibration curve for $c_{Eu} \rightarrow 0$.

[d] For $c_{Eu} = 1 \times 10^{-6}$ mol/l, $n = 10$

3.2. DPP determination of Eu

As can be seen from Fig. 1, the DPP peak of Eu is not distorted or suppressed in the presence of HA. On contrary, the presence of HA causes usually the peak enhancement that may be exploited for the determination of Eu in some kinds of real samples, such as natural waters or soil extracts. The main performance characteristics for the DPP determination of Eu were measured both in the presence as well as in the absence of HA under comparable conditions. As follows from the values listed in Table 2, the limit of detection and limit of quantification decreased, whereas sensitivity increased significantly in the presence of HA. However, it should be pointed out that the presence of HA affects strongly a linearity of the calibration curve, as is demonstrated in Fig. 6. Similar calibration plots were obtained for various concentrations of HA and various concentration ranges of Eu. In principle, it is possible to construct a model calibration curve (adding HA into the calibrating solutions) and to evaluate the measurements using standard procedures for non-linear calibration functions [21]. This approach, however, is not practicable for analyses of real samples with an unknown content of HA. The non-linear calibration dependencies complicate also an evaluation of measurements by the most commonly used method of standard addition. The standard addition method based on

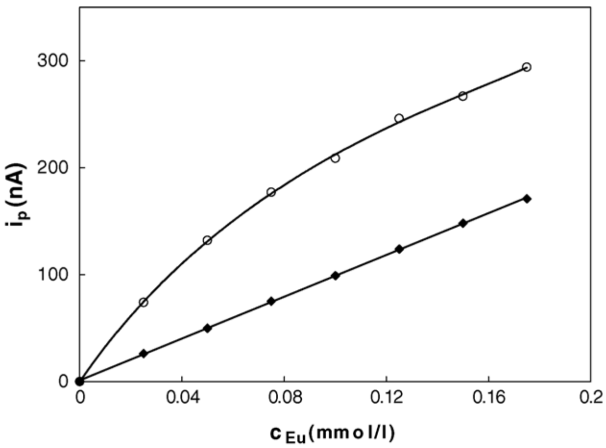

Fig. 6. Calibration curves in the absence (1) and in the presence (2) of HA (5 mg/l). Experimental conditions as in Fig. 1.

a linear extrapolation causes a systematic error with a magnitude depending on the (unknown) concentration of Eu and on the standard addition concentration (and, of course, on the HA concentration). Based on the data from Fig. 6, it was estimated that the standard addition method with one addition may cause a positive error lower than ca. 20% for the Eu concentrations not exceeding 0.02 mmol/l and for an equimolar standard addition, whereas as high as a 100% positive error was obtained for the Eu concentrations about 0.1 mmol/l. The best way to overcome this problem is a sample dilution that allows to work in a linear range of the calibration function. Sometimes, however this is not applicable and the non-linear calibration models have to be adopted.

Although a general shape of the DPP calibration curves affected by the adsorption phenomena may be rather complex (and virtually unpredictable because of a complexity of the respective theories [16]), it seems reasonable to suppose, at least in the first approximation, that they follow the form of some of adsorption isotherms [22], from which the Freundlich and Langmuir isotherms are the most frequently used. It was proved with the aid of a non-linear curve fitting procedure that the calibration function, such as the curve 2 in Fig. 6, can be expressed in the form of the Freundlich-type isotherm (for the data from Fig. 6, the coefficient of multiple determination, R^2, was 0.9972, and the residual sum of squares was 197). It is noticeable that the form of Freundlich isotherm is formally identical with the Lomakin–Scheibe rule [23,24] expressing the relation between an intensity of a spectral line and the concentration of the respective element, which is a very commonly used calibration function in spectrometry.

The Freundlich or Lomakin–Scheibe equations—the power functions, in general—contain two adjustable parameters. It is, therefore possible to determine the europium content using a method of (at least) two standard additions. However, an analytical solution for the respective set of non-linear equations is not possible. Various graphic procedures have been developed to evaluate this kind of non-linear calibration functions; several examples can be found especially in older spectroscopic literature [25–27]. Nowadays, however, an application of interactive computational procedures seems to be more advantageous.

Müller and Oelschläger [28] suggested a special form of the calibration function (Eq. (3)) for describing strongly non-linear calibration curves and presented an interactive FORTRAN program for the evaluation of standard addition determinations.

$$i_\mathrm{p} = K c_\mathrm{Eu}^{m} c_\mathrm{Eu}^{n \ln c_\mathrm{Eu}} \tag{3}$$

K, m, n are constants. Their equation can be used to fit the data in Fig. 6 ($R^2 = 0.9996$, the residual sum of squares 29.1). However, at least three standard additions are required for the evaluation of measurements.

A very good fit was achieved when the Langmuir-type equation was used to model the calibration curve in Fig. 6 ($R^2 = 0.9995$, the residual sum of squares 35.8). The Langmuir equation is a rational function containing only two parameters, and thus two standard additions are necessary for the determination of analyte in an unknown sample.

Again, numerical interactive procedures are recommended for the data treatment. It was found for the spiked samples containing HA and various concentrations of Eu (up to 0.1 mmol/l) that the two-standard addition method utilising the Langmuir-type calibration function gave accurate results with the relative error not exceeding 25%. A comparison of various calibration models is presented in Table 3.

Table 3
Comparison of the calibration models

Calibration model	Concentration of Eu given (μmol/l)	Found (μmol/l)	Error (%)
Linear function	20.0	23.8	+19.0
	50.0	81.2	+62.4
Freundlich (Eq. (1))	20.0	20.5	+2.5
	50.0	22.6	−54.8
Langmuir (Eq. (2))	20.0	21.7	+8.5
	50.0	40.8	−18.4

Synthetic samples containing given amounts of Eu and 5 mg/l HA. Two standard additions were used with concentrations corresponding to 50 and 100% of the given (“unknown”) concentration of Eu.

The proposed polarographic method was used to determine Eu in several synthetic samples originating from investigations of the Eu interactions with HA-containing materials, such as peat, young brown coals (oxihumolites) and solid metal humates. It was tested also for analyses of some natural samples spiked with Eu (waters, soil extracts). A comparison with an inductively coupled plasma emission spectrometry (ICP–OES) suggests that the polarographic determination gives reliable results in a wide range of samples (Table 4).

Table 4
Comparison of the DPP and ICP–OES determinations of Eu

Sample	Concentration of HA (mg/l)[a]	Concentration of Eu (mg/l)	
		DPP	ICP–OES[b]
Extract from the coal-based sorbent loaded with Eu	4.8	3.70	3.55
Soil extract spiked with Eu	7.6	6.76	7.63
Synthetic river water (containing Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-) spiked with Eu	5.6	1.23	0.97
Lake water spiked with Eu	<1	1.31	1.11

[a] Determined spectrophotometrically in the analysed solution containing supporting elecrolyte.

[b] Overall uncertainty of the ICP–OES determinations was ca. 7%.

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