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Fast and simple differential pulse adsorptive stripping voltammetric determination of Ce(III) in natural water samples

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ABSTRACT

This work concerns straightforward, cost-effective, and time-saving adsorptive stripping voltammetric (AdSV) procedure for trace quantification of cerium(III) in natural water samples rich in an organic matrix. The method is based on adsorptive accumulation of the Ce(III)-Alizarin S complex at a glassy carbon electrode (GCE) surface. The experimental parameters (pH and concentration of supporting electrolyte, complexing agent concentration, potential and time of accumulation) and the impact of possible disturbances were studied. It has been proven that interferences caused by organic matrix such as surface-active and humic substances could be removed by the addition of Amberlite XAD-7 resin to the analyzed sample prior to the appropriate voltammetric measurement. Under optimized circumstances, a linear purview of 0.2–8 μmol L^{-1} and a limit of detection value of 0.06 μmol L^{-1} were gained. The featured AdSV procedure was utilized to determine cerium in enriched water samples from the Bystrzyca River and Lake Zemborzyce, which corroborates analytical application.

Keywords: Electrochemical sensors; Cerium; Voltammetry analysis; Alizarin S; Resin

1. Introduction

Cerium belongs to rare earth elements. This group of elements is also called lanthanides. Cerium is the most abundant lanthanide, but rather than occur in one place, it is spread widely throughout the Earth’s crust. It is found in a number of minerals, which include allanite (also known as orthite), monazite, bastnasite, cerite, and samarskite [1]. Its abundance is thought to be as high as 68 parts per million. It makes up about 0.0046% of the Earth’s crust by weight [2]. Cerium has many diverse industrial applications [3–6]. It is used in aluminum and iron alloys, in stainless steels, and in some rare-earth alloys. It is used on a wide scale in the areas of lighting and television as well as in metallurgy and glass and ceramic production. In recent years, applications of cerium as one of the active components of a catalytic converter in motor vehicles have been increasing. Cerium, in conjunction with other rare earth metals, is used in carbon-arc lighting, which is implemented in the motion picture industry. Furthermore, cerium oxide is used as a glass polishing agent. Because of the wide usage of cerium, it increasingly gets into the environment, accumulates in organisms, and finally enters the food chains. Therefore, the development of monitoring techniques for cerium is of most importance.

There are numerous sensitive instrumental techniques applicable for cerium determination. Among these, the most commonly used are spectroscopic techniques such as graphite furnace atomic absorption spectroscopy (GF-AAS) [7], inductively coupled plasma-atomic emission spectroscopy

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(ICP-AES) [7,8], inductively coupled plasma-mass spectroscopy (ICP-MS) [9], and X-ray fluorescence spectroscopy [10]. Others are chromatography [11], spectrophotometry [12], neutron activation analysis (NAA) [13], chemiluminescence [14], and fluorimetry [15]. However, most of these techniques, despite their high sensitivity are complicated and require the use of expensive equipment that most laboratories are not equipped with. Electrochemical methods for cerium determination, such as the potentiometric [16,17] and voltammetric one [18–29], can be competition for these methods due to their ease of handling, great selectivity as well as cost effectiveness. At the same time, these techniques are characterized by a detection limit comparable to the aforementioned spectroscopic techniques, but the most sensitive and effective electrochemical technique for trace measurement of many analytes is stripping voltammetry. The high sensitivity of stripping voltammetry results from the two-stage course of the analytical measurement. In the first stage, called preconcentration, accumulation of the substance on the surface of the working electrode takes place at a constant electrode potential. Thanks to this step, the concentration of the analyte accumulated on the electrode with a relatively small surface area becomes much higher than in the solution. The preconcentration process may take place as a result of electrolysis (anodic striping voltammetry – ASV), adsorption (adsorptive striping voltammetry – AdSV), or an electrode reaction leading to the formation of a sparingly soluble compound on the electrode surface (cathode striping voltammetry – CSV). Out of the voltammetric techniques mentioned above, the AdSV method gives the possibility of obtaining the lowest detection limits due to the use of a complexing agent forming electroactive complexes metal-complexing agent capable of accumulating the electrode surface. Among voltammetric techniques, adsorptive stripping voltammetry (AdSV) [18–26] has commonly been used for cerium determination. To the best of our knowledge, anodic stripping voltammetry (ASV) [27,28] has been used to develop only two cerium detection procedures and cathodic stripping voltammetry (CSV) [29] has been used to develop only one procedure for determination of cerium. The detection limits of these procedures are in a wide concentration range from 1 pmol L^{-1} to 21 μg L^{-1} for accumulation times as high as 600 s. The detection limit of the proposed new procedure is within this concentration range and amounts to 0.06 μg L^{-1}; moreover it should be emphasized that in our case the accumulation time is very short compared to the times used in the procedures described above and is equal to merely 30 s.

In the vast majority of AdSV procedures, working electrodes were based on carbon electrodes, such as carbon paste electrode [18,19] or modified carbon electrode [20–23]. In these last works, carbon paste electrode was modified by using dipyridyl-functionalized nanoporous silica gel [20], ion imprinted polymers [21], nano-sized cerium-imprinted polymer and multiwalled carbon nanotubes [22] or glassy carbon electrode modified with poly-catechol [23]. Among the procedures in which working electrodes are not based on carbon electrodes, we can find two procedures using antimony film [24,25] and only one procedure using solid amalgam alloy electrode [26]. In addition to the selection of a working electrode, the selection of a complexing agent in AdSV procedures is another, but equally important key element. In the procedures described in the literature, several complexing agents have been employed for adsorptive accumulation of cerium, such as alizarin (ALC) [18,24,25], allyl phenoxyacetate (APA) [21], calcein [26], dipyridyl [20], N′-[(2 hydroxyphenyl)methylidene]-2-Furohydrazide (NHMF) [19], methacrylic acid [22], and *o*-phenylenediamine [23].

The voltammetric techniques are ordinarily susceptible to disruptions by organic constituents in an aqueous sample. Therefore, its evasion or minimization is pivotal for reliable determination of miscellaneous elements in the sample. Thereupon, unresponsiveness to the organic matrix is such a key parameter of determination procedures in natural samples. As follows from the above information, numerously papers have been dedicated to the quantification of cerium by the AdSV method. Nevertheless, none of the published procedures have examined the effect of organic compounds on the detection of cerium. As a result of that, in the present work, particular attention was paid to the thorough examination of the leverage of miscellaneous types of surfactants and humic substances on the voltammetric response of cerium and to exclusion of eventual interferences caused by these substances taking advantage of the adsorptive nature of Amberlite XAD-7 resin. It is worth noting that our research was not focused on improving the electrochemical properties of the electrode. It was therefore deliberate to use glassy carbon electrode (GCE) that had not been modified before the voltammetric measurement. The use of a commercially available unmodified electrode makes the procedure faster and easier to perform and, above all, the procedure can also be commonly carried out in the field.

In the present article, we describe the optimization and characterization of a very simple and effective AdSV procedure for cerium(III) trace determinations at a glassy carbon electrode free of interference associated with the presence of organic substances typical in environmental samples. The proposed procedure is based on adsorptive accumulation and oxidation of the Ce(III)-Alizarin S complex. The procedure was applied for the determination of Ce(III) in environmental water samples rich in organic substances.

2. Experimental

2.1. Instrumental and reagents

All voltammetric measurements were carried out with an Autolab PGSTAT 10 analyzer (Utrecht, The Netherlands) and GPES software package produced by Eco Chemie, the Netherlands. A classical three-electrode quartz cell with a volume of 10 mL was used. A glassy carbon electrode (GCE) with a diameter of 1 mm was used as the working electrode. A platinum wire and Ag/AgCl electrode (in saturated NaCl) were used as the auxiliary electrode and reference electrode, respectively. The glassy carbon electrode was polished daily in the following manner. First, the electrode was pre-polished on 2,500 silicon carbide paper and then the electrode was polished using alumina particle suspension (0.3 μm) on a Buehler polishing pad. After polishing, the electrode was washed and sonicated for 30 s in an ultrasonic bath. pH measurements were made on a CI-316 pH meter (Elmetron). A mechanical stirrer (type RZR 2021, Heidolph, Germany) was used during preliminary mixing of the analyzed sample with resin.

The water used for all analysis was deionised in a laboratory purification system (Milli-Q system; 18.2 MV; Millipore, United Kingdom). All chemicals used were of analytical reagent grade or Suprapur. A solution of Ce(III) at a concentration of 1 × 10^{-4} mol L^{-1} was prepared from a dilution of 1 g L^{-1} stock standard solution (Merck) of highest purity. A solution of 1 × 10^{-2} mol L^{-1} Alizarin S (Sodium alizarin sulfonate) was prepared by dissolving 0.0856 g of the reagent in water in a 50 mL voltammetric flask and stored in a refrigerator at a temperature of 6°C. The solutions of 1 mol L^{-1} of the acetate buffers were prepared from acetic acid and sodium hydroxide (Suprapur, Merck).A standard solution of 1 g L^{-1} of Pb(II), polyethylene glycol tert-octylphenyl ether (Triton X-100), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and rhamnolipid (biosurfactant) were purchased from Fluka (Buchs, Switzerland). Humic acid sodium salt (HA) was obtained from Aldrich. The river fulvic acid (FA) and natural organic material (NOM) were obtained from the Suwannee River and purchased from the International Humic Substances Society. Amberlite XAD-7 resin was obtained from Sigma. It was washed four times in water and dried at a temperature of 50°C before use.

2.2. Determination of Ce(III) in the presence of lead

Preliminary measurements, during which the effect of foreign ions was examined, showed that the addition of a small amount of lead to the analysed sample causes an increase in the cerium analytical signal. The AdSV peak current of 2 × 10^{-6} mol L^{-1} Ce(III) in the presence of 0.1 mol L^{-1} acetate buffer with pH = 5.3 and 3 × 10^{-5} mol L^{-1} Alizarin S was measured in the function of Pb(II) concentration over the range of 5 × 10^{-6} mol L^{-1} to 5 × 10^{-5} mol L^{-1}. The cerium peak current increased linearly as the concentration of Pb(II) increased from 5 × 10^{-6} mol L^{-1} to 3 × 10^{-5} mol L^{-1} and then essentially plateaued (Fig. 1). These results showed that at a lead concentration of 3 × 10^{-5} mol L^{-1}, the cerium signal increases twice. It can be assumed that in the presence of lead, besides Ce(III)-Alizarin S complexes, mixed lead and cerium complexes with Alizarin S are also formed, resulting in an increase in the cerium signal. Hence, all subsequent measurements were carried out in the presence of this lead ions added to the analyzed sample.

2.3. Standard procedure of voltammetric measurement

Standard experiments were performed using differential pulse adsorptive stripping voltammetry (DP-AdSV) in the following manner. First, a 10 mL stock solution containing 0.1 mol L^{-1} acetate buffer pH = 5.3, 3 × 10^{-5} mol L^{-1} Pb(II), and 3 × 10^{-5} mol L^{-1} Alizarin S was prepared. After registering the background voltammogram, 1 mL of the analyzed real sample (or a known quantity of the Ce(III) standard solution for the testing procedure) was introduced directly into the electrochemical vessel and the voltammetric signal of cerium was recorded. The measurements were executed in non-deaerated conditions at ambient temperature.

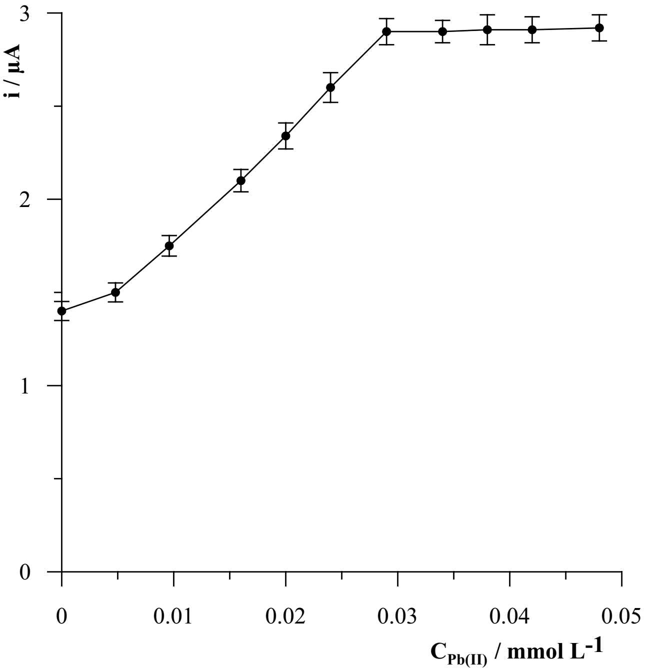

Fig. 1. The influence of lead concentration on the 2 µmol L^{-1} Ce(III) peak current. Accumulation potential 0.2 V and accumulation time 30 s. Fixed concentration: 0.1 mol L^{-1} acetate buffer (pH = 5.3), 3 × 10^{-5} mol L^{-1} Alizarin S.

The accumulation of the Ce(III)-Alizarin S complex was carried out at –0.2 V for 30 s from the stirred dilution. After a 30 s preconcentration period and a subsequent rest period of 5 s, the differential pulse voltammogram was recorded by applying a positive-going potential scan from 0.2 to 0.8 V with a scan rate of 20 mV s^{-1} (at this time, Ce(III) oxidizes to Ce(IV)). The cerium peak was visible at about 0.6 V and its height was directly proportional to the concentration of Ce(III) in the sample. The pulse time and pulse height were 2 ms and 50 mV, respectively.

2.4. Procedure of mixing with resin

Real samples of environmental origin have a complicated matrix rich in organic substances (surfactants and/or humic substances) that may adsorb on the electrode surface, blocking the surface, or form complexes with a specific metal and thus contribute to the disturbance of voltammetric measurement. Therefore, before the voltammetric measurement described in the previous chapter, it is recommended to remove organic substances present in the sample using Amberlite XAD-7 resin. Preliminary experiments show that Ce(III)-Alizarin S complexes undergo adsorption on Amberlite XAD-7 resin and, as a consequence, the voltammetric signal of cerium decreases in time if the resin is present in the voltammetric cell. Considering this, the proposed procedure had to be carried out in two steps. In the first step, 0.5 g of resin was added to the 10 mL of analysed sample (containing 0.2 mol L^{-1} acetate buffer pH = 5.3). Then, the solution was stirred for 5 min using a magnetic stirring bar. During that time the organic matrix of the sample was removed through its adsorption onto the resin. On the other hand, as was tested, in the absence of Alizarin S the cerium ions did not adsorb onto the resin and remained in the solution. In the second-step, after sedimentation of the resin, 5 mL of the sample was pipetted into the electrochemical cell. Next, an appropriate volume of 1 g L^{-1} Pb(II), 1 × 10^{-2} mol L^{-1} Alizarin S, and triply distilled water were successively inserted into the electrochemical cell, so that the desired concentrations were obtained (0.1 mol L^{-1} acetate buffer pH = 5.3, 3 × 10^{-5} mol L^{-1} Pb(II), and 3 × 10^{-5} mol L^{-1} Alizarin S). Finally, the voltammetric measurement was performed as outlined in the previous chapter.

3. Results and discussion

3.1. pH and concentration of supporting electrolyte

To obtain the optimal sensitivity of voltammetric detection of cerium, the determination of Ce(III) was carried out at different pHs and different concentrations of supporting electrolyte. The pH of supporting electrolyte affects the formation of a metal-ligand complex, its stability as well as its adsorption and electrochemical oxidation process. The effect of the pH of the acetate buffer used as supporting electrolyte on the cerium voltammetric signal was investigated in the pH range of 4.0 – 6.4, but in the range from 4.0 to 4.5 no peak of cerium was obtained. The dependence of the stripping peak current of 2 × 10^{-6} mol L^{-1} Ce(III) on the pH of the acetate buffer is shown in Fig. 2. It was shown that the peak current of Ce(III) appeared at a pH equal to 4.6 and increased with an increase in pH from 4.6 to 5.3, and then slightly decreased for the pH range from 5.3 to 6.4. Because the maximum peak current was observed for the acetate buffer pH = 5.3, this supporting electrolyte was chosen for further research.

Subsequently, miscellaneous concentrations of acetate buffer pH = 5.3 in a range of 0.02–0.15 mol L^{-1} were checked at steady cerium and Alizarin S concentrations. The experimental data are depicted in Fig. 3. The results point out that Ce(III) peak current raised with growth of the buffer concentration to 0.1 mol L^{-1}. At buffer concentrations higher than 0.1 mol L^{-1}, an downward trend in the AdSV response can be noticed. Thereupon, a buffer concentration of 0.1 mol L^{-1} was established as the most favorable.

3.2. Alizarin S concentration

The complexing agent concentration is an important parameter in adsorptive stripping voltammetric analysis because the linear range and sensitivity of the method greatly depend on this parameter. First of all, the added analytical ligand must form an electrochemically active complex of suitable stability. Alizarin S is a commonly used organic compound which can form stable complexes with many other metals [30–34] as demonstrated in this study, also with cerium. The effect of Alizarin S concentration was studied by changing the concentration of Alizarin S from 1 × 10^{-5} mol L^{-1} to 1 × 10^{-4} mol L^{-1}, while keeping the analyte concentration and other parameters constant. The results showed that the peak of 2 × 10^{-6} mol L^{-1} cerium linearly increased with the increasing concentration of the complexing agent up to 3 × 10^{-5} mol L^{-1} and finally decreased at higher concentrations (Fig. 4). Therefore, the concentration of the complexing agent equal to 3 × 10^{-5} mol L^{-1} was selected.

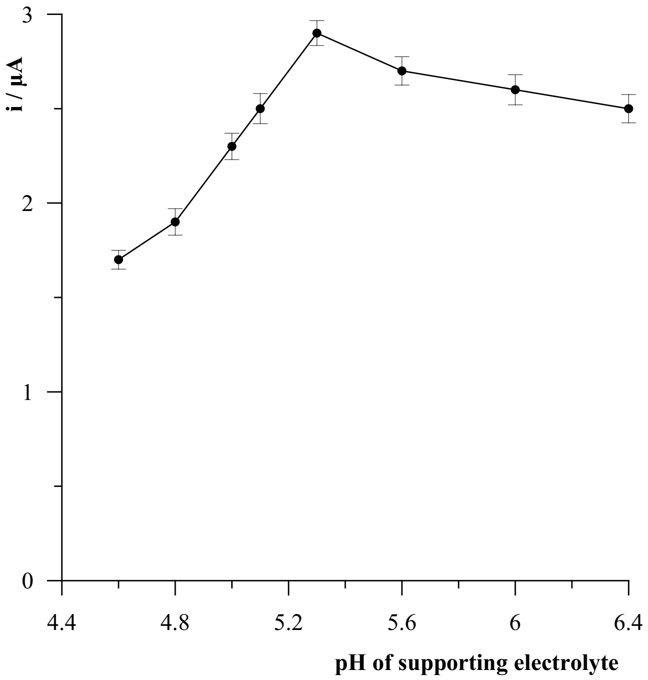

Fig. 2. The influence of pH of supporting electrolyte on the 2 µmol L^{-1} Ce(III) peak current. Accumulation potential 0.2 V and accumulation time 30 s. Fixed concentration: 0.1 mol L^{-1} acetate buffer, 3 × 10^{-5} mol L^{-1} Alizarin S, 3 × 10^{-5} mol L^{-1} Pb(II).

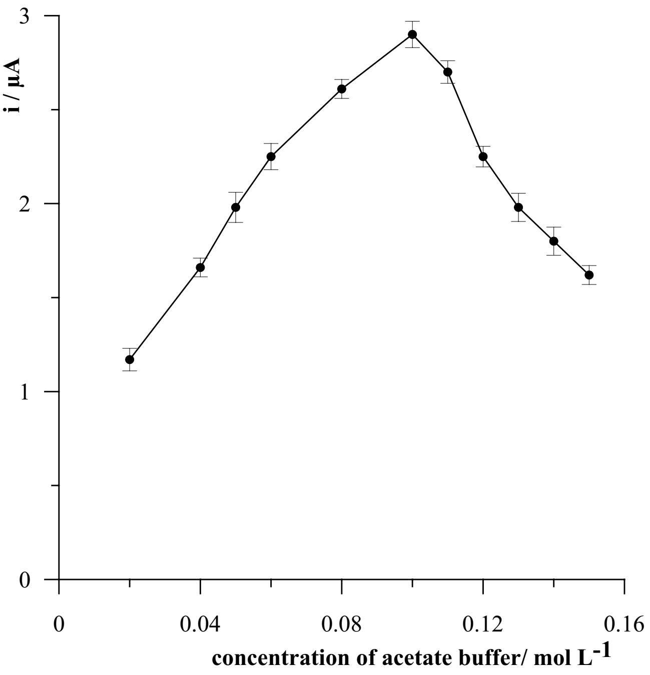

Fig. 3. The influence of acetate buffer (pH = 5.3) concentration on the 2 µmol L^{-1} Ce(III) peak current. Accumulation potential 0.2 V and accumulation time 30 s. Fixed concentration: 3 × 10^{-5} mol L^{-1} Alizarin S, 3 × 10^{-5} mol L^{-1} Pb(II).

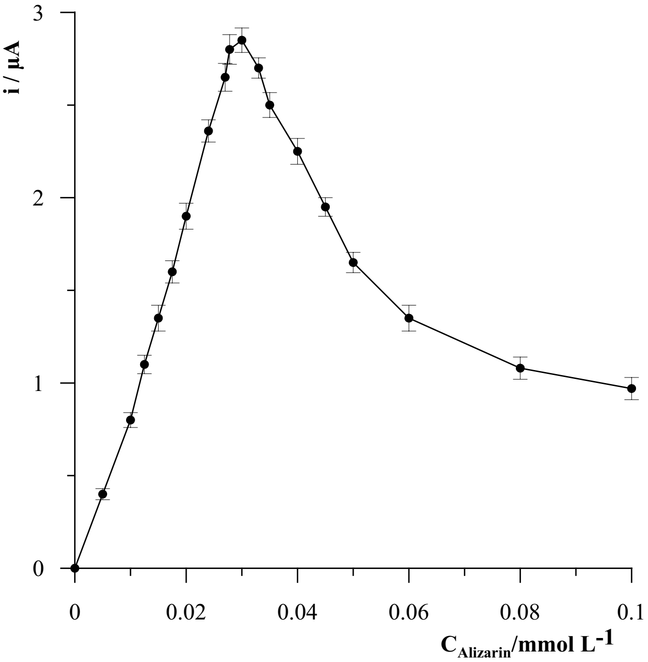

Fig. 4. The influence of Alizarin S concentration on the 2 µmol L^{-1} Ce(III) peak current. Accumulation potential 0.2 V and accumulation time 30 s. Fixed concentration: 0.1 mol L^{-1} acetate buffer (pH = 5.3), 3 × 10^{-5} mol L^{-1} Pb(II).

3.3. Potential and time of Ce(III)-Alizarin S complex deposition

In this part of the optimization experiments, it was assessed how the variability of the potential and time of Ce(III)-Alizarin S complex deposition affects the height of the Ce(III) signal. To check it out, the AdSV response for a concentration of cerium equal to 2 × 10^{-6} mol L^{-1} was investigated over a potential purview from –0.5 to 0.2 V for a fixed period of time of 30 s in the solution containing 0.1 mol L^{-1} acetate buffer pH = 5.3, 3 × 10^{-5} mol L^{-1} Pb(II), and 3 × 10^{-5} mol L^{-1} Alizarin S. The data featured in Fig. 5A permit for the ascertainment that the change in the potential of Ce(III)-Alizarin S complex deposition has a significant impact on the height of the analytical signal of Ce(III). Achieving the highest voltammetric response is possible at the potential of –0.2 V, whereas further alteration of the potential towards more positive values resulted in a reduction of the analytical signal height.

Afterwards, the time of deposition of the Ce(III)-Alizarin S complex was examined for the potential of –0.2 V in the purview from 0 to 70 s. The results are depicted in Fig. 5B. In accordance with the obtained data, it was found that the peak current of cerium raised with drawing out accumulation time up to 30 s, whilst at longer time of Ce(III) deposition, voltammetric response does not exhibit any change.

3.4. Calibration graph, repeatability, and reproducibility

The calibration plot for the accumulation time of 30 s demonstrated a lineal dependence for the Ce(III) concentration of 0.2–8 µmol L^{-1} and was consistent with the regression equation: $y = 1.38x + 0.04$, where y is the peak current (µA) and x is Ce(III) concentration (µmol L^{-1}). Each point of the calibration plot is the mean of three values. The correlation coefficient (R^2) was equal to 0.996. It was calculated that the elaborated procedure exhibits a detection limit of 0.06 µmol L^{-1}. Additionally, the repeatability of the voltammetric response was evaluated on the basis of successive measurements (n = 3) of each studied Ce(III) concentration from the calibration graph. A relative standard

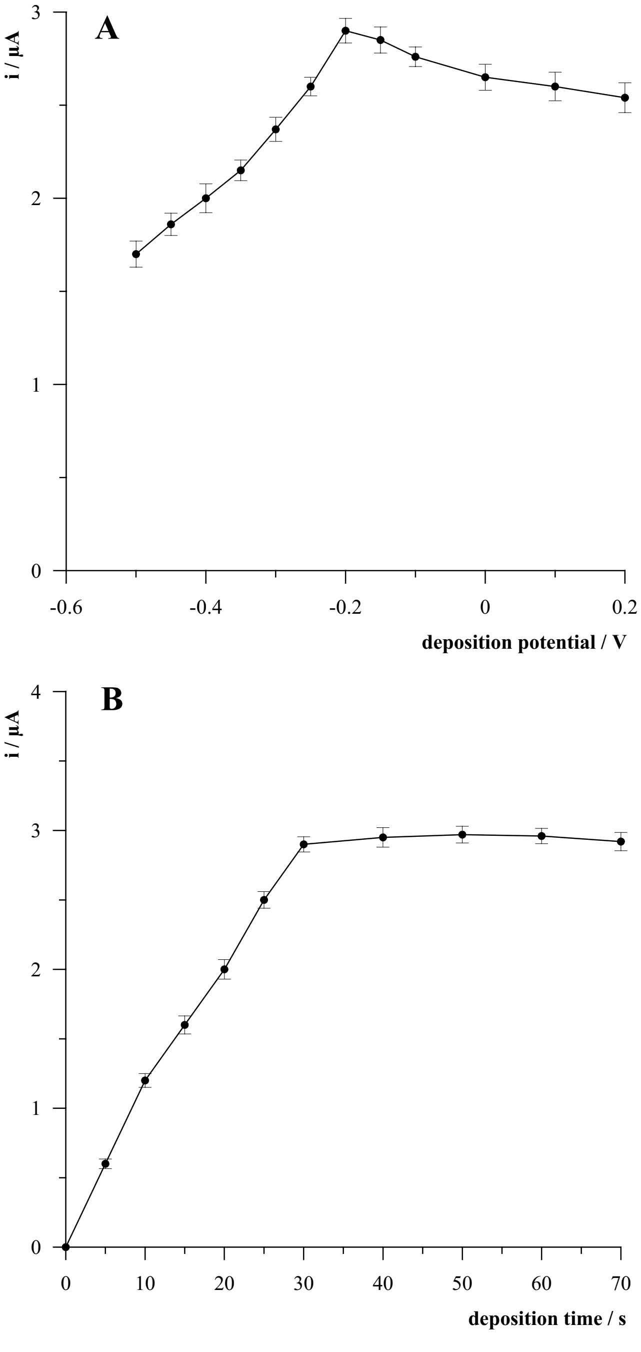

Fig. 5. The influence of potential (A) and time (B) of Ce(III)-Alizarin S complex deposition on the Ce(III) peak current at a concentration of 2 µmol L^{-1}.

deviation of the voltammetric response in the scope from 3.5% to 4.2% was gained. Furthermore, the reproducibility was established in accordance with the measurements executed on five successive days as RSD and it was 6.1%.

3.5. Influence of foreign ions

The leverage of co-existing ions in the sample solution was checked using a steady concentration of 2 μmol L^{-1} Ce(III) and different amounts of foreign ions. The tolerance boundary was appointed as the maximum concentration of potentially interfering ions that generated a relative error not surpassing 5% in the voltammetric response of Ce(III). The experimental data point out that AdSV response of Ce(III) was not dependent on 100-fold excess of Al(III), As(III), As(V), Cd(II), Co(II), Cr(VI), Hg(II), K(I), Mg(II), Mn(II), Na(I), Ni(II), Pt(IV), Se(IV), Se(VI), Sn(II), Ti(IV), U(VI), Zn(II), and 50-fold plethora of Bi(III), Ga(III), Cu(II), Mo(VI). The most interfering nature was shown by Cr(III), Fe(II), Sb(III) and V(V), whose 50-fold plethora caused a decrease in the cerium peak to 70%, 50%, 65% and 30% of its original value, appropriately.

3.6. Influence of surfactants and humic compounds

Adsorptive stripping voltammetry is a voltammetric technique that is especially responsive to organic compounds that are an inherent part of environmental water samples. These substances interfere with the voltammetric response, causing diminution or total disappearance of the peak current s of the elements being determined. In the recommended procedure for cerium quantification, the impact of various kinds of organic compounds, including surfactants with miscellaneous charges and humic substances prevalent in the analyzed natural water samples, was closely explored for the first time. An additional challenge for us, closely related to the problem resulting from the organic matrix, was to elaborate a simple and quick method of deletion of organic substances from the test sample.

At first, the influence of different kinds of surfactants on the Ce(III) voltammetric signal was studied. For this purpose, Triton X-100, CTAB, sodium dodecyl sulfate (SDS), and rhamnolipid, as the representatives for a nonionic, cationic, anionic surfactant and biosurfactant, respectively, were chosen to be tested. The influence of surfactants on the peak current of 2 μmol L^{-1} Ce(III) was investigated by adding Triton X-100, CTAB, SDS, and rhamnolipid to the studied solution in the range from 0.5 to 10 mg L^{-1}. It was observed that both the addition of 10 mg L^{-1} Triton X-100 and SDS did not affect the analytical signal of cerium. However, the addition of 5 mg L^{-1} CTAB caused a total decay of the peak currents of cerium, whilst the same concentration of rhamnolipid decreased the height of the Ce(III) stripping signal to about 40% of its original value.

Subsequently, the impact of commercially available organic matter, such as humic substances, humic acids (HA), fulvic acids (FA), and natural organic matter (NOM), was examined in the concentration range from 0.5 to 10 mg L^{-1}. The measurements were performed similarly as for surface active substances. The results show that the signal of 2 μmol L^{-1} Ce(III) is totally insensitive to the presence of FA and NOM in the solution. However, it was observed that the addition of 5 mg L^{-1} HA reduces the Ce(III) peak to 50% of its original value. Table 1 summarizes all results.

To address this problem, preliminary mixing with the resin before the voltammetric measurement was proposed. It was found that while using the preliminary mixing with Amberlite XAD-7 resin, CTAB, rhamnolipid, and HA did not disturb the analytical signal in the whole range of concentrations (from 0.5 to 10 mg L^{-1}). Similar studies were also carried out with the use of other adsorption resins such as Amberlite XAD-2 and XAD-16, but these resins did not give as spectacular results as the XAD-7 resin. In a solution containing Amberlite XAD-16 resin 10 mg L^{-1} CTAB, rhamnolipid and NOM reduces the cerium current response by approximately 55%, 20% and 15%, respectively. And in the case of pre-mixing the sample with Amberlite

Table 1
Influence of different organic substances on 2 μmol L^{-1} Ce(III) analytical signal using the standard procedure

Kind of organic substance	Concentration of organic substance (mg L^{-1})	Decrease of Ce(III) signal in %
CTAB	0.5	27.5
	1.0	51.0
	2.0	72.0
	5.0	no signal
	10.0	no signal
Rhamnolipid	0.5	10.0
	1.0	12.0
	2.0	43.5
	5.0	63.0
	10.0	71.0
Humic acid	0.5	6.5
	1.0	32.0
	2.0	46.5
	5.0	63.0
	10.0	80.0

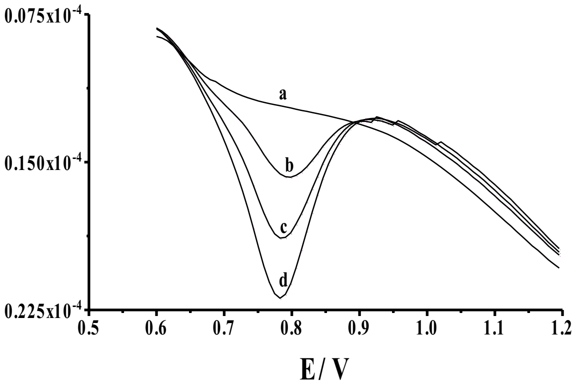

Fig. 6. Differential pulse voltammograms obtained during Ce(III) determination for the Bystrzyca River water: diluted tenfold (a); as (a) +3 × 10^{-7} mol L^{-1} Ce(III) (b); as (a) +6 × 10^{-6} mol L^{-1} Ce(III) (c); as (a) +8 × 10^{-6} mol L^{-1} Ce(III) (d). Fixed concentration: 0.1 mol L^{-1} acetate buffer pH = 5.3, 3 × 10^{-5} mol L^{-1} Pb(II), and 3 × 10^{-5} mol L^{-1} Alizarin S.

XAD-2 the cerium signal was reduced to 50%, 20% and 10%, respectively.

3.7. Application in environmental analysis

In order to prove the applicability and reliability of the developed procedure, recovery tests were carried out by taking two different fresh natural water samples and by adding given amounts of the Ce(III) standard to each sample. The analyzed samples were collected from eastern areas of Poland, river water (the Bystrzyca River) and stagnant water (Lake Zemborzyce). There was no need to prepare the sample for analysis in advance.

Each of the taken samples was tested prior to the addition of Ce(III) but no cerium was detected in any of them. Therefore, various levels of Ce(III) concentration were added to both samples,and then allowed to equilibrate for 1 h. Afterwards, the measurements were taken in a 10 mL voltammetric cell, to which 1 mL of the enriched water sample and the remaining reagents in the amounts as follows from optimization of the procedure were added. For each tested concentration, the measurements were repeated three times, and then their mean values were determined. The recovery values of Ce(III) between 98.2% and 102.4% with RSD ranging from 3.7% to 4.2% for Bystrzyca River as well as between 97.4% and 100.8% with relative standard deviation ranging from 4.0% to 4.9% for Lake Zemborzyce are the evidence of passable accuracy of the proposed method and testify emphatically the applicability of this procedure for determination of Ce(III) in various real water samples. Fig. 6 shows examples of voltammograms recorded during the determination of Ce(III) in the enriched water samples from the Bystrzyca River.

4. Conclusions

Adsorptive stripping voltammetry of Ce(III)-Alizarin S complexes on a glassy carbon electrode turned out to be a straightforward and efficacious method of cerium quantification. Hitherto, the issue of the leverage of disturbances from organic substances on voltammetric determination of cerium has not been brought up in the literature. Contrary to the described before procedures, in this work the influence of miscellaneous types of surfactants and humic substances was thoroughly explored. Besides, it has been revealed that the initial mixing of the sample with the resin removes possible disturbances related to the attendance of these substances. The superiority of the developed procedure is the unchanged voltammetric response of Ce(III) in the attendance of even 10 mg L^{-1} of all examined surfactants or humic substances. The proposed method allows for Ce(III) determination in natural water samples without complicated and time-consuming sample pretreatment, which was confirmed by the passable results gained in course of the analysis of the Bystrzyca River and Lake Zemborzyce water samples.

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