Competitive extraction of Gd(III) into a carbon paste electrode impregnated with a nano-sized Gd(III)-imprinted polymer as a new method for its indirect voltammetric determination

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Abstract We describe an indirect method for the voltammetric determination of Gd(III) ion. It is based on competitive extraction of Gd(III) into an ion-imprinted polymer (IIP) on the surface of a carbon paste electrode (CPE). The nano-sized IIP was synthesized via suspension polymerization in silicone oil and deposited on the CPE. The IIP-modified CPE was then incubated with solutions containing Pb(II) and a solution containing both Pb(II) and Gd(III) ions. The oxidative stripping differential pulse voltammetric signal for Pb(II) was utilized to determine the competitively extracted quantity of Pb(II). The presence of Gd(III) reduces the quantity of electroactive lead ions in the IIP located on the CPE. No such effect was observed for the case of a nonimprinted CPE. The effect of various factors on response were optimized. The drop in the signal for Pb(II) as a result of addition of Gd(III) is proportional to the concentration of Gd(III). The voltammetric response is linearly related to the concentration of Gd(III) in the 6.0 nM to 48 μM range, and the detection limit is 4.5 nM at an SNR of 3. The relative standard deviation is 3.7 % (for $n=5$). The electrode is selective for Gd(III) even in the presence of other lanthanide ions. The method was applied to the determination of G(III) in synthetic and in spiked real samples.

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Introduction

Gadolinium has been classified as one of the rare earth elements. The rare earth elements are divided into the lanthanide and actinide series. Gadolinium and other lanthanide oxides are widely used in the preparation of glass fibers, gasoline-cracking catalysts, optical glasses and polishing compounds. Gadolinium yttrium garnets, fabricated utilizing gadolinium element, are used as phosphors for color TV tubes. This element is also used for the manufacturing of compact discs and computer memories [1, 2]. In addition, gadolinium based compounds are widely employed as a contrast agent for magnetic resonance imaging [3].

Because of the increasing applications of gadolinium in modern industries, its measurement has become important in recent years. Various methods such as: inductively coupled plasma-mass spectroscopy [4, 5], inductively coupled plasma atomic emission spectroscopy [6], laser-based multi step resonance ionization [7], phosphorescence [8] and spectrofluorimetry [9] have been reported for Gd monitoring. However, these methods are expensive and time-consuming. As a result, design of an inexpensive and simple technique which can provide satisfactory selectivity to determine Gd in the presence of other lanthanides is of great value.

Among different available analytical methods the electrochemical techniques can be referred as a really efficient approach, because of their high sensitivity, low cost, high selectivity and easy automation. However, direct electroanalysis of Gd^{3+} ions, using sensitive electrochemical methods like differential pulse voltammetry (DPV), is

not possible; because, this ion is electrically inactive in aqueous solutions and using the traditional electrode materials. The electrochemical methods, used for Gd^{3+} analysis, have been limited to some PVC-based membrane ion selective electrodes [10, 11].

Molecularly imprinted polymer (MIP) can selectively recognize a molecule among closely related structural analogues [12–15]. Similar to MIPs, ion imprinted polymer (IIPs) can recognize a target ion among other metallic ions. Numerous IIP materials have been reported for various kinds of metal ions [16–20].

Previously, we developed a new methodology for Eu^{3+} determination based on Eu^{3+}-imprinted polymer modified carbon paste (CP) electrode [21]. In that work Eu^{3+} concentration in a solution was estimated by monitoring of the decrease in the DPV signal of an electroactive probe ion as the result of competitive extraction of Eu^{3+} in the IIP sites, occupied by the probe ions. Following the mentioned methodology and in order to extend the developed technique, in this study, a DPV method was used for Gd^{3+} determination. Herein, the Gd^{3+}-imprinted polymer was used as the recognition element of carbon paste electrode. In order to overcome the problem of electrochemically inactivity of Gd^{3+}, an electroactive probe ion was utilized to trace the Gd^{3+} adsorption in the IIP, situated in the electrode surface. This is the first indirect voltammetric determination of Gd^{3+} via the IIP-based carbon paste electrode. Compared to our previous work, in this approach the detection limit of the method has been lowered significantly by changing the kind of the electroactive probe ion (from copper ion to lead ion).

Experimental

Instrument and reagents

Electrochemical data was obtained using a potentiostat/galvanostat model PGSTAT302, Metrohm. Carbon paste electrodes, modified with IIP or non imprinted polymer (NIP), were used as a working electrode. An Ag/AgCl electrode and a platinum wire were used as the reference and counter electrodes, respectively. Methacrylic acid (Merck, Germany http://www.merckgroup.com/), Vinyl pyridine (VP) and divinyl benzene (DVB) (Sigma-Aldrich, USA http://www.sigmaaldrich.com/united-states.html) were purified by distillation under reduced pressure. 2, 2′-(2- methyl propionitrile) was obtained from Acros Organic, Geel, Belgium (http://www.exportersindia.com/acrosorganics/) and used as an initiator. $Gd(NO_3)_3$ and other lanthanides were from Merck, Germany. Other chemicals were of analytical grade and purchased from Merck, Germany.

Preparation of MIP nanoparticles by suspension polymerization in silicon oil

In order to prepare, nano-sized IIP, 0.3 mmol of $Gd(NO_3)_3$ (template), 1.8 mmol of vinyl pyridine (functional monomer and complexing ligand), 0.6 mmol of MAA (functional monomer and complexing ligand), 12 mmol of DVB (cross-linker) were dissolved in 5 mL of acetonitrile (porogen). After 1 h, 0.05 g of AIBN (initiator) was added to the mixture. The obtained mixture was transferred to silicon oil (100 mL), purged previously with a stream of nitrogen gas for 15 min. The mixture was then mixed vigorously by a mechanical mixer (1000 rpm for 10 min). This was followed by ultrasonication for 22 min. Before polymerization, a stream of nitrogen gas was blown throughout the solution for 15 min. The polymerization reaction was carried out in a water bath, fixed at 70 °C, for 24 h. The obtained polymeric powder was first washed with petroleum ether and then toluene. After every washing step, high speed centrifugation was applied for the separation of the polymeric particles from the solvents. To extract the non-reacted monomers from the polymer, the particles were further washed with methanol and acetonitrile. Then, Gd^{3+} ions were removed from the polymer by suspending of the particles of the synthesized polymer in a solution of sodium acetate and EDTA for 2 h. Finally, the polymer was successively rinsed with distilled water and dried in vacuum at 50 °C, overnight. In order to prepare the non-imprinted polymer (NIP), exactly, the above-described method was utilized in the absence of Gd^{3+}.

Preparation of the modified electrodes

In order to construct the IIP- and NIP-modified carbon paste electrodes, (IIP-CP and NIP-CP), 0.05 g of graphite was blended with 0.03 g of nano-sized Gd^{3+}-IIP or the related NIP for 10 min. Then, the graphite/IIP (or graphite/NIP) blend was added to the melted n-eicosane (heated at 45–50 °C) and mixed with a stainless steel spatula. Finally, the paste obtained was used to fill a hole (2.00 mm in diameter, 3 mm in depth) at the end of an electrode body, previously heated at 45 ° C. The surface of the electrode was smoothed with the aid of a smooth paper sheet.

Rebinding experiments

The prepared IIP-modified electrodes were inserted into the solution containing both Gd^{3+} (and other aimed ions) and Pb^{2+} (pH=7), being at stirring state (500 rpm). Then, the electrode was placed in the electrochemical cell, filled with 10 mL of HCl solution (0.10 M). In order to record the electrochemical signal, pre-potential of −1.0 V was applied to the electrode for 20 s to reduce the adsorbed probe ions (Pb^{2+}) and then the differential pulse stripping voltammetry was performed in the

potential range of -0.8 to -0.3 V. The obtained signals were compared with the signal of the electrode, immersed in the pure Pb^{2+} solution. The concentration of Pb^{2+} in both described solutions was the same in all experiments.

Results and discussion

Synthesis of Gd(III)-imprinted polymer and its characterization

In order to synthesize Gd^{3+}-imprinted polymer, MAA and VP were contacted with Gd^{3+} (mole ratio 2:6:1). MAA and VP acted either as functional monomers or complexing ligands, canceling the need to additional complexing ligand. This strategy not only resulted in a simple IIP synthesis procedure but also cancelled the risk of removal of the ligands during the washing stage; because, the functional monomers, providing the coordination bonding sites in the IIP, were attached to the polymer network as a result of the polymerization reaction. The so-called suspension polymerization in silicon oil method was utilized as the polymerization method in order to obtain nano-sized imprinted polymers. Scanning electron microscopy images of the synthesized polymeric particles are shown in Fig. 1. It is apparent that the nano-sized polymeric particles are obtained by employing the described synthesis method. Size distribution chart, represented in the inset of the image, indicates that the mean size of the IIP particles is about 50 nm. The FT-IR spectra were also used to investigate further the structure of the obtained polymers. The FT-IR spectra of the unleached IIP, leached IIP and NIP are shown and described in details in Electronic Supplementary Material (Fig. S1, ESM).
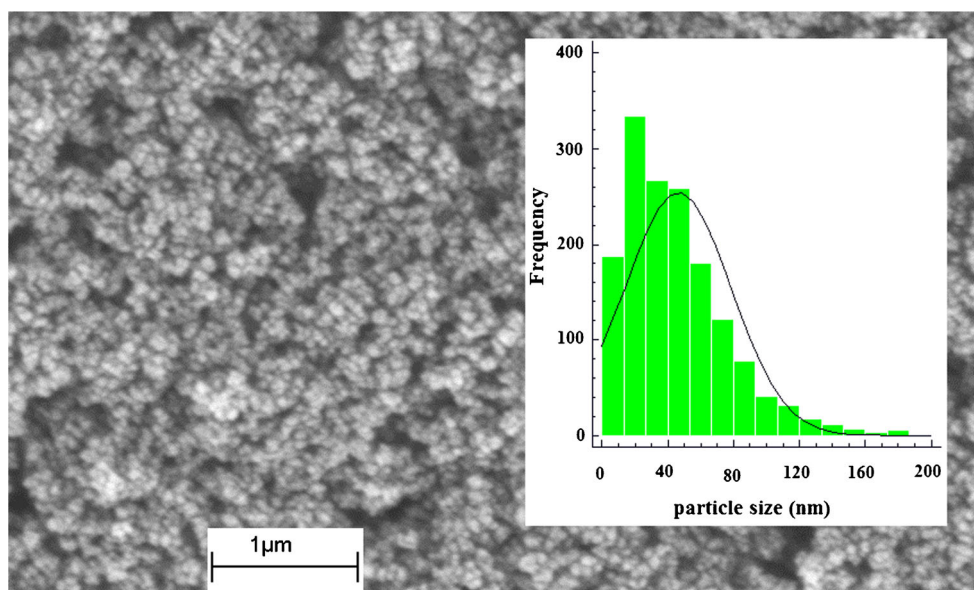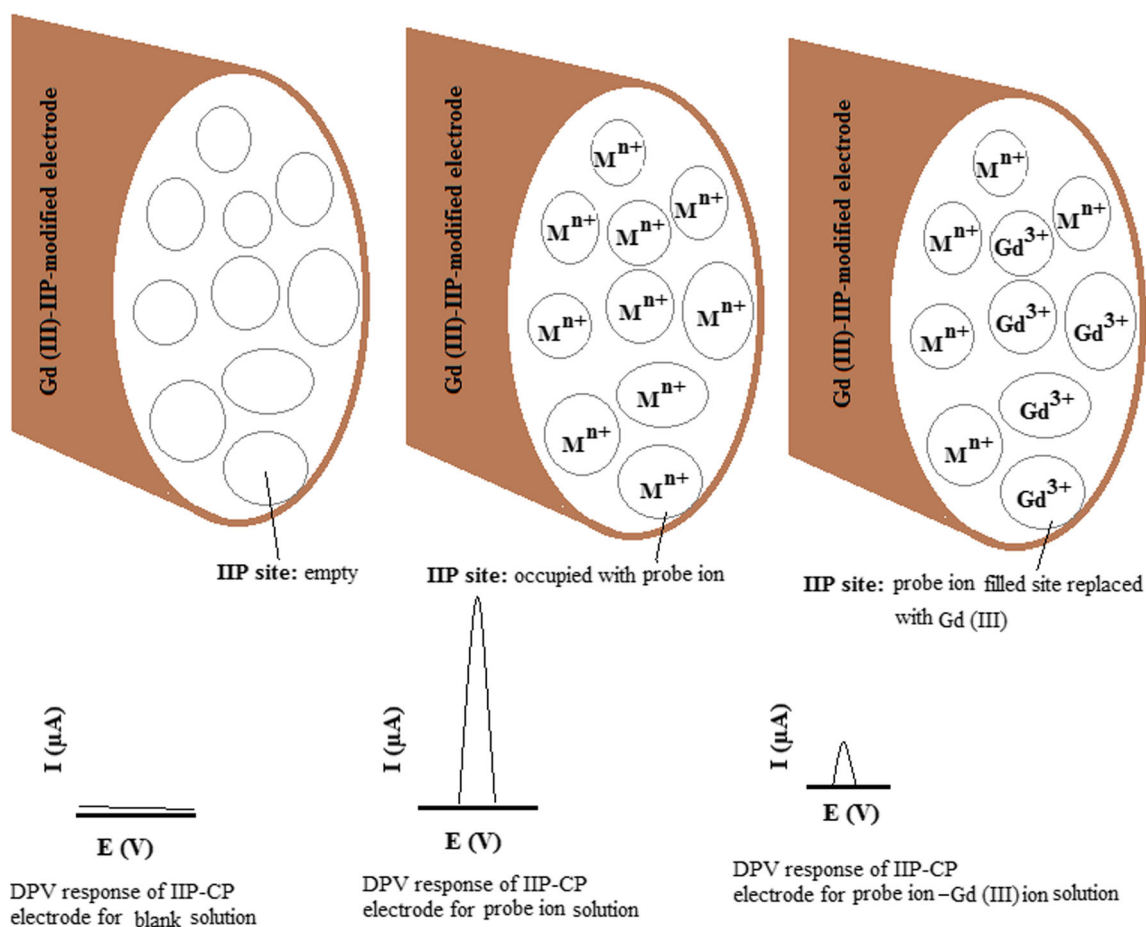
Selection of probe ion

Gd^{3+} is a non-electroactive ion among lanthanides and thus direct electroanalysis methods like voltammetry can not be used for its determination. Therefore, an indirect method was chosen for the investigation of the recognition property of the newly developed Gd^{3+}-IIP. For this purpose, a CP electrode was modified with Gd^{3+}-IIP and immersed in a proper electroactive probe ion solution. By this means, the electroactive ion was adsorbed in the selective sites of the IIP, situated in the carbon paste electrode. The differential pulse voltammetry signal of the described electrode was proportional to the amount of the electroactive probe ions, adsorbed in the electrode surface. However, in the presence of Gd^{3+} ions the electroactive probe ions had to compete with Gd^{3+} to occupy the selective sites of the IIP. This led to a considerable fall in the population of the electroactive probe ion in the selective sites of the IIP. Such a described effect decreased the voltammetric response of the electrode. The extent of the signal reduction was proportional to both Gd^{3+} affinity to the sites of the IIP and the number of Gd^{3+} ions contributed in the competition. Figure 2 illustrates schematically the explained methodology.

The selection of probe ion, however, is very important. The probe ion not only must have a good electroactivity but also have to compete strongly with the target ion for the occupying of the selective site of the IIP. That is to say, the probe ion kind can affect both sensitivity and selectivity of the determination method. Figure 3 represents the results of indirect analysis of Gd^{3+} ion by using two different electroactive probe ions. As can be seen, in the case of Pb^{2+} the decrease in electrode signal, as a result of competitive adsorption of Gd^{3+}, is considerably bigger than that observed when using Cu^{2+} as the

Fig. 1 Scanning electron microscopy images of the prepared IIP

Fig. 2 Schematic representation of the determination mechanism of the developed method

probe ion. This can be attributed to the inherent bigger differential pulse voltammetry signal of Pb^{2+} ions on CP electrode, compared to that of Cu^{2+}. Therefore, removing of Pb^{2+} ions by replacing of target ions can lead to higher drop in initial

signal, compared to exchanging of the same number of Cu^{2+} with Gd^{3+} ions. However, the difference in affinities of theses probe ions to the ion-selective sites of the IIP may be a key point in this case.

Fig. 3 differential pulse voltammetry responses of the IIP-CP electrodes immersed in the solution of pure probe ion (5×10^{-7} mol. L^{-1}) (*a*) and that containing both probe ion (5×10^{-7} mol. L^{-1}) and Gd^{3+}(3×10^{-7} mol. L^{-1}) (*b*); the probe ions utilized: Cu^{2+} (I) and Pb^{2+}(II)
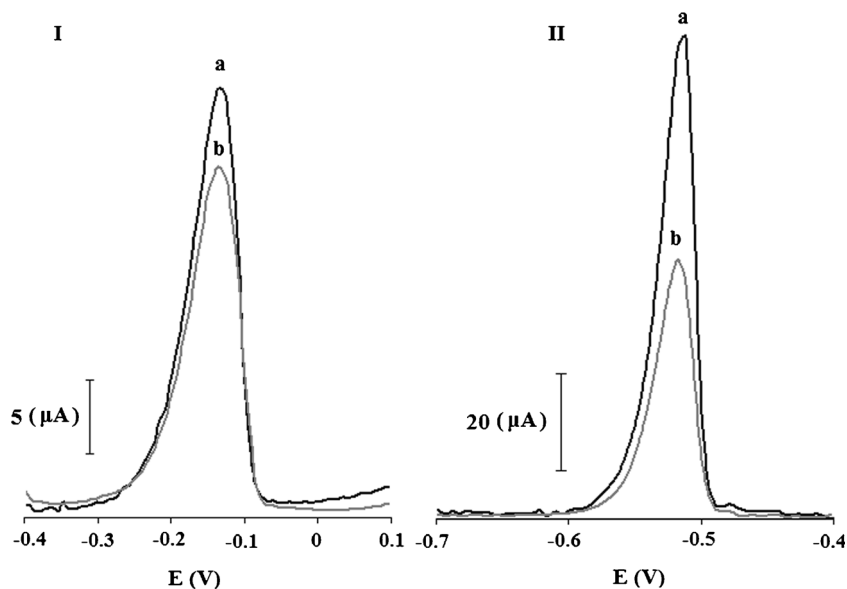
Comparison of the recognition characteristics of the ion imprinted polymer with non-imprinted polymer

After selection of a proper probe ion for indirect analysis of Gd^{3+}, the effectiveness of the ion-selective sites of the IIP for Gd^{3+} recognition was further evaluated. In order to reach this aim, the Gd^{3+} recognition capability of the IIP was compared with that of the NIP particles. In Fig. 4, the voltammograms of (a) and (b) represent the DPV signal obtained for the IIP-CP electrode after 10 min incubation in Pb^{2+} and Pb^{2+} plus Gd^{3+} solutions, respectively. On the other hand, the voltammograms of (c) and (d) are related to the NIP-CP electrode for Pb^{2+} and Pb^{2+} plus Gd^{3+} solutions, respectively. It is clear that the IIP-CP electrode creates bigger Pb^{2+} signal, compared to the NIP-CP electrode, suggesting that the adsorption of Pb^{2+} in the IIP is noticeably higher than that in the NIP material. This may be assigned to the selective sites of the IIP which do not exist in the NIP material. Furthermore, it can be seen that Pb^{2+} signal in the case of IIP-CP electrode is decreased considerably in the presence of Gd^{3+} as the target ions; however, the NIP-CP signal is not affected significantly in the presence of Gd^{3+}. These results indicate that the competition between Gd^{3+} and Pb^{2+} is just for occupying the selective sites of the IIP. In other words, there is no noticeable competition between Gd^{3+} and Pb^{2+} in order to take the non-selective sites
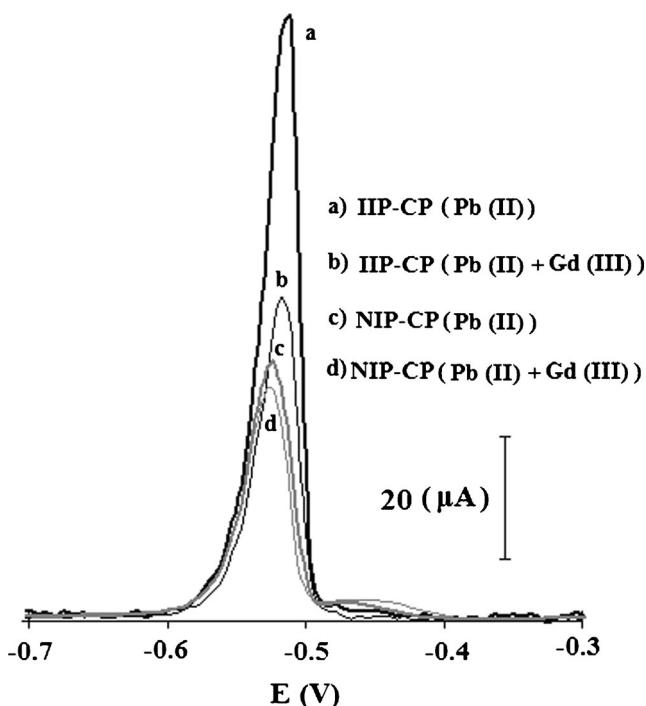
Fig. 4 differential pulse voltammetry responses of the IIP-CP ("*a*" and "*b*") and NIP-CP ("*c*" and "*d*") electrodes immersed in the solution of pure Pb^{2+} ("*a*" and "*c*") and that containing both Pb^{2+} and Gd^{3+}(*b* and *d*); $[Pb^{2+}]=5\times10^{-7}$ mol. L^{-1}, lanthanides ion concentration$=3\times10^{-7}$ mol. L^{-1}, Extraction condition: extraction time= 15 min, agitation speed:400 rpm; electrochemical analysis: 15 ml HCl solution(0.1 mol. L^{-1})

of the IIP; because, the influence of Gd^{3+} on the Pb^{2+} signal of the NIP-CP electrode is very smaller than that on the IIP-CP electrode signal. This experiment suggests that the competitive extraction of Gd^{3+} ion in the IIP-CP, in the presence of Pb^{2+} ion, can be effectively used for the selective determination of Gd^{3+} in the aimed solutions.

The effect of different conditions on the efficiency of the method

Fig. S2a (ESM) represents the dependence of the response of the IIP-CP electrode to the IIP amount in the carbon paste. It is apparent that the electrode response to Pb^{2+} increases with enhancement in the IIP till a limited amount and then it keeps constant. However, the electrode response to the mixture of Pb^{2+} and Gd^{3+} increases continuously as a result of enhancement in the IIP amount. The availability of higher amount of the IIP on the electrode decreases the need to compete between the target and probe ions; since, in such a case, Gd^{3+} ions can enter in the sites, not occupied by Pb^{2+} ions, leading to no suitable information from the target ion recognition by the IIP sites. According to this figure, at a certain amount of the IIP (3 mg) a maximum competition is observed between Gd^{3+} and Pb^{2+} to occupy the positions of the selective sites. Therefore, in order to obtain meaningful signal as a result of target ion recognition, it is necessary to use the optimum amount of the IIP in the modified electrode composition.

The effect of extraction solution pH on the competitive recognition of Gd^{3+} by the IIP-CP electrode is shown in Fig. S2b (ESM). It is obvious that adjusting the solution pH at the range of 6–8 leads to the best condition for the recognition of Gd^{3+} by the IIP; because, at this pH range there is a maximum signal difference between the electrode immersed in the Pb^{2+} solution and that incubated in the Pb^{2+} plus Gd^{3+} solution. Increasing of the acidity of the environment nullify the capability of the functional groups of the IIP sites to link to both Pb^{2+} and Eu^{2+} via coordination bonding. This is because of protonation of the nitrogen groups of vinyl pyridine in the selective sites of the IIP as a result of increasing in H^+ concentration. On the other hand, the swelling of the IIP particles as well as the interference effect of hydroxide ions on Pb^{2+} and Eu^{2+} in alkaline condition may decrease the interaction of both ions with the IIP sites. Therefore, a neutral pH was chosen as an appropriate pH condition for the competitive recognition of Gd^{3+}.

The effect of competitive extraction time on the electrode response was also checked (Fig. S2c, ESM). Herein, the adsorption of the probe ion is initially increased and after a definite time, the adsorption increment rate is decreased strongly. The first adsorption regime is ascribed to the uptaking of Pb^{2+} ion by the high affinity selective sites and the second is related to the adsorption of probe ions to the non-specific binding sites of the IIP. The adsorption behavior of the

Table 1 Comparison of the present method with some previously reported methods

| Method	Analytical characteristics			Reference
	Linear range (nM)	Detection limit (nM)	RSD (%)	
SPE-ICP-MS	3.8–254	1.2	–	[22]
Spectrofluorimetric determination	159–1465	–	8(n=5)	[23]
Membrane electrode	$1 \times 103 – 1 \times 108$	580	–	[24]
Membrane electrode	$938 – 1 \times 107$	500	–	[25]
Membrane electrode	$300 – 1 \times 108$	300	–	[11]
Membrane electrode	10–2500	9.3	1.4(n=7)	[26]
IIP-CP	6.0–48.8	4.8	3.7(n=5)	This work

IIP in the presence of both target and probe ions, however, differ noticeably from that of the previously described behavior. This indicates that there is a real competition between Gd^{3+} and Pb^{2+} for accessing the binding sites of the IIP. It can be seen, that the difference of two curves meets a maximum amount at the extraction time of 10 min. Thus, this extraction time was chosen as the best option for the evaluation of the recognition characteristic of the Gd^{3+}-IIP.

Analytical characterization of the electrode modified with the Gd(III)-imprinted polymer

The interference effects of various species on the target ion analysis by the IIP-CP electrode were examined. The maximum concentrations of foreign species that caused a relative error of 5 % in the analytical signal were accepted as tolerance limit. The obtained results are given in Table 1. According to results obtained, the developed sensor response was not influenced by presence of 100-fold excess of Ca^{2+}, Mg^{2+} and Zn^{2+} as well as 50-fold excess of Hg^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Fe^{3+} and Ag^+. Presence of 20-fold excess of Cd^{2+}, Cu^{2+} and Pt^{2+} influenced significantly the electrode signal. Among the tested lanthanide ions, the interfering effect of Eu^{3+} and Sm^{3+} was the highest and observed at about 7-fold concentration excess. Dy^{3+} and Er^{3+} showed interfering effect when their concentrations were 10 times higher than Gd^{3+} concentration. La^{3+} and Ce^{3+} showed no significant effect on Gd^{3+} response up to 15-foldconcentration excess.

Fig. 5 decreasing of the IIP-CP signal for Pb^{2+} as function of addition of different concentration of Gd3+ (a= 0.0 b=6.0×10^{-9}, c=3.0×10^{-8}, d=1.0×10^{-7}, e=1.8×10^{-7}, f g=2.8×10^{-7}, h=3.2×10^{-7}, i=3.8×10^{-7}, j=4.5×10^{-7}) (I) and the plot of the decrease amounts as a function of Gd^{3+} concentration used as the calibration curve of the method (II); I_0: the electrode signal in the pure Pb^{2+} solution (3×10^{-7} mol. L^{-1}) I: the electrode signal in the solution containing Pb^{2+} (3×10^{-7} mol. L^{-1}) and different concentration of Gd^{3+}
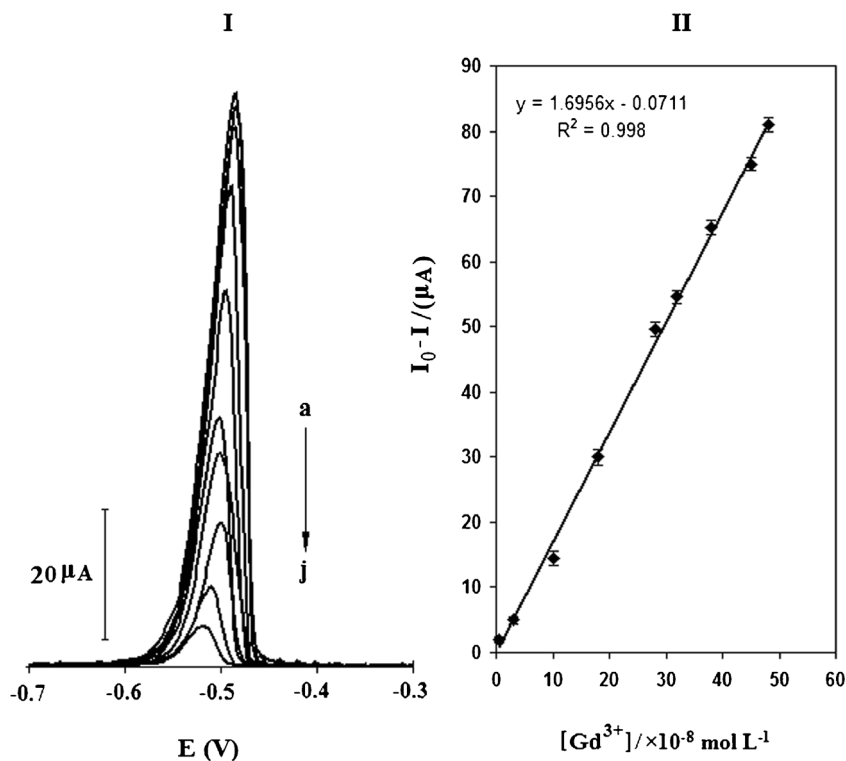
Table 2 Determination of Gd^{3+} in different synthetic and spiked real samples ($n=5$)

Sample	Added (nM)	Found (nM)	Recovery (%)	ICP-OES
Synthetic water$^{(a)}$	8.0	7.7	96.2(±3.8)	–
	25.0	26.5	106.0(±3.9)	23.9
	20.0	21.1	105.5(±4.3)	–
Tap water	3.0	2.8	93.3(±4.3)	3.1
	40.0	41.6	104.0(±5.5)	41.7
River water	15.0	15.7	108.7 (±5.2)	–
	30.0	28.3	94.3(±4.5)	30.8

^{a} (containing : Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, NO$_3$ $^-$, Cl$^-$)

Figure 5(I) shows the successive decreases in the initial voltammetric signal of the probe ion as a result of Gd^{3+} concentration increment in the solution. The depicted results were used for the plotting of an applicable calibration curve. For this aim, the voltammetric responses of the IIP-CP electrodes, obtained for the solutions of different concentrations of Gd^{3+} and fixed concentration of Pb^{2+} (3×10^{-7} mol L^{-1}) were subtracted from the voltametric signal of the IIP-CP electrode, incubated in the pure Pb^{2+} solution (3×10^{-7} mol L^{-1}). Figure 5(II) represents the obtained calibration curve in which the decrease in voltammetric signal is plotted as a function of Gd^{3+} concentration in the solution. As can be seen, this electrode exhibits concentration linear range of 6×10^{-9} – 4.8×10^{-7} mol L^{-1}. The detection limit was calculated to be equal to 4.5×10^{-9} mol L^{-1} (S/N). Relative standard error percent of 5 separate determinations by the sensor was found to be 3.71 %.

In Table 1, some analytical characteristics of this method are compared with some previously reported methods. It can be seen that compared to Gd(III) membrane electrodes, spectrofluorimetric technique and optical sensor our developed technique can led to very better detection limit. Among the depicted methods, the inductively coupled plasma-mass spectroscopy method, coupled with solid phase extraction (SPE-ICP-MS) shows relatively better detection limit, in comparison to this method. However, our developed method is cheaper, easier and much rapid, compared to the SPE-ICP-MS method.

The developed method was used to determine Gd^{3+} in several synthetic and real samples. Since, no Gd(III) was found in the tested real samples, the samples were spiked with the known amounts of Gd(III) solutions and then their Gd^{3+} contents were determined by both developed technique and reference method. A comparison with an inductively coupled plasma emission spectrometry (ICP–OES), used as reference method, suggested that the developed voltammetric determination method gave reliable results in a wide range of samples (Table 2).

Conclusion

Nano-sized Gd^{3+}-imprinted polymer was prepared and used as a selective recognition element of a carbon paste electrode. An indirect voltammetric method based on competitive extraction of Gd^{3+} in the IIP-CP electrode, in the presence Pb^{2+} was introduced for highly selective and sensitive determination of Gd (III) in water samples. The competition of Gd^{3+} ions against probe ions to occupy the Gd^{3+}-selective sites of the IIP, existing in CP electrode, lead to an effective reduction in the DPV signal of the electrode to the probe ion. Both Cu^{2+} and Pb^{2+} were tested as probe ions and the later was found to be the better option; since, it led to better sensitivity in target ion analysis. The IIP amount, used for the CP modification, was a crucial factor for achievement the best condition. This developed electrode showed high selectivity to Gd^{3+} determination, even in the presence of other lanthanide ions. The sensor was capable of determination of Gd^{3+} in spiked water samples.

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