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Quantitative Determination of Gadolinium Ion by a Gd^{3+}-Liquid Membrane Sensor Based on 1-(4-Nitrophenyl)-3-(4-phenylazophenyl)triazene as a Sensing Material

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In this work, a new gadolinium(III) PVC-membrane potentiometric sensor for the Gd^{3+} ion based on 1-(4-Nitrophenyl)-3-(4-phenylazophenyl)triazene (PPAT) has been prepared. The sensor shows a Nernstian slope of 19.9±0.2 $mVdecade^{-1}$ in a wide concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with a detection limit of 4.7×10^{-7} mol L^{-1}. It has a very short response time of about 10 s. The proposed electrode revealed high selectivity for Gd^{3+} ions over a number of cations including alkali, alkaline earth, transition and heavy metal ions and could be used in a pH range of 2.6–8.7. The fabricated Gd^{3+} electrode was successfully used as an indicator electrode in potentiometric determination of Gd(III) ions with standard solution of EDTA and the monitoring of Gd(III) ions in mixtures of different metal ions with quantitative results.

Keywords: Ion selective electrode, Sensor, Potentiometry, PVC membrane

1. INTRODUCTION

During the last decade, there has been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and nondestructive analysis of different samples with small volume samples [1-3]. The utility of ion selective electrodes (ISE) is being increasingly appreciated by analytical chemists, in view of the rapid, world-wide growth of industry and technology, because they represent rapid, accurate, and low cost procedures for trace metal analysis. In general, a liquid membrane sensor is a device comprised of a nonpolar solvent supported by a highly porous polymeric layer [4].

Gadolinium is one of the rare chemicals, which can be found in houses in equipment such as colour televisions, fluorescent lamps, energy-saving lamps and glasses. Gadolinium is dumped in the environment in many different places, mainly by petrol-producing industries. Gadolinium will gradually accumulate in soils and water soils and this will eventually lead to increasing concentrations in humans, animals and soil particles. Gadolinium salts irritate skin and eyes and are suspected to be tumorigens [5]. Other lanthanide oxides and gadolinium oxide are widely used in preparation of polishing compounds, carbon arcs, gasoline-cracking catalysts optical glasses, and glass fibers [6]. Some reports on measurements of gadolinium are spectroscopic methods such as atomic emission spectroscopy, high-resolutionˆI3-spectroscopy, phosphorescence opto-sensing, inductively coupled plasma-mass spectrometry (ICP-MS), laser-based multi step resonance ionization, quenching of gadolinium fluorescence, and electron spin resonance. But almost all of these are expensive and time consuming. In this report we are going to introduce a new simple and nonexpensive method that is based on an electrochemical sensor with a sensitive and selective component 1-(4-Nitrophenyl)-3-(4-phenylazophenyl)triazene. A literature survey indicates that there are only a limited number of reports regarding gadolinium determination by ion selective electrodes [7-11].

Recently, several studies concerning the selective and sensitive ion-selective electrodes have been reported for some metal ions by our research team and other researchers [12-45]. In this work, the use of 1-(4-Nitrophenyl)-3-(4-phenylazophenyl)triazene (PPAT) as an excellent ionophore is introduced for the preparation of a highly Gd(III) ion-selective electrode (Fig. 1). This sensor has relatively high selectivity and a low detection limit relative to the other sensors that have been developed for determination of one of the lanthanides, even in presence of other lanthanides.

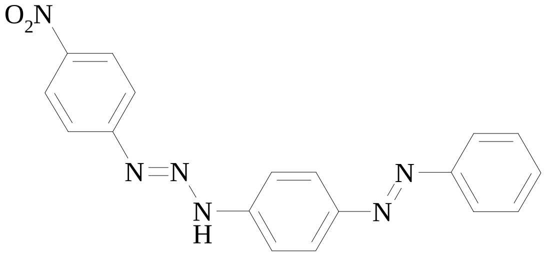


Figure 1. The Chemical structure of PPAT.

2. EXPERIMENTAL

2.1. Chemicals and reagents

The Merck and the Aldrich Chemical Co. were the providers of the following reagent. grades: benzyl acetate (BA), nitrobenzene (NB), dibutyl phthalate (DBP), acetophenone (AP), oleic acid (OA), ionophore 1-(4-Nitrophenyl)-3-(4-phenylazophenyl)triazene, high relative molecular weight PVC, sodium tetraphenyl borate (NaTPB) and tetrahydrofurane (THF). Chloride and nitrate salts of the cations used (from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. During the experiments, doubly distilled de-ionized water was used.

2.2. ISE membrane preparation

The general procedure to prepare the PVC membrane was to thoroughly mix 30 wt.% of powdered PVC, 60 wt.% of nitrobenzene and 4 wt.% of the additive NaTPB in 3mL of THF. To this mixture 6 wt.% 1-(4-Nitrophenyl)-3-(4-phenylazophenyl)triazene (PPAT) was added and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 5 s, so that a non-transparent membrane (about 0.3 mm in thickness) is formed. The tube was, then, removed from the mixture, kept at room temperature for about 24 h and filled with an internal filling solution (1.0×10^{-3} mol L^{-1} $GdCl_3$). Finally, the electrode was conditioned by soaking in a 1.0×10^{-3} mol L^{-1} $GdCl_3$ solution for 24 h [46-61]. As an internal reference electrode, a silver/silver chloride electrode was used.

2.3. The EMF measurements

All emf measurements were carried out with the following assembly:

Ag–AgCl| 1.0×10^{-3} mol L^{-1} $GdCl_3$ | PVC membrane: test solution| Hg–Hg_2Cl_2, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. The activities were calculated according to the Debye–Huckel procedure [62].

3. RESULTS AND DISCISSION

3.1. Response of the Gd^{3+} sensor

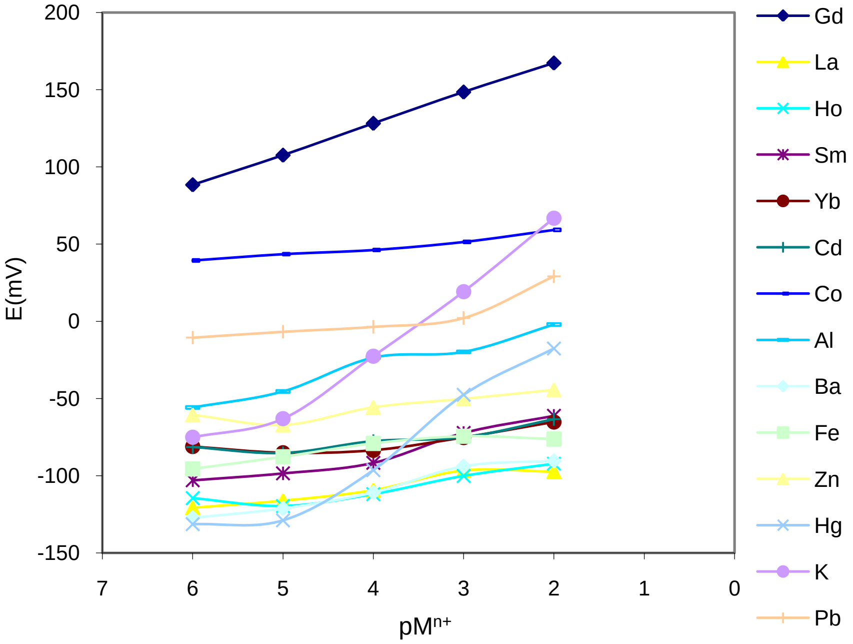


Figure 2. Potential responses of various ion-selective electrodes based on PPAT.

At first, for checking the stability as well as the selectivity of PPAT as a sensing ionophore, it was tested for the preparation of a variety of ions: mono, di, and trivalent metal ion-selective sensors. Their potential responses were measured and the resulting data are summarized in Figure 2. It can be observed that the response slopes of the other ion-selective electrodes are much lower than the values expected from the Nernstian equation, covering only a limited concentration range. Among the tested cations, only the Gd^{3+} ion illustrated a strong response (with a slope of 19.9±0.2 mV $decade^{-1}$) to the PPAT-based membrane sensors in comparison with the other tested cations. This observation can be attributed to the selective behavior of the PVC membrane system against Gd^{3+} in comparison with the tested metal ions, including other lanthanide ions.

3.2. Evaluation of the membrane composition effect on the potential response of the Gd(III) sensor

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition of the membrane (wt, %)				Slope / $mVdecade^{-1}$	Dynamic Linear range / $molL^{-1}$
	PVC	Plasticizer	PPAT	Additive		
1	30	NB, 66	2	NaTPB,2;OA,0	13.3 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
2	30	AP, 66	2	NaTPB,2;OA0	6.5 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
3	30	BA, 66	2	NaTPB,2;OA,0	7.7 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
4	30	DBP, 66	2	NaTPB,2;OA,0	6.0 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
5	30	NB, 60	1	NaTPB,9;OA,0	13.5 ± 0.4	1.0×10^{-4}-1.0×10^{-2}
6	30	NB, 60	2	NaTPB,8;OA,0	13.5 ± 0.2	1.0×10^{-4}-1.0×10^{-2}
7	30	NB, 60	3	NaTPB,7;OA,0	12.8 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
8	30	NB, 60	4	NaTPB,6;OA,0	10.3 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
9	30	NB, 60	5	NaTPB,5;OA,0	15.4 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
10	30	NB, 60	6	NaTPB,4;OA,0	19.9 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
11	30	NB, 60	7	NaTPB,3;OA,0	17.0 ± 0.4	1.0×10^{-6}-1.0×10^{-3}
12	30	NB, 60	8	NaTPB,2;OA,0	12.6 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
13	30	NB, 60	9	NaTPB,1;OA,0	9.4 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
14	30	DBP, 60	6	NaTPB,4;OA,0	16.2 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
15	30	BA, 60	6	NaTPB,4;OA,0	15.9 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
16	30	AP, 60	6	NaTPB,4;OA,0	15.8 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
17	30	NB, 62	6	NaTPB,2;OA,0	23.5 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
18	30	NB, 61	6	NaTPB,3;OA,0	22.3 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
19	30	NB, 55	6	NaTPB,4;OA,5	17.3 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
20	30	NB, 50	6	NaTPB,4;OA,10	18.7 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
21	30	NB, 45	6	NaTPB,4;OA,15	16.3 ± 0.6	1.0×10^{-6}-1.0×10^{-2}

In general, the membrane electrode response depends on some parameters, such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore,, and the nature and amount of the additives [63-75]. Thus, different aspects of the preparation of a Gd^{3+}-selective membrane based on PPAT were optimized. Table 1 lists the membrane data, having various ratios of different constituents. According to Table 1, PPAT amount increase up to 6% in the membrane (membrane no. 10) resulting in Nernstian slope. A maximum slope of 19.9±0.2 mVdecade^{-1} of gadolinium concentration was observed for membrane no.10 with 6% of PPAT. Because the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of ligand, it was expected to play a key role in determining the selectivity, working concentration range, and response time of the membrane electrode. As shown from Table 1, except NB, among three other plasticizers used (AP, BA and DBP), the resulting membranes revealed no stable potential response. This is due to the high polarity of NB that facilitates the extraction of gadolinium ions with high charge density from aqueous solution to the organic membrane phase.

The presence of ionic additives with large lipophilic anions in the composition of cationic-selective membrane electrodes not only diminishes the ohmic resistance and enhances the potential behavior and selectivity, but also in poor extraction capacities, increases the sensitivity of the membrane electrodes [75–81]. Table 1 reveals that the slope of the Gd(III) membrane sensor, NaTPB is a suitable additive. Clearly from Table 1, the NaTPB addition of 4% will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a near Nernstian behavior (membrane no. 10).

All in all the best response behavior of 19.9±0.2 mVdecade^{-1}, in a wide concentration range of 1.0×10^{-6}–1.0×10^{-2} mol L^{-1} was found to be achievable for a composition of 30 mg of PVC, 6 mg of the ionophore, 60 mg of NB as the plasticizer and 4 mg of NaTPB (No. 10).

3.3. The calibration curve

The critical response characteristics of the Gd^{3+} sensor were assessed according to IUPAC recommendations [82]. The potential response of the membrane at varying concentration of Gd^{3+} ions (Fig. 3) indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The slope of the calibration curve was 19.9±0.2 mVdecade^{-1} of Gd^{3+} concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 4.7×10^{-7} mol L^{-1}.

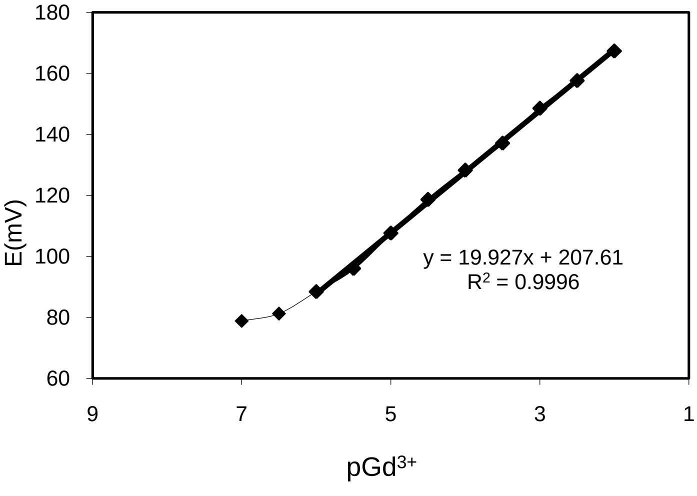


Figure 3. Calibration curve of the PPAT-based gadolinium electrode.

3.4. The pH effect

The pH dependence on the response of the Gd(III) membrane electrode in test solution (1.0×10^{-3} mol L^{-1} of Gd(III)) was studied in a pH range 1.0-11.0, and the results are illustrated in Figure 4. The pH of the solutions was adjusted by either HNO_3 or NaOH solutions [83-86]. As seen, the potential was found to stay fairly constant in the pH range 2.6–8.7. Beyond the range, a relatively drastic drift was observed. The observed drift at higher pH values could be due to the formation of insoluble $Gd(OH)_3$ in the solution. In acidic solutions having pH values less than the minimum of this range, the ionophore used could be protonated to some extent, resulting in improper functioning of the membrane electrode to the Gd(III) ion concentration at pH values less than 2.6.

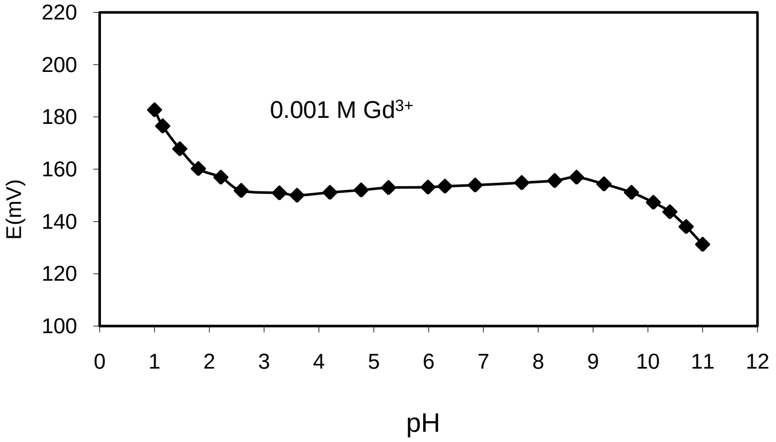


Figure 4. pH effect of the test solution (1.0×10^{-3} mol L^{-1} of Gd^{3+}) on the potential response of the Gd^{3+} ion-selective electrode.

3.5. Dynamic response time

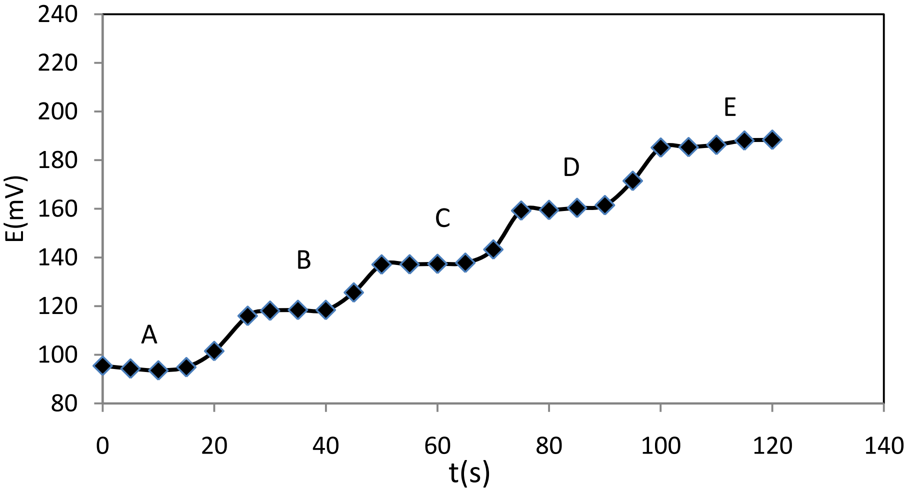


Figure 5. Dynamic response time of the gadolinium electrode for step changes in the Gd^{3+} concentration: A) 1.0×10^{-6} mol L^{-1}, B) 1.0×10^{-5} mol L^{-1}, C) 1.0×10^{-4} mol L^{-1}, D) 1.0×10^{-3} mol L^{-1}, E) 1.0×10^{-2} mol L^{-1}.

For analytical applications, dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the Gd^{3+} concentration in solution in a concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The results are shown in Figure 5. As can be seen, in the whole concentration range the electrode reached its equilibrium response in a very short time (~10 s). This is most probably due to the fast exchange kinetics of the complexation–decomplexation of Gd^{3+} ions with the ionophore at the test solution–membrane interface.

3.6. The selectivity of the Gd(III) sensor

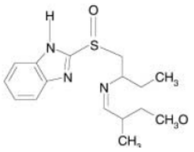
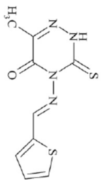
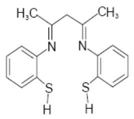
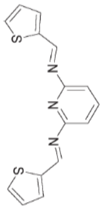
The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients, $K^{Pot}_{A,B}$. In this work, matched potential method (MPM) was used for calculation of selectivity coefficient [87, 88]. According to the MPM, a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before by adding primary ions. The selectivity coefficient, $K^{Pot}_{A,B}$ is determined as $K^{Pot}_{A,B}=a_A/a_B$. The resulting values are listed in Table 2. As can be seen from Table 2, for the all mono and bivalent metal ions and trivalent lanthanide ions tested, the selectivity coefficients are in the order 8.0×10^{-3} or smaller, indicating they would not radically disturb the function of the developed Gd^{3+} membrane sensor.

Table 2. Selectivity coefficients of the developed Gd^{3+} electrode based on MPM method .

Interfering Ions	K^{MPM}
Lu^{3+}	5.0×10^{-3}
Eu^{3+}	2.5×10^{-3}
Tb^{3+}	5.8×10^{-3}
Nd^{3+}	1.0×10^{-3}
Pr^{3+}	2.8×10^{-4}
Yb^{3+}	7.2×10^{-3}
Cr^{3+}	7.8×10^{-4}
Al^{3+}	3.8×10^{-3}
K^{+}	4.7×10^{-4}
Ba^{2+}	5.5×10^{-4}
Sr^{2+}	5.8×10^{-4}
Ca^{2+}	8.0×10^{-3}
Pb^{2+}	4.2×10^{-3}
Co^{2+}	5.8×10^{-3}
Ni^{2+}	5.4×10^{-4}

A comparison is exhibited in Table 3 between the selectivity coefficients, linear range, detection limit, slope, pH range and response time of the developed Gd^{3+} sensor with those of the best previously reported Gd^{3+} electrodes [7-11]. It is instantly clear that the concentration range, the response time, the detection limit of the recommended electrode and the selectivity coefficients are superior to those stated by other researchers.

Table 3. Comparison table of the characterization of reported Gd(III) potentiometric electrodes.

Character / reference	Ref. 7	Ref. 8	Ref. 9	Ref. 10	Ref. 11	This work
LR (mol L^{-1})	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}	2.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-2}
DL (mol L^{-1})	5.0×10^{-6}	5.8×10^{-7}	3.0×10^{-6}	7.0×10^{-7}	5.0×10^{-6}	4.7×10^{-7}
Response time (s)	3	10	10	20	15	~10
pH range	4.0-10.0	3.2-8.7	4.0-8.0	3.5-8.0	4.0-10.0	2.6-8.7
Slope (mV/decade)	19.3±0.3	19.8±0.2	19.8±0.3	19.4±0.4	30.0	19.9±0.2
Log K_{sel}>-2.2	La^{3+}, Sm^{3+}, Ce^{3+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+}	-	La^{3+}, Sm^{3+}, Eu^{3+}, Yb^{3+}, Dy^{3+}, Cu^{2+}	-	Not available	-
Ionophore structure					Not available	Fig. 1

3.7. Analytical application

The proposed Gd^{3+}-PVC membrane sensor was successfully applied as an indicator electrode in titration of Gd^{3+} (1.0×10^{-4} mol L^{-1}) with a standard EDTA solution (1.0×10^{-2} mol L^{-1}) and the resulting titration curve is shown in Figure 6. As can be seen, the amount of Gd^{3+} ions in solution can be determined with the sensor.

The proposed sensor was also successfully applied to the determination of Gd^{3+} ions in mixtures of different metal ions, and the results of triplicate measurements are summarized in Table 4. As can be seen from Table 4, the amounts of the gadolinium ions added to the solution could be determined by the sensor with relatively good accuracy.

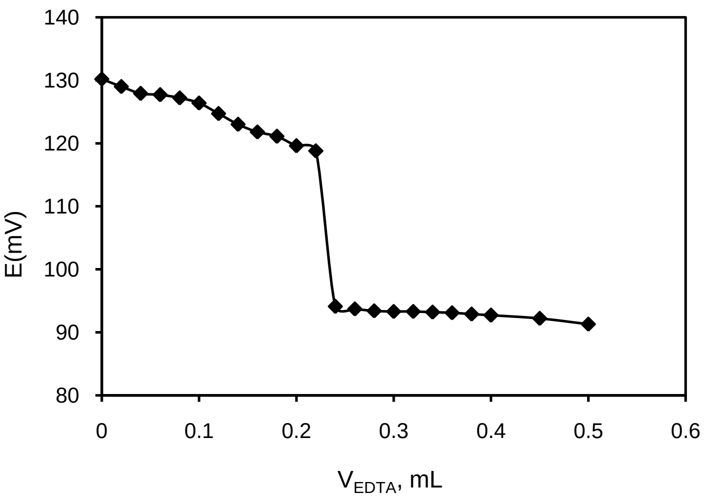


Figure 6. Potential titration curve of 25.0 mL from a 1.0×10^{-4} mol L^{-1} Gd^{3+} solution with 1.0×10^{-2} mol L^{-1} of EDTA (pH=10).

Table 4. Determination of Gd^{3+} ions in mixtures of different ions.

Serial no.	Composition	Observed content (mol L^{-1})
1	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Yb(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Tm(NO_3)_3$	1.01×10^{-5}
2	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Nd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Sm(NO_3)_3$	9.8×10^{-6}
3	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Er(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Eu(NO_3)_3$	9.6×10^{-6}
4	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $La(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Tb(NO_3)_3$	1.02×10^{-5}
5	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Pr(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Al(NO_3)_3$	1.03×10^{-5}
6	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Ho(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Dy(NO_3)_3$	1.01×10^{-5}
7	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Pb(NO_3)_2$	9.7×10^{-6}
8	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $Co(NO_3)_2$+ 1.0×10^{-3} mol L^{-1} $Cd(NO_3)_2$	1.04×10^{-5}
9	1.0×10^{-5} mol L^{-1} $Gd(NO_3)_3$ + 1.0×10^{-3} mol L^{-1} $NaNO_3$ + 1.0×10^{-3} mol L^{-1} KNO_3	9.8×10^{-6}

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