

Design and fabrication of a novel optical sensor for determination of trace amounts of lutetium ion

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ABSTRACT

In this study, for the first time we report a highly selective and sensitive lutetium ions chemical optical sensor based on immobilization of an asymmetrically S–N Schiff's base, namely *N*-(thien-2-ylmethylene)pyridine-2,6-diamine (TPD) on a triacetylcellulose membrane. This optode exhibits a linear range of 5.0×10^{-7} – 1.0×10^{-5} M of the Lu(III) ion concentration with a detection limit of 9.3×10^{-8} M at a wavelength of 336 nm. The influence of responsible factors for improving sensitivity of the sensor was studied and identified. Response time of the newly designed optode was within 20–30 s depending on the Lu(III) ion concentration. Response of the optical sensor is independent of the pH of the solution in the range of 3.0–9.0. It manifests advantages of fast response time, low detection limit and most significantly, very good selectivity with respect to a number of lanthanide ions. The sensor can readily be regenerated with thiourea solutions and its response was reversible and reproducible. This optode was applied to the determination of Lu(III) in aqueous and CRM samples.

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1. Introduction

Lutetium is one of the rare earth elements (REEs) that can be found in houses in equipments such as fluorescent lamps, energy-saving lamps, color televisions and glasses. Use of lutetium is still growing, as it is suitable for catalyzer production and glass polish. In addition, lutetium is dumped in the environment in many different places, mainly from petrol-producing industries. It can also enter the environment when household equipment is thrown away¹.

The biological properties of the lutetium compounds as well as other lanthanide ions, primarily based on their similarity to calcium, have been the bases for research into potential therapeutic applications of lanthanides since the early part of the twentieth century²⁻³. Lutetium texaphyrin has

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been used as photosensitizer in photodynamic therapy and photoangioplasty⁴. Due to the increasing industrial use of Lu(III) compounds as well as their enhanced discharge, monitoring of Lu(III) has been of a recent increasing concern.

Some recent methods for determination of lanthanide ions such as lutetium include inductively coupled plasma mass spectroscopy (ICP-MS)⁵⁻⁶, inductively coupled plasma atomic emission spectroscopy (ICP-AES)⁷⁻⁸, flame atomic absorption spectroscopy (FAAS)⁹, activation analysis¹⁰, photometric determination¹¹ and fluorimetry¹². As a result, design of an inexpensive and simple technique, which can provide the necessary selectivity to determine Lu(III) in the presence of other lanthanides that are very similar to Lu(III) is of great value.

Optical sensors, besides Lu(III) potentiometric ion-selective electrodes which have been already reported¹³⁻¹⁶, can be proper for the Lu(III) assessment, as they may easily be incorporated into low cost, easy to use kits. Furthermore, they can offer the required selectivity and sensitivity for the environmental monitoring¹⁷⁻²². Basic principles and theoretical description of bulk optode membranes, based on the reversible mass analyte transfer from sample in the bulk of the sensing layer have been well elucidated²³⁻²⁵.

Beside to other method of analysis of rare earth ions, optical sensors have attracted the attention of many researchers with respect to cost, freedom from electrical interference, safety and the possibility of remote sensing. Also by using optodes, real time analysis can be performed. Sensing material of an optical sensor can be adsorbed on the surface of support materials chemically and physically²⁶; chemically immobilized in an appropriate support²⁷⁻²⁸ or physically entrapped in polymeric matrices²⁹⁻³¹.

In this work, a novel lutetium optical sensor based on immobilization of *N*-(thien-2-ylmethylene) pyridine-2,6-diamine (TPD) on a triacetylcellulose membrane is introduced. The proposed method offers a more selective and sensitive method for Lu(III) analysis in real samples with lower detection limit in comparison with to the other reported methods.

2. Experimental

2.1 Reagents

All reagents were prepared from analytical reagent grade chemicals supplied from Merck (Darmstadt, Germany), except LuCl₃ which was obtained from Aldrich. The 10⁻² M lutetium standard stock solution was prepared by dissolving 0.2813 g of LuCl₃ in a 100 mL volumetric flask and diluting to the mark with distilled water. Universal buffer solutions were prepared from boric acid/citric acid/phosphoric acid solutions (0.04 M each). The final pH was adjusted with the addition of a 0.5 M sodium hydroxide solution.

2.2 Synthesis of TPD

The procedure for the preparation of *N*-(thien-2-ylmethylene) pyridine-2,6-diamine (Fig. 1) was as follows. A mixture of thiophene-2-carboxaldehyde (0.01 mol, 1.12 g), 2,6-diaminopyridine (0.01 mol, 1.09 g) and catalytic amount of acetic acid was refluxed for 1 h in absolute ethanol (20 ml). Then the reaction mixture was then cooled to the room temperature and the yellow precipitate was filtered, washed with ethanol, and dried under the reduced pressure, mp 225–227 °C, 1.6 g, yield 80%; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3340 and 3186 (NH), 1610, 1477, 1448, 1354, 1292, 1225, 1040, 791, 700. MS, m/z (%): 203 (M⁺, 5), 202 (15), 183 (4), 128 (24), 109 (100), 82 (55), 55 (15), 45 (14), 39 (18). Anal. Calcd for C₁₀H₉N₃S (203.27): C, 59.09; H, 4.46; N, 20.67. Found: C, 60.1; H, 4.7; N, 20.4%. ¹H NMR (90 MHz, DMSO-*d*₆ solution): δ 6.10–6.40 (4 H, br. m, 2 CH and NH₂), 6.95 (1 H,

d, $J = 6.1$ Hz, CH), 7.10–7.35 (4 H, m, 4 CH); ^{13}C NMR: δ 108.24, 113.41, 121.04, 127.69, 130.74, and 135.63 (6 CH), 138.55 (C), 149.88 (CH), 159.09 and 161.05 (2C) 13 .

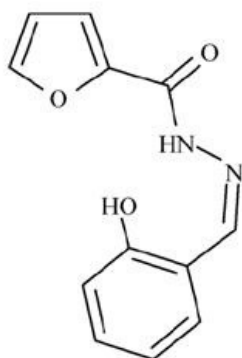


Fig. 1. Structure of N-(thien-2-ylmethylene)pyridine-2,6-diamine (TPD)

2.3 Apparatus and measurement procedures

Spectrophotometry measurements were recorded on a PerkinElmer Lambda 2 UV/vis Spectrophotometer which connected to a Pentium II computer with 1-cm quartz cells. The sensing membrane, which was prepared as mentioned above, was placed and fixed in a disposable plastic cuvette. The length of the film was exactly as the length of the cuvette. Thus, the optode was placed in the cell and could not move during the determinations. All measurements were performed in a batch mode. Optode membrane response to different metal ions was investigated in universal buffer (0.04 M) at pH value of 4. Membrane was first exposed to buffer solution and absorbance was measured at 336 nm. Then, the sample solution was added and absorbance at 336 nm was again measured after 1 min. All results are based on 5 replicate measurements.

2.4 Preparation of the membrane sensor

Transparent triacetylcellulose optode were produced from waste photographic film tapes, which were previously treated with commercial sodium hypochlorite for several seconds in order to remove the colored gelatinous layers. The triacetylcellulose film was hydrolyzed in order to de-esterify the acetyl groups and to increase the porosity of the membrane by treating the membrane into 0.10M NaOH solution for 24 h. Films (1 × 4 cm) were treated with a TPD solution (0.005 g) in 10 mL ethylene diamine for 2 min at ambient temperature. Afterwards, they were washed with water for the removal of ethylene diamine and the loosely trapped indicator (used ligand). Prepared membranes were kept under water, when not in use.

3. Results and Discussion

The ionophore TPD, recently have been used as a sensing materials in construction of a selective Lu (III) membrane sensor. Potentiometric selectivity of the TPD base sensor revealed that that among a number of metal ions tested (including alkali, alkaline metal, heavy and transition metal ions) 13 . Lu (III) has a special tendency to TPD. Thus, in this work TPD was used as a sensing material in construction of a lutetium optical sensor.

3.1 Spectral characteristics

Fig. 2(a) and (b) show the absorption spectra in a solution of acetonitrile and immobilized TPD on hydrolyzed cellulose acetate which were obtained after equilibration in buffer solution (pH=4) containing different concentrations of Lu(III) ions. The spectral characteristic of this optical sensor

indicate maxima at 336 nm Fig. 2(b). The spectral change is result of the addition of Lu(III) and complex formation in the optode Fig. 2(b). Also this maxima shifted with increasing Lu(III) concentration in the optode 336 nm. It is important to note that the absorption spectrum of the immobilized indicator show red shift in comparison to those of their soluble form 315 nm. This observation could be attributed to the fact that the structured conformation of the immobilized indicators is more planar than that of its soluble analogue³². As can be seen from Fig. 2b the increase in the absorption band at 336 nm is more pronounced in the membrane as the Lu(III) concentration increases. For our additional studies, the wavelength of 336 nm was selected, because of higher selectivity and sensitivity at this wavelength.

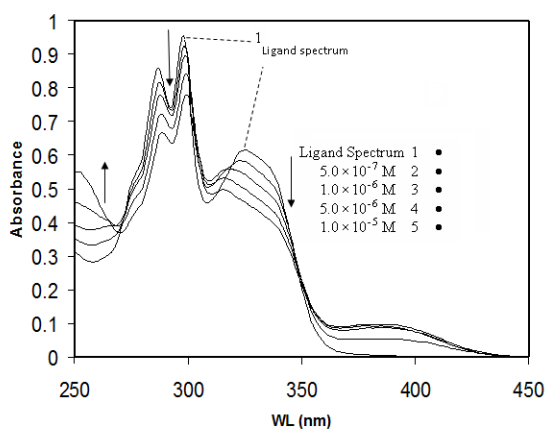


Fig. 2. (a)

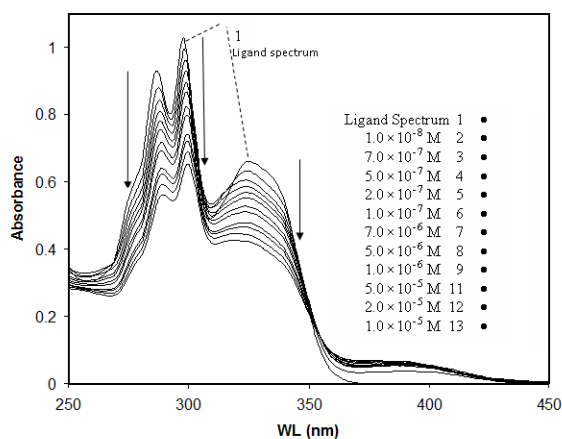


Fig. 2. (b)

Fig. 2. Absorption spectra of solution (a) and optode film (b) response to Absorption spectra of optode film response to Lu(III) in the range of 5.0×10^{-7} – 1×10^{-5} M at pH 4.

3.2 pH effect

pH influence on the response of the proposed optical sensor was studied in the range of 3.0–9.0 by changing the universal buffer. As it can be noticed in Fig. 3, as the pH of the solution is increased, the response of the membrane to Lu(III) ions is decreased. The sensor response is almost constant in pH range of 7-9. A maximum value in the optical sensor response was obtained at pH value of 4.0. This pH was selected for our subsequent investigations.

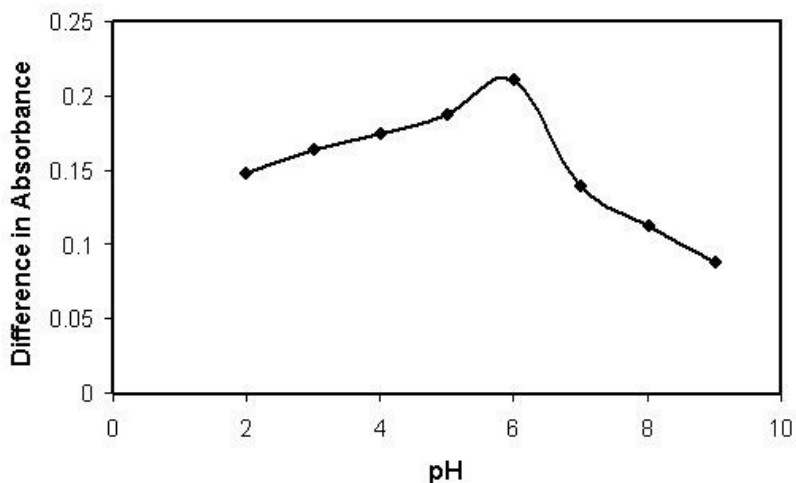


Fig. 3. pH effect on the optode film response

The observed drift at higher pH values could be attributed to the hydrolysis of lutetium ions in the solution which decrease the Lu(III) ions concentration in the solution and inhibits the formation of complex between Lu(III) ions and the TPD. Thus, the optode response decreases. At pH values lower than 3, the heteroatoms of the ligand in the membrane of the optode are protonated and not able to form complex with Lu(III) ions in the solution³³.

3.3 Response time

In this research, the optode film was found to reach 95 % of the final signal at 20-30 s, depending on lutetium ions concentration. Fig. 4 shows the time course for the absorption intensity of the membrane at 336 nm. The response time was tested by recording the absorbance change from a pure buffer (pH=4) to a buffered Lu(III) solution of 2.5×10^{-6} M.

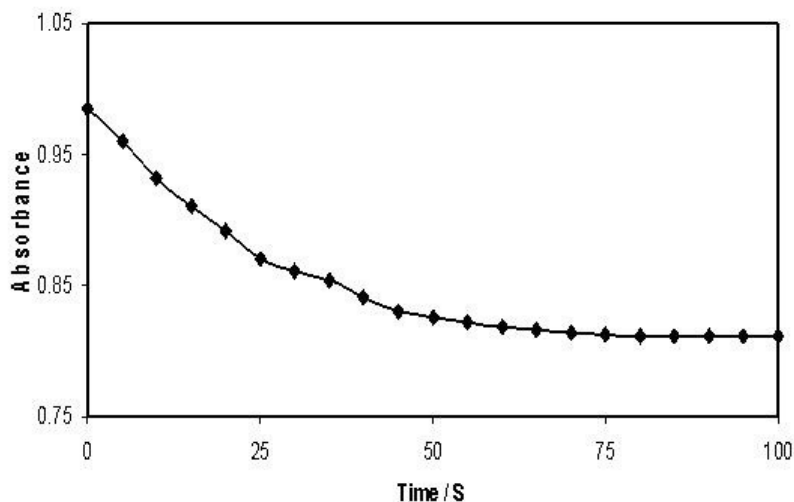


Fig. 4. Response time curve of the film optode at 336 nm when the film was exposed to 1×10^{-6} M Lu(III) ion

At high Lu(III) concentrations, a rapid response was achieved, which resulted in a large change in response. At low Lu(III) concentrations, a longer response time was produced by the optode film. In general, the response time of the optode film is governed by three processes: (1) film diffusion, (2) complex formation rate between metal ion and ligand and (3) complex dissociation rate³⁴. It should be noted that binding of the Lu(III) ion to ligand TPD is a kind of charge dipole interaction.

3.4 Dynamic range

Under the optimum conditions, calibration graphs for Lu(III) was constructed by plotting absorbance change values as a function of the analyte concentration during a time of 60 s after the solution contact with sensing phase. The calibration graphs were linear in the range of 5.0×10^{-7} – 1.0×10^{-5} M for Lu(III) ion concentrations. The results are shown in Table 1.

Table 1. Characteristics of calibration graphs for the determination of Lu (III) ion at pH=4

Slope ($L \text{ mol}^{-1}$)	Intercept	Correlation coefficient	Linear range (M)	Limit of detection (M)
32222	0.0132	0.9925	5.0×10^{-7} – 1.0×10^{-5}	9.3×10^{-8}

The calibration graph is linear up to the Lu(III) concentration of 1.0×10^{-5} M, described by the equation:

$$\Delta Abs = 32222 [\text{Lu(III)}] + 0.0132, R^2 = 0.9925$$

ΔAbs is the absorbance difference (defined as the difference between the absorbance of the immobilized TPD alone and the absorbance of Lu(III)-TPD complex), $[Lu(III)]$ is the lutetium concentration (M) and R^2 is the R-squared value of the calibration curve. Moreover, the detection limit of the sensor film was found to be 9.3×10^{-8} M. In this case, detection limit can be defined as the sample concentration yielding a signal which is equal to the blank signal plus three times of its standard deviation.

3.5 Optode regeneration

For an optode membrane to perform suitably, absorbance change must be reversible. Tests were conducted with a number of reagents to reverse the absorbance of Lu(III) complex. Complexing agents such as EDTA and sulfosalicylic acid have a partial reverse effect, and prolonged exposure to them have no further improvement in reversibility of the optode. Thiourea (1.0 M) was concluded to be the best reagent, giving a short regeneration time (less than 1 min). The on use durability of the sensor phase was obtained by subsequently placing the film in Lu(III) solutions and regenerating. After regenerating these solutions twice, a drift of about 2.3% was obtained in response of the sensor film.

3.6 Reproducibility

Repeatability and reproducibility of the optical sensors are two important characteristics. Both parameters were studied in this research. To evaluate the discrepancies in the response for successive runs using a single sensor, the repeatability was evaluated by performing 10 determinations with the same Lu(III) standard solution. The coefficient of variation of sensor response for 8.0×10^{-6} M Lu(III) was 1.2 %. Fig. 5 shows the absorbance changes versus time for the optode membrane. The mean absorbance values with the standard deviation were found to be 0.736 ± 0.007 ($n=7$, $8.0 \mu\text{M}$ Lu(III) ion) and 0.439 ± 0.011 ($n=7$, 1.0 M thiourea solution).

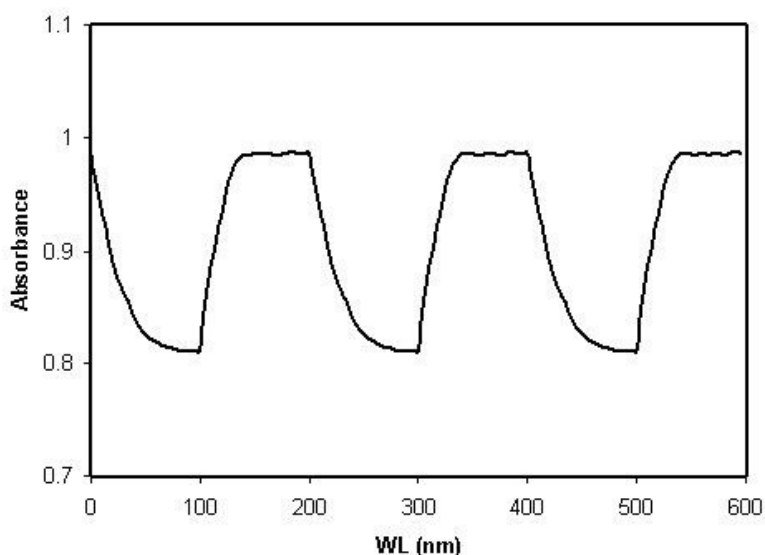


Fig.5. Absorbance variation of the membrane at 336 nm for repeatedly exposing into 8×10^{-6} M Lu (III) solution and 1.0 M thiourea solution

For the evaluation of differences in responses of individual sensors, four membranes were prepared from the same mixture. Reproducibility was obtained by determining 8×10^{-6} M lutetium ions (Seven replicate determinations). Coefficient variation of the responses between the membranes was 2.7%.

3.7 Lifetime and stability

The lifetime of the optode film was determined by adding a buffer solution (pH=4) in to the cuvette, containing the film. The signal was recorded at wavelength of 336 nm over a period of time (about 10 h). No significant indicator loss occurred during that time. When the film was exposed to light, no drift in the signal took place and the optode was found to be stable during the experiment with no indicator leakage. However, the prepared membranes were kept under water, when not in use, to prevent them from drying out. Additionally, stability of film response was investigated over six weeks under ambient conditions, which is indicated that the film was stable over this period.

3.8 Effect of the foreign ions

The interference for a number of common species of the absorbance determination of Lu(III) ions was investigated using the prepared sensor. To determine the selectivity of the sensor film, the optode film was tested under lutetium ions concentration of 1×10^{-6} M in the presence of other metal ions. Limit of tolerance was taken as the concentration causing an error of $\pm 5\%$ in the lutetium ions assay. The results are summarized in Table 2. The surprisingly high selectivity of the optode film for Lu(III) ions over other cations used, most probably arises from the strong tendency of the TPD for formation of stable complex with Lu(III) ions.

Table 2. Influence of the foreign ions on the Lu (III) determination of 1×10^{-6} M

Interferent	Tolerance ^a limit
La(III), Sm (III), Gd(III), Eu(III), Tm(III), Ca ²⁺ ,	500
Ho(III), Dy(III), Nd(III), Ce(III), Pb ²⁺ , Na ⁺ , SCN ⁻	700
Ni ²⁺ , Cd ²⁺ , Sn ²⁺ , Cu ²⁺ , K ⁺ , Ag ⁺ , Mg ²⁺ , Hg ²⁺ , CO ₃ ²⁻ , NO ₃ ⁻ , Cl ⁻ , Br ⁻ , SO ₄ ²⁻	1500

^a Maximum ratio of the foreign ions to the cerium ions (1.0×10^{-6} M) giving an error of $< 5\%$

3.9 Recovery tests

The recovery tests were performed using three different samples (tap, mineral and river water) by using spike method. The test for each sample was carried out in triplicate measurements and the results were given in Table 3. As it is evident from Table 3, lutetium recovery values were between 98 and 103.

Table 3. Results of the recovery test

Sample	Lu (III) Added (μ M)	Lu (III) Found (μ M)	R.S.D. %	Recovery (%)
River Water	0.00	ND ^a	-	-
	1.00	1.03	1.80	103
Mineral Water	0.00	ND	-	-
	1.00	0.98	0.94	98

^a Not detected

3.10 Application to synthetic sample and real samples

The developed lutetium optical sensor device was applied to the detection of lutetium ions in synthetic and river water samples. Table 4 lists the respective resulting data of these applications. The result, derived from seven replicates measurements with the same sensor, was found to be in satisfactory agreement with that determined by Arsenazo (III) method³⁵.

Table 4. Results of the Lu(III) ion concentration measurements in real samples

Sample	Lu (III) Added (μM)	Lu (III) Found (μM) by Arsenazo method	Lu (III) Found (μM) by proposed method	R.S.D. (%) for proposed method (n=7)
Synthetic sample 1	0.00	ND	ND	-
Synthetic sample 1	1.00	1.02	0.99	1.40
Synthetic sample 2	5.00	5.06	4.94	1.20
River Water	1.00	0.98	1.01	0.97

The characteristics of the proposed lutetium optical sensor were also compared with other methods for determination of lutetium reported in the literature (Table 5). The linear range and detection limit of the proposed optical sensor is acceptable compared to the reported methods; however, literature survey shows that there is no report on an optical sensor membrane with chip reagents for determination of Lu(III) ions in solutions.

Table 5. Comparison of proposed Lu(III) optical sensor with other methods for determination of Lutetium

Method	DL ^a (M)	LR ^b (M)	Samples	References
ISE	6.7×10^{-7}	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	CRM sample	15
Fluorimetry	29 ng/ml	$1.8 \times 10^{-7} - 8.8 \times 10^{-6}$	synthetic sample	12
Spectrophotometry	0.114 $\mu\text{g/ml}$	0.68 - 10 $\mu\text{g/ml}$	synthetic sample	11
Optical sensor	9.3×10^{-8}	$5.0 \times 10^{-7} - 1.0 \times 10^{-5}$	river water & CRM	this work

^a Detection limit

^b Linear range

The proposed sensor was also applied to Lu(III) determination concentration in the certified reference material (CRM), called Coal and Fuel Ash (FFA 1 Fly Ash). According to Table 6, where the CRM analysis was summarized, the Lu(III) concentration was 0.658 mg kg^{-1} . Alternatively, the calibration method was employed, illustrating a Lu(III) concentration value of $0.667 \pm 0.3 \text{ mg kg}^{-1}$. These experimental data revealed that the proposed optode performed a trustworthy detection regarding the Lu(III), despite the presence of other rare earth elements.

Table 6. Results from the Coal and Fuel Ash Analysis (FFA 1 Fly Ash)

Certified values for (mg kg^{-1})					
Al	14.87	Hf	6.09	Sm	10.9
As	53.6	La	60.7	Sr	250
Ba	835	Li	128	Ta	2.11
Ce	120	Lu	0.658	Tb	1.38
Co	39.8	Mn	1066	Th	29.4
Ca	156	Na	2.19	Tm	0.705
Cs	48.2	Nd	56.8	U	15.1
Cu	158	Ni	99.0	V	260
Dy	9.09	P	725	W	10.5
Er	4.52	Pb	369	Y	45
Eu	2.39	Rb	185	Yb	4.24
F	198	Sb	17.6	Zn	569
Fe	4.89	Sc	24.2	-	-
Gd	10.0	Si	22.48	-	-

4. Conclusion

The optical sensor described in this work is easily prepared and provides a simple and inexpensive means for the determination of Lu(III) ions. The optical sensor can be regenerated readily with a solution of thiourea and it has a long lifetime. The optode response was concluded to be reproducible with a good Lu(III) selectivity over other lanthanide ions. Since the optical sensor required no solvent

extraction, it could compete satisfactorily with the standard optical fibers. This optical sensor was applied to the determination of Lu(III) in spike and different water samples with good precision and accuracy.

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