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Optical Chemical Sensor of Lutetium(III) in Water Based On 2-Nitro-6-(thiazol-2-yldiazenyl)phenol Immobilized on Polymethyl meth-acrylate and 2-Nitrophenyl octyl ether Matrix

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ABSTRACT

Objectives: An optical chemical sensor membrane obtained by physical inclusion of a 2-nitro-6-(thiazol-2-yl-diazenyl)phenol (NTDP) as a selectophore and polymethyl methacrylate (PMMA) and 2-nitrophenyl octyl ether (NPOE) as a plasticizer. **Methods:** The adsorption of Lu(III) causes the colour of the membrane to change from orange to pink with maximum absorbance (λ_{max}) at 606 nm. The sensor membrane gives the best response towards Lu(III) ion at pH 6.5, after 10 min of contact time, at 150 ng mL^{-1} Lu(III), and 10 mL solution. **Results:** A linear Lu(III) calibration curve can be developed in the concentration range of 5.0–280 ng mL^{-1} with R^2 = 0.9990. The molar absorptivity is found to be 9.06 x 10^6 L mol^{-1} cm^{-1}. The detection and of quantification limits are found to be 1.63 and 4.95 ng mL^{-1}, respectively. **Conclusion:** The optical sensor membrane analytical characteristics was performed as interference of anions and cations, equilibrated time, reusability, detection limit, etc. and compared with the previous different conventional methods for Lu(III) using various chromophores. The optical sensor membrane investigated in this work was examined in real samples with excellent results comparing with the previous ICP-OES method.

Keywords: optical chemical sensor, 2-nitro-6-(thiazol-2-yldiazenyl) phenol, Lu(III) analysis, poly(methyl methacrylate)

INTRODUCTION

One of the rare earth elements (REEs) is Lutetium which present in houses in instruments as energy-saving lamps, color televisions, fluorescent lamps, and glasses. Lutetium Uses is still growing, as it is optimum for glass polish and catalyzer production. It is introduced in the environment in many various places, mainly as petrol-producing industries. Lutetium able to enter the environment when household instrument is thrown away [1].

The last member of lanthanide group occurs in association with the element yttrium is Lutetium and sometimes introduced in metal alloys and as a catalyst in different chemical reactions. Lanthanide family has an enormous applications ranging from the ceramic industry and production of glass to agriculture, and metallurgy electronics. The main problem in quantitative detection of lanthanides is the selectivity. Various reagents have been examined for their spectrophotometric determination but they have not been specific and even the most selective requires extractive separation to remove interfering ions. Hence, an easy procedure to detect these elements selectively is of great importance [2].

Since the early part of the twentieth century [3–4]; lutetium compounds has a biological characters as well as other lanthanide ions, primarily depended on their similarity to calcium, have been the principles for research into potential therapeutic applications of lanthanides. Lutetium texaphyrin has been applied as photosensitizer in photoangioplasty and photodynamic therapy [5]. The increasing industrial apply of Lu(III) compounds as well as their enhanced discharge, monitoring of Lu(III) has been of a recent increasing concern.

Recently, some procedures to determine lanthanide ions such as lutetium include inductively coupled plasma mass spectroscopy (ICP-MS) [6-8], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [9–11], flame atomic absorption spectroscopy (FAAS) [12], neutron activation analysis [13], photometric determination [14,15] and fluorimetry [16]. Design of an inexpensive and simple technique, can provide the selectivity for Lu(III) determination in the presence of other lanthanides that are very similar to Lu(III) is of great value. These methods are sensitive and selective. However, it is relatively expensive and requires a skilled person to do the job. The chemo-optic sensor is an alternative method for metal analysis. It is part of the green analytical methods since it can significantly reduce energy consumption, organic solvents, and gas emission. Therefore, it is much more environmentally friendly [17–20].

Lu(III) potentiometric ion-selective electrodes, besides optical membrane sensors, have been already reported [21–24], can be applied for the Lu(III) determination, as they may easily be incorporated into easy to use kits, and low cost. In addition, they can offer the required sensitivity and selectivity to environmental monitoring [25-30]. Bases and theoretical description of bulk optode sensor membranes, depended on the reversible mass analyte transfer from sample in the bulk of the sensing layer have been well investigated [31–33].

Optical membrane sensors have reported much attention in analytical chemistry, because of some advantages as low cost, high, easy fabrication, sensitivity, and selectivity [34–38]. Various strategies have been applied to investigate optical membrane sensors for some target ions. Visual test strips or optical allow the simple detection of analyte by the naked eye, or by a portable spectrophotometer without any specific pretreatment [39].

Preconcentration procedure based on membrane sensors can be tailor-made for a specific analytical application. The analyte selective membrane can be changed to optical chemical sensor (optode) by immobilizing the indicator that responds to analyte in a concentration dependent manner [40–42]. The optical membrane sensors have been formed by immobilizing the indicator (chromoionophores, ionophores, and fluoroionophores) with or without extractant in the solid matrix applying highly diversified procedures [43–46]. These optical membrane sensors are depended on the preconcentration of the analyte as a chromogenic species on a solid substrate and subsequent detection of the absorbance/reflectance of the solid phase, without stripping the chromogenic species. The presence of extractant confirms an increase in selectivity and sensitivity of optical membrane sensors compared to the corresponding solution spectrophotometry using same chromophore.

EXPERIMENTAL

Chemicals and Instruments

Doubly distilled water and analytical reagent grade chemicals were applied throughout. Tetrahydrofuran (THF), 2-nitrophenyl octyl ether (NPOE) and polymethyl methacrylate (PMMA) were achieved from Sigma–Aldrich (Steinheim, Switzerland). Tris(2-ethylhexyl) phosphate was achieved from Koch-Light Laboratories (Coinbrook Bucks, England). Lutetium standard stock solution (10^{-3} M) was prepared by dissolving 0.0389 g of $LuCl_3.6H_2O$ in a 100 mL volumetric flask and diluting to the mark with distilled water. Triethanolamine buffer was prepared by dissolving an appropriate weight of triethanolamine in distilled water and neutralizing with perchloric acid (pH 6.5). 2-nitro-6-(thiazol-2-yldiazenyl) phenol (NTDP) used in this work was prepared according to the method described previously [47].

The thickness of the optode was detected by a digital micrometer (Mitutoy, Japan) with an accuracy of ± 0.001 mm. A microprocessor-based pH meter model Orion research model 601 A/digital ionalyzer was applied for all pH measurements. UV–vis spectrophotometer model V 53 from JASCO (Tokyo, Japan) was achieved for recording the spectra and the absorbance measurements. The absorbance measurements were given by mounting the optical membrane sensors samples (3.0 cm x 1.0 cm) inside a quartz cuvette. The absorbance measurements of the optical membrane sensors samples were obtained with respect to air as well as blank optode sample.

Preparation of the Optical Membrane Sensors

The optical membrane sensor were prepared by dissolving 0.30 g PMMA and 0.05 g of the chromophore NTDP, and 150 µL NPOE in 10 mL THF, and stirring the mixture at a constant speed for 30 min at room temperature. Subsequently, the obtained casting solution was homogenized by ultrasonication for 3.0–5.0 min. The casting solution was introduced in a Petri dish to allow the formation of the homogeneous transparent membrane with slow evaporation of THF.

Uptake Experiments

The optical membrane sensor strips (3.0 cm x 1.0 cm) were equilibrated in sample solutions of desired medium (~10^{-4} M bicarbonate/carbonate solution in TEA buffer) and agitated with magnetic stirring bar at a rate of 800

rpm. TEA buffer (3.0 mL) was introduced in 10 mL (sample volume) to obtain a pH of 6.5 ± 0.2 unless stated otherwise. It should be noted that Lu(III) precipitation was observed in the absence of bicarbonate medium. The optical membrane sensor strips were left out of the sample solutions and washed with a jet of distilled water. The colour of optical membrane sensor strips converted from orange to pink based on the Lu(III) concentration in the sample solution. The change in absorbance of Lu(III)–NTDP complex was measured at λ_{max}= 606 nm under various experimental conditions.

RESULTS AND DISCUSSION

Composition of the Optical Membrane Sensors

Different combinations of the matrix forming polymer, plasticizer (PMMA /NPOE), chromophore NTDP, were invstigated to optimize the lutetium uptake in the optical membrane sensors matrix from aqueous samples having pH of 6.5. It is shown that NTDP immobilized in the optical membrane sensor could form complex with Lu(III) in absence of a carrier in the matrix. This seems to suggest that NTDP itself act as a carrier to facilitate the transfer of Lu(III) from equilibrating solution to the optical membrane sensors matrix. Among the various carriers investigated, it was found that no efficient for facilitating the transfer of Lu(III) from equilibrating solution to optical membrane sensor matrix was achieved.

Spectral Characteristics

NTDP is a reagent of the most sensitive ones for the spectrophotometric analysis of copper in different aqueous/organic phase samples. It forms 1:1 stable complex with Cu(II) at pH 7.1 [47]. The comparison of UV–vis spectra of optical membrane sensor samples equilibrated with various aqueous matrix having same concentration of Lu(III) (150 ng mL^{-1}) is drown in **Figure 1**. It is seen from this figure that TEA buffer (pH 6.5 ± 0.2) in the equilibrating solution enriched the colour change in optical membrane sensor sample corresponding to the formation of Lu(III)–NTDP complex. In seawater matrix, the optode response towards Lu(III) was significantly lower as compared to other aqueous matrices, and may not be applicable for quantification of Lu(III) in seawater. The change in absorbance spectra of optical membrane sensor samples, equilibrated with solutions having different samples of Lu(III) in TEA buffer is recommended (**Figure 1**). The comparison of spectra indicated that there was large bathochromic shift in absorbance of optical membrane sensor samples from 456 nm (blank) to 606 nm on equilibration with buffer solutions having Lu(III) ranging from 5.0 to 280 ng mL^{-1}. The absorbance maxima at 606 nm is recommended for Lu(III)–NTDP complex, indicating that the optical membrane sensor is responsive towards change in the lutetium concentrations in the equilibrating solution. The absorbance of the blank optical membrane sensor sample (without lutetium) is significantly lower as compared to that at 606 nm. Hence, the change in the absorbance at 606 nm can be applied for quantitative determination of Lu(III) in the aqueous samples. It was also illustrated that pink colour of Lu(III)-loaded optical membrane sensor sample changes back to orange on immersing this optode in well-stirred 0.02 M HNO$_3$ for 10 min. This indicated that Lu(III)–NTDP complex formed in the optical membrane sensor is broken at pH 2.0 to regenerate the NTDP in the optical membrane sensors.
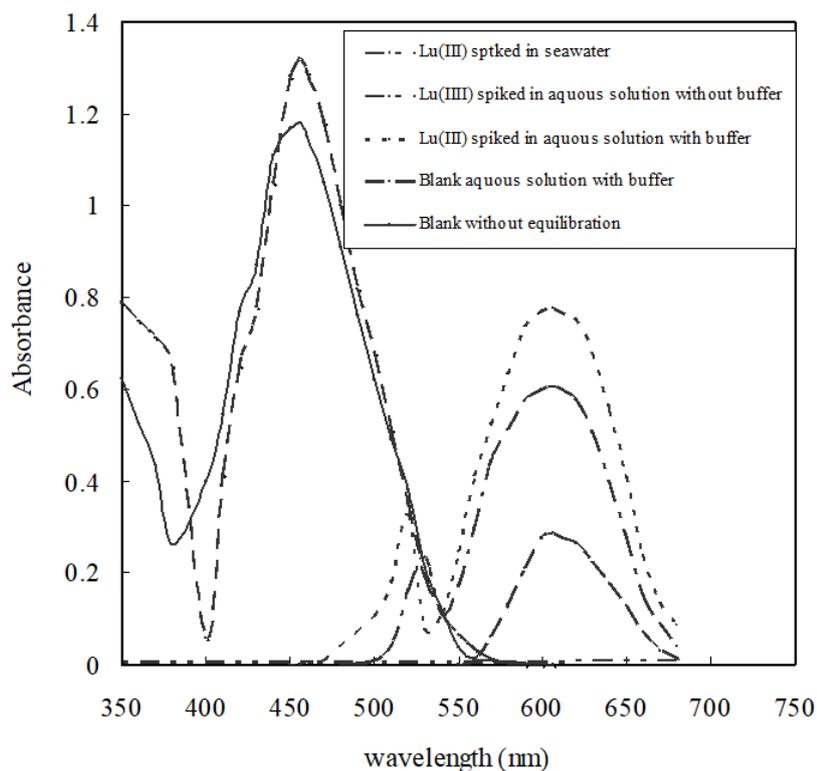
Figure 1. UV-vis spectra of sensor samples (1.0 cm× 3.0 cm) equilibrated with 10 mL of various aqueous samples spiked with 150 ng mL^{-1} of Lu(III) in bicarbonate medium

Table 1. Response of membrane sensor samples after 10 min equilibration with well-stirred aqueous solution containing Lu(III) and 10^{-3} M NaHCO$_3$ at pH 6.5

Composition	Response
PMMA/ NPOE (75 wt.%) + NTDP (25 wt.%)	No color change
PMMA/ NPOE (50 wt.%) + NTDP (50 wt.%)	No color change
PMMA/ NPOE (80 wt.%) + NTDP (20 wt.%)	No color change
PMMA/ NPOE (87.5 wt.%) + NTDP (12.5 wt.%)	Color changes from orange to pink

Optimization

PMMA was chosen as a supporting matrix for NTDP due to its hydrophobicity, transparency, resistance to acid, base and salt solutions [48], and low absorbance in the UV-Vis range [49]. These will keep the sensor membrane stable during analysis of Lu(III) in environmental samples and allow quantitative analysis by UV-Vis spectrophotometry.

The optical membrane sensor response based on the rate of diffusion of anionic lutetium existing in the aqueous phase to the membrane sensor interface to form complex with the NTDP molecule present in the sensor matrix. The high concentration of NTDP was found to degrade the optical quality of the sensor. The concentrations of NTDP and PMMA used in preparation of the optical membrane sensors are recorded in **Table 1**. The optical membrane sensor samples were equilibrated for 10 min in 10 mL buffer solution well-stirred, having 150 ng mL^{-1} Lu(III). The Lu(III) uptake increase with increase in amount PMMA and NPOE in the membrane sensor indicates that they enhances the Lu(III) loading capacity of the sensor. However, the kinetics of lutetium uptake (10 min) was too slow to allow its apply as a chemical sensor for wide range of applications.

To study the properties of plasticizer and their relative amounts in the sensor matrix, it was investigated that increase in plasticizer concentration, leads to increases the diffusion rate of anions in the plasticized sensors [50]. So, the sensor samples having varying of two various plasticizers (e.g. PMMA and NPOE) were prepared and investigated for their response time towards Lu(III) ions in carbonate aqueous buffered medium.
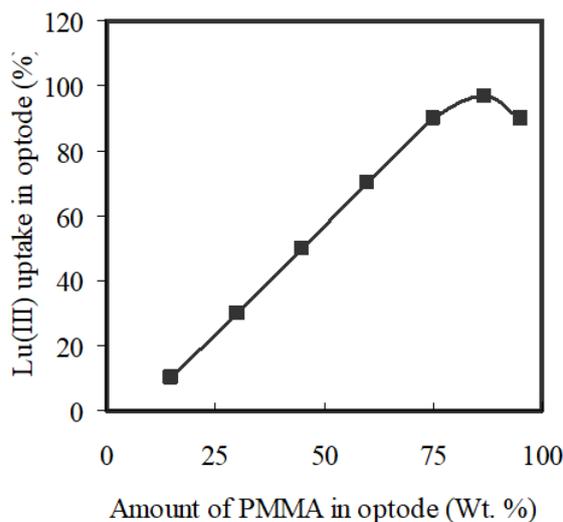
Figure 2. Variation of lutetium uptake with PMMA concentration in the sensor; Lu_{total}=150 ng mL^{-1}; sample volume=10 mL; duration=10 min; pH 6.5
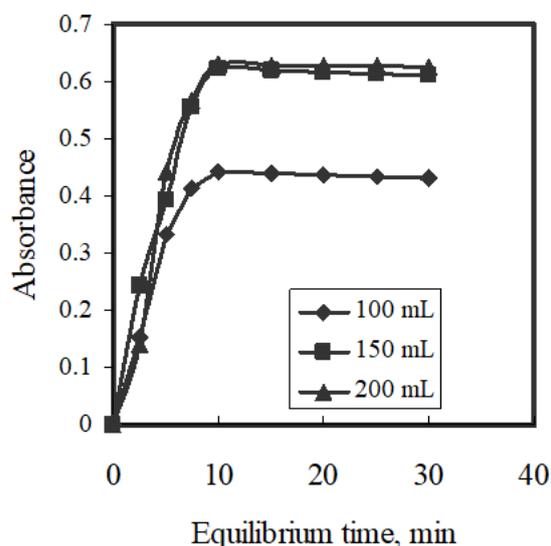

Figure 3. Lutetium uptake kinetics as a function of plasticizer NPOE amount in the sensor; Lu_{total}=150 ng mL^{-1}; sample volume=10 mL; pH 6.5

The difference in absorbance of the sensor samples, plasticized with changing concentrations of PMMA and NPOE, was illustrated by equilibrating these with 10 mL buffered sample solutions well-stirred, having 150 ng mL^{-1} Lu(III) in bicarbonate/carbonate medium (**Figure 2**). The sensor samples were taken out at regular time intervals to measure the absorbance of Lu(III)–NTDP complex at 606 nm as a function of equilibration time. The difference of absorbance at λ_{max} in the sensor samples as a function of equilibration time are presented in **Figure 3**, suggesting the kinetics of sorption of anionic Lu(III) species in the sensor. As can be shown from **Figure 3**, the rate of sorption of lutetium anionic species increases with increase in plasticizer in the sensor concentration. The matrix forming PMMA chains in the liquid fraction of sensor (plasticizer) matrix introduces obstruction in the path of the moving ion-pair.

The Effect of pH on Sensing Performance

The pH of the test solutions plays an important role in obtaining a better membrane performance. The analyte solution has been subjected to pH variation, from 5.0 to 8.0. **Figure 4** suggests that the solution pH of 6.5 gives the best response. Furthermore, at optimum pH, the amount of OH- ion in the solution is larger and the donor atom in the ligand tends to release H$^+$ ion (deprotonated) and thus becomes partially negative-charged species (L$^-$). This condition enhances the reaction between Lu(III) or [Lu(OH)$_2$]$^+$ in the solution and NTDP ligand in the matrix to
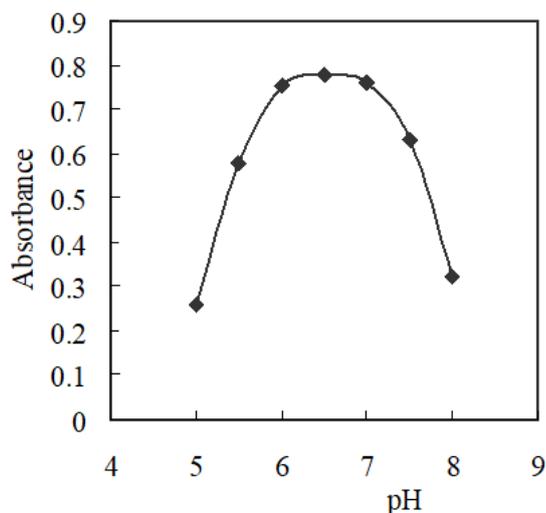
Figure 4. Effet of pH on the optical sensor of 150 mL^{-1} Lu^{3+} complexed with NTDP at the optimum conditions

form Lu–NTDP. On the other hand, at lower pH, large amount of H$^+$ in the solution causes the formation of free metal ion (M^{n+}) and the hydroxyl group in the ligand remains protonated. This situation causes the interaction between metal ion and ligand much more difficult to occur due to charge repulsion between positive metal ion and positively protonated ligand. At higher pH (> 8.5), the absorbance is getting smaller possibly due to leaching process of NTDP ligand from the membrane matrix as indicated by the orange-color change of the solution. For all of the tested pH, the absorbance has been observed to reach its maximum value after 10 min of reaction.

The major component of liquid phase is the plasticizer, which acts as a medium for diffusion transport of ions in the sensor. The sensor could not be plasticized more than 90 wt.% of the plasticizer as mechanical strength of the sensor was not enough to apply it in well-stirred solution. Out of two plasticizer applied in the preparation of sensor, the sensor sample with 1.0 wt.% NPOE gave faster increase in absorbance corresponding to Lu(III)–NTDP complex than the sensor formed by TEHP. Although the equilibration time needed for complete Lu(III) sorption is longer than 10 min, the shorter equilibration time could be applied for quantitative analysis of Lu(III) as % uptake remains constant at fixed equilibration time. The equilibration time of 10 min could be applied for constructing calibration graph for aqueous sample containing Lu(III) greater than 280 ng mL^{-1}. The detection limit for lutetium would be better after 10 min equilibration of the sensor sample as more than 97% of Lu(III) sorption in the sensor is obtained. So, the composition of sensor was kept as: 86.5 wt.% PMMA + 1.0 wt.% NPOE + 12.5 wt.% NTDP for lutetium uptake investigates with an equilibration time of 10 min.

The measured absorbance at 606 nm for a long period over 18 h did not indicate the evidence of leaching of Lu(III)–NTDP complex from the sensor sample to equilibrating bicarbonate aqueous medium with TEA buffer. There was no drift in the absorbance when the film applied for lutetium uptake was exposed to light. No appreciable variation in the sensor absorbance value was presented when the film was dipped in de-ionized distilled water overnight. These results ilustrated that the sensor film was quite stable under the optimum conditions for this works.

Stoichiometric Ratio

The complex nature was illustrated at the optimum experimental conditions investigated above applying the molar ratio and continuous variation procedures. The plot of the molar ratio of NTDP to Lu(III) versus absorbance, obtained by changing the NTDP concentration, illustrated inflection at a molar ratio of 2.0, indicating the presence of two NTDP molecules in the formed complex. Also, the Job method illustrated a ratio of NTDP to Lu(III) = 2.0. Consequently, the results investigated that the stoichiometric ratio was (2 : 1) [NTDP : Lu(III)]. The conditional formation constant (log K), calculated applying the Harvey and Manning equation using the data given in the above two procedures, was calculated to be 6.67, whereas the true constant was 5.55.

$$2 \text{ NTDP} + \text{Lu(III)} \rightleftharpoons [(\text{NTDP})_2\text{Lu}]$$

Analytical Data

The sensor response, change in absorbance at 606 nm, towards lutetium concentration is up to 280 ng mL^{-1} after correcting for the blank. The blank absorbance at 606 nm was monitored after equilibrating sensor sample with

Table 2. Analytical features of the proposed procedure

Parameters	Using optode	Parameters	Using optode
pH	6.5	Regression equation	
equilubrium time (min)	10	Slope ($\mu g\ mL^{-1}$)	25.18
Stirring time (min)	3.0-5.0	Intercept	0.15
Beer's range (ng $mL^{-1)}$	5.0-280	Correlation coefficient (*r*)	0.9990
Ringbom range (ng mL^{-1})	20- 265	RSD [a] (%)	1.87
Molar absorptivity (L $mol^{-1}\ cm^{-1}$)	9.06×10^6	Detection limits (ng mL^{-1})	1.63
Sandell sensitivity (ng cm^{-2})	0.019	Quantification limits (ng mL^{-1})	4.95

Table 3. Results of the recovery test

Sample	Lu(III) ng mL^{-1}			R.S.D. %	Recovery (%)
	Added	Lu(III) Found			
		proposed	ICP-OES		
River Water	0.00	ND[a]	ND	-	-
	50	51.0	48.0	1.45	102.00
	100	99.2	102.9	1.60	99.20
	150	151.5	151.8	1.33	101.00
	200	201.6	198.8	1.75	100.80
	250	248.4	252.5	1.55	99.36
Mineral Water	0.00	ND	ND	-	-
	60	58.8	61.5	0.94	98.00
	120	121.0	118.7	1.39	100.83
	180	178.5	183.4	1.57	99.17
	240	241.8	238.1	1.41	100.75
	280	278.7	284.5	1.82	99.54
Tap water	0.00	ND	ND	-	-
	75	74.5	76.0	1.11	99.33
	150	150.7	148.8	1.37	100.47
	225	224.1	227.5	1.25	99.60

[a] Not detected

blank solution at pH 6.5, without lutetium. The linearly changes as a function of Lu(III) concentration range of 5.0–280 ng mL^{-1}. However, the calibration line did not pass through the zero. This may be due to the chemical varies produced on sorption of Lu(III) in the sensor matrix that might have varied the absorbance. These chemical variations may be counter ions or water content in the sensor matrix. The water contents before and after Lu(III) sorption in sensor sample were found to be within 1.2 wt.%. The minimum concentration of Lu(III) needed in the 10 mL equilibrating solution to produce distinct color change of sensor (dimensions 3.0 cm x 1.0 cm) was calculated to be 280 ng mL^{-1}. However, the detection limit of Lu(III) concentration can be further enhanced by applying larger volume of aqueous sample.

The obtained linear regression equation was A = 5.18C ($\mu g\ mL^{-1}$) + 0.13 (r = 0.9990). The molar absorptivity was found to be 9.06×10^6 L $mol^{-1}\ cm^{-1}$ at 606 nm, whereas the Sandell sensitivity was calculated to be 0.019 ng cm^{-2} (**Table 2**). The standard deviations of the absorbance monitors were investigated from a series of 13 blank solutions. The detection (K = 3) and of quantifiation (K = 10) limits of the procedure were illustrated [51] and presented in **Table 2**, according to the IUPAC definitions ($C_1 = KS_o/s$ where C_1 is the limit of detection, S_o is the standard error of blank, s is the slope of the standard curve and K is the constant related to the confidence interval. The RSD was 1.87% calculated from a series of 10 standards each having 150 ng mL^{-1} of Lu(III).

The membrane sensor reproducibility was investigated applying standard lutetium solution. Suitable aliquots were spiked from standard lutetium solution in to the medium of uptake experiments, e.g., pH 6.5, TEA buffer, volume = 10 mL; and [Lu]=150 ng mL^{-1}. The membrane sensor sample was taken out for the absorbance monitors after equilibration for 10 min. The mean absorbance values with the RSD were calculated to be 0.77 ± 0.02 (n = 6). The small deviations in absorbance values indicate that membrane sensor responses are reproducible under the optimum expermental conditions.

To enhance the change in absorbance at 606 nm in the membrane sensor, the sensor samples of various dimensions were equilibrated in bicarbonate medium with buffered solutions having 1.0 μg of Lu(III) in 10 mL. As can be shown from **Figure 5**, the absorbance increases from 0.29 to 0.78 by decreasing area of sensor samples from 4.0 to 1.0 cm^2. This can be attributed to increase in Lu(III) amounts in the unit volume of the sensor. Therefore, the possibility exist to improve Lu(III) detection limit of sensor by decreasing its volume.
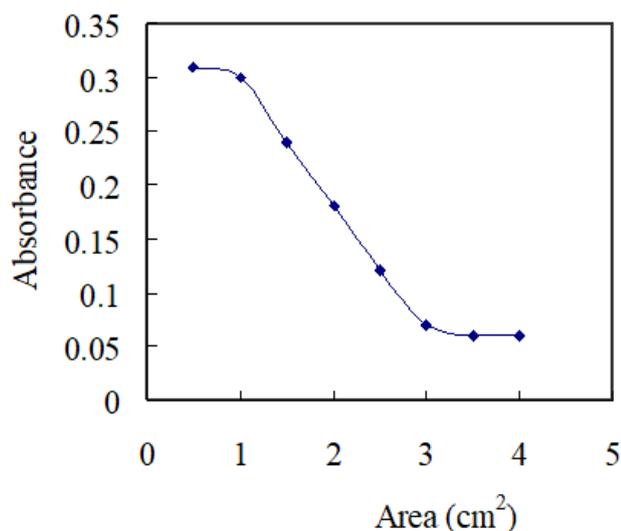
Figure 5. Variation in absorbance of the sensor samples at 606 nm equilibrated with buffered solution containing 1.0 µg of Lu(III). The area of membrane sensor was varied by changing length and keeping same breadth 1.0 cm

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

| Sample | Lu(III) ng mL^{-1} | | | R.S.D. (%) | t-test[b] | F-value[b] |
| | Lu(III) Added | Lu(III) Found | | | | |
		ICP-OES	proposed			
Synthetic sample 1	100	98.5	100.6	1.27	1.62	3.03
Synthetic sample 1	140	141.2	140.6	1.75	1.32	2.87
Synthetic sample 1	180	182.2	180.9	1.36	1.98	4.56
Synthetic sample 1	220	218.3	221.2	1.55	1.78	3.59
Synthetic sample 2	150	151.5	149.4	1.65	2.12	3.96
Synthetic sample 2	200	202.7	199.0	1.83	2.34	4.26
Synthetic sample 2	240	237.8	241.2	1.49	1.87	3.56
Synthetic sample 2	280	283.5	278.7	1.34	1.73	3.42

The performance of the proposed procedure was assessed by calculation of the F-test (for precision) and t-value (for accuracy) compared with the AAS ones. The mean values were obtained in F-tests and Student's t- at 95% confidence limits for six degrees of freedom [52]. The results indicated that the investigated values (**Table 4**) did not exceed the theoretical values. The higher accuracy, wider range of determination, increased stability and lower time consumption indicate the advantages of the proposed procedure over the other ones.

Interfering Ions

The selectivity of the sensor was investigated by equilibrating sensor samples with solutions containing various cations (Th^{4+}, La^{3+}, Sc^{3+}, Y^{3+}, Sm^{3+}, Nd^{3+}, Eu^{3+}, and Fe^{3+}) and anions (F$^-$, I$^-$, NO$_3^-$, CO$_3^{2-}$, PO$_4^{3-}$ and C$_2$O$_4^{2-}$). The absorbance spectra of sensor samples did not vary on its equilibration with solution containing 5.0–400 µg of Th^{4+}. However, some of these ions were found to affect the Lu(III) sorption in the sensor. To study the effects of these ions on Lu(III) sorption in the sensor, the uptake investigates were recorded out in the presence of trace concentrations of cations such as Th^{4+}, Nd^{3+}, Fe^{3+}, and anions as F$^-$, C$_2$O$_4^{2-}$ at pH 6.5 in TEA buffer with 150 ng mL^{-1} Lu(III). In all cases except C$_2$O$_4^{2-}$, the absorbance changes in the sensor samples were within ± 5.0%, indicating that the presence of these cations/anions in the trace amounts will not significantly affect the Lu(III) determination. The tolerance limit was taken as 5.0% deviations in the mean absorbance values in Lu(III)–NTDP complex at 606 nm in the absence of the competing cations/anions. In case of C$_2$O$_4^{2-}$, the absorbance was decreased to 15% which illustrated that C$_2$O$_4^{2-}$ ions interfere in the sorption of Lu(III) in the sensor. A 1.0 mL of 1.0 x 10^{-3} M ammonium molybdate was added to prevent the interference of C$_2$O$_4^{2-}$ upto 400 fold molar excess.

Analytical Application to Synthetic and Real Samples

The lutetium optical sensor device was developed and used to detect lutetium ions in synthetic and river water samples. **Table 3** and **4** records the respective resulting data of these applications. The result, derived from six replicates monitors with the same sensor, was calculated to be in satisfactory agreement with that detected by

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

Method	DL ^{a} (M)	LR^b (M)	Samples	Ref.
Spectrophotometry	0.114 µg/mL	0.68 – 10 µg/mL	synthetic sample	14
Fluorimetry	29 ng/mL	1.8×10^{-7} - 8.8×10^{-6}	synthetic sample	15
ISE	6.7×10^{-7}	1.0×10^{-6} - 1.0×10^{-2}	CRM sample	23
Optical sensor	9.3×10^{-8}	5.0×10^{-7} - 1.0×10^{-5}	river water & CRM	50
Optical sensor	1.63 ng mL^{-1}	4.95 ng mL^{-1}	river water & CRM	this work

^{a} Detection limit
^{b} Linear range

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

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

Arsenazo (III) procedure [53]. The characteristics of the proposed lutetium optical sensor were also compared with other procedures to determine lutetium presented in the literature (**Table 5**). The linear range and detection limit of the proposed optical sensor is acceptable compared to the reported procedures; however, literature survey presents that there is no work on optical sensor membrane with chip reagents to determine Lu(III) ions in solutions.

The proposed sensor was also applied to determine Lu(III) 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 recorded, the Lu(III) amounts was 0.658 mg kg^{-1}. Alternatively, the calibration procedure was employed, representing a Lu(III) value of 0.667 ± 0.3 mg kg^{-1}. These data revealed that the proposed sensor performed a trustworthy detection regarding the Lu(III), despite the presence of other rare earth elements.

The membrane sensor was successfully applied in the spectrophotometric titration of Lu(III) with EDTA. A 10 mL (150 ng mL^{-1}) solution of Lu(III) was titrated with 1.0×10^{-5} M solution EDTA (pH = 10.0). The sharp break point corresponds to the stoichiometry of Lu(III)-EDTA complex.

As a result of very low detection limit and the high selectivity of the investigated lutetium sensor, it was applied to Lu(III) ion determination in the soil where domestic devices were stored. Samples were taken from ten various locations. From each location, 2000 g of soil were taken, powdered and mixed well. Each sample of 10 g was taken, dissolved in 5.0 mL of HNO$_3$ (10%) and then stirred for 25 min at 600 ^{o}C.

The resulting mixture was filtered and the residues were washed with distilled water three times (each time with 2.0 mL). The resulting solution was diluted to 10 mL with 1.0 M CH$_3$COO/NaCH$_3$COO). Afterwards, the absorbance was monitored by applying the developed Lu(III) optode as well as its calibration curve achieved after mokitoring a series of lutetium ion standard solutions. The amounts of lutetium ion in the samples was detected. The result, derived from triplicate mokitorts with the same sensor, was investigated to be in satisfactory agreement with that determined by Arsenazo procedure [54], as it can be recorded from **Table 7**.

Table 7. Determination of lutetium in soil samples (the results are based on triplicates measurements)

Samples	Lu(III) ng Kg^{-1}			
	Proposed	ICP-OES	t-test[a]	F-value[a]
1	41 ± 0.3	39 ± 0.3	1.32	2.66
2	28 ± 0.2	27 ± 0.2	1.65	2.95
3	37 ± 0.2	35 ± 0.2	1.82	3.03
4	18 ± 0.4	20 ± 0.4	2.12	3.48
5	46 ± 0.2	48 ± 0.2	1.45	2.89
6	15 ± 0.3	19 ± 0.3	2.27	3.73
7	22 ± 0.4	23 ± 0.5	1.84	3.11

CONCLUSIONS

A PMMA-based optical membrane sensor has been developed to lutetium preconcentrate, separate and its determination. The optical membrane sensor varies color due to lutetium uptake in the presence of TEA buffer of pH 6.5 in bicarbonate/carbonate medium (~10^{-4} M). The intensity of color in the optical membrane sensor sample was illustrated to be dependent on the lutetium uptake from the sample solution as well as the composition of membrane. The detection limit of the optical membrane sensor film (dimension: 3.0 cm x 1.0 cm) was calculated to be 1.63 ng mL^{-1}. The presence of trace amounts of cations as Th^{4+}, Nd^{3+}, Fe^{3+}, and of anions as F^-, I^-, NO_3^-, and CO_3^{2-}, etc. can not be tolerated during lutetium determination. At higher concentration of these ions, the negative bias was obtained in the most cases except for $C_2O_4^{2-}$ ions. The optical membrane sensor film was quite stable under the experimental conditions.

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