

Yttrium Selective Poly(Vinyl) Chloride Sensor Based on Derivative of 2-Amino-1,4-Naphthoquinone

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The ligand (ionophores H) based on 2-amino-1,4-naphthoquinone have been synthesized and explored as neutral ionophores for preparing polyvinyl chloride-based membrane sensor for the determination of yttrium(III). During the optimization, the addition of potassium tetrakis(4-chlorophenyl) borate and various plasticizers, viz., o-NPOE, DBP, DBBP, DOP and CN have improved performance of the sensors. The best performance was obtained with the sensor number 8, with composition (% w/w) ionophore H (3.5%): PVC (30.0%): o-NPOE (63.0%): KTpCIPB (3.5%). This sensor exhibits Nernstian response with slope 19.8 mV/decade of activity in the concentration range 2.3×10^{-7} to 1.0×10^{-2} M yttrium (III), performs satisfactorily over wide slight acidic pH range of (2.5–6.5) with a fast response time (12 s). The sensor was also found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of acetonitrile, ethanol and methanol. The proposed sensor can be used over a period of 2.5 months without significant drift in potentials. The quantitative application of sensor number 8 was also evaluated in comparative analysis of yttrium(III) with Flame-AAS.

Keywords: Yttrium(III); 2-amino-1,4-naphthoquinone; PVC based sensor

1. INTRODUCTION

Yttrium is a transition metal of group 3 (IIIB). It is moderately abundant element in the Earth's crust. Its abundance is estimated to be about 28 to 70 parts per million. Traditionally, yttrium has had many of the same uses as the rare earth elements. For example, it has been used in phosphors. Yttrium phosphors have long been used in color television sets and in computer monitors[1]. They have also been used in specialized fluorescent lights. Other uses include the production of electrodes, electronic filters, lasers, superconductors, computer monitors, trichromatic fluorescent lights, temperature sensors, X-ray intensifying screens[2] and various medical applications and also as traces in various

materials to enhance their properties. Yttrium is an important element used in atomic reactors for control rods. It is also used in manufacturing of glass and ceramics. It is also used for the production of labeled monoclonal antibodies for tumor therapy studies Yttrium also used in making of alloys and Laser. In spite of being such huge applications in different areas it's accurately measurement of concentration always problematic.

Detection of Yttrium(III) element usually carried out by different methods; Solvent extraction technique[3], ICP-MS [4] and AAS[5]. However most of these techniques are costly and required manpower as a technical expert. The pre-sample treatment is most necessary requirement before the analysis of samples and even not completely considered to be accurate for the detection of yttrium[6].

A simplest analytical technique; ion-selective electrodes (ISEs) has been utilized since long time in determination of cations, anions and organic molecules in different real samples. ISE is a low-cost portable device and can be used without pre-treatment of samples. This has led to increasing interest by our research group in the development and application of ion-selective membrane sensors using various organic ionophores and ion-pairs for the determination of metal [7–34], nonmetals [35–44] and some selective drugs [45–62]. In the present study a derivative of 2-amino-1,4-naphthoquinone have been synthesized and explored in PVC-based membrane sensor as an ionophore for the analysis of yttrium.

2. EXPERIMENT

2.1 Reagents and materials

High molecular weight polyvinyl chloride (PVC), 2-amino-1,4-naphthoquinone and isopropanaldehyde Aldrich (Wisconsin, USA), o-nitrophenyl octyl ether (o-NPOE), CH₃OH, C₆H₅CHO, dioctylphthalate (DOP) and trifluoroacetic acid (CF₃COOH) Fluka (Ronkonkoma, NY), tri-n-butylphosphate (TBP) BDH (Poole, England), chloronaphthalene (CN), dibutylphthalate (DBP), sodium tetraphenylborate (NaTPB) and dibutyl(butyl) phosphonate (DBBP) Mobile (Alabama, USA), potassium fluoroborate (KBF₄), potassium tetrakis (p-chlorophenyl)borate (KTpCIPB) and oleic acid (OA) Sisco Research Lab. (Mumbai, India).

2.2 Synthesis of Ligand (H)

To a solution of 250mg (1.45 mmol) 2-amino-1,4-naphthoquinone, 1ml of bezalaldehyde (excess) in 50 ml of chloroform, trifluoroacetic acid(3 drops) was added. The reaction mixture was stirred at 50° C for 3days. Then , the solvent was removed and the residue was recrystallized from CH₃OH to produce 150mg (24%) of ligand; H m.p.238-239. IR(KBr): 3406(s), 1608 (s), 1586 (s),1494 (m), 1350(m), and 1298 (m)cm⁻¹. ¹HNMR δ(CDCl₃): 5.82(br,2H), 5.86(s,1H),6.15 (d,J=6Hz,1H), 6.90 (d,J=6Hz,1H),7.40 (m,2H), 7.71 (m,2H),8.01 (m,3H), 8.12 (m,1H). C-13 NMRδ: 52.78, 102.93, 112.78, 126.03, 126.20, 126.40, 126.76, 128.11, 129.17, 130.11, 130.53, 132.16, 132.48, 132.87,133.41, 134.72,134.96,138.04, 145.68, 147.49, 181.27, 181.73, 182.04, 183.40. m/z: 434(M+,

100%). Anal. Calcd for $C_{27}H_{18}N_2O_4$: C,74.64; H,4.17; N,6.44. Found: C, 74.57; H, 4.12; N, 6.36 on the basis of structure given in Figure 1.

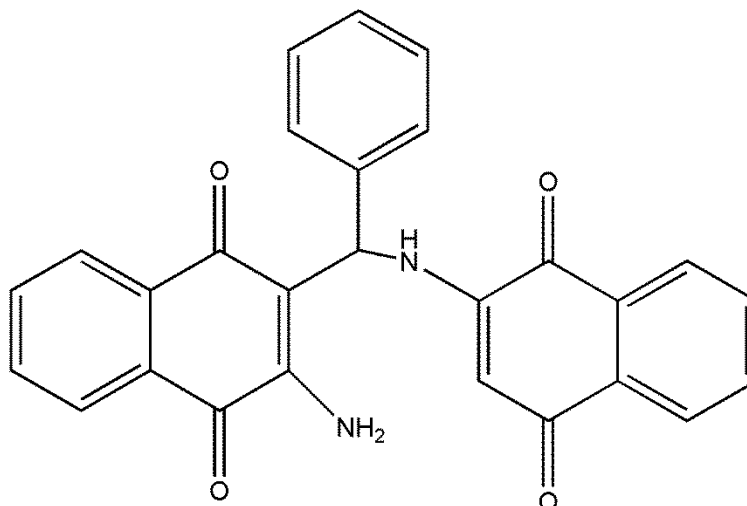


Figure 1. Structure of ligand (ionophore H) derivative of 2-amino-1,4-naphthoquinone.

2.3 Fabrication of PVC Membrane sensor

The membranes have been fabricated as suggested by Craggs et al. [55]. The PVC-based membranes have been prepared by dissolving appropriate amounts of ionophore (H), different anionic additives NaTPB, OA, KTpClPB, KBF₄ and plasticizers DBBP, DBP, o-NPOE, CN, DOP, THB and PVC in THF (5 mL). The components were added in terms of weight percentages. The homogeneous mixture was obtained after complete dissolution of all the components, concentrated by evaporating THF and it has been poured into polyacrylate rings placed on a smooth glass plate. The viscosity of the solution and solvent evaporation was carefully controlled to obtain membranes with reproducible characteristics and uniform thickness otherwise the response of the membrane sensors have shown a significant variation. The membranes of 0.4-mm thickness were removed carefully from the glass plate and glued to one end of a “Pyrex” glass tube. It is known that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition and nature of plasticizer used [63,64]. Thus, the ratio of membrane ingredients, time of contact, concentration of equilibrating solution, etc. were optimized after a good deal of experimentation to provide membranes, which generate reproducible and stable potentials. The membranes having only

PVC as membrane ingredient (dummy membranes) have also been prepared to observe whether any background potentials being produced due to binding material or not. The potentials were not generated without the electroactive material in the membrane. The activities of metal ions were calculated from the modified form of the Debye–Huckel equation.

2.4 Equilibration of membranes and potential measurements

The prepared membranes were equilibrated for two days in 0.01M Y(III) solution. The potentials were measured by varying the concentration of Y^{3+} in the test solution in the range 1.0×10^{-9} to 1.0×10^{-2} M using a buffer solution Tris–HCl (pH 4.0) with a digital potentiometer (model 5652 A, ECIL, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrode.



3. RESULT AND DISCUSSION

3.1 Determination of stability constant

Formation constant of the ion–ionophore complex within the membrane phase is a very important parameter that dictates the practical selectivity of the sensor. In this method, two membrane segments are fused together, with only one containing the ionophore, to give a concentration-polarized sandwich membrane.

Table 1. Binding constants measured for ligand H with different cations

Cation	Formation constant ($\log \beta_{ILn}$)* \pm SD	Cation	Formation constant ($\log \beta_{ILn}$)* \pm SD
Pr(III)	4.15 \pm 0.05	Na(I)	0.45 \pm 0.13
Sc(III)	5.45 \pm 0.03	K(I)	0.51 \pm 0.14
Y(III)	6.68 \pm 0.05	Ca(II)	1.22 \pm 0.12
Nd(III)	4.96 \pm 0.06	Mg(II)	1.44 \pm 0.11
Pm(III)	4.76 \pm 0.19	Pb(II)	1.53 \pm 0.13
Dy(III)	4.58 \pm 0.15	Al(III)	3.21 \pm 0.23
Tl(III)	4.11 \pm 0.13	In(III)	3.42 \pm 0.15
Co(II)	1.31 \pm 0.14	Ga(III)	3.52 \pm 0.23
Ag(I)	1.01 \pm 0.20	Cr(III)	1.98 \pm 0.21

*triplicate measurement

A membrane potential measurement of this transient condition reveals the ion activity ratio at both interfaces, which translates into the apparent binding constants of the ion–ionophore complex [65]. In this method complex formation constants obtained by neglecting ion pairing. As reported, the membrane potential E_M is determined by subtracting the cell potential for a membrane without ionophore from that for the sandwich membrane. The formation constant is then calculated from the following equation.

$$\beta_{ILn} = \left(L_T - \frac{nR_T}{Z_I} \right)^{-n} \exp \left(\frac{E_M z_I F}{RT} \right) \quad (1)$$

Where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion–ionophore complex stoichiometry, and R , T and F are the gas constant, the absolute temperature, and the Faraday constant. The ion I carries a charge of z_I . The determined formation constants ($\log \beta_{ILn}$) for the examined different complexes were recorded in Table 1. The elapsed time between sandwich fusion and exposure to electrolyte was typically <1 min. The potential was recorded as the mean of the last minute of a 5 min measurement period in the appropriate salt solution. The potential of such sandwich membranes remains free of diffusion-induced potential drifts for about 20 min. Standard deviations were obtained based on the measurements of sets of at least three replicate membrane disks that were made from the same parent membrane.

3.2 Effect of internal solution

The influence of the concentration of internal solution on the potential response of the polymeric membrane sensors for Y(III) based on H ionophore was studied. The concentration was varied from 1.0×10^{-1} to 1.0×10^{-4} M and the potential response of the sensors has been observed. It was found that the best results in terms of slope and working concentration range has been obtained with internal solution of activity 1.0×10^{-2} M. Thus, 1.0×10^{-2} M concentration of the reference solution was quite appropriate for the smooth functioning of the proposed sensors.

3.3 Optimization of membrane composition

Table 2. Effect of plasticizers on the performance of ionophore H based membrane sensors.

Sensor No.	Composition of membrane sensors (% w/w)				Working Range (M)	*Slope ± 0.5	Response Time(s)
	Ionophore	PVC	Additives	Plasticizers			
1	0.0 (H)	30.0	4.0 (KTpCIPB)	66.0	-	-	20
2	13.0 (H)	73.0	14.0(KTpCIPB)	0.0	4.6×10^{-3} - 1.0×10^{-2}	16.8	25
3	3.5 (H)	30.0	3.5 (KTpCIPB)	63.0(DBP)	4.6×10^{-5} - 1.0×10^{-2}	17.7	18
4	3.5 (H)	30.0	3.5 (KTpCIPB)	63.0(DBBP)	3.5×10^{-4} - 1.0×10^{-2}	17.8	21
5	3.5 (H)	30.0	3.5 (KTpCIPB)	63.0(TEHP)	2.9×10^{-4} - 1.0×10^{-2}	18.3	19
6	3.5 (H)	30.0	3.5 (KTpCIPB)	63.0 (CN)	5.8×10^{-4} - 1.0×10^{-2}	19.2	17
7	3.5 (H)	30.0	3.5 (KTpCIPB)	63.0 (DOP)	5.5×10^{-4} - 1.0×10^{-2}	18.4	15
8	3.5 (H)	30.0	3.5 (KTpCIPB)	63.0 (<i>o</i> -NPOE)	2.3×10^{-7} - 1.0×10^{-2}	19.8	12

*S.D with Triplicate measurement

In order to get the best responsive results from membrane sensors, the different membranes as in Table 2; with different composition have been prepared and their response characteristics were

evaluated according to the IUPAC recommendations [66] as it is often known that selectivity is highly dependent on the incorporation of additional membrane components [67].

3.3.1 Effect of addition of plasticizer

It is well known that the sensitivity and selectivity of cation-selective membrane sensors strongly depend on the membrane composition and the nature of the plasticizer used [68,69]. Once the membrane sensors based on ligand H have been prepared and as their responses were checked against different concentration of Y(III) further to get the best results, membrane compositions have been optimized using different concentration of plasticizers having a different dielectric constants (ϵ); TEHP ($\epsilon = 4.8$), DBBP ($\epsilon = 4.6$), DBP ($\epsilon = 6.4$), *o*-NPOE ($\epsilon = 24$), CN ($\epsilon = 5$), DOP ($\epsilon = 5$) and PVC ($\epsilon = 3.9$). The effect of plasticizer on Y(III) membrane sensors based on ligand H is shown in (Tables 2). It is clear from the table that *o*-NPOE is more effective plasticizer than others in preparing the Y(III) ISEs because of its high dielectric ($\epsilon = 24$) constant that increases the Y(III) selectivity for proposed ionophores. The plasticizers except *o*-NPOE has less dielectric constant therefore they will solvate the extracted cation in ionophore-free membranes or membrane segments more strongly than *o*-NPOE-based membranes, which lead to smaller binding constants. It is noteworthy that the lipophilicity of plasticizer influences both dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex [70,71].

3.3.2 Effect of addition of anionic additives

Table 3. Effect of different anionic additives on the performance of best optimized membrane sensor based on ionophores H.

Membrane sensor composition	**Anionic additives	Working concentration range (M)	Detection limit(M) ± 0.5	*Slope ± 0.5
H : PVC : <i>o</i> -NPOE (w/w%) 3.5 : 30.0 : 63.0	-	4.5×10^{-4} to 1.0×10^{-2}	3.8×10^{-4}	17.5
	(KTpCIPB)	2.3×10^{-7} to 1.0×10^{-2}	1.3×10^{-7}	19.8
	NaTPB	6.3×10^{-7} to 1.0×10^{-2}	4.2×10^{-7}	19.7
	KBF ₄	7.8×10^{-7} to 1.0×10^{-2}	5.5×10^{-7}	19.0
	OA	8.4×10^{-7} to 1.0×10^{-2}	6.4×10^{-7}	19.3

* \pm Standard deviation, Triplicate measurement

To determine the effect of different lipophilic anionic additives added to the membrane phase influencing the working sensitivity of the sensor, a series of membranes was studied by using lipophilic additives like NaTPB, KTpCIPB, OA and KBF₄ (Table 3). Incorporating KTpCIPB in the membrane composition in the proportion of 3.5% (w/w) relative to the total membrane composition showed best performance characteristics. This is due to fact that KTpCIPB acts as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction.

3.4 Measurement of selectivity coefficient for different cationic species

Table 4, The selectivity coefficient ($-\log K_{Y(III),B}^{Pot}$) measured by FIM (Fixed interference method) for different cations based on sensor number 8.

Cation ^a	Selectivity coefficient ^b ($-\log K_{Y(III),B}^{Pot}$)	Cation ^a	Selectivity coefficient ^b ($-\log K_{Y(III),B}^{Pot}$)
Pr(III)	2.15 ± 0.52	Na(I)	4.45 ± 0.41
Sc(III)	1.65 ± 0.32	K(I)	4.51 ± 0.44
Ce(III)	3.08 ± 0.51	Ca(II)	3.22 ± 0.51
Nd(III)	1.86 ± 0.42	Mg(II)	3.44 ± 0.40
Pm(III)	1.90 ± 0.43	Pb(II)	3.15 ± 0.33
Dy(III)	2.01 ± 0.33	Al(III)	2.31 ± 0.23
Tl(III)	2.21 ± 0.43	In(III)	2.42 ± 0.51
Co(II)	3.31 ± 0.44	Ga(III)	2.52 ± 0.43
Ag(I)	4.01 ± 0.42	Cr(III)	2.94 ± 0.41

^aOnly selected cations are mentioned, however during measurement a number of cations considered.

^bSelectivity coefficient measurement was done in triplicate measurement, (\pm S.D) standard deviation.

The selectivity is one of the most important characteristics of an electrode, as it often determines whether a reliable measurement in the sample is possible or not. The selectivity coefficient has been introduced in the Nikolski-Eisenman equation. The selectivity coefficient values of the best responsive membrane sensor (number 8), for different cationic species (M^{n+}) was evaluated by using fixed interference method (FIM) [72]. In the FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} M) and varying amount of Y(III) ions. The selectivity coefficient is calculated from the following equation:

$$K_{Y(III),B}^{Pot} = \frac{aY^{(III)}}{(aB)^{zA/zB}} \quad (2)$$

where aY^{3+} is the activity of the primary ion (Y^{3+}) at the lower detection limit in the presence of interfering ion B with activity of B, having zA and zB their respective charges. The values of selectivity coefficient so determined for best responsive membrane sensor (number 8) are compiled in Table 4. It is clear from the corresponding table that the selectivity of sensor no. 8 towards Y^{3+} is higher over most of the cations. As sensor no. 8 is better than the other membrane sensors in terms of wider working concentration range, lower detection limit, high selectivity and Nernstian compliance, further studies were carried out with it only.

3.5 pH and non-aqueous effect

Table 5. The performance of best Y(III) selective sensor (number 8) in non-aqueous content.

Non-aqueous content (% v/v)	Working concentration range (M)	Slope (± 0.5 mV decade ⁻¹ of activity) ^a
0	2.3×10^{-7} to 1.0×10^{-2}	19.8
Methanol		
10	2.5×10^{-7} - 1.0×10^{-2}	19.8
20	2.6×10^{-7} - 1.0×10^{-2}	19.8
25	6.8×10^{-7} - 1.0×10^{-2}	19.5
30	2.6×10^{-6} - 1.0×10^{-2}	19.2
35	4.4×10^{-6} - 1.0×10^{-2}	19.2
Ethanol		
10	2.5×10^{-7} - 1.0×10^{-2}	19.8
20	2.5×10^{-7} - 1.0×10^{-2}	19.7
25	7.5×10^{-7} - 1.0×10^{-2}	19.6
30	3.2×10^{-6} - 1.0×10^{-2}	19.4
35	5.2×10^{-6} - 1.0×10^{-2}	19.4
Acetonitrile		
10	2.5×10^{-7} - 1.0×10^{-2}	19.8
20	2.5×10^{-7} - 1.0×10^{-2}	19.8
25	8.5×10^{-7} - 1.0×10^{-2}	19.5
30	5.1×10^{-6} - 1.0×10^{-2}	19.4
35	7.1×10^{-6} - 1.0×10^{-2}	19.4

^a \pm Standard Deviation

The pH dependence of the sensor (number 8) has been tested over the pH range 1.0–12.0 at two fixed concentrations (1.0×10^{-2} and 1.0×10^{-3}) of Y^{3+} with the equimolar concentration of sodium citrate. Due to the interference of H^+ at lower pH range (1–2) and OH^- at higher pH range (higher to pH 7) in the aqueous solution. It is necessary to find the optimum pH range where the sensors functions without interference from the hydrogen or hydroxyl ions. The pH was adjusted with dilute nitric acid or sodium hydroxide solutions. The potential of the sensor was determined as a function of pH and the results are demonstrated in Figure 2. The potential remained constant over the pH range of 2.5–6.5, which may be taken as the working pH range for analytical analysis of real samples. The performance of the sensor no. 8 was further assessed in partial non-aqueous media, i.e. methanol–water, ethanol–water and acetonitrile–water mixture. The results obtained are compiled in Table 5 and show that up to 20% non-aqueous content no significant change occurs in the slope and working concentration of the sensor. However, above 20% non-aqueous content, the working concentration range of the sensor is significantly reduced, and thus the sensor can only be utilized in mixtures containing up to 20% non-aqueous content.

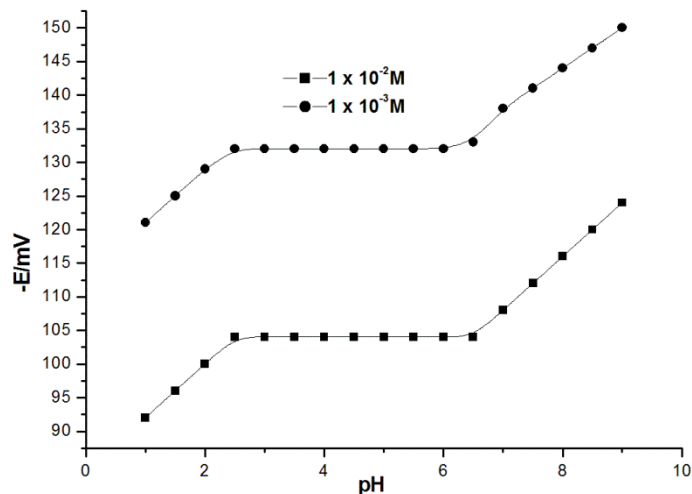


Figure 2. Optimization of working pH range for sensor number 8.

3.6 Dynamic Response and Life Time measurement

To measure the dynamic response time of the proposed sensor the concentration of the test solution has been successively changed from 1.0×10^{-6} to 1.0×10^{-2} M. The resulting data depicted in Figure 3, shows that the time needed to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of Y(III) ions, each having a tenfold difference in concentration is 12 for sensor number 8.

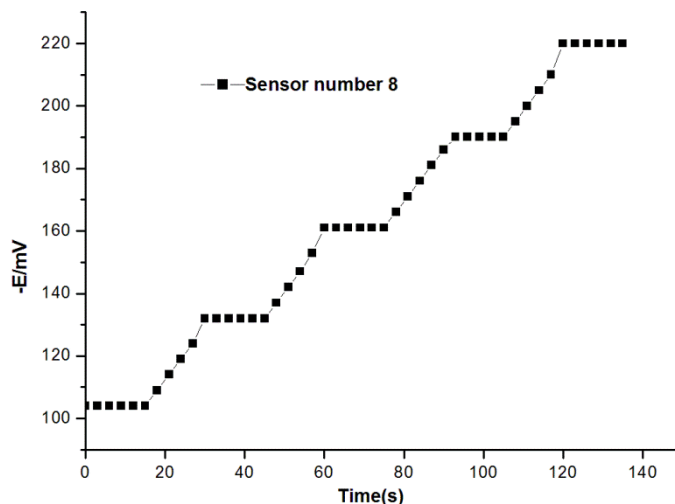


Figure 3. Dynamic response study of best optimized sensor number 8.

This is most probably due to the fast exchange kinetics of complexation–decomplexation of Y(III) ions with the H-ionophore at the test solution–membrane interface. The reduction of the

sensitivity in the polymeric membrane may be dependent upon the lipophilicity and chemical stability of the ionophores, which can result in the ionophore leaking from the membrane. Since Y(III) chelates with ionophore having high lipophilicity, the membranes containing them should provide very low leaking of the ionophore. The membrane could be used over a period of 2.5 months without significant drift in potentials. However, it is important to emphasize that it should be stored in 0.01M Y^{3+} solution when not in use.

4. ANALYTICAL APPLICATION IN REAL SAMPLE ANALYSIS

Table 6. Comparative evaluation of proposed sensor number 8 with Flame-AAS in analytical measurement of yttrium concentration in different glass factory's discharge.

S. no.	Known concentration of Y(III)			Effluent discharge from different companies		
	Known sample concentration	Flame-AAS	Sensor number 8	Company sample number	Flame-AAS	Sensor number 8
1	3ppm	2.7ppm±0.5	2.6ppm±0.5	1	3.2ppm±0.5	2.8ppm±0.4
2	4 ppm	3.8ppm±0.4	3.6ppm±0.3	2	2.8ppm±0.6	2.3ppm±0.3
3	5ppm	4.6ppm±0.6	4.3ppm±0.5	3	3.7ppm±0.2	3.4ppm±0.5
4	6ppm	5.7ppm±0.5	5.3ppm±0.4	4	3.2ppm±0.5	2.8ppm±0.4
5	6.5ppm	6.1ppm±0.3	5.8ppm±0.3	5	3.5ppm±0.4	3.2ppm±0.4
6	7ppm	6.6ppm±0.4	6.2ppm±0.5	6	3.2ppm±0.3	2.9ppm±0.4

*± Standard deviation, Triplicate measurement

The analytical application of Proposed sensor number 8 has been evaluated by measuring concentration of Y(III) in effluent discharge from glass factory. The analysis of samples has been done in acidic condition by controlling the pH <7 using HCl or Tris-HCl buffer may also be used. To check the authenticity of proposed sensor we also did comparative analysis with flame-AAS using different known concentration of of Y(III).

The effluent discharge has been collected from different glass industries near the city. After collecting the different samples we had put all samples in closed clean amber color glass bottles overnight at room temperature, just to let down the big debris of unwanted materials. Next morning we had collected supernatant from bottles and adjust the pH near 4.5 (optimized) and measure the potential for each sample. For flame-AAS we filtered all samples via 0.5µm pore size filter and adjust the pH near 5.5. All the known concentration samples were made in Tris-HCl buffer (pH 4.5-5.5) and calibration graph drawn, Figure 4. The obtained results were mentioned in Table 6.

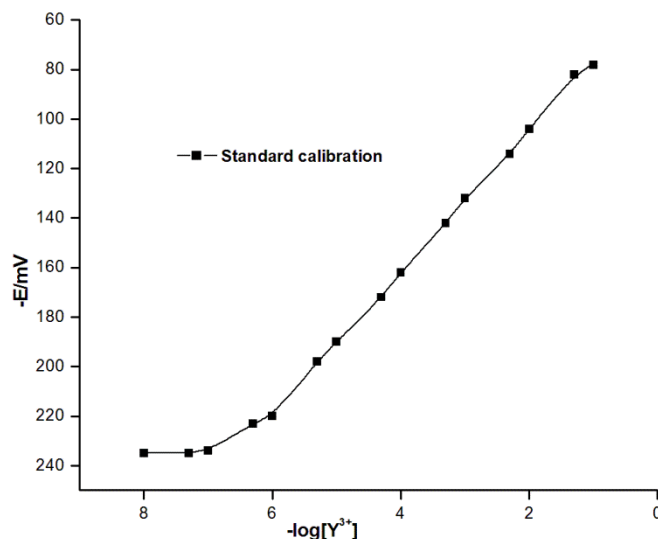


Figure 4. Calibration graph drawn for sensor number 8 using known concentration of sample.

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