

A new ion-selective electrode based on aluminium tungstate for Fe(III) determination in rock sample, pharmaceutical sample and water sample

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Abstract. An inorganic cation exchanger, aluminum tungstate (AT), has been synthesized by adding 0.1 M sodium tungstate gradually into 0.1 M aluminium nitrate at pH 1.2 with continuous stirring. The ion exchange capacity for Na⁺ ion and distribution coefficients of various metal ions was determined on the column of aluminium tungstate. The distribution studies of various metal ions showed the selectivity of Fe(III) ions by this cation exchange material. So, a Fe(III) ion-selective membrane electrode was prepared by using this cation exchange material as an electroactive material. The effect of plasticizers viz. dibutyl phthalate (DBP), dioctylphthalate (DOP), di-(butyl) butyl phosphate (DBBP) and *tris*-(2-ethylhexylphosphate) (TEHP), has also been studied on the performance of membrane sensor. It was observed that the membrane containing the composition AT: PVC: DBP in the ratio 2 : 20 : 15 displayed a useful analytical response with excellent reproducibility, low detection limit, wide working pH range (1–3.5), quick response time (15 s) and applicability over a wide concentration range of Fe(III) ions from 1×10^{-7} M to 1×10^{-1} M with a slope of 20 ± 1 mV per decade. The selectivity coefficients were determined by the mixed solution method and revealed that the electrode was selective for Fe(III) ions in the presence of interfering ions. The electrode was used for at least 5 months without any considerable divergence in response characteristics. The constructed sensor was used as indicator electrode in the potentiometric titration of Fe(III) ions against EDTA and Fe(III) determination in rock sample, pharmaceutical sample and water sample. The results are found to be in good agreement with those obtained by using conventional methods.

Keywords. Aluminium tungstate; Fe(III) ion-selective membrane electrode; PVC; rock sample; pharmaceutical sample.

1. Introduction

Although a lot of work has already been done on the synthesis of inorganic ion exchangers but the development of new inorganic ion exchangers with characteristic properties still needed attention and their utility in various fields is yet to be explored. The need of selective determination of heavy metal ions has increased immensely during last few decades due to growing environmental problems. Over the past decades, ion-selective electrode based potentiometry has become a well-established electro analytical technique for the determination and identification of metal ions even in traces. The ion-selective electrodes (ISEs) are of wide spread interest because of their simplicity, low cost, sufficiently reliable and reasonable selectivity, non-destructiveness and fast provision for analytical results (Oesch *et al* 1978). Precipitate based ion-selective membrane electrodes are well known as they are successfully

used for the determination of several anions and cations (Amini *et al* 1999a, b; Li *et al* 1999; Hassan *et al* 2000; Lindfors and Ivaska 2000; Ganjali *et al* 2001; Shamsipur *et al* 2001). Although iron is an essential element to all forms of life, biologically, it plays an important role in oxygen and electron transport and provides fundamental structure of myoglobin, hemoglobin, hemoenzymes and many cofactors involved in enzyme activities. Approximately 10–15 mg of iron is present in the food ingested during a day (Teixeira *et al* 1998). The absence of iron in the organism causes anemia which results decreased red blood cell content. So we can say that, with only a few possible exceptions in the bacterial world, there would be no life without iron. But, if iron concentration exceeds the normal level it may become potential health hazard. Excess iron in the body causes liver and kidney damage (haemochromatosis), gastric irritation, vomit, pallor and circulatory collapse. Hence the need for iron ion determination in clinical, medicinal, environmental and different industrial samples has led to a number of methods for the measurement of this analyte (Costa and Araújo 2001;

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Carneiro *et al* 2002; Nagabhushana *et al* 2002; Safavi *et al* 2002; Zolgharnein *et al* 2002). However, despite the urgent need for iron selective sensors for the potentiometric monitoring of Fe(III) ions, there have been only limited reports on Fe(III) ion selective electrodes in the literature (Buhlmann *et al* 1998; Mahmoud 2001). Some of them were prepared with ion exchangers (Hassan *et al* 1994; Buhlmann *et al* 1998) and a few of them with ionophores (Chem *et al* 1998; Saleh 2000). An iron selective electrode (Sil *et al* 2005) using PVC and 1,4,8,11-tetraazocyclotetradecane as ionophores had a slope of 60 mV and working concentration range 10^{-6} to 10^{-2} was used for the analysis of alloys and pharmaceutical preparations. A few examples for the use of solid-state ISEs for Fe(III) were also reported (Umezawa 1990; Volkov and Kruchinina 1993; Koenig and Granber 1995; Marco *et al* 1999; Marco and Mackay 2000). Most of these ion-selective electrodes were less selective and had long response time, low pH range and poor stability. The effect of various types of plasticizers on the selectivity of carrier based PVC electrodes has been reported (Ammann *et al* 1975; Marcus 1994), but the systematic investigations about the role of the plasticizers in ion-selective electrodes are still desired. Our present work has been undertaken to make a Fe(III) ion selective electrode by using aluminium tungstate (as electroactive material), PVC and different types of plasticizers and it was found that the electrode which has DBP plasticizer displayed a useful analytical response with excellent reproducibility, low detection limit, wide pH range, quick response time and applicability over a wide concentration range of Fe(III) ions from 1×10^{-7} M to 1×10^{-1} M with a slope of 20 ± 1 mV per decade. Application of this electrode for the determination of iron in rock sample, water sample and commercially available pharmaceutical sample is presented. Although there are various methods for the determination of iron but the advantages of this ISE are its simplicity, low cost, fast response, wide working pH range and wide analytical range.

2. Experimental

2.1 Reagents

Aluminium nitrate and sodium tungstate (E-Merck, India), high molecular weight poly (vinyl chloride) powder and tetrahydrofuran (Fluka, Switzerland), di-butyl phthalate (DBP), di-octylphthalate (DOP), di-(butyl) butyl phosphate (DBBP) (Riedal, India) and *tris*-(2-ethylhexylphosphate) (TEHP) (E-Merck, India). All other reagents and chemicals were of analytical reagent grade. Pharmaceutical sample containing iron was obtained from the local drug market. Double distilled water was used throughout the experiment. All Fe(III) solutions were prepared with FeCl_3 in 0.1 M HCl to prevent hydrolysis and working solutions were prepared daily to prevent ageing.

2.2 Instrumentation

A single electrode pH meter (Toshniwal, India), a UV-Vis spectrophotometer (Elico EI 301E, India), a water bath incubator shaker and a digital potentiometer (Equiptronics EQ 609, India) with silver-silver chloride electrode as reference electrode were used.

2.3 Preparation of aluminium tungstate

Aluminium tungstate was prepared by adding aqueous solution of 0.1 M sodium tungstate gradually into 0.1 M aluminium nitrate solution with continuous stirring at pH 1.2. The pH of the mixture was adjusted by adding 1 M HNO_3 and NH_3 solutions. The mixing ratio of the reactants was 1 : 1 (v/v). The precipitate formed was kept in the mother liquor for 24 h. The supernatant liquid was decanted and the precipitate was washed with demineralized water several times to remove excess of acid and finally filtered using suction pump. The product was dried completely at $40 \pm 2^\circ\text{C}$ in an oven. The final product was immersed in demineralized water to get small granules. The granular particle of the material was then converted into the H^+ ion form by keeping it in 1 M HNO_3 solution for 24 h with occasional shaking and replacing the supernatant liquid with a fresh quantity of acid. The excess acid was removed by several washings with demineralized water. It was finally dried at $40 \pm 2^\circ\text{C}$ and sieved to obtain particles of desired size ($\sim 125 \mu\text{m}$) and stored in a dessicator.

2.4 Ion exchange capacity

1 g (dry mass) of the material in H^+ form was packed in a glass column with a glass wool support at the base. 0.1 M solution of NaCl was passed through the column at a flow rate of 0.5 mL min^{-1} . The effluent was collected and titrated against a standard 0.1 M solution of sodium hydroxide using phenolphthalein as an indicator. The hydrogen ions released were then calculated.

2.5 Distribution studies

In order to get an idea of partition behaviour of the exchanger towards the separation of metal ions of analytical interest, distribution coefficients (K_d) were determined in several solvent systems (table 1). A 0.4 g exchanger in H^+ form was treated with 40 mL solution of metal ions in required solvent medium in a 100 mL Erlenmeyer flask. The mixture was shaken for 6 h at $25 \pm 2^\circ\text{C}$ in a temperature controlled incubator shaker. The amount of metal ions before and after adsorption was determined by titration against a standard solution of 0.01 M di-sodium salt of EDTA. The K_d values may be expressed as follows:

$$K_d = \frac{\text{milli equivalent of metal ions/g of ion-exchanger}}{\text{milli equivalent of metal ions/mL of solution}},$$

$$K_d = \frac{I-F}{F} \times \frac{V}{M} \text{ mL g}^{-1}, \quad (1)$$

where I is the initial amount of the metal ion in the solution phase, F the final amount of metal ion in the solution phase after treatment with the exchanger, V the volume of the solution (mL) and M , the amount of ion exchanger taken (g).

2.6 Quantitative separation of metal ions in binary synthetic mixtures

Quantitative separations of some important metal ions of analytical utility were achieved on aluminium tungstate columns. 1.5 g of exchanger in H^+ form was packed in a glass column of 0.9 cm internal diameter with a glass wool support at the end. The column was washed thoroughly with demineralized water and the mixture of two metal ions having initial concentration of 0.1 M of each with different volume ratios, was loaded onto it and allowed to pass through the column at a flow rate of 0.50 mL min^{-1} till the solution level was just above the surface of the material. The column was then rinsed with demineralized water so that the metal ions, which were not exchanged, could be removed. Individual metal ions adsorbed on the exchanger, were then eluted using the appropriate eluting reagents (table 2). The flow rate of the eluent was maintained at 0.5 mL min^{-1} throughout the elution process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

Table 1. Distribution coefficient (K_d) of metal ions on aluminium tungstate in different solvent systems.

Metal ions	pH 1.50	pH 2.00	pH 3.61	pH 5.20
Mg ²⁺	20	68	90	138
Ca ²⁺	109	128	150	186
Sr ²⁺	79	98	140	177
Ba ²⁺	90	102	135	360
Mn ²⁺	88	102	132	156
Fe(III)	891	1914	2714	3915
Co ²⁺	60	182	280	305
Ni ²⁺	150	150	168	170
Cu ²⁺	150	164	166	166
Zn ²⁺	180	160	140	113
Cd ²⁺	118	118	122	118
Hg ²⁺	169	138	120	98
Pb ²⁺	263	228	192	166
Al ³⁺	133	210	260	340
Zr ⁴⁺	614	602	540	478
Th ⁴⁺	119	318	720	1580
La ³⁺	300	329	358	492

2.7 Membrane preparation

The membranes were prepared as suggested by Coetzee and Benson (1971). The electroactive material, aluminium tungstate cation exchanger, was ground to fine powder and different amounts of this was mixed thoroughly with a fixed amount of PVC and dissolved in 10 mL of tetrahydrofuran (THF). For studying the effect of solvent mediators, DBP, DOP, DBBP and TEHP were also added to get different compositions. The mixtures were vigorously shaken and when the solution got viscous, it was poured in a dust free Pyrex glass circles and solutions were allowed to evaporate at room temperature. After 48 h, a transparent membrane was obtained.

2.8 Conditioning and characterization of membrane

The physicochemical properties of the membrane viz. water content, porosity, thickness and swelling etc were determined as described elsewhere (Jain and Singh 1981; Amarchand *et al* 2000) after conditioning the membrane.

For conditioning, the membranes were equilibrated with 1 M NaCl and a few mL of CH_3COONa to adjust the pH in the range 5–6.5 (to maintain acid present in the film).

To find out the water content, the conditioned membranes were first dipped in water to elute diffusible salts and blotted with Whatmann filter paper to remove surface moisture and weighed water content was calculated as

$$\% \text{ Total weight} = \frac{(W_w - W_d) \times 100}{W_w}, \quad (2)$$

where W_w is the weight of the wet membrane and W_d the weight of dry membrane.

Porosity (ϵ) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data:

$$\epsilon = \frac{W_w - W_d}{AL\rho_w}, \quad (3)$$

where A is the area of the membrane, L the thickness of the membrane and ρ_w the density of water.

Membrane thickness was measured by taking the average thickness of the membrane by using screw gauze and the swelling was measured as the difference between the average thicknesses of the membrane before and after equilibration with 1 M NaCl for 24 h. Details of characterization and conditioning are given in table 3.

2.9 Electrode preparation

A transparent membrane of 5 mm diameter was cut from master membrane, glued to one end of a Pyrex glass tube with the help of araldite. The glass tube was filled with a

Table 2. Quantitative separation of metal ions from a binary mixture using aluminium tungstate column at room temperature.

Metal ions separation	Amount loaded (mg)	Amount found (mg)*	% Recovery	% Error	Volume of eluent used (mL)	Eluent used
Mg ²⁺	0.73	0.68	93.15	-6.85	50	pH 1.5
Fe(III)	1.68	1.60	95.23	-4.77	70	pH 1.5
Ca ²⁺	1.20	1.12	93.33	-6.67	60	pH 1.5
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Zn ²⁺	1.96	1.96	96.42	-3.58	60	pH 5.2
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Cd ²⁺	3.37	3.10	91.98	-8.02	50	pH 5.2
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Hg ²⁺	6.02	5.40	89.70	-10.30	60	pH 5.2
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Pb ²⁺	6.22	6.20	99.67	-0.23	60	pH 5.2
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Mn ²⁺	1.65	1.55	93.93	-6.07	50	pH 1.5
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Al ³⁺	0.81	0.75	92.59	-7.41	50	pH 1.5
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Th ⁴⁺	6.97	6.90	98.99	-1.01	60	pH 1.5
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5
Co ²⁺	1.77	1.70	96.05	-3.95	60	pH 1.5
Fe(III)	1.68	1.60	95.23	-6.85	70	pH 1.5

*Average of three replicate determinations

Table 3. Characterization of ion-exchanger membrane.

Sl. no.	Membrane composition (W/W)						Thick-ness (mm)	Water content as % weight of net membrane	Porosity	Swelling as %wt of wet membrane	Working conc. range (molar)	Slope (± 1 mV/decade of activity)	Response time
	AT	PVC	DBP	DOP	DBBP	TEHP							
M-1	20	200	-	-	-	-	0.39	1.50	0.053	0.16	1.6×10^{-5} to 1.0×10^{-1}	22	40
M-2	20	200	150	-	-	-	0.42	1.50	0.052	0.16	1.0×10^{-7} to 1.0×10^{-1}	20	15
M-3	20	200	-	150	-	-	0.44	1.58	0.064	0.18	1.7×10^{-4} to 1.0×10^{-1}	24	17
M-4	20	200	-	-	150	-	0.44	1.60	0.065	0.20	1.6×10^{-6} to 1.0×10^{-1}	23	16
M-5	20	200	-	-	-	150	0.50	1.61	0.067	0.18	1.9×10^{-6} to 1.0×10^{-1}	25	17
M-6	30	200	150	-	-	-	0.44	1.70	0.058	0.18	2.1×10^{-6} to 1.0×10^{-1}	21	24
M-7	40	200	150	-	-	-	0.48	1.82	0.065	0.20	2.5×10^{-6} to 1.0×10^{-1}	22	16

0.1 M Fe(NO₃)₃ solution. Silver/silver chloride electrodes were used as internal and external reference electrodes. All the potential measurements using the following cell were made at $25 \pm 0.1^\circ\text{C}$. The whole arrangement can be shown as

Internal reference electrode (Ag/AgCl) | 3.0 M KCl | Internal electrolyte, 0.1 M Fe(III) | Membrane | Sample solution | 3.0 M KCl | External reference electrode (AgCl/Ag).

The performance of the electrode was investigated by measuring the e.m.f. of Fe(III) ion solution over the pH

range of 1×10^{-10} to 1×10^{-1} M. The membrane electrode was conditioned by soaking in a 0.1 M Fe(NO₃)₃ solution for 3 days and atleast 1 h before use. After performing the experiment, membrane electrode was removed from the test solution and kept in 0.1 M Fe(NO₃)₃. Potential measurement of the membrane electrode was plotted against the selected concentration of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted four times to check the reproducibility of the system.

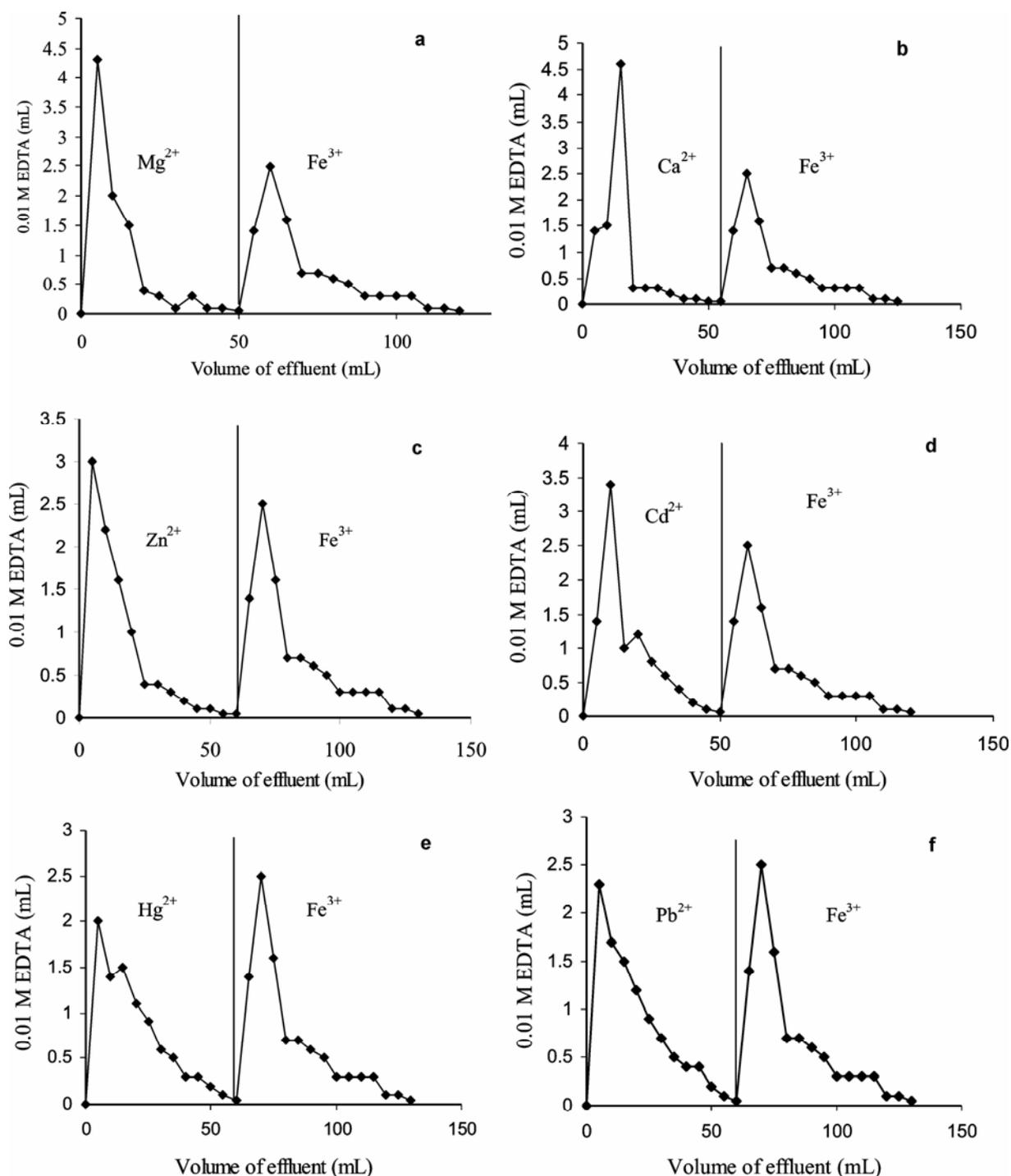


Figure 1. Binary separation curves of a. Mg^{2+} and Fe(III), b. Ca^{2+} and Fe(III), c. Zn^{2+} and Fe(III), d. Cd^{2+} and Fe(III), e. Hg^{2+} and Fe(III) and f. Pb^{2+} and Fe(III).

3. Results and discussion

An inorganic cation exchanger, aluminum tungstate, has been synthesized by adding 0.1 M sodium tungstate gradually into 0.1 M aluminium nitrate at pH 1.2 with continuous stirring. This cation exchange material has good ion exchange capacity (1.17 meq g^{-1} for Na^+). In

order to explore the potentiality of this new inorganic cation exchange material in the separation of metal ions, distribution studies for 17 metal ions have been performed in buffer solutions of different pH (table 1). It has been observed that K_d values increase with the increase in the pH of the buffer solutions for all metal ions except Zn(II), Pb(II), Hg(II), Zr(IV) and La(III). It may be due

Table 4. Selective separations of Fe(III) from a synthetic mixture of Zn²⁺, Fe(III), Cu²⁺ and Cd²⁺ on a column of aluminium tungstate.

Sl. no.	Amount of Fe(III) loaded (mg)	Amount of Fe(III) found* (mg)	% Recovery	% Error	Eluent used pH 1.5 (mL)
1	2.79	2.76	98.92	-1.08	75
2	5.58	5.54	99.28	-0.72	75
3	8.37	8.20	97.96	-2.04	80

*Average of three replicate determinations

to faster release of H⁺ ions from the exchange material in less acidic medium. So greater adsorption of metal ions takes place by this exchange material. The separation capability of the material has been demonstrated by achieving a number of binary separations of some important metal ions (table 2). The sequential elution of ions through column depends upon the metal–ligand stability. The weakly retained metal ions eluted first and strongly retained at last. The order of elution and eluents used for binary separations are also shown in figure 1. The separations are quite sharp and recovery was quantitative and reproducible. High K_d values of Fe(III) enable its selective separation from a mixture of synthetic mixture of Fe(III), Zn(II), Cd(II) and Cu(II) (table 3). The high uptake of Fe(III) ions in all solvent systems demonstrated not only the ion exchange properties but also the ion-selective characteristics of the cation exchanger, aluminium tungstate. So aluminium tungstate has also been used as an electroactive material for the preparation of Fe(III) ion-selective membrane electrode. Many samples of aluminium tungstate membrane were prepared using different mixing ratios of aluminium tungstate (electroactive material) and plasticizers with a fixed amount of PVC. It was found that the membrane having DBP exhibited widest working concentration range, quick response time and Nernstian slope of 20 ± 1 mV/decade of activity among all these prepared by using DBP, DOP, DBBP and TEHP. These membranes were also characterized on the basis of thickness, porosity, swelling etc to find out the membrane of good electrochemical performance for the purpose of preparation of an ion-selective membrane electrode (table 4). Generally an ideal membrane should have less thickness, moderate swelling and water content capacity. Membrane, M-2, has low order of water content, swelling porosity, thickness and shows wide working concentration range and quick response. So membrane, M-2, was selected for the preparation of ion selective electrode for detailed studies. The composition (w/w) of the membrane (M-2) was AT: PVC: DBP in the ratio 2 : 20 : 15.

3.1 Working concentration range and slope

The electrode potential measurement of all membrane sensors was studied in the range of 1×10^{-10} to 1×10^{-1} M and 0.1 M Fe(NO₃)₃ solution was taken as internal solu-

tion. It is clear from table 4 that membrane 1 with the aluminium tungstate and PVC in the ratio 1 : 10, respectively showed a linear working concentration range of 1.6×10^{-5} to 1.0×10^{-1} M with an average slope of 22 mV/decade of activity. When the amount of aluminium tungstate was increased in a fixed amount of PVC, the thickness, water content and response time increased and working concentration range was decreased. Plasticizers have been used to improve the response characteristics of the membrane (Gupta *et al* 2006a, b). Therefore, DBP, DOP, DBBP and TEHP plasticizers were also added and it was observed that among all plasticizers employed, the use of DBP resulted in the best response characteristics by the membrane sensor (M-2). It should be noted that the nature of plasticizers affect the dielectric constant of membrane (Masuda *et al* 1998; Ez *et al* 2003; Zare *et al* 2005). The electrode prepared from membrane M-2 showed response for the Fe(III) ions in the concentration range of 1×10^{-7} to 1×10^{-1} M with an average slope of 20 ± 1 mV (figure 2). A calibration curve was made by measuring the electrode response to standard solution prepared by serial dilution method without the addition of extra indifferent salts.

3.2 Response time and lifetime of membrane electrode

The response time (figure 3) of a membrane sensor is an important factor. The practical response time required for Fe(III) sensor to reach a potential of equilibrium value after successive immersion of a series of Fe(III) ion solutions, each having 10-fold difference in concentration was measured. The response time of membrane sensor without plasticizer was found to be 40 s. The plasticizers played an important role in reducing the response time and best results were observed in the case of DBP as the response time was 15 s, which is the lowest among all. The membrane electrode could be used for at least 5 months without any measurable divergence in its response for Fe(III) ions. It is very important that the performance of any ion-selective electrode should be checked every time before using it for any analytical purpose. However, the sensor was stored in 0.1 M Fe(III) solution during non-usage. Repeated monitoring of the potential on the same portion of the sample (1×10^{-3} M) gave a standard deviation of ± 2 mV and there was no significant

change in the slope. It is interesting to note that the electrode in our present work gave a quicker response time of 15 s with stable reading and works over a lower concentration range of Fe(III) ions as compared to ion-selective electrode developed earlier for Fe(III) (Teixeira *et al* 1998; Sil *et al* 2005).

3.3 Effect of pH on test solution

In order to determine the useful pH range over which the electrode can be used without any pH interference, the potential of the electrode was determined over a pH range of 1–8 (figure 4). pH was adjusted by drop wise addition of a 0.1 M solution of HNO₃ or NaOH and the e.m.f. of the electrode was measured at each pH value. It is clear from the figure that the potential remained constant in the pH range 1–3.5 which can be taken as the working pH range of the proposed sensor. Above pH 3.5 the potential

starts decreasing sharply, this may be because of the formation of ferric hydroxide in the solution at higher pH (Sil *et al* 2005). At low pH, the potential increased indicating that the membrane sensor responds to hydrogen ions (Gupta *et al* 2006a).

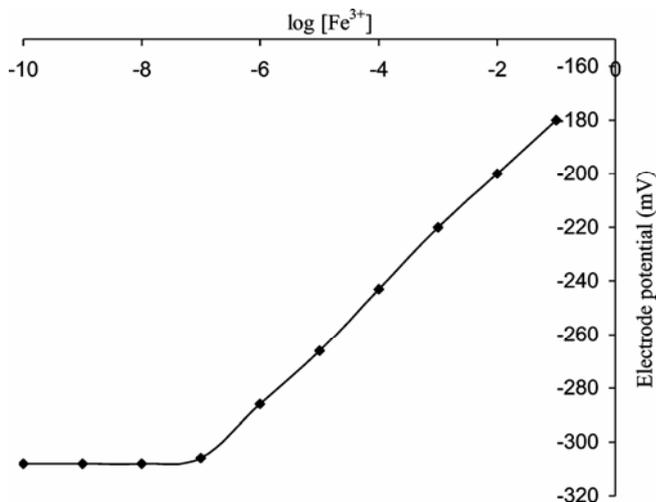


Figure 2. Calibration curve for aluminium tungstate membrane electrode in aqueous solution of Fe(NO₃)₃.

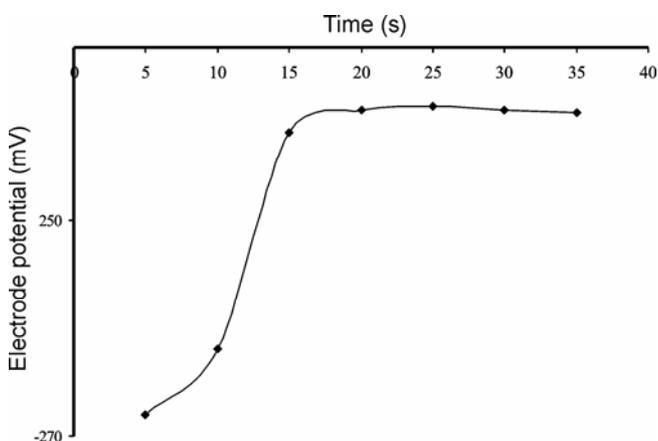


Figure 3. Response of Fe(III) ion-selective aluminium tungstate membrane electrode at different time intervals.

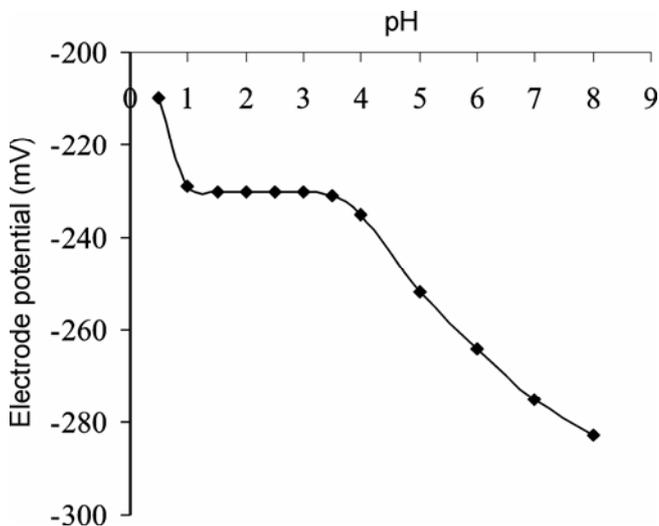


Figure 4. Effect of pH on electrode response of Fe(III) ion-selective aluminium tungstate membrane electrode.

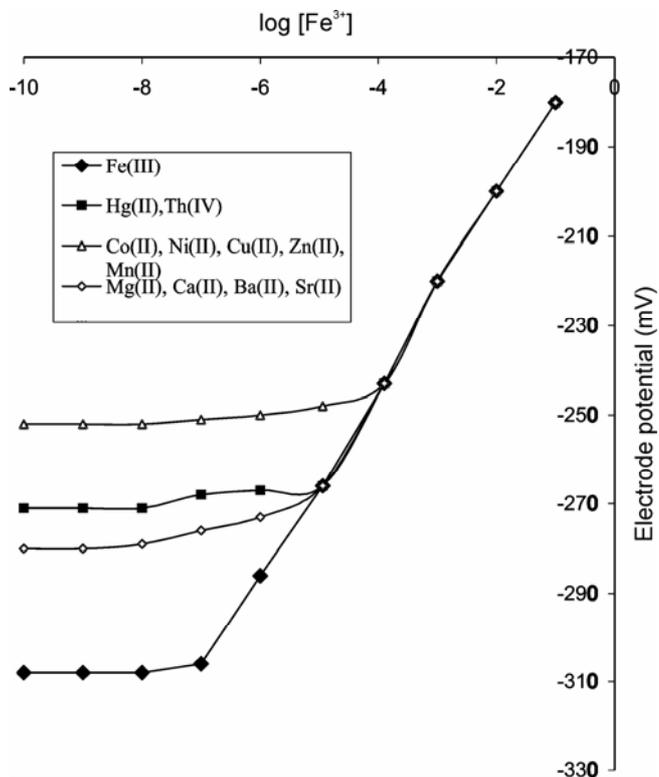


Figure 5. Selectivity coefficients of various interfering ions for aluminium tungstate PVC membrane electrode.

3.4 Selectivity coefficients

One of the important characteristics of any ion-selective electrode is its relative response to the primary ions over other ions present in the solution, which is termed as selectivity coefficient, $K_{A,B}^{POT}$. It determines the extent to which a sensor can be used for the analysis of real samples (Gupta *et al* 2006a). The selectivity coefficients of the electrode were studied with respect to closely associated metals by the mixed solution method as discussed elsewhere (Craggs *et al* 1974). A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-3} M) and varying concentrations (1×10^{-1} to 1×10^{-10} M) of the primary ion. Now, the potential measurements were made by using the membrane electrode assembly and the results are summarized in table 5. It is shown from figure 5 as well as table 5 that interference due to presence of alkaline earth metal ions is negligible and Hg^{2+} , Th^{4+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Mn^{2+} register slight interference in the order of 1×10^{-4} or smaller, with the determination of ferric ions.

Table 5. Selectivity coefficients ($K_{Fe,M}^{POT}$) of various interfering ions for Fe(III) ion-selective electrode.

Interfering ion (M^{n+})	Selectivity coefficients ($K_{Fe,M}^{POT}$)
Hg^{2+}	1×10^{-5}
Th^{4+}	1×10^{-5}
Co^{2+}	1×10^{-4}
Ni^{2+}	1×10^{-4}
Cu^{2+}	1×10^{-4}
Zn^{2+}	1×10^{-4}
Mn^{2+}	1×10^{-4}
Mg^{2+}	1×10^{-6}
Ca^{2+}	1×10^{-6}
Ba^{2+}	1×10^{-6}
Sr^{2+}	1×10^{-6}

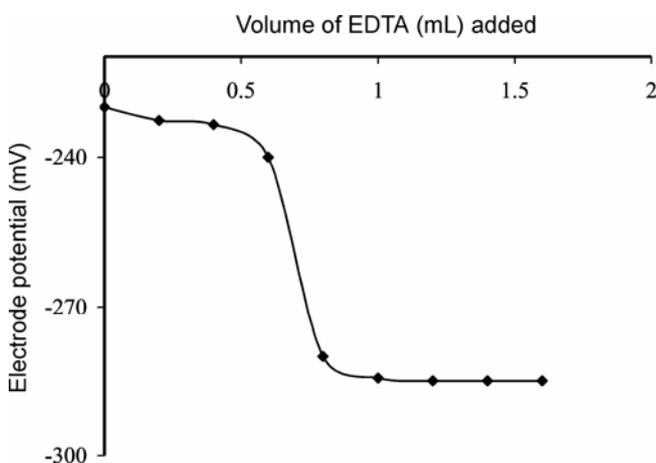


Figure 6. Potentiometric titration of Fe(III) against EDTA solution.

Thus, the results indicate that these interfering cations would not significantly disturb the functioning of Fe(III) ion-selective electrode and electrode is selective in the presence of these cations.

4. Analytical Applications

4.1 Determination of Fe(III) in real samples

In order to test the analytical validity of this approach, the electrode has been used for the determination of iron in rock sample (Hawain Basalt, United States Geological rock sample), pharmaceutical sample (Fefol Z, Glaxo, India) and water sample (Hinden river, India).

Pharmaceutical sample was prepared by dissolving one tablet of Fefol-Z in 10 mL HCl and heated to dryness. After that, the sample was dissolved in 10 mL DMW, filtered and transferred to a 25 mL standard flask and this volume was completed with DMW. Rock sample was prepared by dissolving 1 g rock sample in 5 mL hydrofluoric acid by heating. The solution was filtered and the filtrate was diluted to 50 mL with DMW in standard flask. Two other techniques viz. AAS and UV-Vis spectrophotometer, were also used for the determination of iron contents in these samples. The results obtained are presented in table 6 and compared with those obtained by using AAS and UV-Vis spectrophotometer. The sensor is found to be in satisfactory agreement with that obtained from atomic absorption spectrometer (AAS) and UV-Vis spectrophotometer. These observations and results have been confirmed that present electrode can be used for practical analysis.

4.2 Potentiometric titration

The analytical utility of this membrane electrode has been established by using it as an indicator electrode in the potentiometric titration of Fe(III) ions with an EDTA solution as a titrant (figure 6). A 10 mL of 1×10^{-3} solution of Fe(III) was titrated against 0.01 M EDTA solution at working pH of this electrode (3). The addition of EDTA causes a decrease in potential as a result of the decrease in free Fe(III) ion concentration due to the formation of Fe(III)-EDTA complex which gives the idea of end point and therefore, the proposed sensor can be used as an indicator electrode for the potentiometric determination of Fe(III) ions.

5. Conclusions

In the present study, we have reported a new aluminium tungstate based Fe(III) ion-selective electrode. The selectivity, response time, working concentration range of the electrodes are influenced by the amount of the electroac-

Table 6. Determination of Fe (III) in real samples using AAS, spectrophotometer and proposed sensor.

Sample	Adjusted pH	Labeled amount	AAS	Spectrophotometer	Proposed sensor
Water sample	3.0	4.47 mg L ⁻¹	4.46 ± 0.02 mg L ⁻¹	4.43 ± 0.04 mg L ⁻¹	4.42 ± 0.08 mg L ⁻¹
Rock sample	3.0	172 mg L ⁻¹	171 ± 0.01 mg L ⁻¹	170 ± 0.03 mg L ⁻¹	169 ± 0.05 mg L ⁻¹
Pharmaceutical sample (Fefol-Z)	3.0	50 mg/tablet	49.4 ± 0.02 mg/tablet	48.6 ± 0.03 mg/tablet	47.2 ± 0.04 mg/tablet

tive material (aluminium tungstate) and types of plasticizers. So the electrode was fabricated by taking appropriate amount of electrode constituents, which had good operation characteristics e.g. sensitivity, stability response time and wide working range. The electrode could successfully be employed as indicator electrode in the potentiometric titration of Fe(III) against EDTA as well as to determine Fe(III) ions quantitatively in rock sample, pharmaceutical sample and water sample.

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