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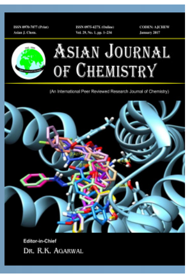

Synthesis, Characterization and Analytical Applications of Novel Electroactive Sensor based on Titanium(IV) Tungstovanadate for Determination of Cadmium

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The novel exchanger titanium(IV) tungstovanadate has been prepared by sol-gel method. The characterization of sensor has been done with FTIR, SEM, EDS and X-ray diffraction studies. Membranes containing different composition of electroactive material and epoxy resin as binder were prepared. The membrane with 60 % electroactive material and 40 % epoxy binder gives the best response. Potentiometric result shows that the sensor can be used in the concentration range of 10^{-7} to 10^{-1} M Cd(II) ions with a near Nernstian slope of 21 mV/decade. The electrode shows a fast response time of < 10 sec. The working pH range of the electrode is 2.62 to 8.66 and it behaves well in the partially non aqueous medium upto 30 % concentration of ethanol, methanol and acetone. Fixed interference method was used for determining the selectivity coefficient with respect to different metal ions like Pb^{2+}, Cr^{3+}, La^{2+}, Co^{2+}, Hg^{2+}, As^{3+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Sm^{3+} *etc.* and effect of internal solution was also studied. The developed sensor can be used as an indicator electrode in the potentiometric titration of Cd(II) against EDTA and oxalic acid.

Keywords: Titanium(IV) tungstovanadate, Electroactive sensor, Cadmium, Selectivity coefficient.

INTRODUCTION

Cadmium is used as a barrier in nuclear fission, as neutron absorber, in steel galvanization, paints, pigments, cosmetics, nickel cadmium batteries, in television screens, lasers and in welding of seals along with zinc. In United States, 600 tonnes of cadmium is produced annually and about 150 metric tonnes of cadmium is imported [1,2]. Cadmium enters in human body through inhalation or ingestion. The most significant source of cadmium exposure is cigarette smoking. The people working in welding and soldering industry are more significantly exposed to inhalation of cadmium and it can cause severe chemical pneumonitis [3-5]. About 30 % of absorbed cadmium is deposited in the liver and 30 % in the kidneys [6]. Cadmium initiates tissue injury by creating oxidative stress and it also changes DNA epigenetically [7-9]. Cadmium interferes competitively with physiological action of zinc [10-13]. Cadmium prevents formation of heme and it blocks the functioning of mitochondria and causes apoptosis [14-18]. The main target of cadmium toxicity is kidney where the reabsorption of protein, amino acids, bicarbonates and phosphate (Fanconi syndrome) is affected to a large extent. Cadmium poisoning also affects diabetic's patients more drastically as it leads to renal tubular damage [19,20]. Cadmium reduces level of osteocalcin. It interferes with calcium channels and leads to constriction of blood vessels [21-25]. Cadmium increases rates of autoimmunity and synthesis of non-specific antibodies. It reduces production of antigen-specific antibodies [26,27]. Keeping in view all harmful effects of cadmium, it becomes manadatory to check the presence of cadmium in the environment. The novel sensor titanium(IV) tungstovanadate has been successfully used for the detection of cadmium.

Titanium based ion exchangers have excellent ion exchange properties. These exchangers are prepared using different composition of materials so as to increase their selectivity. Three component based ion exchangers of titanium have been reported in literature *i.e.* titanium(IV)iodovenadate [28], polyaniline titanotungstate [29], sodium irontitinate [30], titanium antimonite [31], titanium phosphate [32], titanium tungstosilicate [33], titaniummolybdo silicate [34], titanium-molybdate [35] have been synthesized. The present work deals with the synthesis, characterization, ion exchange properties and analytical applications of a novel three component based exchanger *i.e.* Ti(IV) tungstovanadate.

EXPERIMENTAL

A digital pH-conductivity meter-101 (Sr.No.-1402046) was used to measure pH and temperature was measured with a temperature meter -18. The sample was dried with a temperature controlled electric oven (Universal). Digital potentiometer-118 (Sr.No.1312575) was used for EMF measurement.

Titanium chloride ($TiCl_4$), sodium tungstate and ammonium metavanadate were used. All the chemicals were supplied by CDH, Qualikems and S.D. Fine Chemicals Pvt. Ltd. The reagents used were of highest purity.

Synthesis of titanium(IV) tungstovanadate: Titanium(IV) tungstovanadate was synthesized by adding solution of titanium tetrachloride to a mixture of sodium tungstate and ammonium metavanadate at 60 °C in different volume ratios. The pH of the mixture was maintained by adding conc. HCl (Table-1). The mixture was stirred continuously. Yellow coloured gel was obtained which was filtered and washed with double distilled water so as to remove any traces of chlorides and sulphates. The ppts. were dried and converted in the form of granules by putting them in the distilled water. The granules were kept overnight in 0.1 M HCl to convert them into H^+ ion form [36]. The exchanger was washed with double distilled water and dried finally at 50 °C.

Physico-chemical characterization

Ion exchange capacity (IEC) and distribution coefficient studies: Column operation method was used to find ion exchange capacity of the exchanger [37] (Table-1). It was found to be maximum for the S-1. So, S-1 was selected for further potentiometric studies.

Distribution coefficient studies *i.e.* (K_d) values for different metal ions like Sm^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, La^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, Hg^{2+} and As^{3+} were calculated by the formula given below [38]:

$$K_d = \frac{(I-F)}{F} \cdot \frac{V}{W}$$

K_d values are summarized in the Table-2.

TABLE-2
DISTRIBUTION COEFFICIENT (K_d) VALUES FOR DIFFERENT METAL IONS ON SENSOR

Metal ions	K_d values	Metal ions	K_d values
Sm(III)	50.0	Cu(II)	40.0
Mn(II)	92.0	Cr(III)	75.0
Ni(II)	33.3	Cd(II)	500.0
Co(II)	25.0	Hg(II)	100.0
Pb(II)	60.0	As(III)	50.0
La(II)	33.3		

Infrared spectra: Infrared spectroscopy was recorded using KBr pellet medium and was used to find different attacking sites of heteropolyacids salts. Structure elucidation of polyoxometalate chemistry was characterized by four types of metal oxygen linkages exhibiting characteristic vibrational bands (Fig. 1).

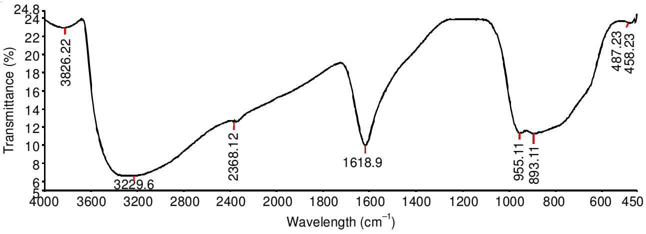

Fig. 1. FTIR of titanium(IV) tungstovanadate

M-O-X (weak and long bands *i.e.* X-M bonds containing 4 internal oxygen atoms).

1 M atom connected to 12 terminal oxygen atoms having almost double bond character (M-O bonds).

Metal atoms connected to 12 edge sharing oxygen atoms (M-O-M) (12 edge-sharing oxygen connecting M's).

M_3O_{13} units containing 12-corner sharing oxygen (M-O-M).

The metal oxygen bonding present in heteropoly acid was explained by infrared spectroscopy.

Thermal gravimetric, X-ray diffraction, SEM and EDS analysis of Ti(IV) tungstovanadate: To find the number of water molecules in Ti(IV) tungstovanadate, the exchanger was heated at a constant heating rate of 10 °C/min. A TGA curve was obtained between 10 °C and 800 °C maintaining the nitrogen flow at a rate of 20 mL/min. The thermal stability, number and nature of water molecules present in the Ti(IV) tungstovanadate can be calculated with the help of the TGA (Fig. 2).

The nature of the heteropoly acid *i.e.* whether the compound is amorphous or crystalline as well as the orientation of crystallites was deduced with the help of XRD analysis using powder diffraction method (Fig. 3).

SEM technique was used to show the external texture, topography, morphology, crystalline structure and orientation of materials where as EDS technique was used to determine

TABLE-1
PREPARATION AND PROPERTIES OF TITANIUM(IV) TUNGSTOVANADATE USING DIFFERENT CONDITIONS

Sample No.	Name of constituent	Volume ratio	Molar conc. (M)	Temp. (°C)	pH	Morphology	Colour in H^+ ion	IEC (meq/g)
S-1	TC	2	1.0	40	1.0	Amorphous	Yellow	0.520
	ST	1	1.0					
	AMV	1	1.0					
S-2	TC	1	0.5	60	0.0	Amorphous	Yellow	0.320
	ST	1	0.5					
	AMV	1	0.5					
S-3	TC	2	1.0	60	1.0	Amorphous	Yellow	0.240
	ST	1	1.0					
	AMV	1	1.0					
S-4	TC	1	0.5	60	1.0	Amorphous	Yellow	0.300
	ST	1	0.5					
	AMV	1	0.5					

TC = Titanium tetrachloride, ST = Sodiumtungstate, AMV = Ammoniummetavanadate

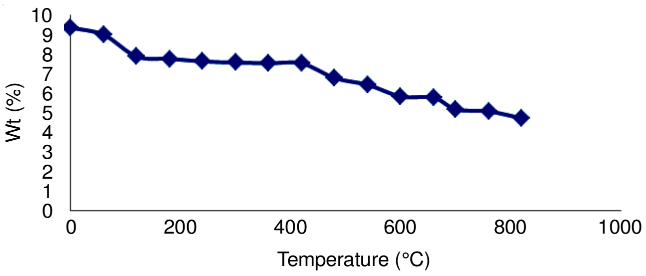

Fig. 2. TGA curve of Ti(IV) tungstovanadate

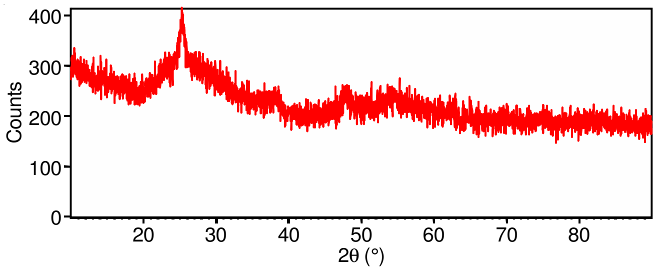

Fig. 3. XRD of titanium(IV) tungstovanadate

the chemical composition and elemental analysis of Ti(IV) tungstovanadate (Fig. 4).

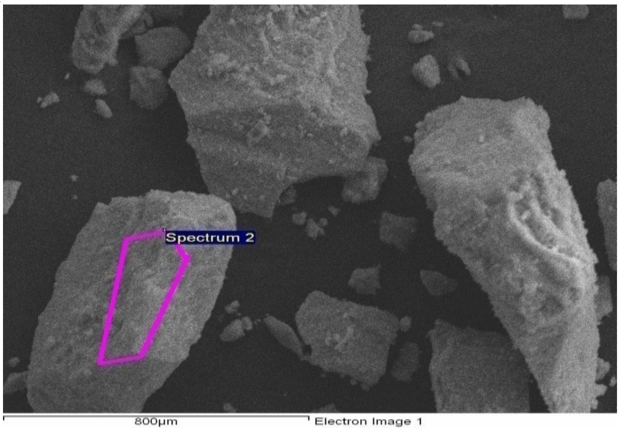

Fig. 4. SEM image of titanium(IV) tungstovanadate

Potentiometric studies

Preparation of membranes and measurement of EMF: For potentiometric studies, membranes were prepared by mixing exchanger and epoxy resin in different amount (w/w). The prepared membranes were diced in circular shape of diameter 2 cm. The finest membrane that gave reproducible results and best performance was selected for further potentiometric studies [39].

To measure EMF, the selected membrane was attached to one end of the glass tube with 1.8 cm internal diameter using araldite [40]. The membrane was equilibrated by keeping it in 0.1 M Cd^{2+} ions solution and washed with double distilled water. All EMF measurements were carried out by using the following cell assembly:

$Hg\text{-}Hg_2Cl_{2(S)}$ | KCl (sat)|| 0.1M Cd^{2+} || membrane ||
test solution || KCl (sat), Hg_2Cl_2-Hg

The potential was measured at 25 °C. Debye-Huckel equation [41] was used to calculate the activities. 0.1 M Cd^{2+} ion solution was diluted to obtain the test solutions of concentration from 10^{-8} to 10^{-1} M. Unbuffered solutions were used to measure EMF.

Effect of internal solution and pH: To check the effect of internal solution on the response of the electrode, the EMF was measured by varying the concentration of the internal solution from 1×10^{-1} M to 1.0×10^{-3} M.

The response of the electrode was also studied under different pH conditions. For this purpose, few drops of HCl (0.01 M) or NaOH (0.01M) was added as needed and EMF was measured.

RESULTS AND DISCUSSION

IR spectrum: The presence of external water molecules along with –OH groups and other metal oxides were identified with the help of IR spectrum. IR spectrum of the exchanger was studied in the H^+ ion form.

In FTIR studies, the interstitial water molecules and V-OH group stretching was confirmed by a strong band at 3229 cm^{-1} [42]. In all TiO_2 spectra, stretching vibrations of hydrogen bonded surface water molecules and –OH group were characterized by a strong band at 3826.22 cm^{-1} [43]. A band at 1618.9 cm^{-1} was due to bending vibrations of coordinated water as well as due to Ti-OH group [44,45]. A peak around 487.23 cm^{-1} was due to vibrations in the rutile crystalline structure of Ti-O [46]. A small peak at 2368.12 cm^{-1} was due to Ti-O vibrations [47].

There are four kind of oxygen atoms and four Ti-O bonds in Keggin structure of $[TiW_{12}O_{40}]_4$ by which the oxygen atom get bonded with the exheteroatom (Ti), 12 W-O_b-W oxygen bridging, corner sharing oxygen bridges and 11 W-O_t terminal oxygen atoms. In general the symmetric and asymmetric stretching vibrations were observed. A band at 893.11 cm^{-1} was due to W-Ob-W, a band at 955.11 cm^{-1} was due to W-O_t and a band at 458.23 cm^{-1} was due to (Ti-O) or (O-Ti-O) [48]. All of which correspond to the spectrum of Ti(IV) tungstovanadate complex of Keggin structure previously reported. Results are shown in Fig. 1.

The vibration bands were either broadened or shifted from their normal modes due to coupling of outer valence electronic states with the vibrational states of the molecules.

Electron diffraction spectra of the Ti(IV) tungstovanadate showed that it contains Ti, W and V and O which were characterized by the respective peaks in the spectrum. Atomic ratio of these elements was Ti:W:V:O was 4.90:9.78:1.44:83.88, respectively. The oxygen content in the empirical formula includes the molecular water, hydroxyl group and oxide. Based on the data, the empirical formula of the synthesized exchanger can be represented as:

$$[(TiO_2)_{3.41}(H_3VO_3)_3(H_3WO_4)_{16.802}]\cdot nH_2O$$

The external water molecules were consistent only upto 200 °C as shown by thermogravimetric studies. The sensor lost a 18 % weight up to 200 °C. When sensor was heated above than recommended temperature, the sensor lost external water molecules. To calculate the number of external water mole-cules ('n'), Alberti 'n' formula [49] was used which is given as:

$$18\ n = X\ (M+18n)/100$$

where X = loss in weight (%) at 200 °C, (M+18n) is the molar mass of the exchanger and 'n' represents external water molecules. The value of 'n' was calculated as 24. So the formula of the sensor would be

$$[(TiO_2)_{3.41}(H_3VO_3)_3(H_3WO_4)_{16.802}]\cdot 24H_2O$$

The molecular weight of the exchanger was deduced and it was 2447.62 a.m.u. The weight loss of 16 % was further observed upto 550 °C. This weight loss was due to rearrangement of coordinated water, hydroxyl molecules and other functional groups. A regular trend in the weight loss was noticed even upto 800 °C *i.e.* 21 % which was due to loss of coordinated water and hydroxyl groups.

X-ray diffraction studies proved lack of particular angle of diffraction line and it was concluded that the heteropoly acid salt is amorphous in nature. Scanning electron microscopic studies revealed that the particles of heteropoly acid *i.e.* Ti(IV) tungstovanadate (a) have an irregular shape, (b) don't have crystalline structure and (c) are broad in size.

Effect of membrane composition: The electrode is characterized on the basis of different parameters like response time, measuring range and slope of calibration curve. The results are given in Table-3. As seen from the results, the best response was shown by the electrode with 60 % composition having very less response time (< 10 s) and measuring range of 10^{-7} to 10^{-1} M.

Calibration curve and statistical data: The selected electrode was used to measure EMF for different concentrations of Cd^{2+} ions. The best response was shown by the electrode with Ti(IV) tungstovanadate (60 %) and epoxy 40 % in the concentration range of 10^{-7} to 10^{-1} M Cd^{2+} ion with a slope of 21 mV/decade. The electrode shows a fast response time of less than 10 s. Whereas the electrode with composition 40 % and 50 % shows a Nernstian slope in the range of 18-19 mV/decade in the concentration range of 10^{-6} to 10^{-1} M with response time of 14 and 15 s. A standard deviation of ± 1.0 mV/decade was observed. EMFs were plotted against log of activities of the cadmium ion. The intersection of the two extrapolated linear portions of the curve [50] shows the detection limit of the electrode. The measurement range remains the same whether the EMF is measured from higher to lower or lower to higher concentration.

Effects of internal solution concentration and pH of the solution: It is clearly visible from Fig. 5 that behaviour of the electrode remains unaffected by change in the concentration. There is an expected change in the intercept of the calibration curve which is same as observed by Kumar *et al.* [51]. Results are given in Table-3.

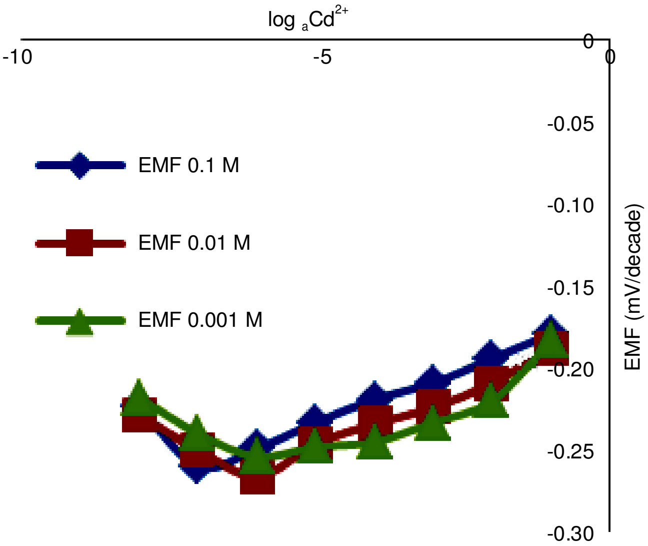

Fig. 5. Effect of internal solution on the electrode (60 %) based on titanium(IV) tungstovanadate selective for Cd^{2+} ions

To check the effect of pH on the performance of electrode, few drops of 0.01 M HCl and 0.01 M NaOH were introduced in the testing solution and the potential was determined over a pH range of 2-12 with 1×10^{-2} M external concentration of Cd^{2+} ion. It was found that the sensor works well in the pH range of 2.62 to 8.66. The potential remains the same even with change of pH from acidic to basic (Fig. 6).

Selectivity coefficient of Cd^{2+} selective electrode: Values for selectivity coefficient helps to find the response of elecro-active material even when other interfering metal ions are present. Selectivity coefficient of electrode was determined with fixed interference method (FIM) [52,53]. The interfering ion solutions with concentration 2×10^{-3} M and 2×10^{-4} M solutions were mixed with 2×10^{-1} to 2×10^{-8} M solutions of Cd^{2+} ions. The equation used for calculating values for selectivity coefficient is as below:

$$K_{A,B}^{POT} = \frac{a_A}{(a_A)z_A / z_B}$$

The selectivity coefficient values (Table-4) indicate that the developed sensor exhibits highest selectivity for Cd(II) ions over a number of cations but it is only moderately selective in the presence of Mn(II) ions.

TABLE-3
EFFECT OF INTERNAL SOLUTION CONCENTRATION ON THE RESPONSE OF ELECTRODE BASED ON TITANIUM(IV) TUNGSTOVANADATE

Solution No.	Concentration of internal solution (M)	Membrane composition (%)	Slope (mV/decade)	Response time (s)	Detection limit (M)
1	1.0×10^{-1}	60	21	10	10^{-7}
	1.0×10^{-1}	50	18	14	10^{-6}
	1.0×10^{-1}	40	19	14	$10^{-6.4}$
2	1.0×10^{-2}	60	17	12	$10^{-6.2}$
	1.0×10^{-2}	50	10	16	10^{-7}
	1.0×10^{-2}	40	12	17	$10^{-6.2}$
3	1.0×10^{-3}	60	19	15	$10^{-6.2}$
	1.0×10^{-3}	50	12	15	$10^{-6.3}$
	1.0×10^{-3}	40	15	13	$10^{-6.4}$

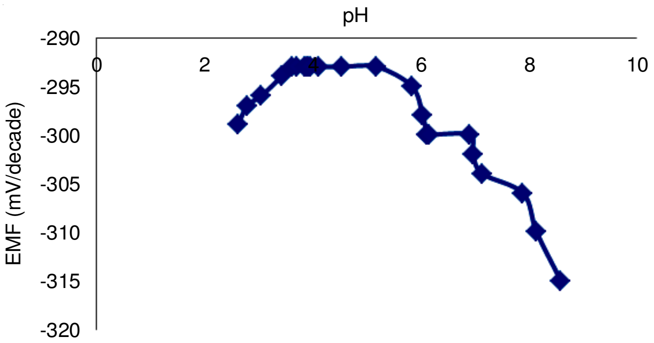

Fig. 6. Effect of change of pH on the response of Cd^{2+} selective electrode based on titanium(IV) tungstovanadate

TABLE-4
SELECTIVITY COEFFICIENT FOR Cd^{2+} SELECTIVE ELECTROACTIVE SENSOR BASED ON TITANIUM(IV) TUNGSTOVANADATE

Interfering ion (B)	Selectivity coefficient values	$K^{POT}_{A,B}$
	Interfering ion solution (2×10^{-3}M)	Interfering ion solution (2×10^{-4}M)
Pb^{2+}	0.445	0.204
Ni^{2+}	0.301	0.230
Cu^{2+}	0.334	0.230
Sm^{3+}	0.494	0.411
La^{2+}	0.398	0.369
Cr^{3+}	0.754	0.376
Co^{2+}	0.301	0.176
Mn^{2+}	0.361	0.010
Hg^{2+}	0.345	0.245
As^{3+}	0.338	0.289

Effect of partial non-aqueous solutions and analytical applications: The working of electrode was also studied in solvents like methanol, ethanol and acetone with water (partially non-aqueous medium). The calibration curves are plotted to check the response of the electrode with 10 %, 20 %, 30 % methanol, ethanol and acetone (Fig. 7, Table-5). Results show that there is no change in the slope with partially non-aqueous solvents so the electrode can be successfully used in partially non-aqueous solvent also. The sensor was also used as indicator electrode in the potentiometric titrations for EDTA and oxalic acid solutions. For this purpose 5.0×10^{-3} oxalic acid/5.0×10^{-3} M EDTA was used (Fig. 8). The sharp inflection point at the titrant volume confirms the presence of 1:1 volume.

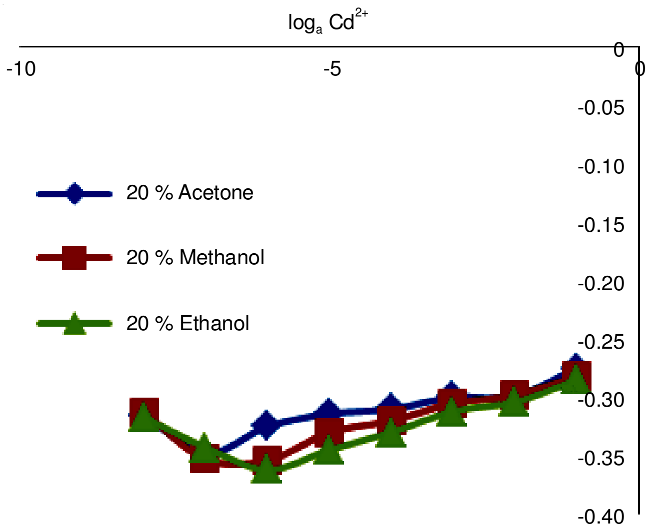

Fig. 7. Effect of partially non aqueous solvents on Cd^{2+} selective electrode based on titanium(IV) tungstovanadate

TABLE-5
EFFECT OF PARTIALLY NON-AQUEOUS SOLVENTS ON Cd^{2+} SELECTIVE ELECTRODE BASED ON TITANIUM(IV) TUNGSTOVNADATE

Name of solvent used	% (v/v)	Slope (m/V) decade	Range of measuring (M)
Acetone	10 %	19.8	10^{-7} to10^{-1}
	20 %	19.9	10^{-7} to 10^{-1}
	30 %	20.0	10^{-7} to 10^{-1}
Ethanol	10 %	20.0	10^{-7} to10^{-1}
	20 %	20.0	10^{-6} to 10^{-1}
	30 %	19.3	10^{-7} to 10^{-1}
Methanol	10 %	20	10^{-7} to 10^{-1}
	20 %	20	10^{-7} to 10^{-1}
	30 %	20	10^{-7} to 10^{-1}

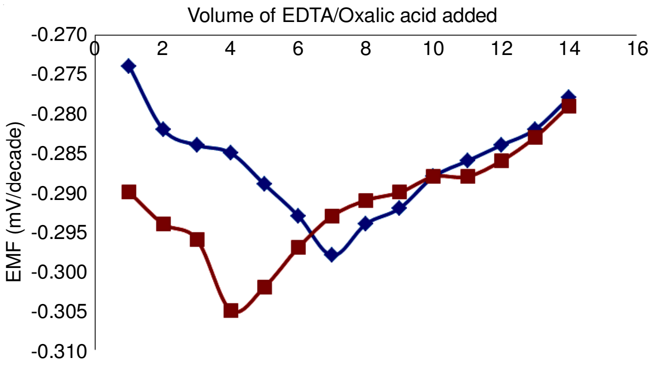

Fig. 8. Potentiometric titration curve using proposed sensor as an indicator electrode (5×10^{-3} M oxalic acid/5×10^{-3} M EDTA)

Response time and life time: Response time is the average time required time for the sensor to reach a potential with in ± 1 mV/decade for final equilibrium value and was found to be < 10 s. For the determination of the life time of the electrode, the potential measurement were made each and every day by keeping the electrode in standard solution. The slope of the calibration curve was determined every time. It was found that the slope remained the same for a period of 6 months for the detection of cadmium(II)ions. It can be also used as an indicator electrode.

Conclusion

Titanium(IV)tungstvanadate can be successfully used as an electrode for making a cadmium(II) selective membrane electrode. The electrode has reasonably good lifetime, detection limit, pH range, selectivity coefficient and can be used as an indicator electrode also.

REFERENCES

1. K.H. Wedepohl, *Geochim. Cosmochim. Acta*, **59**, 1217 (1995); https://doi.org/10.1016/0016-7037(95)00038-2.
2. M.O. Roll, Geological Survey- Mineral Commodity Summaries, USA (2012).
3. L. Friberg, *Annu. Rev. Public Health*, **4**, 367 (1983); https://doi.org/10.1146/annurev.pu.04.050183.002055.

4. G.F. Nordberg, K. Nogawa, M. Nordberg, L. Friberg and B.M. Fowler, Handbook on the Toxicology of Metals, Academic Press, edn 3, p. 445 (2007).
5. D.R. Abernethy, A.J. De Stefano, T.L. Cecil, K. Zaidi and R.L. Williams, *Pharm. Res.*, **27**, 750 (2010); https://doi.org/10.1007/s11095-010-0080-3.
6. M. Nordberg and G.F. Nordberg, Heavy Metals in the Environment, Chap. 8, p. 231 (2002).
7. A. Buha, Z. Bulat and D. Dukic-Cosic and V. Matovic, *Arch. Ind. Hygiene Toxicol.*, **62**, 65 (2011); 10.2478/10004-1254-63-2012-2217
8. R.C. Patra, A.K. Rautray and D. Swarup, *Vet. Med. Int.*, Article ID 457327 (2011); https://doi.org/10.4061/2011/457327.
9. A. Cuypers, M. Plusquin, T. Remans, M. Jozefczak, E. Keunen, H. Gielen, K. Opdenakker, A.R. Nair, E. Munters, T.J. Artois, T. Nawrot, J. Vangronsveld and K. Smeets, *Biometals*, **23**, 927 (2010); https://doi.org/10.1007/s10534-010-9329-x.
10. M. Abdulla and J. Chmielnicka, *Biol. Trace Elem. Res.*, **23**, 25 (1989); https://doi.org/10.1007/BF02917176.
11. J.M. Moulis, *Biometals*, **23**, 877 (2010); https://doi.org/10.1007/s10534-010-9336-y.
12. G.S. Shukla and R.L. Singhal, *Can. J. Physiol. Pharmacol.*, **62**, 1015 (1984); https://doi.org/10.1139/y84-171.
13. A. Schauder, A. Avital and Z. Malik, *J. Environ. Pathol. Toxicol. Oncol.*, **29**, 137 (2010); https://doi.org/10.1615/JEnvironPatholToxicolOncol.v29.i2.70.
14. G. Cannino, E. Ferruggia, C. Luparello and A.M. Rinaldi, *Mitochondrion*, **9**, 377 (2009); https://doi.org/10.1016/j.mito.2009.08.009.
15. F. Thevenod, *Nephron*, **93**, 87 (2003); https://doi.org/10.1159/000070241.
16. M.L. Robles-Osorio and E. Sabath, *Nefrologia*, **36**, 577 (2016); https://doi.org/10.1016/j.nefro.2016.05.004.
17. E.F. Madden and B.A. Fowler, *Drug Chem. Toxicol.*, **23**, 1 (2000); https://doi.org/10.1081/DCT-100100098.
18. Y. Fujiwara, J.Y. Lee, M. Tokumoto and M. Satoh, *Biol. Pharm. Bull.*, **35**, 1892 (2012); https://doi.org/10.1248/bpb.b212014.
19. A. Akesson, T. Lundh, M. Vahter, P. Bjellerup, J. Lidfeldt, C. Nerbrand, G. Samsioe, U. Strömberg and S. Skerfving, *Environ. Health Perspect.*, **113**, 1627 (2005); https://doi.org/10.1289/ehp.8033.
20. T. Kjellstrom, *IARC Sci. Publ.*, **118**, 301 (1992).
21. E.R. Youness, N.A. Mohammed and F.A. Morsy, *Toxicol. Mech. Methods*, **22**, 560 (2012); https://doi.org/10.3109/15376516.2012.702796.
22. M. Sughis, J. Penders, V. Haufroid, B. Nemery and T.S. Nawrot, *Environ. Health*, **10**, 104 (2011); https://doi.org/10.1186/1476-069X-10-104.
23. M.V. Varoni, D. Palomba, S. Gianorso and V. Anania, *Vet. Res. Commun.*, **27**, 807 (2003); https://doi.org/10.1023/B:VERC.0000014277.06785.6f.
24. S. Abu-Hayyeh, M. Sian, K.G. Jones, A. Manuel and J.T. Powell, *Arterioscler. Thromb. Vasc. Biol.*, **21**, 863 (2001); https://doi.org/10.1161/01.ATV.21.5.863.
25. W.C. Prozialeck, J.R. Edwards and J.M. Woods, *Life Sci.*, **79**, 1493 (2006); https://doi.org/10.1016/j.lfs.2006.05.007.
26. M. Ohsawa, *Yakugaku Zasshi*, **129**, 305 (2009); https://doi.org/10.1248/yakushi.129.305.
27. M. Fortier, F. Omara, J. Bernier, P. Brousseau and M. Fournier, *J. Toxicol. Environ. Health*, **71**, 1327 (2008); https://doi.org/10.1080/15287390802240918.
28. S.A. Nabi and M. Naushad, *Chem. Eng. J.*, **158**, 100 (2010); https://doi.org/10.1016/j.cej.2009.12.011.
29. M. El-Naggar, E.S. Zakaria, I.M. Ali, M. Khalil and M.F. El-Shahat, *Arab. J. Chem.*, **5**, 109 (2012); https://doi.org/10.1016/j.arabjc.2010.09.028.
30. A.A. Khan, M. Khalid and U. Baig, *React. Funct. Polym.*, **70**, 849 (2010); https://doi.org/10.1016/j.reactfunctpolym.2010.07.020.
31. E.S. Zakaria, I.M. Ali and I.M. El-Naggar, *Colloids Surf A*, **210**, 33 (2002); https://doi.org/10.1016/S0927-7757(02)00216-9.
32. M. Qureshi and V. Kumar, *Chromatogr. J.*, **62**, 431 (1971); https://doi.org/10.1016/S0021-9673(00)91395-5.
33. Z.M. Siddiqi and D. Pathania, *Chromatogr. J.*, **987**, 147 (2003); https://doi.org/10.1016/S0021-9673(02)01659-X.
34. S.A. Nabi, A.H. Shalla, A.M. Khan and S.A. Ganie, *Colloids Surf A*, **302**, 241 (2007); https://doi.org/10.1016/j.colsurfa.2007.02.034.
35. M. Qureshi and S.A. Nabi, *J. Inorg. Nucl. Chem.*, **32**, 2059 (1970); https://doi.org/10.1016/0022-1902(70)80614-5.
36. H.K. Sharma, P. Dogra, A. Kumar and F. Koohyar, *Quim. Nova*, **37**, 1324 (2014); https://doi.org/10.5935/0100-4042.20140198.
37. H.K. Sharma, P. Dogra and N. Sharma, *Res. J. Chem. Environ.*, **15**, 897 (2011).
38. H.K. Sharma and N. Sharma, *E-J. Chem.*, **6**, 1139 (2009); https://doi.org/10.1155/2009/301016.
39. S.K. Mittal, R. Kumar, P. Dogra and H.K. Sharma, *Res. J. Chem. Environ.*, **11**, 47 (2007).
40. K.S. Harish, V. Neha and J.K. Kapoor, *E-J. Chem.*, **8**, 155 (2011); https://doi.org/10.1155/2011/358039.
41. E. Bakker, *Electroanalysis*, **9**, 7 (1997); https://doi.org/10.1002/elan.1140090103.
42. H.K. Sharma and P. Dogra, *Am. Chem. Sci. J.*, **4**, 457 (2014); https://doi.org/10.9734/ACSJ/2014/5527.
43. C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, p. 353 (1963).
44. J.R.S. Brownson, M.I. Tejedor-Tejedor and M.A. Anderson, *Chem. Mater.*, **17**, 6304 (2005); https://doi.org/10.1021/cm051568f.
45. Y. Gao, Y. Masuda, W.S. Seo, H. Ohta and K. Koumoto, *Ceram. Int.*, **30**, 1365 (2004); https://doi.org/10.1016/j.ceramint.2003.12.105.
46. G.V. Jere and C.C. Patel, *Can. J. Rev. Chem. Rev. Can. Chim.*, **40**, 1576 (1962); https://doi.org/10.1139/v62-238.
47. T. Busani and R A B. Devine, *Semicond. Sci. Technol.*, **20**, 870 (2005); https://doi.org/10.1088/0268-1242/20/8/043.
48. D.P. Padiyan, S.J. Ethilton and R. Murugesan, *Phys. Status Solidi (a)*, **185**, 231 (2001); https://doi.org/10.1002/1521-396X(200106)185:2<231::AID-PSSA231>3.0.CO;2-8.
49. C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983); https://doi.org/10.1021/ic00144a006.
50. G. Alberti, P. Cardini-Galli, U. Costantino and E. Torracca, *J. Inorg. Nucl. Chem.*, **29**, 571 (1967); https://doi.org/10.1016/0022-1902(67)80063-0.
51. H.K. Sharma and N. Sharma, *Int. Res. J. Pure Appl. Chem.*, **4**, 118 (2014); https://doi.org/10.9734/IRJPAC/2014/4347.
52. R. Kumar, H.K. Sharma and P. Dogra, *Int. J. Environ. Anal. Chem.*, **91**, 280 (2011); https://doi.org/10.1080/03067310903278528.
53. Y. Umezawa, K. Umezawa and H. Sato, *Pure Appl. Chem.*, **67**, 507 (1995); https://doi.org/10.1351/pac199567030507.