

# A Novel Carbon Paste Electrode for Potentiometric Determination of Vanadyl Ion

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**ABSTRACT:** Carbon paste electrode was modified by disodium 2,4-diamino-7-methylbenzo[g]pteridine-5,10-dioxide to fabricate a sensor for potentiometric determination of vanadyl ion ( $VO^{2+}$ ) in aqueous medium. The new ligand was synthesized in three steps with high yield. The optimal composition of the carbon paste was made of graphite powder (64.5%), ionophore (16.6%), paraffin oil (17.8%), and sodium tetraphenylborate (NaTPB, 1.1%). The electrode exhibited a constant sensitivity of  $30.20 \pm 0.5$  mV to  $VO^{2+}$  ions over a concentration range of 5  $\mu$ M to 1 mM. The detection limit was calculated to be 5  $\mu$ M with a response time of less than 35 s. The electrode showed to be highly reproducible over a period of 3 weeks. This sensor exhibits high selectivity to  $VO^{2+}$  ions and was successfully employed for potentiometric titration of  $VO^{2+}$  ions with EDTA.

**KEY WORDS:** Carbon paste electrode, Potentiometry, Vanadyl ion, 2,4-diamino-7-methylbenzo[g]pteridine- 5,10-dioxide.

## INTRODUCTION

Vanadium is a trace element that is believed to have an essential role in normal cell growth, but at  $\mu$ g/mL concentrations can be considered as a serious threat to environment [1]. The main sources of pollution are vanadium refining industries, alloy industries, fossil fuel

combustion process and wastes of steel-industry slags. The toxicity of vanadium is dependent on its oxidation state [2,3]. For instance, V(V) as vanadate is more toxic than V(IV). Although vanadium can exist in different oxidation states from II to V in aqueous solutions,

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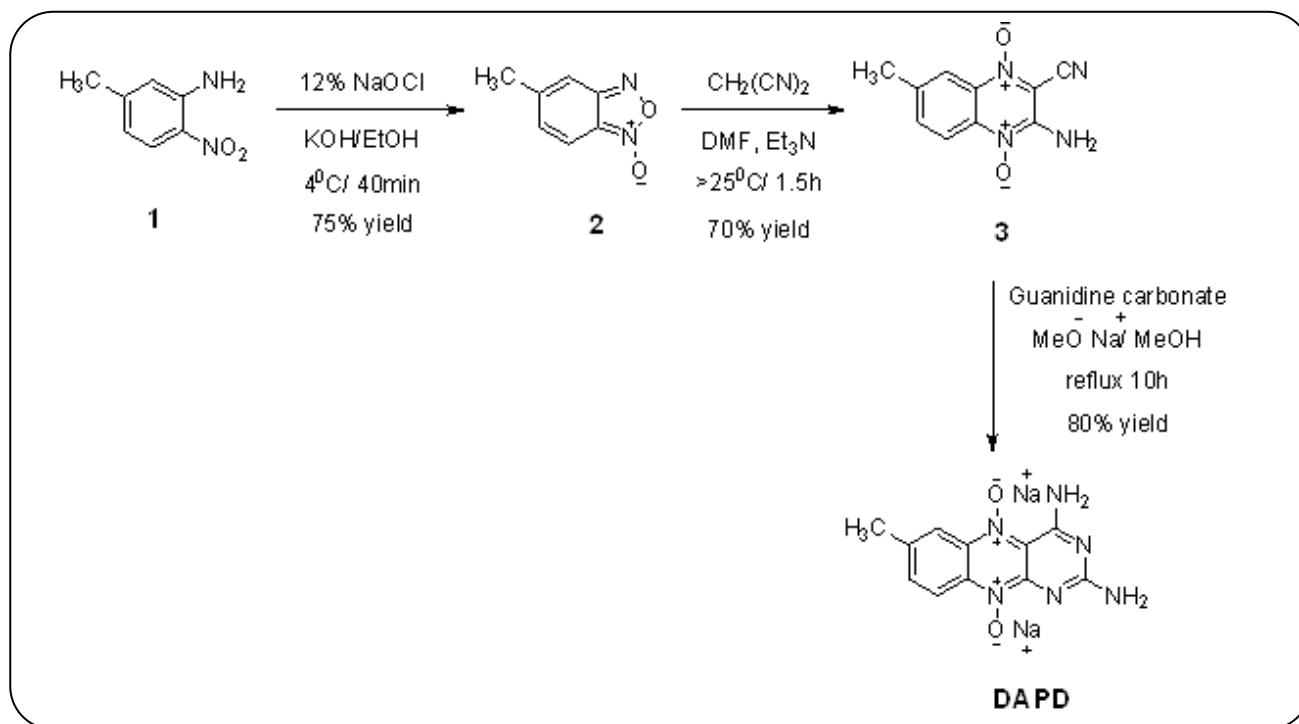


Fig. 1: Scheme of synthesis of DAPD.

more attention has been paid to its determination in oxidation states of IV and V as they are commonly found in inorganic and biological systems. V(IV) is usually found in the form of oxovanadium,  $\text{VO}^{2+}$ . There are different methods for determination of vanadyl.

Several methods have been used to determine vanadium species, including dispersive liquid-liquid microextraction coupled with digital colorimetry [19], electrothermal atomic absorption spectrometry [20,21], Inductively Coupled Plasma (ICP) detection [22] ion selective electrode [17].

Among them, potentiometric methods using Ion Selective Electrodes (ISE) are very attractive strategy as they allow direct determination of ion concentration in liquid samples and provide various benefits including high selectivity, simplicity and fast responses. There are a few reports on carbon paste electrode developed for  $\text{VO}^{2+}$  ion [6], PVC-based DAN [4], arene [5], Tri-n-octylphosphine oxide [16] and thiacalix [4] arene [18].

Recent advances in this field have shown that ionophores could provide conditions for specific interactions between the sensor and the target metal ion. The results shows that the new ligand, 2,4-diamino-7-methylbenzo[g] pteridine-5,10-dioxide (DAPD), illustrated in Fig. 1,

can be used as an ionophore for construction of a novel carbon paste electrode for vanadyl ion.

## EXPERIMENTAL SECTION

### Reagents and materials

All the chemical used in this work were purchased from Merck (Darmshtate-Germany). Multiwalled carbon nanotube was purchased from Fluka. Double distilled water was used for preparing all the aqueous solutions.

### Apparatus

Melting points were recorded on an electro thermal type 9100 melting point apparatus. The IR spectra were obtained on a AVATAR 370 FT-IR Thermo Nicolet Spectrometer. Elemental analysis was performed using a Thermo Finnigan Flash EA microanalyzer. A Velp Scientifica model:F20520162 Stirrer was used for stirring the solutions.

### Electrode preparation

Graphite powder (175 mg), ionophore (45 mg), NaTPB (3 mg) and paraffin oil (60  $\mu\text{L}$ ) were thoroughly mixed to produce a uniform paste. The electrode body was made of a disposable polyethylene 1 mL syringe.

To construct electrodes with thicker bodies, the tip of the syringe was cut off with a razor blade. Smooth surfaces were obtained by applying manual pressure to the piston while holding the electrode surface against a smooth solid support. A fresh electrode surface was obtained by squeezing out a small amounts of paste, scrapping off the excess against a conventional paper and polishing the electrode on a smooth paper to obtain a shiny appearance. The electrical connection was made with a copper wire and the electrode was kept at room temperature for about 3 h and was finally conditioned for 22 h by soaking in 1 mM VOSO<sub>4</sub> solution.

### Potentiometric measurements

All potentiometric measurements were carried out with the following assembly at 25.0 ± 0.1 °C:

Ag // AgCl, (KCl, Stad) || VO<sup>2+</sup> sample solution / carbon paste electrode

The reference electrode was obtained from Metrohm. pH Adjustments were made using a solutions of H<sub>2</sub>SO<sub>4</sub> and NaOH.

## RESULTS AND DISCUSSION

### Preparation of DAPD

DAPD synthesis was fulfilled in three steps. First, 5-Methyl-benzo(1,2,5)oxadiazole 1-oxide was synthesized from 4-Methyl-2-nitro-aniline and sodium hypochlorite in a solution of sodium hydroxide in 96% ethanol. The product was purified by recrystallization with 70% ethanol to produce compound **2** (75% yield) as small yellow needles and mp of 95-96 °C [7]. Subsequent reaction of compound **2** with malononitrile in DMF in the presence of Et<sub>3</sub>N, produced 3-amino-6-methyl-2-quinoxalinecarbonitrile-1,4-dioxide as a red solid with 70% yield and m.p. of 241-242°C. <sup>1</sup>H NMR (100 MHz, DMSO) showed the following chemical shifts δ: 2.55 (s, 3H, CH<sub>3</sub>), 7.40-7.53 (m, 1H, H<sub>7</sub> arom.), 7.69-7.82 (m, 1H, H<sub>8</sub> arom.), 7.90-8.15 (m, 3H, H<sub>5</sub> arom. and NH<sub>2</sub>). The IR spectrum showed peaks at ν<sub>max</sub> (cm<sup>-1</sup>) 3330, 3272, 2234, 1337 cm<sup>-1</sup>. Finally, condensation of **3** with guanidine carbonate in boiling dry methanol, in the presence of sodium methoxide, produced disodium 2,4-diamino-7-methylbenzo[g] pteridine-5,10-dioxide (DAPD) as a green solid with 80% yield and m.p. of greater than 300°C. The IR spectrum of this compound showed disappearance of CN bond of compound **2** (Fig. 2).

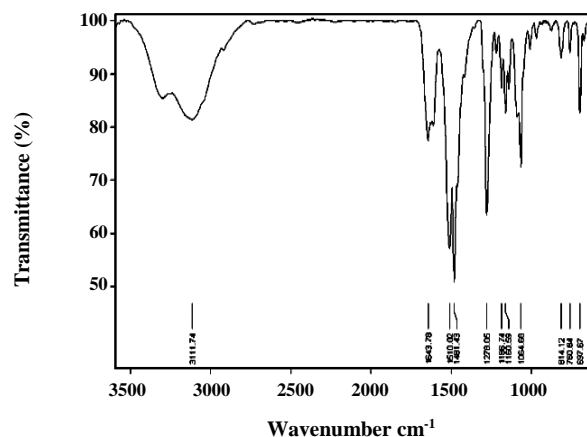


Fig. 2: The IR spectrum of DAPD.

Because DAPD is salt, it is not soluble in any organic solvent to obtain the NMR spectrum. Due to the ionic nature of this compound and the presence of its ionic bonds, DAPD has a high melting point and therefore, its mass spectrum couldnot be established.

IR ν<sub>max</sub> (cm<sup>-1</sup>) 3297, 3119, 2921, 1642, 1278 cm<sup>-1</sup>; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>2</sub>: C, 42.43; H 3.31; N, 27.63; Found: C, 44.32; H, 2.88; N, 24.99.

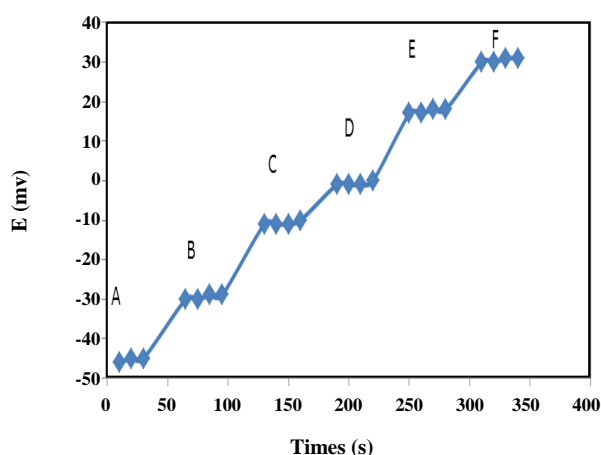
### Effect of carbon paste composition

It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the electrode composition and the properties of the additives employed[8,9]. Thus, the influence of the carbon past electrode composition, nature and amount of carbon (graphite and nanotube), the amount of paraffine oil and NaTPB as lipophilic additive on the potential response of the electrode was thoroughly investigated. Several electrode were prepared with different compositions and the optimized electrode compositions are summarized in Table 1.

As can be seen the use of 17.8% paraffin oil in the presence of 64.5% graphite powder, 16.6% ionophore and 1.1% NaTPB (No .6, Table 1) results in best sensitivity, with a Nernstian slope of 30.20 ± 0.5 mV per decade with a good correlation coefficient. It should be noted that the presence of a lipophilic anion in carbon paste electrode not only diminishes the ohmic resistance and enhances the response behavior and selectivity but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes [10,11].

Table 1: Optimization of paste ingredients.

NO.	Graphite (Wt%)	MWCNT (Wt%)	Paraffine oil (Wt%)	Ionophore (Wt%)	NaTPB (Wt%)	Slope	Linear range	r 2
1	68	0	9.9	21	1.1	43.5	5 $\mu$ M to 1 mM	0.925
2	69	0	17	12.9	1.1	20.1	0.5 $\mu$ M to 1 mM	0.971
3	67	0	12.9	19	1.1	35.1	5 $\mu$ M to 1 mM	0.947
4	62	0	16.9	20	1.1	15.4	5 $\mu$ M to 1 mM	0.791
5	64.5	0	17.8	16.6	1.1	30.2	5 $\mu$ M to 1 mM	0.995
6	63	2.3	17	16.6	1.1	15.2	5 $\mu$ M to 0.5 mM	0.980
7	64	3.7	21.7	9.5	1.1	33.5	5 $\mu$ M to 1 mM	0.888
8	61	5.6	22.5	9.8	1.1	24.2	1 $\mu$ M to 0.5 mM	0.919
9	56	3.7	23	16.2	1.1	36.9	0.5 $\mu$ M to 0.5 mM	0.880
10	59	4.4	22.7	12.7	1.2	26.9	1 $\mu$ M to 0.5 mM	0.831
11	55	5.6	22.1	16.2	1.1	30.8	10 $\mu$ M to 0.5 mM	0.853
12	65.2	0	18.2	16.6	0	18.9	5 $\mu$ M to 1 mM	0.984

Fig. 3: Dynamic response of membrane electrode for step change in concentration of  $VO^{2+}$ .

#### Response time

Dynamic response time is an important factor for an ISE. The practical response time was recorded by changing the  $VO^{2+}$  concentration over a concentration range of 5 to 1000  $\mu$ M. The actual potential versus time is shown in Fig. 3. As seen, the electrode reaches the equilibrium response in less than 35 s over the entire concentration range.

#### Potentiometric selectivity

Fig. 5 clearly shows the selective behavior of the Carbon paste electrodes based on DAPD for  $VO^{2+}$  ion

in respect with other cationic species. The selectivity coefficients of the proposed paste selective electrode were determined against a number of interfering ions by mixed solution method[12]. In this method, the potentiometric selectivity coefficients ( $K^{Pot}_{VO^{2+}}$ ) were evaluated from potential measurements on solutions containing a fixed amount of  $VO^{2+}$  ion (0.1 mM) and varying amounts of the interfering ions ( $M^{n+}$ ) according to the following equation:

$$K^{Pot}_{VO^{2+},M} a^{2/n}_M = a_{VO^{2+}} \{ \exp [(E_2 - E_1)F/RT] - a_{VO^{2+}} \} \quad (1)$$

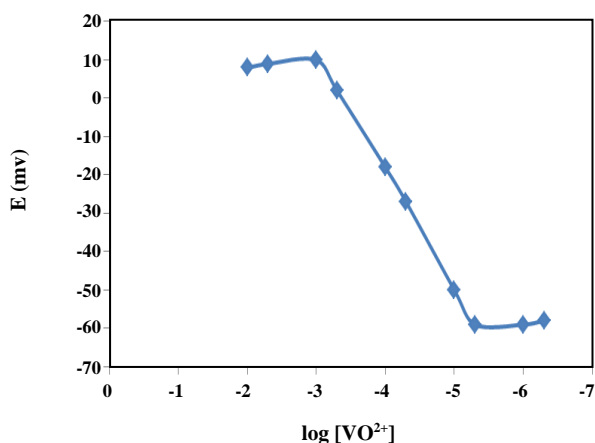
where  $E_1$  and  $E_2$  are the measured e.m.f. for the solution of  $VO^{2+}$  ions alone and for the mixed solution, respectively,  $K^{Pot}_{VO^{2+},M}$  is the Nikolskii coefficient,  $a_{VO^{2+}}$  and  $a^{2/n}_M$  the sample activities of the primary ion ( $VO^{2+}$ ) and interfering ion ( $M^{n+}$ ) and R, T and F have their usual meanings. According to Eq. (1),  $K^{Pot}_{VO^{2+},M}$  can be evaluated from the slope of the graph of  $a_{VO^{2+}} \{ \exp [(E_2 - E_1)F/RT] - a_{VO^{2+}} \}$  versus  $a^{2/n}_M$ . The data in Table 2 show that the selectivity coefficient of different interfering ions for the proposed carbon paste electrodes based on DAPD for  $VO^{2+}$  ion are in the order of  $10^{-1}$  or lower indicating that they would not significantly interfere in functioning of the  $VO^{2+}$  ion-selective electrode.

#### Effect of pH

The influence of pH on the potential response of 0.1mM vanadyl ion sensor was investigated in the pH

Table 2: Selectivity coefficients of various interfering ions ( $M^{n+}$ ).

$M^{n+}$	Selectivity of coefficients
$Ni^{2+}$	$8.2 \times 10^{-2}$
$Mn^{2+}$	$4.1 \times 10^{-2}$
$Cr^{3+}$	$4.4 \times 10^{-2}$
$Zn^{2+}$	$8 \times 10^{-4}$
$Ca^{2+}$	$7.2 \times 10^{-3}$
$Sr^{2+}$	$9.3 \times 10^{-3}$
$Co^{2+}$	$1.09 \times 10^{-2}$
$Al^{3+}$	$2.4 \times 10^{-2}$
$Na^+$	$5.9 \times 10^{-1}$
$K^+$	$6.7 \times 10^{-1}$
$NH_4^+$	$1.2 \times 10^{-1}$

Fig. 4: Calibration graph for the proposed  $VO^{2+}$  ion-selective electrode.

range of 1.5–7 (Fig. 6). As shown in Fig. 6, the potential remained constant within the pH range of 4.0–6.5 but a drastic decrease was observed between 1.5 to 4. The observed change in potential response at lower pH values (than 4) may be due to the protonation of the ionophore and responding the electrode to hydrogen ions as an interfering species, and hence resulting in an increased potential by increasing the acidity of the solution[13]. At pHs higher than 6.5 vanadyl ion is converted to other oxidation forms of vanadium. Based on pourbaix diagram, more details about the effect of pH on other species of vanadium ions have been previously reported[14].

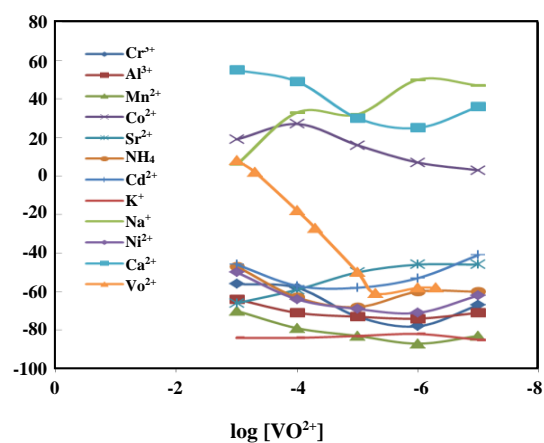


Fig. 5: Potential response of various metal ion-selective electrodes based on 2,4-diamino-7-methylbenzo[g]pteridine-5,10-dioxide.

#### Calibration curve

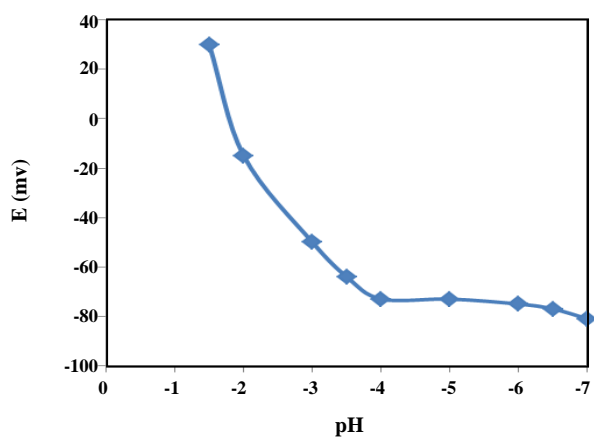
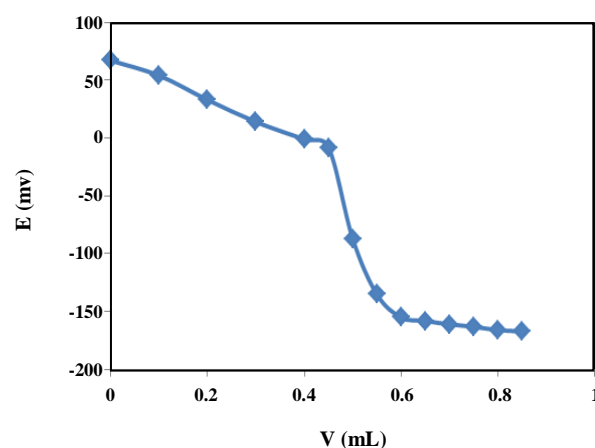
The potential response of the carbon paste electrode based on DAPD is shown in Fig. 4. The e.m.f. vs. the negative logarithm of  $VO^{2+}$  concentration in the carbon paste based on DAPD, indicated a rectilinear range from 5  $\mu$ M to 1 mM. The slope of the calibration curve was  $30.20 \pm 0.5$  mV per decade of  $VO^{2+}$  concentration. The limit of detection calculated from the intersection of the two extrapolated segments of the calibration graph, was 5  $\mu$ M. The standard deviation of four replicate measurements is  $\pm 0.5$  mV. The prepared carbon paste electrodes could be used for 3 weeks without any measurable change in their potentials.

**Table 3: Result of determination of vanadyl in tap water.**

Sample	Added vanadyl(mM)	Found vanadyl(mM)	Recovery (%)
Tap water	-	Detection limit>	-
Tap water	0.1	0.095	95.0
Tap water	0.01	0.0104	104.0

**Table 4: Comparison of some VO<sub>2</sub><sup>+</sup> electrode parameters.**

Reference	Linear range	Detection limit	pH range	Slope (mV per decade)	Application
[15]	10 $\mu$ M to 100 mM	-	1.8 – 2.5	29.1	Potentiometric titration
[16]	10 $\mu$ M to 10 mM	1 $\mu$ M	3.5 - 6	29.5	-
[4]	10 $\mu$ M to 100 mM	7.9 $\mu$ M	2.8 - 4	29.7	Potentiometric titration
[17]	0.11 $\mu$ M to 110 mM	0.11 $\mu$ M	2.5 - 4	29.3	Spiked sample
[5]	10 $\mu$ M to 100 mM	3.9 $\mu$ M	3.0–6.0	29.9	Spiked sample
This Work	5 $\mu$ M to 10 mM	5 $\mu$ M	4.0 - 6.5	30.2	Potentiometric titration and Spiked sample

**Fig. 6: Effect of pH of test solution on the potential response of the VO<sub>2</sub><sup>+</sup> selective electrode at 0.1 mM of VO<sub>2</sub><sup>+</sup>.****Fig. 7: Potentiometric titration curve of 10 mL of 0.5 mM VO<sub>2</sub><sup>+</sup> solution with 0.01 M EDTA, using the proposed electrode as an indicator electrode.**

#### Potentiometric titration

The proposed VO<sub>2</sub><sup>+</sup>carbon paste electrode was successfully applied for titration of VO<sub>2</sub><sup>+</sup> (0.5 mM, 10 mL) with EDTA (1×10<sup>-2</sup> M) at pH 4.5. The addition of EDTA to VO<sub>2</sub><sup>+</sup> solution causes the formation of a stable VO<sub>2</sub><sup>+</sup> EDTA complex, resulting in a decrease of VO<sub>2</sub><sup>+</sup> concentration and thereby a decrease in cell potential. Fig. 7 shows that of VO<sub>2</sub><sup>+</sup> ions in solution can be determined accurately by the proposed ion-selective electrode.

#### Analytical application

The proposed VO<sub>2</sub><sup>+</sup>carbon paste electrode was applied to obtain recovery of VO<sub>2</sub><sup>+</sup> in tap water sample with

satisfactory results. The results are summarized in Table 3. Good recovery was obtained for tap water.

#### CONCLUSIONS

The construction of a sensor is reported using a newly synthesized ionophore for potentiometric determination of VO<sub>2</sub><sup>+</sup> ion. The electrode has a fast response time and good Nernstian behavior over a wide concentration range with good selectivity. The electrode was successfully applied as an indicator electrode in potentiometric titration. Table 4 compares the electrode characteristics with other works.

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