



## Construction of an Ion-Selective Electrode for Determination of permanganate Ion

V. Zare Shahabadi <sup>a,\*</sup> and F. Abbasitababar <sup>b</sup>

<sup>a</sup> Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran.

<sup>b</sup> Department of Chemistry, Marvdasht Branch, Islamic Azad University, Marvdasht, Fars, Iran

### Abstract

A PVC ion-selective membrane electrode based on Cd-tetraphenyl porphyrine as a carrier was prepared for determination of  $MnO_4^-$  ion. This electrode revealed good selectivity toward permanganate ion over a wide variety of anions. Effects of some experimental parameters such as nature of the plasticizer, the amounts of carrier and additive, and concentration of the internal solution on the potential response of the proposed sensor were investigated. The electrode exhibited a sub-Nernstian slope of  $51.0 \pm 1.0$  mV per decade for  $MnO_4^-$  over a concentration range of  $3.3 \times 10^{-6}$ – $7.5 \times 10^{-2}$  M in the pH range 5.0–10.0. The detection limit and response time of the electrode were  $1.7 \times 10^{-6}$  M and 14 s, respectively. The electrode can be used within 3 days without any considerable divergence in its potential. This electrode was successfully employed for indirect determination of Mn(II).

**Keyword:** Cd- Tetraphenyl Porphyrin, Permanganate Determination, Ion-Selective Electrode, PVC Membrane Electrode.

### Introduction

Manganese appears to be an essential trace element for all living organisms. Its concentration in organisms primarily depends on the species. It is particularly stored and concentrated in tissues rich in mitochondria. Manganese, a co-factor for the enzyme pyruvate carboxylase [1], is also thought to act as a nonspecific activator for the enzymes succinate dehydrogenase, prolidase, arginase, alkaline phosphatase, farnesyl pyrophatase, superoxide dismutase, glycosyl tranferases, and adenosine triphosphatases [2]. Manganese deficiency in animals causes impaired growth, skeletal abnormalities, and changes the metabolism of carbohydrates and lipids [3]. Furthermore manganese is considered as an essential trace element for humans however there is no direct evidence for this [4].

The presence of manganese can be detected by measuring the absorbance of permanganate

produced through an oxidation reaction between Mn(II) and periodate in acidic solution. In the present work, a permanganate ion-selective electrode based on Cd-tetraphenyl porphyrin (Cd-TPP) was developed and employed for indirect determination of Mn(II). To the best of our knowledge, there is only one report on developing a permanganate ion-selective electrode [5].

### Experimental section

#### Reagents

Dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl sebacate (DBS), dibutyl phthalate (DBP), dioctyl sebacate (DOS), poly(vinyl chloride) (PVC), tetrahydrofuran (THF) and cetyl trimethyl ammonium bromide (CTAB), were obtained from Fluka or Merck companies.

Cd-TPP used as carrier in the proposed electrode was synthesized and purified as described elsewhere [6]. Doubly distilled deionized water was used throughout the

Corresponding author.  
e-mail: valizare@gmail.com

experiments. Potassium permanganate stock solution was prepared and standardized as described in reference [7]. Potassium and sodium salts of anions provided from Merck or Fluka were used without further purification.

#### Membrane preparation

For preparation of the PVC membrane, the appropriate amounts of PVC (high molecular weight), carrier (Cd-TPP), CTAB, and plasticizer (DES) as solvent mediator were weighted. The mixture was stirred until the PVC was wet and it was then dissolved in 2 ml of THF. The resulting clear mixture was placed to evaporate slowly until an oily concentrated solution obtained. The membrane was prepared by dipping Pyrex tube (3.0 mm internal diameter and 5.0 cm long) into the provided solution for 10 second. The tube was stored for 2 h at 25-30 °C to complete drying. The tube was then

filled with internal filling solution of the interest anion. Finally, the electrode was conditioned by soaking in a solution of the respective anion. A silver-silver chloride coated wire or a calomel reference electrode was used as an internal reference electrode.

#### Electrode system

All emf measurements were carried out with the following assembly:

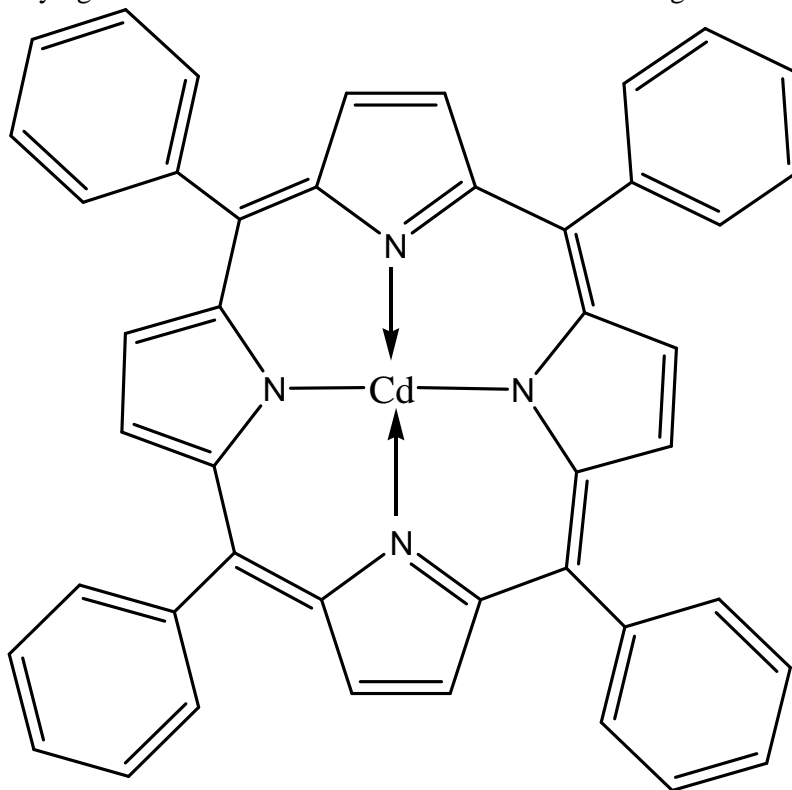
“Ag|AgCl (or SCE)|  $K_n(A)$  (xM) | sensor membrane | test solution | SCE”

A HIOKI digital hitester (Model 3256-01) was used for measuring the potential.

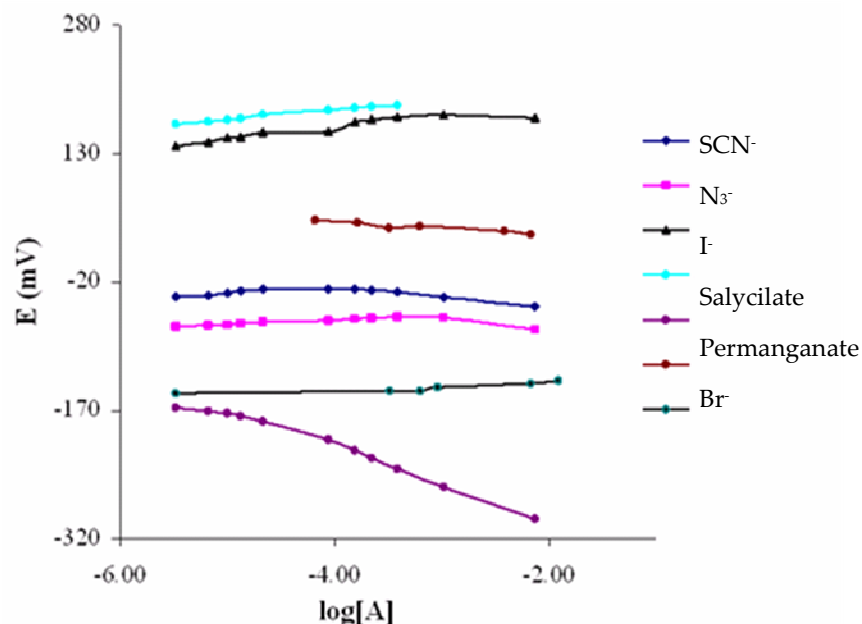
#### Results and discussion

##### *The potential responses of membrane electrodes to various anions*

The structure of the carrier (Cd-TPP) is shown in Figure 1., and the potential responses of the membrane electrode based on this carrier are given in Figure 2.



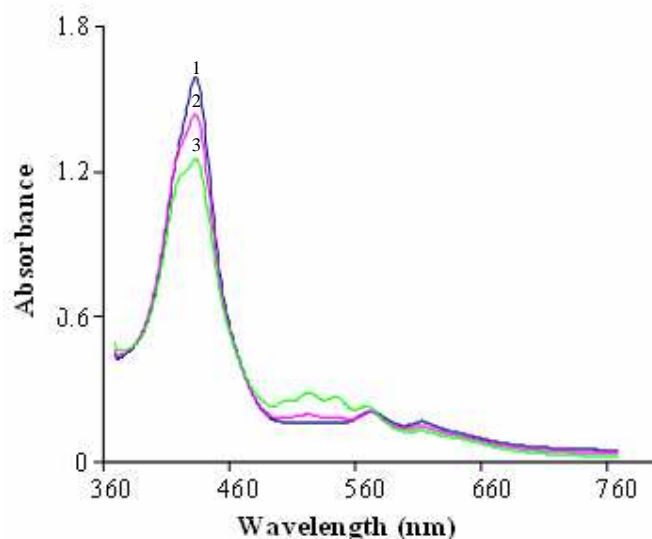
**Fig 1.** Chemical structure of Cd-TPP



**Fig 2.** Potential responses of the ion-selective electrode based on Cd-TPP toward different anions

As can be seen in Figure 2, the proposed membrane electrode exhibits a linear response to the  $\text{MnO}_4^-$  in the range  $5.0 \times 10^{-6}$ – $8.0 \times 10^{-3}$  M with a slope of  $-35.1$  mV per decade and a square correlation coefficient of 0.993. Probably charge transfer interaction between  $\text{MnO}_4^-$  and carrier in the membrane, i.e. Cd-TPP, is responsible for good response of the electrode toward  $\text{MnO}_4^-$ . This interaction is

also confirmed by UV-Vis spectrophotometric studies as illustrated in Figure 3. As seen, by addition of permanganate solution into a solution containing Cd-TPP causes to decrease in absorbance of Cd-TPP at 430 nm. The membrane electrode also shows a negligible response toward the other anions in the range  $5.0 \times 10^{-6}$  to  $4.0 \times 10^{-2}$  M, indicating very weak interaction between them and the carrier.



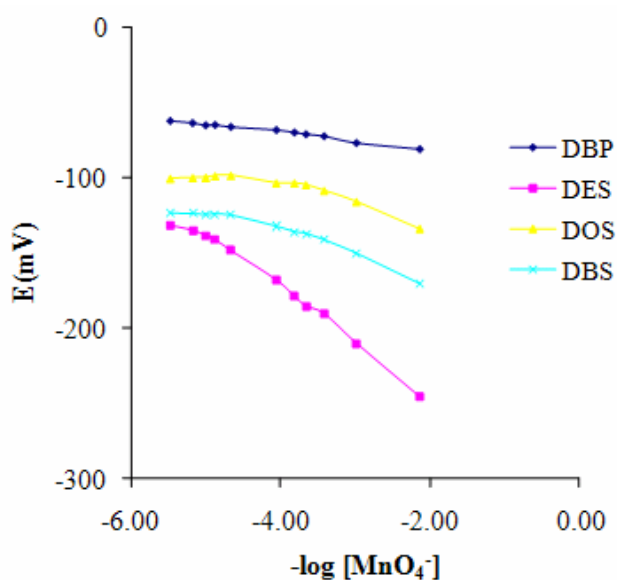
**Fig 3.** (1): Spectra of a solution containing  $1 \times 10^{-6}$  M of Cd-TPP; (2) and (3) were recorded after addition of 10.0 and 25.0  $\mu\text{L}$  from a 0.001 M permanganate solution, respectively.

### Optimization of the membrane composition

It is well known that the sensitivity and selectivity obtained for a given carrier depend significantly on the membrane composition and the nature of solvent mediator [8]. Thus, the influences of nature of the plasticizer, amounts of the carrier and CTAB as a lipophilic additive, and the nature of solvent mediator on the response behavior were investigated.

In order to have a homogenous organic phase, the membrane solvent must be physically compatible with the polymer

[19,20]. In this work, several solvent mediators (DES, DBS, DOS, and DBP) were tested. The electrode based on DES had better characteristic than the others (Figure 4). As it is shown, this electrode has a linear response in the range  $3.3 \times 10^{-6}$ - $6.6 \times 10^{-2}$  M of  $\text{MnO}_4^-$  with a sub-Nernstian slope of -34.8 mV per decade. Moreover, the electrode based on DES showed faster and more stable response than the electrodes based on the others.



**Fig 4.** Calibration curves of permanganate ion-selective electrode membranes constructed using various plasticizers.

Nine electrodes were prepared to investigate the effect of membrane composition on the response of the permanganate ion-selective electrode (Table

1). It is obvious from the data given in Table 1 that the best electrode has a composition of 3% Cd-TPP, 1% CTAB, 64% DES, and 32% PVC.

**Table 1.** Effect of membrane composition on response of the proposed electrode

Material	1	2	3	4	5	6	7	8	9
CTAB%	0.0	0.0	0.0	0.0	0.0	0.1	0.5	0.8	1.0
Cd-TPP%	0.0	1.0	2.0	3.0	3.0	3.0	3.0	3.0	3.0
PVC%	33.3	33.0	32.7	32.3	32.3	32.3	32.2	32.1	32.0
DES %	66.7	66.0	65.3	64.7	64.7	64.6	64.3	64.1	64.0
Slope (mV per decade)	-14.8	-36.6	-37.8	-39.4	-39.2	-43.7	-47.1	-49.0	-51.4
R <sup>2</sup>	0.993	0.993	0.993	0.995	0.992	0.996	0.993	0.990	0.997

The effect of concentration of internal standard solution of  $\text{KMnO}_4$  in the range 0.001-0.01 M on the potential response of the electrode was also investigated. It had only a slight effect on the response of the membrane electrode. A solution of 0.01 M  $\text{KMnO}_4$  was used as the internal solution throughout all the experiments.

#### *The effect of pH*

The effect of pH of the test solution on the potential response of the proposed electrode was studied for  $1.0 \times 10^{-4}$  M  $\text{MnO}_4^-$ . Potential was found to be mostly constant in the pH range of 5.0-10.0.

#### *Analytical figures of merit*

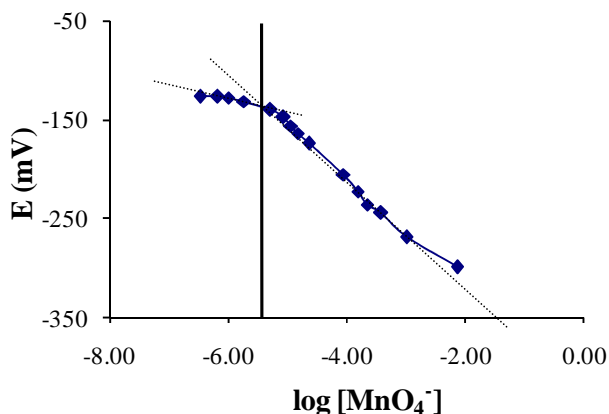
Several figures of merit of the proposed membrane electrode including repeatability, response time, detection limit, and selectivity were studied.

Four electrodes were prepared and applied for determining permanganate ion in the same condition to judge about the repeatability of

the proposed electrode. All electrodes revealed a sub-Nernstian potentiometric response for  $\text{MnO}_4^-$ . The standard deviations for slopes and square correlation coefficients obtained by considering all calibration curves were 0.89 and 0.005, respectively, indicating that the proposed permanganate-selective electrode had stable response toward  $\text{MnO}_4^-$  ion.

Response time is one of the most important characteristics for ion-selective electrode. Lower response time is always desirable due to providing more analysis in a short time period [Error! Bookmark not defined.]. Response time of  $\text{MnO}_4^-$  selective membrane electrode is about 14 seconds for change the  $\text{MnO}_4^-$  concentration from  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  M.

Detection limit of the electrode was determined by the method described in previous [21]. Figure 5 illustrates the procedure and gives the detection limit of about  $1.7 \times 10^{-6}$  M.



**Fig 5.** Extrapolating the two linear parts of the calibration curve to calculate the detection limit.

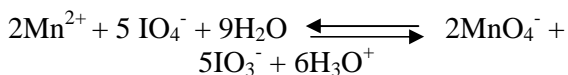
Potentiometric selectivity coefficients describing the membrane preference for an interfering  $A^{n-}$  ion relative to  $\text{MnO}_4^-$  were determined by the matched potential method as described elsewhere [22]. These coefficients for some anions are given in Table 2.

**Table 2.** Selectivity coefficients for  $\text{MnO}_4^-$  ISE

Anions	Selectivity coefficient
$\text{SCN}^-$	$1.7 \times 10^{-2}$
$\text{I}^-$	$2.6 \times 10^{-2}$
$\text{N}_3^-$	$4.1 \times 10^{-3}$
Salicylate	$1.4 \times 10^{-3}$
$\text{CN}^-$	$3.0 \times 10^{-4}$
$\text{OH}^-$	$2.1 \times 10^{-4}$
$\text{Br}^-$	$2.8 \times 10^{-5}$
$\text{ClO}_4^-$	$8.0 \times 10^{-3}$
$\text{Cr}_2\text{O}_7^{2-}$	$< 1.0 \times 10^{-6}$

**Analytical application**

Indirect determination of  $Mn^{2+}$  was achieved by measuring the released  $MnO_4^-$  from the following reaction [23]:



The proposed permanganate-selective membrane electrode was employed for determination of  $MnO_4^-$ . The results were satisfactory and are shown in Table 3.

**Table 3.** Results of indirect determination of Mn(II) using the proposed electrode

Sample	Actual concentration (M)	Found concentration	Relative error%
1	$2.00 \times 10^{-5}$	$1.92 \times 10^{-5}$	-3.85
2	$1.00 \times 10^{-4}$	$9.67 \times 10^{-5}$	-3.30
3	$5.00 \times 10^{-3}$	$5.21 \times 10^{-3}$	4.20

**Conclusion**

As a conclusion, Cd-TPP was a perfect carrier for permanganate ion in the PVC-membrane electrode. It was suggested that the main interaction between permanganate and Cd-TPP was of charge transfer type. The resulted electrode was highly selective toward permanganate ion and applied successfully for

indirect determination of Mn(II). The main drawback of the proposed electrode was its low lifetime which was due to decomposing of permanganate ion in the internal standard solution and precipitating of  $MnO_2$  on the membrane.

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