Fabrication of a New Modified Tm³⁺- Carbon Paste Sensor Using Multi-Walled Carbon Nanotubes (MWCNTs) and Nanosilica Based on 4-Hydroxy Salophen

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In this research, a new modified carbon paste electrode (CPE) including multi-walled carbon nanotube (MWCNT) and nanosilica (NS) and 4-Hydroxy Salophen (HS) as a suitable ionophore was constructed and applicated as Tm³⁺-ion selective sensor. This electrode shows a Nernstian response (19.2 ± 0.1 mV/decade) over concentration range of 1.0×10^{-8} to 1.0×10^{-3} mol L⁻¹. The electrode detection limits was found to be 9.0×10^{-9} mol L⁻¹ at a pH range of 3.1–7.8. The sensor has a response time of ~14 s. This electrode displays very good selectivity with respect to different interfering ions, including alkali, alkaline earth, transition and heavy metal ions. The created sensor was satisfactory applied to determine Tm³⁺ ions in presence of metal ions mixture and used as an indicator electrode in the potentiometric titration of Tm³⁺ ions with EDTA.

1. INTRODUCTION

Thulium is in the lanthanide series in the periodic table of elements with sign Tm and atomic number 69.The most common oxidation status of thulium compounds (in halides, oxide, and other compounds) is +3.It is just found on the earth in the trace quantities and used in the portable X-ray equipments and in the solid-state lasers as the radiation fountain. It has no noticeable biological role and is not particularly toxic. It also applied in the microwave equipment as ceramic magnetic materials, that is called ferrites. Thulium as an easily workable metal has been used in the dosimeters to form of thulium-doped calcium sulphate. Thulium and other lanthanide oxides are widely applied in construction of the optical devices with the provision of optical glasses and glass fibers, to purging of

sulfur in the iron and steel industries, gasoline-cracking catalysts, burnishing compounds and carbon arcs, and etc [1-5].

The main methods for low-level determination of Tm^{3+} ions and other lanthanide elements in solutions are inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), Isotope dilution mass spectrometry, spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, etc. These methods are either low sensitivities, are time-consuming, involving multiple sample manipulations, or too expensive [6-9].

Carbon paste ion-selective electrodes incorporating MWCNT and NS were successfully used to the monitoring of many metal ions in different industrial, biochemical and environmental samples [10-12]. The advantages of this sensors are inexpensive, fast, portability, simplicity, and trusty response in a abroad concentration range in comparison with other electrochemical systems. A literature study revealed that there are very little records on Tm^{3+} carbon paste electrodes [13, 14].

During the past decade, other researchers and our team have used some of ion carriers in construction of a number of PVC-membrane ISEs for anions and cations [15–30].

This present research focuses on the construction of a new nano composite Tm^{3+}CPE based on 4-Hydroxy Salophen (HS) [Fig. 1] as a suitable selective element, and its application in the monitoring of Tm^{3+} ion concentration .
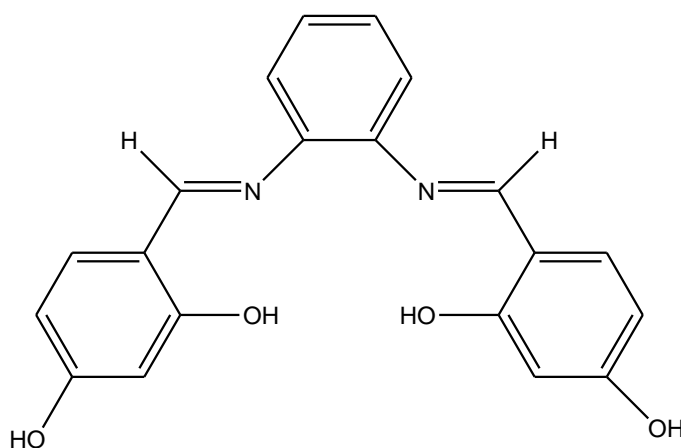

Figure 1. The structure of HS.

2. EXPERIMENTAL

2.1. Reagents and materials

The chemical companies of the Aldrich and Merck were the providers for the salts (chloride and nitrate) of all cations, high-purity paraffin oil and graphite powder (1–2 μm particle size). Nanosilica (NS), and multi-wall carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length) with 95% purity were purchased from Research Institute of the Petroleum Industry (Iran). An Ag/AgCl electrode purchased from Azar electrode, Iran Co. as a reference electrode. Doubly distilled de-ionized water was used throughout.

2.2. The creation of Tm³⁺-CPE

Appropriate amount of graphite powder along with different amounts of the ion carrier HS, NS and MWCNTs were thoroughly mixed. The obtained mixture was transferred into a glass tube. The sensor body was constructed from a glass tube of i.d. 5 mm and a height of 3 cm. The mixture homogenization, was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper [31-33]. A new surface was produced by scraping out the old surface and replacing the carbon paste. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L-1 $Tm(NO_3)_3$ solution.

2.3. The measurements of EMF

The monitoring of the electromotive force measurements (emf) can be represented as follows:
Tm^{3+}CPE | sample solution | Ag–AgCl (satd.)
Using a Corning ion analyzer 250 pH/mV meter at 25.0 ^{0}C. The activities of the ions tested were calculated according to the Debye–Huckel procedure [34].

$$\log\gamma = -0.511z^2\left[\frac{\mu^{1/2}}{1+1.5\mu^{1/2}} - 0.2\mu\right]$$

3. RESULTS AND DISCISSION

In preliminary experiments, to get a clear result about the selectivity of the HS as a neutral ion carrier for common metal ions, a series of experiments was performed. In detail, it was used to create the PVC membrane ion-selective sensors for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. Their potential responses were measured. Among the different cations tested, only the Tm^{3+} ions showed a strong response (with a slope of 19.2±0.1 mVdecade^{-1}) to the HS based membrane electrodes in comparison with the other used cations. In the next experiments, Tm^{3+}-CPE based on the same ion carrier was fabricated for determine of Tm^{3+} ion concentration. For this purpose, various CP compositions were tested and the corresponding results are provided in Table 1. In this Table, the effect of the amount of the HS, binder, MWCNT and NS on the potential response of the Tm^{3+}-CPE was studied. The addition of the ligand HS to the compositions of CPE increases the potential responses of the Tm^{3+}-CPEs (Nos. 1, 4, 5). It can be seen that addition of 3% HS to the CPE increases the slope of the electrode from 15.4 to 17.6 mV decade^{-1}.

Using multi-walled carbon nanotube (MWCNT) in the CP composition improves the conductivity of the electrode and the transduction of the chemical signal to electrical signal. The dynamic working range and response time of the electrode improves by increasing of the conductivity. The CP sensor compositions were modified by adding %1, %2 and %3 wt. of MWCNT to the composition (Nos. 6-8) which led to improvements in the sensitivity of the CP sensor from the sub-

Nerstian value of 16.3 mV decade^{-1} to 22.9 mV decade^{-1}. From Table 1, addition of 2% MWCNT to CP electrode shows the best response.

Nanosilica as a filler compound in the carbon paste composition which has high specific surface area that helps extraction of the ions into the surface of the CPE. Obviously from Table 1, addition of 0.1% wt of nanosilica (NS) to the CPE (no. 9) improves the response of the CP sensor.

According to this Table, the paste composition of 25% Paraffin oil, 3% HS, 2% MWNCT, 0.1% NS and 69.9% graphite powder exhibited a better Nernstian potential response (slope 19.2±0.1 mV decade^{-1}) with response time and a better linearity in linear response range (1.0×10^{-8} to 1.0×10^{-3} mol L^{-1}).

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition of CP (wt.%)					Slope (mVdecade^{-1})	Dynamic linear range (mol L^{-1})
	Binder (Paraffin oil)	HS	Graphite Powder	MWCNTs	NS		
1	25	1	74	0	0	15.4±0.3	1.0×10^{-7}-1.0×10^{-3}
2	30	1	69	0	0	12.7±0.5	1.0×10^{-6}-1.0×10^{-3}
3	35	1	64	0	0	12.3±0.1	1.0×10^{-6}-1.0×10^{-3}
4	25	2	73	0	0	16.7±0.3	1.0×10^{-7}-1.0×10^{-3}
5	25	3	72	0	0	17.6±0.4	5.0×10^{-8}-1.0×10^{-3}
6	25	3	71	1	0	16.3±0.7	5.0×10^{-8}-1.0×10^{-3}
7	25	3	70	2	0	18.8±0.3	1.0×10^{-8}-1.0×10^{-3}
8	25	3	69	3	0	22.9±0.7	1.0×10^{-8}-1.0×10^{-3}
9	25	3	69.9	2	0.1	19.2±0.1	1.0×10^{-8}-1.0×10^{-3}
10	25	3	69.8	2	0.2	18.2±0.8	1.0×10^{-8}-1.0×10^{-3}
11	25	3	69.7	2	0.3	17.1±0.4	1.0×10^{-8}-1.0×10^{-3}

3.2. Measuring range and calibration curve

The measuring range of an ISE is defined the linear section of the calibration graph [35-37]. The potential response of the nano-composite based Tm^{3+}-CPE (composition No. 9) displays a linear response in Tm(III) ion concentration in the range 1.0×10^{-8}-1.0×10^{-3} mol L^{-1} (Fig. 2). As can be seen from Fig. 2, the calibration graph slope is 19.2 ± 0.1 mV per decade. To calculate the detection limits

of the Tm^{3+}-CPE, by extrapolating of the linear portion of the electrode's calibration curve, was calculated to be 9.0×10^{-9} mol L^{-1}.
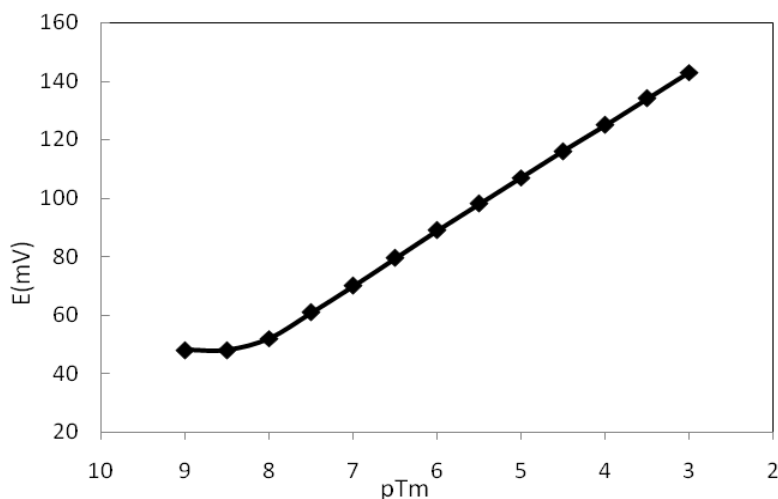

Figure 2. Calibration curves of the HS-based Tm^{3+} sensor.

3.3. The pH effect

For investigate the pH effect on the performance of the optimal modified Tm^{3+}-CPE (no. 9), the potentials were determined for a fixed concentration of Tm^{3+} solution (1.0×10^{-3} mol L^-) in the pH range of 1.0-11.0 (the pH was adjusted by using concentrated NaOH or HCl) and the recorded potentials are depicted in Fig.3 [38-43]. The results displayed the potential of sensor is constant between pH (3.1-7.8). Potential fluctuations at higher pH values (greater than 7.8) could be due to the formation of some hydroxyl complexes of Tm^{3+} in the solution. At the lower pH values than 3.1 can be attributed to partial protonation of the donor atoms of HS in the constructed Tm^{3+}-CPE.
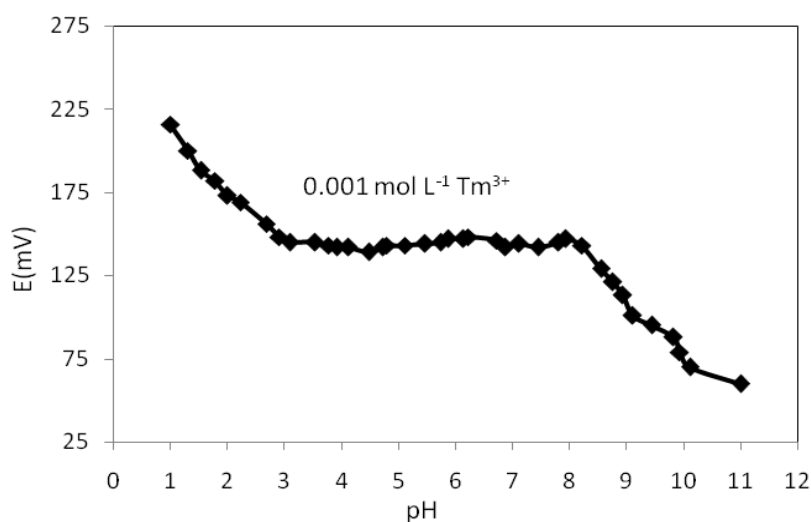

Figure 3. pH effect of the test solution (1.0×10^{-3} mol L^{-1} of Tm^{3+}) on the performance characteristics of the Tm^{3+} sensor based on HS.

3.4. Response time of the Tm^{3+}-CPE

In order to explore the response time of the Tm^{3+}-CPE, the practical response time was measured by changing the Tm^{3+} concentration in solution, each having a 10-fold difference in concentration (in the range 1.0×10^{-8}-1.0×10^{-3} mol L^{-1}) and the results are shown in Fig 4 [44-52]. As can be seen, in whole concentration range the Tm^{3+}-CPE reaches its equilibrium response in a very short time (~14 s).
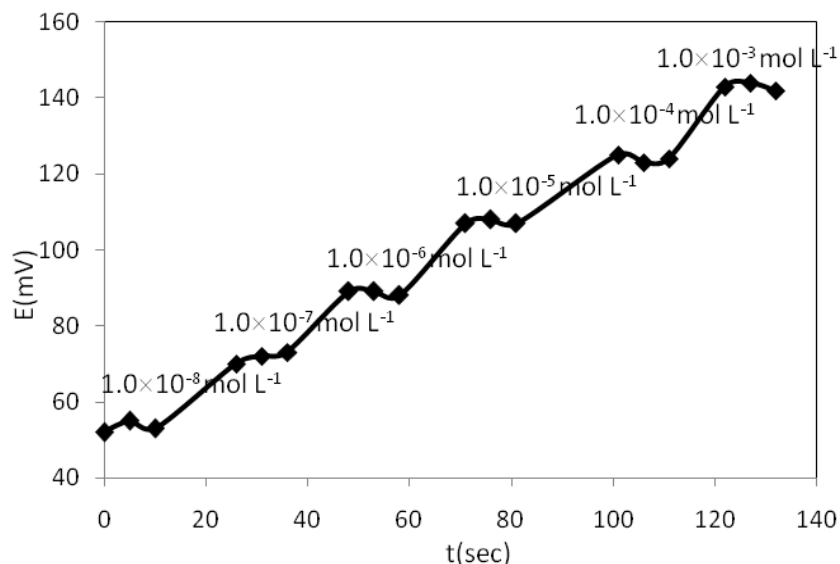

Figure 4. Dynamic response time of Tm^{3+} sensor based on HS.

3.5. Selectivity of the Tm^{3+}-CPE

In order to evaluate of the selectivity ability of the Tm^{3+}-CPE, the matched potential method (MPM) was used for this purpose and the results are given in Table 2. [53-63]. The selectivity coefficients, K^{MPM}, is defined as its tendency to respond to the activity (concentration) ratio of the primary (A) ion in the presence of interfering species (B), $K^{MPM} = a_A/a_B$. According to the MPM, the specified activity (concentration) of the main ion is added to a reference solution and the potential is recorded. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. As can be seen from Table 2, for all the mono-, di- and trivalent ions used, the selectivity coefficients of the CPE are in the range 5.5×10^{-4} to 6.8×10^{-5} mol L^{-1} indicating that they would not disturb the function of the Tm^{3+}-CPE.

Table 3 compares the linear (concentration) range, limit of detection, response time, and major interfering cations of the suggested Tm^{3+}-CPE with the previously reported Tm^{3+}-CPEs in the literature [13, 14]. As seen, the Tm^{3+}-CPE not only in the case of linear range and limit of detection, but also in the case of selectivity coefficients is superior to the previously reported Tm^{3+}-CPEs.

Table 2. Selectivity coefficients ($K^{MPM}_{Tm^{3+},B}$) of various interfering species for Tm^{3+}-CPE.

Interfering Ion	$K^{MPM}_{Tm,B}$	Interfering Ion	$K^{MPM}_{Tm,B}$
Lu^{3+}	2.4×10^{-4}	Cr^{3+}	3.8×10^{-4}
La^{3+}	8.8×10^{-5}	Mg^{2+}	2.7×10^{-4}
Yb^{3+}	2.8×10^{-4}	Pb^{2+}	2.3×10^{-4}
Nd^{3+}	1.0×10^{-4}	Na^{+}	4.9×10^{-4}
Eu^{3+}	8.3×10^{-5}	K^{+}	5.5×10^{-4}
Ho^{3+}	7.9×10^{-5}	Co^{2+}	8.0×10^{-5}
Gd^{3+}	8.2×10^{-5}	Fe^{3+}	2.8×10^{-4}
Sm^{3+}	8.9×10^{-5}	Ca^{2+}	2.2×10^{-4}
Er^{3+}	6.8×10^{-5}	Al^{3+}	4.1×10^{-4}
Tb^{3+}	7.9×10^{-5}	Cu^{2+}	2.1×10^{-4}
Pr^{3+}	9.0×10^{-5}	Ni^{2+}	8.7×10^{-5}

Table 3. Comparison of previously reported Tm^{3+}-CPEs with the proposed Tm^{3+}-CPE.

Ion	Ref. 13	Ref. 14	This work
Linearity rang (molL^{-1})	1.0×10^{-6}- 1.0×10^{-2}	1.0×10^{-6}- 1.0×10^{-2}	1.0×10^{-8}- 1.0×10^{-3}
Detection limit (molL^{-1})	8.3×10^{-7}	2.0×10^{-7}	9.0×10^{-9}
Response time (s)	15	25	~14
Slope (mV decade^{-1})	19.9	19.7	19.2
$K^{MPM}>10^{-3}$	Ca, Ho, Gd, Yb, Tb, Pr, Lu, Er, Nd	Pb, Ca, Gd, Yb, Tb, Dy, Pr, Lu, Er	-

3.6. Analytical application

The practical utility of the Tm^{3+}-CPE was investigated by its use as an indicator electrode for the potentiometric titration of a 1.0×10^{-4} mol L^{-1} Tm^{3+} ion solution with a standard 1.0×10^{-2} mol L^{-1} of EDTA and the results are shown in Figure 5. As seen, the amount of Tm^{3+} ions in solution can be accurately determined from the titration curve providing a sharp end-point.
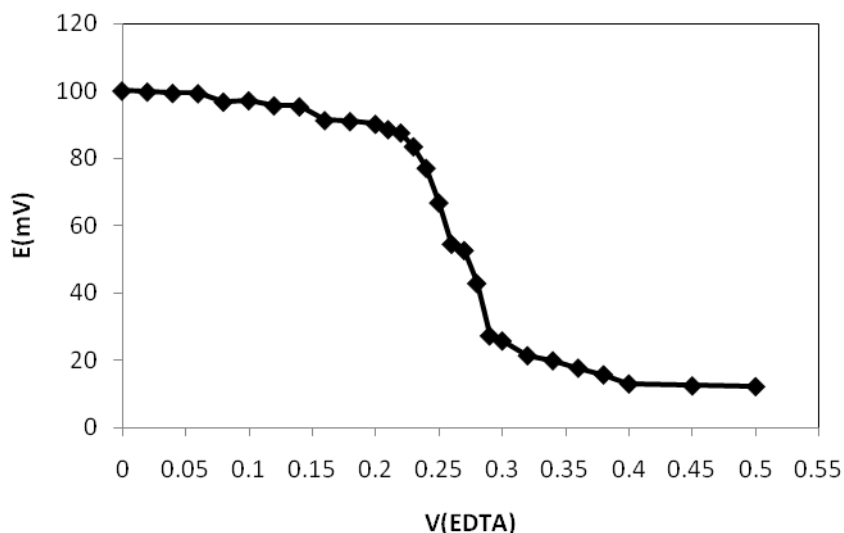

Figure 5. Potential titration curves of 25 mL 1.0×10^{-4} mol L^{-1} Tm^{3+} solution with 1.0×10^{-2} mol L^{-1} of EDTA.

In order to evaluate the applicability of the proposed Tm^{3+}-CPE, it was used to the monitoring of Tm^{3+} ion content in presence of metal ions mixture. The resulting values of the Tm^{3+}-CPE are listed in Table 4. It should be noted that the recovery of thulium ions to be very good (97.0%-104.0%).

Table 4. Determination of Tm^{3+} ion in presence of metal ions mixture.

Tm^{3+} (mol L^{-1})	Added cations (mol L^{-1})	Found[a] (mol L^{-1})	Recovery (%)
1.0×10^{-8}	$(0.0001)Gd(NO_3)_3$ & $(0.0001)Pr(NO_3)_3$	1.00×10^{-8}	100
1.0×10^{-8}	$(0.0001)Eu(NO_3)_3$ & $(0.0001)Er(NO_3)_3$	0.99×10^{-8}	99
1.0×10^{-8}	$(0.0001)La(NO_3)_3$ & $(0.0001)Ho(NO_3)_3$	0.99×10^{-8}	99
1.0×10^{-8}	$(0.0001)Sm(NO_3)_3$ & $(0.0001)Yb(NO_3)_3$	0.98×10^{-8}	98
1.0×10^{-8}	$(0.0001)Tb(NO_3)_3$ & $(0.0001)Nd(NO_3)_3$	0.97×10^{-8}	97
1.0×10^{-8}	$(0.0001)Na(NO_3)$ & $(0.0001)Cu(NO_3)_2$	1.04×10^{-8}	104
1.0×10^{-8}	$(0.0001)Pb(NO_3)_2$ & $(0.0001)Ni(NO_3)_2$	1.01×10^{-8}	101
1.0×10^{-8}	$(0.0001)Co(NO_3)_2$ & $(0.0001)Al(NO_3)_3$	1.01×10^{-8}	101
1.0×10^{-8}	$(0.0001)K(NO_3)$ & $(0.0001)Mg(NO_3)_2$	1.03×10^{-8}	103
1.0×10^{-8}	$(0.0001)Pb(NO_3)_2$ & $(0.0001)Ca(NO_3)_2$ & $(0.0001)K(NO_3)$	0.98×10^{-8}	98
1.0×10^{-8}	$(0.0001)Al(NO_3)_3$ & $(0.0001)Na(NO_3)$ & $(0.0001)Cu(NO_3)_2$	1.02×10^{-8}	102

[a]Results are based on three measurements.

4. CONCLUSION

A new modified Tm^{3+}-CPE including MWCNT and NS and 4-Hydroxy Salophen (HS) as a suitable ionophore was designed and applied as an electrochemical Tm^{3+}-CPE for the determining of Tm^{3+} ions in solution. The proposed Tm^{3+}-CPE revealed a Nernstian behavior (slope 19.2 ± 0.1 mV decade^{-1}) over a wide applicability range from 1.0×10^{-8} to 1.0×10^{-3} mol L^{-1} with an detection limit of 9.0×10^{-9} mol L^{-1}, a fast response time of 14 s and its potential response were pH independent across the range of 3.1 to 7.8.

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