

## Construction of a New Modified Nano-Composite $Tm^{3+}$ - Carbon Paste Electrode Based on N, N'-bis (pyridine-2-carboxamido)-2-aminobenzylamine

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A new modified nano-composite  $Tm^{3+}$ -carbon paste electrode (CPE) including nanosilica (NS) and multi-walled carbon nanotube (MWCNT) based on N, N'-bis (pyridine-2-carboxamido)-2-aminobenzylamine (BPCA) as an ion carrier was constructed. The electrode displays a Nernstian response ( $19.9 \pm 0.3$  mV/decade across a broad range ( $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>); a detection limits of  $3.9 \times 10^{-9}$  mol L<sup>-1</sup> between the pH range of 3.1–8.8 and a fast response time of ~5 s. The proposed  $Tm^{3+}$ -CPE showed a good  $Tm^{3+}$  selectivity over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The created  $Tm^{3+}$ -CPE was satisfactory applied to the  $Tm^{3+}$  recovery from different metal ions mixture. It was also used as an indicator electrode in the potentiometric titration of  $Tm^{3+}$  ions with EDTA.

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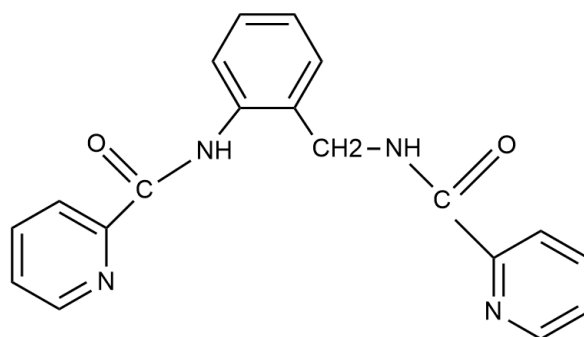
**Keywords:** Sensor, Carbon Paste Electrodes, Ion selective electrode, Potentiometry, Nano-Composite

### 1. INTRODUCTION

Thulium with sign Tm is one of the lanthanide metal ions in the periodic table of elements. Thulium has found many applications such as using as a portable sources of diagnostic X- radiation devices, the microwave equipment (ferrites), the construction of the optical devices, glass fibers, gasoline-cracking catalysts, as a dopant in tunable fiber lasers, burnishing compounds, as emitting materials in electroluminescence devices, carbon arcs, and etc [1-4].

In recent years, several methods have been developed for the determination of thallium such as X-ray fluorescence spectrometry, square-wave anodic stripping voltammetry, fluorescence enhancement, isotope dilution mass spectrometry, neutron activation analysis, spectrofluorimetry, flame atomic absorption spectrometry, coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), Isotope dilution mass spectrometry, spectrofluorimetry, X-ray fluorescence spectrometry, flotation spectrophotometric method, etc. Although these methods are very sensitive, but almost all of them either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories [5-8]. 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 [9-11]. In this work, we are going to introduce a new simple and inexpensive electrochemical sensor based on N, N'-bis (pyridine-2-carboxamido)-2-aminobenzylamine (BPCA) (Fig. 1). Library search shows that currently there only a limited number of reports on  $Tm^{3+}$ -carbon paste electrodes [12-14].

Lately, other researchers and our team have used some of ionophores in creation of a number of ion selective electrodes (ISEs) for anions and cations [15–60]. The aim of this research is the fabrication of a new nano composite  $Tm^{3+}$ -carbon paste electrode for the determination of  $Tm^{3+}$  based on N, N'-bis (pyridine-2-carboxamido)-2-aminobenzylamine (BPCA) a sensing component.



**Figure 1.** The chemical structure of BPCA.

## 2. EXPERIMENTAL

### 2.1. Reagents and materials

The high-purity paraffin oil and graphite powder (1–2  $\mu\text{m}$  particle size) and the salts of all cations (chloride and nitrate) were purchased from the Merck chemical company. The Nanosilica (NS) and multi-wall carbon nanotubes (MWCNTs) with 1-25  $\mu\text{m}$  length, 10-40 nm diameters, core diameter: 5–10 nm, SBET: 40–600  $\text{m}^2/\text{g}$ ,  $V_{\text{total}}$ : 0.9  $\text{cm}^3/\text{g}$ , bulk density 0.1  $\text{g}/\text{cm}^3$ , true density 2.1  $\text{g}/\text{cm}^3$  and 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 preparation of $Tm^{3+}$ -CPE based on BPCA

The modified CPEs were prepared through a general procedure as follows: The desired amounts of graphite powder, paraffin, various amounts of the ion carrier BPCA, nanosilica (NS) and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube. The electrode body was fabricated from a glass tube with an inner diameter of 5 mm and a height of 3 cm. The pasty mixture was homogenized before being packed into the tube tip to avoid possible air gaps which can increase the electric resistance of the electrodes. Then, a copper wire was inserted into the opposite end of the modified CPE to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste. The electrode was finally conditioned for 72 h by soaking in a  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>  $Tm(NO_3)_3$  solution [27, 61–66].

## 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.)

A Corning ion analyzer 250 pH/mV meter at 25.0 °C was used for the potential measurements. The activities of the ions tested were calculated according to the Debye–Huckel procedure [67].

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

## 3. RESULTS AND DISCUSSION

The selectivity and sensitivity for an ion selective electrode is greatly related to the chemical structure of the ion carrier used. Based on our previous studies [68] which indicated a strong interaction between BPCA with  $Tm^{3+}$  ions, it was used in creation of a series of nano-composite carbon paste electrodes with a variety of compositions some of which were modified using NS and MWCNT.

In the CPEs, the sensitivity, selectivity and linearity of the electrode not only depend on the nature of the employed ionophore BPCA but also on CP compositions. Thus, the influences of CP compositions were studied and the data are summarized in Table 1. According to Table 1, the BPCA amount 1% value results in the best sensitivity. As can be seen from Table 1, the electrode no. 9 shows a better Nernstian slope of 19.9 mV per decade with a better linear range ( $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>) and the electrode composed of 1% BPCA, 30% paraffin oil, 66.9% graphite powder, 2% MWCNT, 0.1% nanosilica was found to be optimal for the  $Tm^{3+}$  electrode. It was selected for further examination.

In the carbon paste composition, Nanosilica (NS) act as a filler compound that helps extraction of the ions into the surface of the CPE, due to high specific surface area. Due to advantages of carbon paste electrodes (CPEs) such as renewability, stable response, low ohmic resistance, and no need for

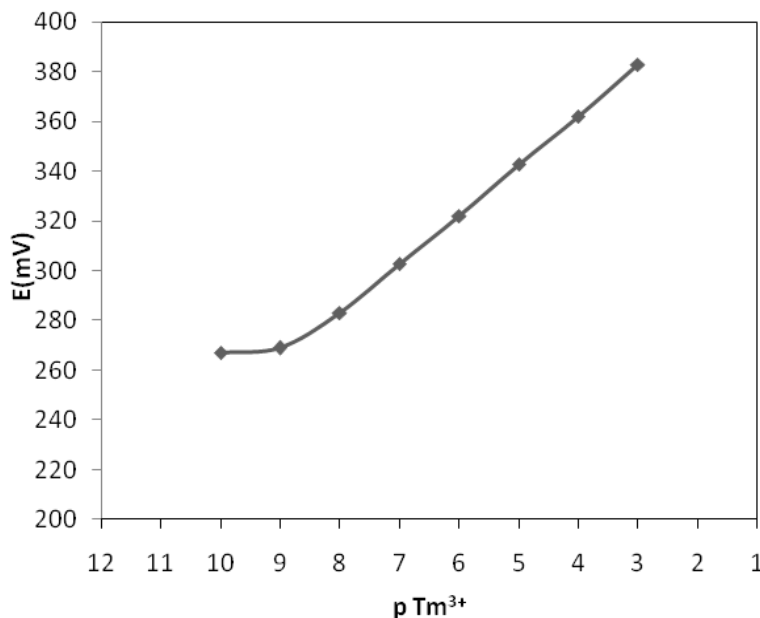
internal solution, they have recently attracted attention to use as sensors. During the past years, the carbon nanotubes (CNTs) with interesting physicochemical properties such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area have been used [69-73]. The conductivity of the CPE and the conversion of the signal (chemical to electrical) improves with the application of MWCNT in the carbon paste composition. By improving the conductivity of sensor, the dynamic working range and response time of the electrode improve.

**Table 1.** Optimization of the membrane ingredients.

Electrode No.	Composition of Carbon Paste (wt.%)					Slope (mV/decade)	Dynamic linear range (M)
	Binder (Paraffin oil)	BPCA	Graphite Powder	MWCNTs	Nano-Silica		
1	25	1	74	-	-	15.2 ± 0.4	1.0×10 <sup>-7</sup> _ 1.0×10 <sup>-3</sup>
2	30	1	69	-	-	17.6 ± 0.2	1.0×10 <sup>-7</sup> _ 1.0×10 <sup>-3</sup>
3	35	1	64	-	-	14.5 ± 0.5	1.0×10 <sup>-7</sup> _ 1.0×10 <sup>-3</sup>
4	30	2	68	-	-	16.8 ± 0.3	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>
5	30	3	67	-	-	15.7 ± 0.2	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>
6	30	1	68	1	-	17.8 ± 0.4	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>
7	30	1	67	2	-	18.6 ± 0.2	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>
8	30	1	66	3	-	17.2 ± 0.5	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>
9	30	1	66.9	2	0.1	19.9 ± 0.3	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>
10	30	1	66.8	2	0.2	19.1± 0.2	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>
11	30	1	66.7	2	0.3	18.8 ± 0.4	1.0×10 <sup>-8</sup> _ 1.0×10 <sup>-3</sup>

### 3.1. Calibration curve and detection limit

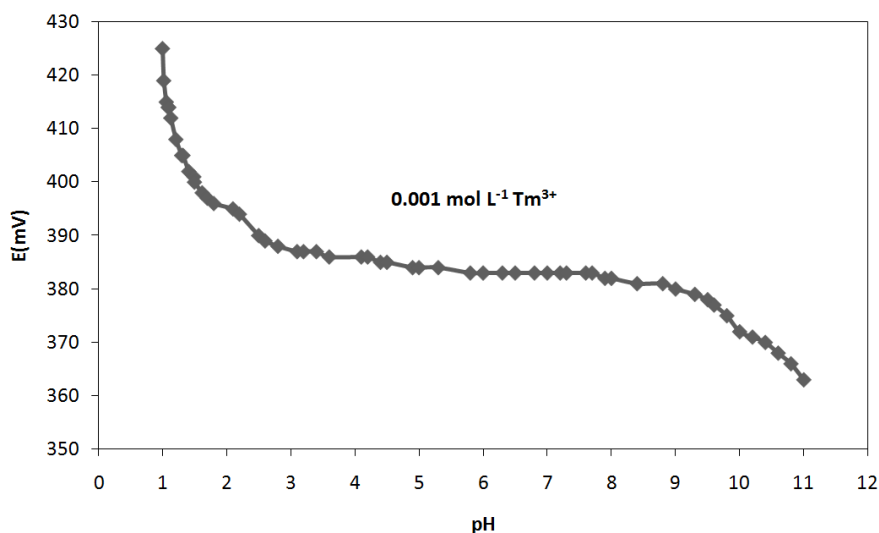
The potential response of the modified nano-composite Tm<sup>3+</sup>-CPE (no. 9) was investigated across Tm<sup>3+</sup> ion concentration range of 1.0×10<sup>-10</sup>-1.0×10<sup>-3</sup> mol L<sup>-1</sup>. The proposed Tm<sup>3+</sup>-CP sensor shows a linear range in the range 1.0 ×10<sup>-8</sup>-1.0 × 10<sup>-3</sup> mol L<sup>-1</sup> (Fig. 2). By extrapolating based on the linear portion of the electrode's calibration curve, the detection limit of the Tm<sup>3+</sup>-CPE was calculated to be 3.9×10<sup>-9</sup> mol L<sup>-1</sup> [69-74].



**Figure 2.** Calibration curves of the Tm<sup>3+</sup>-CPE based on BPCA.

### 3.2. The pH effect

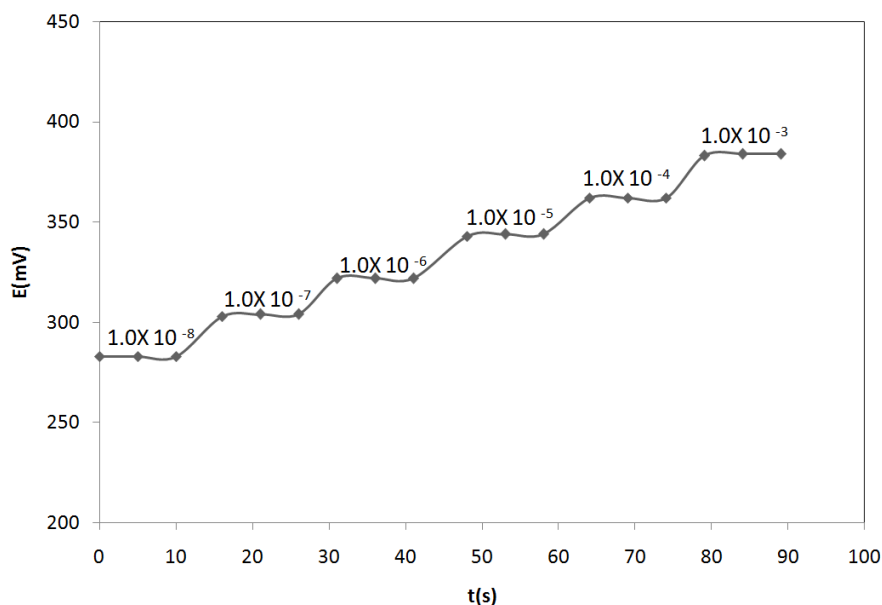
In order to study of the influence of pH on the response of the new modified Tm<sup>3+</sup>-CPE (no. 9), the potentials were recorded in the pH range of 1.0-11.0 (the pH was adjusted by using concentrated NaOH or HCl) for a fixed concentration of Tm<sup>3+</sup> solution (1.0×10<sup>-3</sup> mol L<sup>-1</sup>) and the results are showed in Fig.3 [75-83]. As it can be seen, the potentials remain constant in the pH range of 3.1-8.8. The observed drift at the higher pH values (> 7.8) could be due to the formation of some hydroxyl complexes of Tm<sup>3+</sup> in the solution. At the lower pH values (< 3.1) can be attributed to partial protonation of the donor atoms of BPCA.



**Figure 3.** pH effect of the test solution (1.0×10<sup>-3</sup> mol L<sup>-1</sup> of Tm<sup>3+</sup>) on the performance characteristics of the Tm<sup>3+</sup> sensor based on BPCA.

### 3.3. Response time of the $Tm^{3+}$ -CPE

Since the dynamic response time of a CPE is one of the most important factors in its evaluation, the dynamic response time was studied by immersing the  $Tm^{3+}$ -CP sensor in various solutions, each having a 10-fold different in concentration (in the range  $1.0 \times 10^{-8}$ - $1.0 \times 10^{-3}$  mol L<sup>-1</sup>) and the results are depicted in Fig 4 [84-92]. As can be seen, for the proposed modified  $Tm^{3+}$  sensor, the response time in the whole concentration range reaches its equilibrium response in a very short time (~5 s).



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

### 3.4. Selectivity of the $Tm^{3+}$ -CPE

Selectivity coefficients describing the membrane preference towards an interfering ion. In order to evaluate of the potentiometric selectivity ability of the  $Tm^{3+}$ -CPE, the matched potential method (MPM) was used for this proposed [93-108]. According to the MPM method, a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution until the measured potential matches that obtained before the primary ion addition. The matched potential method selectivity coefficient, KMPM, is then given by the resulting primary ion to interfering ion activity (concentration) ratio,  $K^{MPM} = a_A/a_B$ . The experimental conditions and the resulting for the  $Tm^{3+}$ -CPE are listed in Table 2. In line with the information of Table 2, the selectivity coefficients for the monovalent ( $Na^+$ ,  $K^+$ ), the divalent ( $Mg^{2+}$ ,  $Sr^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Ca^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ) and trivalent ( $Pr^{3+}$ ,  $Dy^{3+}$ ,  $Yb^{3+}$ ,  $Ho^{3+}$ ,  $Eu^{3+}$ ,  $Sm^{3+}$ ,  $Er^{3+}$ ,  $Gd^{3+}$ ,  $Tb^{3+}$ ,  $Cr^{3+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ) tested cations are smaller than  $7.0 \times 10^{-4}$ . 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  $2.1 \times 10^{-5}$  to  $7.0 \times 10^{-4}$  indicating that they would not disturb the function of the  $Tm^{3+}$ -CPE.

**Table 2.** Selectivity coefficients ( $K_{Tm^{3+},B}^{MPM}$ ) of various interfering species for  $Tm^{3+}$ -CPE based on BPCA.

Interfering Ion	$K_{Tm,B}^{MPM}$	Interfering Ion	$K_{Tm,B}^{MPM}$
$Pr^{3+}$	$7.6 \times 10^{-5}$	$Tb^{3+}$	$2.8 \times 10^{-4}$
$Dy^{3+}$	$7.9 \times 10^{-5}$	$Zn^{2+}$	$3.6 \times 10^{-4}$
$Yb^{3+}$	$4.8 \times 10^{-5}$	$Pb^{2+}$	$8.9 \times 10^{-5}$
$Ho^{3+}$	$3.1 \times 10^{-4}$	$Ni^{2+}$	$1.0 \times 10^{-4}$
$Eu^{3+}$	$6.8 \times 10^{-4}$	$Mg^{2+}$	$2.5 \times 10^{-5}$
$Cr^{3+}$	$2.1 \times 10^{-5}$	$Co^{2+}$	$2.1 \times 10^{-5}$
$Al^{3+}$	$1.3 \times 10^{-4}$	$Cd^{2+}$	$7.7 \times 10^{-5}$
$Sm^{3+}$	$2.8 \times 10^{-5}$	$Ca^{2+}$	$3.1 \times 10^{-4}$
$Er^{3+}$	$5.6 \times 10^{-4}$	$Sr^{2+}$	$1.9 \times 10^{-4}$
$Gd^{3+}$	$7.0 \times 10^{-4}$	$K^+$	$2.3 \times 10^{-5}$
$Fe^{3+}$	$4.6 \times 10^{-5}$	$Na^+$	$3.5 \times 10^{-5}$

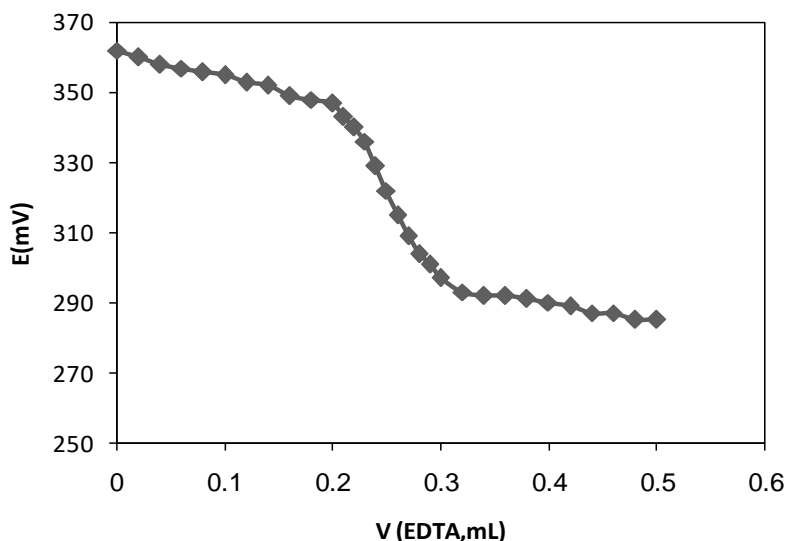
Table 3 also compares the Linearity rang, detection limits, response times, slope and the selectivity coefficients of the  $Tm^{3+}$ -CPE with those of the best previous  $Tm^{3+}$ -CPE reported in the literature by other researchers [12-14]. From the data given in Table 3, the proposed sensor in all of terms in the proposed Table is superior to the previously reported  $Tm^{3+}$ -CPEs.

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

Ion	Ref. 12	Ref. 13	Ref. 14	This work
Linearity rang ( $molL^{-1}$ )	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-3}$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-3}$
Detection limit ( $molL^{-1}$ )	$9.0 \times 10^{-9}$	$8.3 \times 10^{-7}$	$2.0 \times 10^{-7}$	$3.8 \times 10^{-9}$
Response time (s)	~14	15	25	~5
Slope ( $mV decade^{-1}$ )	19.2	19.9	19.7	19.9
$K^{MPM} > 10^{-3}$	-	Ca, Ho, Gd, Yb, Tb, Pr, Lu, Er, Nd	Pb, Ca, Gd, Yb, Tb, Dy, Pr, Lu, Er	-

### 3.5. Analytical application

The suggested  $Tm^{3+}$ -CPE was found to work well under the laboratory conditions. The selective thulium carbon paste electrode was used as an indicator electrode in the titration of a  $1.0 \times 10^{-4} mol L^{-1} Tm^{3+}$  ion solution (pH=4; sodium acetate buffer) with a standard  $1.0 \times 10^{-2} mol L^{-1}$  of EDTA (pH=10). The results are shown in Figure 5. According to this figure, the sensor is capable of monitoring the amount of thulium ions from the titration curve providing a sharp end-point.



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

Because of high selectivity and low detection limit of the developed Tm $^{3+}$ -CPE (electrode No. 9), it was also used to the monitoring of Tm $^{3+}$  ion content in mixtures of two and three different ions and the results are shown in Table 4. The corresponding results in Table 4 reveal that the recovery of Tm $^{3+}$  ions in all mixtures is acceptable.

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

Tm $^{3+}$ (mol L $^{-1}$ )	Added cations (mol L $^{-1}$ )	Found <sup>a</sup> (mol L $^{-1}$ )	Recovery (%)
$1.0 \times 10^{-8}$	(0.00001)Pr(NO $_3$ ) $_3$ & (0.00001)Sr(NO $_3$ ) $_2$	$1.04 \times 10^{-8}$	104
$1.0 \times 10^{-8}$	(0.00001)Eu(NO $_3$ ) $_3$ & (0.00001)Er(NO $_3$ ) $_3$	$1.03 \times 10^{-8}$	103
$1.0 \times 10^{-8}$	(0.00001)Yb(NO $_3$ ) $_3$ & (0.00001)Gd(NO $_3$ ) $_3$	$1.05 \times 10^{-8}$	105
$1.0 \times 10^{-8}$	(0.00001)Dy(NO $_3$ ) $_3$ & (0.00001)Sm(NO $_3$ ) $_3$	$1.02 \times 10^{-8}$	102
$1.0 \times 10^{-8}$	(0.00001)Ho(NO $_3$ ) $_3$ & (0.00001)Zn(NO $_3$ ) $_2$	$1.03 \times 10^{-8}$	103
$1.0 \times 10^{-8}$	(0.00001)Na(NO $_3$ )& (0.00001)Mg(NO $_3$ ) $_2$	$1.01 \times 10^{-8}$	101
$1.0 \times 10^{-8}$	(0.00001)Lu(NO $_3$ ) $_3$ & (0.00001)Ni(NO $_3$ ) $_2$	$1.02 \times 10^{-8}$	102
$1.0 \times 10^{-8}$	(0.00001)Co(NO $_3$ ) $_2$ & (0.00001)Fe(NO $_3$ ) $_3$	$1.04 \times 10^{-8}$	104
$1.0 \times 10^{-8}$	(0.00001)KNO $_3$ & (0.00001)Mg(NO $_3$ ) $_2$	$1.02 \times 10^{-8}$	102
$1.0 \times 10^{-8}$	(0.00001)Pb(NO $_3$ ) $_2$ & (0.00001)Ca(NO $_3$ ) $_2$ & (0.00001)KNO $_3$	$1.03 \times 10^{-8}$	103
$1.0 \times 10^{-8}$	(0.00001)Fe(NO $_3$ ) $_3$ & (0.00001)NaNO $_3$ & (0.00001)Ca(NO $_3$ ) $_2$	$1.01 \times 10^{-8}$	101

<sup>a</sup>Results are based on three measurements.

#### 4. CONCLUSION

The experiment data of this research show that the potentiometric method using a new modified Tm $^{3+}$ -CPE including MWCNT and NS provides an attractive alternative for the monitoring



of  $\text{Tm}^{3+}$  ion in solution. The proposed  $\text{Tm}^{3+}$ -CPE displayed linear response over a wide applicability range (from  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-3}$  mol  $\text{L}^{-1}$ ) with a Nernstian slope ( $19.9 \pm 0.3$  mV decade $^{-1}$ ), a detection limit of  $3.8 \times 10^{-9}$  mol  $\text{L}^{-1}$ , fast response time ( $\sim 5$  s), selective to thulium ion, and is easy to prepare. Its selectivity towards the thulium ions was not influenced by the presence of the common alkali, alkaline earth, or transition and heavy metal ions, since the interference of these substances was low. The proposed sensor can be successfully applied to the determination of thulium ions in in presence of metal ions mixture.

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