Fabrication of a Tb\(^{3+}\) Carbon Paste Ion Selective Electrode by Using Nanosilica and Multi-Walled Carbon Nanotubes (MWCNTs)

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A new Tb\(^{3+}\) carbon paste ion selective electrode based on 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid (DAPTA) for determination of trace amount of terbium was prepared. Using nanosilica and multi-walled carbon nanotube (MWCNT) in the composition of carbon paste electrodes cause improvement in their characterizations. The electrode composition of 20% paraffin oil, 52% graphite powder, 3% DAPTA, 3% WCNTs, and 0.3% nanosilica showed the stable potential response to Tb\(^{3+}\) ions and the Nernstian slope of 20.1±0.3 mV decade\(^{-1}\) with a detection limit of 9.0×10\(^{-10}\) mol L\(^{-1}\) in the wide linear concentration range of 10\(^{-9}\) - 10\(^{-2}\) mol L\(^{-1}\). It has a fast response time (~6 s) in the pH range of 3.0 – 9.2. This sensor presented very good selectivity and sensitivity towards the Tb\(^{3+}\) ions over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The practical utility of the proposed chemical sensor has been observed by using it as an indicator electrode in the titration of Tb\(^{3+}\) ions with EDTA.

**Keywords:** sensor, multi-walled carbon nanotubes, potentiometry, ion-selective electrode, nanosilica

1. **INTRODUCTION**

Lanthanides are widely used in the field of glass and ceramic industries, metallurgy, electronics, agriculture and natural science. The main application involve the use of mixed rare-earth as gasoline-cracking catalysts, and as starting materials for making misch metal, the use of rare-earth silicides for various metallurgical applications and as polishing compounds, and for carbon arcs used in movie projectors and searchlights [1]. Terbium is one of the more costly lanthanides, mainly because there are few applications for this element and consequently very little is produced. Terbium
has no known biological role. Terbium is also used in alloys and in the production of electronic devices, its oxide is used in green phosphors in fluorescent lamps and color TV tubes.

In general, most reported carbon paste (CP) potentiometric sensors, comprise of an ionophore incorporated into a carbon paste, typically consisting of graphite powder dispersed in a non-conductive mineral oil, which is used to give carbon paste electrodes (CPEs) some disadvantages. Mineral oils, on the other hand, do not have fixed components due to the fact that they are derived during the process of refining crude oil or petroleum. The presence of contaminants or matrix components used in the construction of sensors may unpredictably influence detection. Furthermore, carbon nanotubes (CNTs) have recently been used in composition of carbon paste electrodes. CNTs have very interesting physicochemical properties, such as an ordered structure with a high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area. The combination of these characteristics makes CNTs unique materials with the potential for diverse applications [2-15].

Many techniques have been used for determination of terbium which most of them have been spectroscopic methods such as inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), electron spin resonance, high resolution γ-spectroscopy, atomic emission spectroscopy, spectrophotofluorimetric, laser-based multi step resonance ionization and some nucleic methods. Nevertheless, almost all of these methods are expensive and time consuming, with the exception of one; the ion selective electrode (ISE) method. On the other hand application of carrier-based ion-selective electrodes (ISEs) can offer inexpensive and convenient analyses methods for different anions and cations [16-40] including rare-earth ions, if the used sensors enjoy levels acceptable sensitivity and selectivity.

![Figure 1. Chemical structure of DAPTA.](image)

Previous selectivity studies [41] showed a strong interactions between DAPTA (Figure 1) and Tb$^{3+}$ ions, while the same interactions were found to be low for other common interfering ions, we decided to construct a high performance potentiometric electrode with improved mechanical resistant and renewable surface for determination of Tb$^{3+}$ ions in solution using DAPTA as a sensing material in new proposed carbon paste composition based on nanosilica and multi-walled carbon nanotubes (MWCNTs).
2. EXPERIMENTAL

2.1. Reagents

The 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid (DAPTA), nanosilica, graphite powder with a 1–2 μm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for the construction of the carbon pastes. The multi-wall carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length, SBET: 40-600 m²/g and with 95% purity were purchased from Research Institute of the Petroleum Industry (Iran). The chloride and nitrate salts of the cations were all purchased from Merck Co. Triply distilled de-ionized water was used throughout.

2.2. Preparation of the carbon paste electrode

Different amounts of the ionophore DAPTA along with appropriate amount of graphite powder, nanosilica and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube. The electrode body was fabricated from a glass tube of i.d. 5 mm and a height of 3 cm. After the mixture homogenization, the paste 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. 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 $1.0 \times 10^{-3}$ mol L⁻¹ Tb(NO₃)₃ solution.

2.3. The emf measurements

The glass cell in which carbon paste electrode was placed into contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode. The Tb³⁺ CPE was used as an indicator electrode. Both electrodes were connected to a milivoltmeter.

The following cell was assembled for the conduction of the EMF (electromotive force) measurements:

Carbon paste electrode | sample Tb³⁺ ion solution | Ag/AgCl–KCl (satd.)

3. RESULTS AND DISCUSSIONS

3.1. Carbon paste electrode composition

The fact that selectivity of carbon paste and PVC membrane ion-selective electrodes is highly dependent on the ion carrier used is very well known [42-55]. Upon the addition of the ionophore, in amounts of 2-5%, to the composition of carbon paste electrodes considerable increases in the potential response of the CP electrodes (composition 7-10) was observed and presence of 3% of DAPTA to CP electrode was found to lead to a very good response behavior, increasing the potential response from
17.9 to 20.1 mV decade$^{-1}$. Based on previous selectivity studies [41], DAPTA shows a selective behavior toward Tb$^{3+}$ ion. Different CPE compositions were prepared and the results of the application of each are shown in Table 1. The results revealed that the best CPE (CPE No. 7), shows a near Nernstian slope about 20.1 mV decade$^{-1}$.

Using MWCNT in the composition of the carbon paste not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. As it is seen in electrode no. 7, 3% MWCNTs in the paste composition affects the electrode response drastically. This is due to the electrical properties of MWCNTs which can improve the transduction and amplification of the signal. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values (CPE Nos. 6-8). It is clearly seen from Table 1, CPE No. 7. Nano-silica is also known to improve the response of CPEs, if used as filler compound, due to its high specific surface area that helps extraction of the ions into the surface of the CPE. Furthermore, the application of nano-silica in CPE compositions can lead to enhancements in the mechanical properties of the electrodes. The results in Table 1 show that CPE comprising 0.3% nano-silica, 3% MWCNT, 3% L, 30% paraffin oil and 63.7% graphite respond the best (CPE No. 7).

<table>
<thead>
<tr>
<th>Electrode No.</th>
<th>Composition of Carbon Paste (wt.%)</th>
<th>Slope (mV/decade)</th>
<th>Dynamic linear range (mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binder (Paraffin oil)</td>
<td>DAPT</td>
<td>Graphite powder</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>3</td>
<td>70.7</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>3</td>
<td>65.7</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>3</td>
<td>65.9</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>3</td>
<td>65.8</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>3</td>
<td>65.5</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
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<tr>
<td>7</td>
<td>30</td>
<td>3</td>
<td>63.7</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>2</td>
<td>64.7</td>
</tr>
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<td>9</td>
<td>30</td>
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<td>62.7</td>
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<tr>
<td>10</td>
<td>30</td>
<td>5</td>
<td>61.7</td>
</tr>
</tbody>
</table>

3.2. Calibration graph and statistical data

The potential response of the Tb$^{3+}$-CPE at varying concentrations of terbium nitrate (Fig. 2) indicates a linear working concentration range from 1.0×10$^{-9}$ to 1×10$^{-2}$ mol L$^{-1}$. The slope of the calibration graph was 20.1±0.3 mV per decade of terbium ions concentration. The detection limit of the electrode that determined from the intersection of the two extrapolated segments of the calibration graph was 9.0×10$^{-10}$ mol L$^{-1}$ [56-60]. The standard deviation for ten replicate measurements was ±0.6 mV.
3.3. pH effect and response time

In order to study the effect of pH on the performance of the Tb\(^{3+}\)-CP sensor, the potentials were determined in the pH range of 1.0-11.0 (the pH was adjusted by using concentrated NaOH or HCl) at one concentrations (1.0×10\(^{-3}\) mol L\(^{-1}\)) of Tb\(^{3+}\) and the result is depicted in Figure 3 [61-67]. As it is seen, the potential remained constant from pH 3.0 to 9.2, beyond which some drifts in the potentials were observed. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Tb\(^{3+}\) in the solution. At the lower pH values, the potentials increased, indicating that the membrane sensor responded to protonium ions, as a result of the some extent protonation of nitrogen atoms of the ionophore.

![Figure 3](image_url)  
**Figure 3.** pH effect of the test solution (1.0×10\(^{-3}\) mol L\(^{-1}\)) of the Tb\(^{3+}\) sensor based on DAPTA.
Dynamic response time is an important factor for terbium carbon paste electrodes [68-72]. In this study, the practical response time was recorded by changing solution with different Tb$^{3+}$ concentrations from $1.0 \times 10^{-9}$ to $1.0 \times 10^{-2}$ mol L$^{-1}$. The actual potential versus time trace for the electrode based on DAPTA is shown in Figure 4. As can be seen, the electrode reaches the equilibrium response in a very short time of about 6 s.

![Figure 4. Dynamic response time of Tb$^{3+}$-CP sensor based on DAPTA.](image)

### 3.4. Electrode selectivity of the Tb$^{3+}$-CP sensor

Potentiometric selectivity coefficients of the sensor were determined by the matched potential method (MPM) [73-76]. According to this 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 the one obtained before adding primary ions. The matched potential method selectivity coefficient, $K_{\text{MPM}}$, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{\text{MPM}} = a_A/a_B$.

The resulted potentiometric selectivity coefficients values are summarized in Table 2. The data given in Table 2, show the selectivity coefficients of the proposed Tb$^{3+}$-CP sensor were $5.8 \times 10^{-4}$ or smaller and revealed that the proposed Tb$^{3+}$-CPE is highly selective with respect to most of transition and heavy metal ions. The surprisingly high selectivity of the carbon paste electrode for terbium ions over other cations used, most probably arises from the strong tendency of the carrier molecules for terbium ions.
Table 2. Selectivity coefficients ($K_{MPM}^{Tb^{3+}}$) of proposed Tb$^{3+}$-CP sensor.

<table>
<thead>
<tr>
<th>Interfering Ion (B)</th>
<th>$K_{MPM}^{Tb^{3+}}$</th>
<th>Interfering Ion (B)</th>
<th>$K_{MPM}^{Tb^{3+}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy$^{3+}$</td>
<td>7.8×10$^{-5}$</td>
<td>Yb$^{3+}$</td>
<td>6.2×10$^{-5}$</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>7.5×10$^{-5}$</td>
<td>Cr$^{3+}$</td>
<td>3.5×10$^{-4}$</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>8.5×10$^{-5}$</td>
<td>Fe$^{3+}$</td>
<td>7.0×10$^{-5}$</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>5.5×10$^{-4}$</td>
<td>Ca$^{2+}$</td>
<td>5.0×10$^{-5}$</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>7.9×10$^{-5}$</td>
<td>Mg$^{2+}$</td>
<td>7.1×10$^{-5}$</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>8.0×10$^{-5}$</td>
<td>Co$^{2+}$</td>
<td>1.0×10$^{-4}$</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>2.0×10$^{-4}$</td>
<td>Cd$^{2+}$</td>
<td>8.3×10$^{-5}$</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>5.3×10$^{-4}$</td>
<td>Ni$^{2+}$</td>
<td>6.9×10$^{-5}$</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>5.0×10$^{-4}$</td>
<td>Pb$^{2+}$</td>
<td>7.8×10$^{-5}$</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>5.8×10$^{-4}$</td>
<td>Na$^{+}$</td>
<td>2.0×10$^{-4}$</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>1.0×10$^{-4}$</td>
<td>K$^+$</td>
<td>2.3×10$^{-4}$</td>
</tr>
</tbody>
</table>

3.5. Analytical application

The proposed Tb$^{3+}$-CPE was successfully used as an indicator electrode in the titration of 25.0 mL of a 1.0×10$^{-4}$ mol L$^{-1}$ Tb$^{3+}$ solution with a 1.0×10$^{-2}$ mol L$^{-1}$ EDTA. The resulting titration curve is given in Figure 5, demonstrating that the amount of Tb(III) ion in the solution can be determined with the electrode.

![Figure 5. Potentiometric titration curves of 25 mL 1.0×10$^{-4}$ mol L$^{-1}$ Tb$^{3+}$ solution with 1.0×10$^{-2}$ mol L$^{-1}$ of EDTA.](image-url)
4. CONCLUSION

Having a basis the resulting data of this work, Diaminopropane-N,N,N',N'-tetraacetic acid (DAPTA) can be used as an electroactive ion carrier to produce Tb(III)-CPE. The Tb$^{3+}$-CP sensor based on Diaminopropane-N,N,N',N'-tetraacetic acid as a selective and sensitive chemical material shows the best response characteristics with Nernstian behavior across the concentration range of 1.0×10$^{-9}$-1.0×10$^{-2}$ mol L$^{-1}$ Tb$^{3+}$, a detection limit of 9.0× 0$^{-10}$ mol L$^{-1}$ with the slope of 20.1±0.3 mV per decade of activity. The proposed Tb$^{3+}$-CP sensor was found to work well in the pH range of 3.0–9.2 with response time about 6 s and showed reproducible and stable potentiometric signals. Its selectivity towards the terbium 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.

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References


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