Construction of a Fe$^{3+}$ Carbon Paste Electrode Based on Multi-walled Carbon Nanotubes (MWCNTs)/Nanosilica

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The results of our previous studies showed a selective interaction between Di-tert-butylazodicarboxylate (TBADDC) and Fe$^{3+}$ ions respect to other metal ions. A new carbon paste ion selective electrode for determination of iron amount was prepared. Using multi-walled carbon nanotube (MWCNT) and nanosilica in the composition of carbon paste electrodes (CPEs) cause improvement in their characterizations. The best performance for nano-composite sensor was obtained with electrode composition of 4% TBADDC, 0.3% nanosilica, 30% paraffin oil (binder), 62.7% graphite powder, and 3% MWCNT. The new Fe$^{3+}$-CPE showed a Nernstian slope of 19.9±0.4 mV per decade with a detection limit of 8.0×10$^{-10}$ mol L$^{-1}$ in the range of 1.0×10$^{-9}$-1.0×10$^{-2}$ mol L$^{-1}$. The sensor could be used in a pH window of 1.6–4.3 and the response time of the sensor was at least 5 s, in addition to its very good Fe$^{3+}$ selectivity over many mono-, di- and trivalent transition and heavy metal ions. The proposed sensor was successfully applied as an indicator electrode for the potentiometric titration of 25 mL of a 10×10$^{-2}$ mol L$^{-1}$ Fe$^{3+}$ ions with a 10×10$^{-3}$ mol L$^{-1}$ EDTA and the monitoring of the Fe(III) concentration ions in some cationic mixtures.

Keywords: multi-walled carbon nanotubes, nanosilica, sensor, carbon paste ion selective, potentiometry, Di-tert-butylazodicarboxylate

1. INTRODUCTION

Multi-walled carbon nanotubes (MWCNTs) have been recently used in composition of carbon paste electrodes [1-4]. CNTs have very interesting physicochemical properties, such as an 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 [5]. The combination of these characteristics makes CNTs unique materials with the potential for diverse
applications. Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical signal [6].

The increasing use of ion sensors in the field of environmental, agricultural, industry and medicinal analysis is putting more and more pressure on analytical chemists to develop new sensors for a fast, accurate, reproducible and selective determination of various species. Iron is widely distributed in nature and is one of the most important elements in biological systems. It is well known that an iron deficiency is the most common cause of anemia. On the other hand, too much iron can cause several health problems. High levels of iron are associated with an increased risk for cancer, hearth disease and other illnesses such as haemochromatosis [7-9]. Regarding its industrial use, iron and its compounds have numerous important industrial applications. However, despite the urgent need for iron-selective sensors for the potentiometric monitoring of Fe$^{3+}$ ions in chemical, biological, industrial and environmental samples, very little work has been done on the development of potentiometric sensors for iron ion [10-16].

Previous selectivity studies [11] showed a selective interaction between Di-tert-butylazodicarboxylate (TBADC)(Fig. 1) and Fe$^{3+}$ ions respect to other common cations. This research focuses on the introduction of a highly Fe$^{3+}$-carbon paste electrode (Fe$^{3+}$-CPE) based on Di-tert-butylazodicarboxylate (TBADC), as an ionophore for determination of Fe$^{3+}$ ion concentration.

![Figure 1. Structure of TBADC.](image-url)

### 2. EXPERIMENTAL PART

#### 2.1. Reagents and materials

The di-tert-butylazodicarboxylate (TBADC), 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. Apparatus

The electrochemical cell used for the determination of EMF the included the Fe(III) sensor as the indicator electrode and an Ag/AgCl electrode (Azar electrode, Iran) as the reference electrode and had a format as below:
2.3. Carbon paste electrode preparation

The modified CPEs were prepared through a general procedure as follows: Desired amounts of TBADC, graphite powder, nano silica, the paraffin oil and MWCNT were thoroughly mixed and then transferred into a glass tube (5 mm i.d. and 3 cm in length). To avoid the formation of air gaps in the structure of the CPE, the mixture was then homogenized before being packed into the tube tip. This can help avoid unwanted increases in the electric resistance of the electrodes. Next copper wire was inserted into the opposite end act as an electrical contact and the external surface of the CPE was cleaned with soft abrasive paper, which was repeated prior to any measurement. The electrode was finally rested for 48 h by being soaked in a $1.0 \times 10^{-3}$ mol L$^{-1}$ of Fe(NO$_3$)$_3$ solution [6, 17-21].

Table 1. The optimization of the nano-composite based Fe(III) carbon paste ingredients

<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>Nano-Silicon</td>
<td>MWCNTs</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>0.3</td>
<td>3</td>
</tr>
</tbody>
</table>

In this research, Fe$^{3+}$-CPE based on the TBADC was created in order to determine Fe(III) ion concentration. Therefore, different carbon paste compositions were tested and the results were summarized in Table 1. The ion carrier is the main ingredient of any ISE [17-21]. To test the selectivity of TBADC as well as the role of the composite concentration on its behavior, the ionophore was used to fabricate a series of nano-composite CPEs having a variety of compositions.

Addition of MWCNT in the composition of the carbon paste electrode not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. Improvement in the conductivity of CPEs, can further improve the dynamic working range and
response time of the sensor. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values (CPE Nos. 9 & 10). Using paraffin oil in the carbon paste electrodes yields more efficient extraction of ions with high charge density into the carbon paste surface (CPE Nos. 1-3). Using nanosilica in the composition of the carbon paste can also improve the response of the electrode. Nanosilica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the CPE. Also, it enhances the mechanical properties of the electrode. However, the composition of 30% paraffin oil, 3% MWCNT, 0.3% nanosilica, 4% TBADC and 62.7% graphite powder illustrate a Nernstian potential response (CPE No. 10).

3.2. Slope and detection limit

The potential response of the created Fe$^{3+}$-CPE at varying concentration of Fe$^{3+}$ ions displays a linear response with respect to the concentration of Fe$^{3+}$ ions in the range of $1.0 \times 10^{-9}$ to $1.0 \times 10^{-2}$ mol L$^{-1}$ (Fig. 2). The slope of calibration graph was 19.9±0.4 mV per decade of the activity of Fe$^{3+}$ ions. The detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph was $8.0 \times 10^{-10}$ mol L$^{-1}$ [22-48]. The standard deviation of 10 replicate measurements is ±0.6 mV.

![Figure 2. Calibration curves of the TBADC-based Fe$^{3+}$-CPE.](image)

3.3. The pH effect

In order to study the effect of pH on the performance of the sensor [49-59], the potentials were determined in the pH range of 0.5-8.0 (the pH was adjusted by using concentrated NaOH or HCl) at concentrations ($1.0 \times 10^{-3}$ mol L$^{-1}$) of Fe$^{3+}$ and the results is depicted in Figure 3. As it is seen, the potential remained constant from pH 1.6 to 4.3, 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 Fe$^{3+}$ 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.** pH effect of the test solution (1.0×10^{-3} mol L^{-1} of Fe^{3+}) of the Fe^{3+}-CPE based on TBADC.

### 3.4. Response time

For analytical applications, dynamic response time is one of the most important factors for any sensor [71-85].

**Figure 4.** Dynamic response time of Fe^{3+}-CPE based on TBADC.
Parameters including the temperature, type and speed of stirring, the concentration and composition of each solution, and preconditioning of the electrode are also known to influence the response time the sensors and they were hence kept at constant values throughout the experiments. In this study, the dynamic response time of the Fe$^{3+}$-CPE was recorded at various concentrations (1.0×10^{-9} to 1.0×10^{-2} mol L^{-1}) of the test solutions and the results are illustrated in Figure 4. As it is obvious, in the whole concentration range the electrode reaches its equilibrium response, very fast (~5 s). This is probably due to the very fast exchange kinetics of complexation-decomplexation of Fe$^{3+}$ with TBADC on the test solution-composite interface.

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

One of the most important characteristics of the CPEs is its relative response towards the primary ion over other ions present in the solution, which is usually expressed in terms of potentiometric selectivity coefficients. In this work, the matched potential method was used for the evaluation of the selectivity of the sensor [60-62]. The matched potential method selectivity coefficient, $K_{MPM}$, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{MPM} = a_A/a_B$. The resulting values are listed in Table 2. For all tested ions, the selectivity coefficients are in the order of 2.0×10^{-4} or smaller, indicating they would not radically disturb the function of the developed Fe$^{3+}$-CPE.

<table>
<thead>
<tr>
<th>Interfering Ion</th>
<th>$K_{MPM}^{Fe^{3+}}$</th>
<th>Interfering Ion</th>
<th>$K_{MPM}^{Fe^{3+}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho$^{3+}$</td>
<td>4.5×10^{-5}</td>
<td>Dy$^{3+}$</td>
<td>6.0×10^{-5}</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>1.0×10^{-4}</td>
<td>Ca$^{2+}$</td>
<td>2.0×10^{-4}</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>5.5×10^{-5}</td>
<td>Co$^{2+}$</td>
<td>6.0×10^{-5}</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>5.0×10^{-5}</td>
<td>K$^+$</td>
<td>9.0×10^{-5}</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>4.0×10^{-5}</td>
<td>Pb$^{2+}$</td>
<td>8.0×10^{-5}</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>6.0×10^{-5}</td>
<td>Ni$^{2+}$</td>
<td>5.0×10^{-5}</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>7.0×10^{-5}</td>
<td>Mg$^{2+}$</td>
<td>7.0×10^{-5}</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>8.5×10^{-5}</td>
<td>Cd$^{2+}$</td>
<td>8.0×10^{-5}</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>6.0×10^{-5}</td>
<td>Na$^+$</td>
<td>1.0×10^{-4}</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>4.0×10^{-5}</td>
<td>Al$^{3+}$</td>
<td>9.0×10^{-5}</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>2.0×10^{-4}</td>
<td>Yb$^{3+}$</td>
<td>8.0×10^{-5}</td>
</tr>
</tbody>
</table>

3.6. Analytical Applications

3.6.1. Titration with EDTA

The proposed Fe$^{3+}$-CPE was successfully applied as an indicator electrode in the titration of 25 mL of Fe$^{3+}$ solution (1.0×10^{-4} mol L^{-1}) with a standard EDTA solution (1.0×10^{-2} mol L^{-1}) and the
resulting titration curve is shown in Figure 5. As can be seen from Figure 5, the endpoint of the titration is sharp and the sensor can monitor the amount of iron ions with good accuracy from the resulting titration curve.

![Graph showing potential titration curves](image)

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

### 3.6.2 Determination of Fe$^{3+}$ in some cationic mixtures

The applicability of the Fe$^{3+}$-CPE was evaluated for monitoring of the Fe$^{3+}$ concentration ions in some cationic mixtures and the results are summarized in Table 3. As can be seen from Table 3, the determination of Fe$^{3+}$ in a low concentration, in the presence of other ions with higher concentration, is possible. As can be seen from Table 3, the recovery of iron ion in the ternary and quaternary mixtures is in the range of 93-104%.

### 4. CONCLUSIONS

In the present study, Fe$^{3+}$ nano-composite carbon paste electrode based on MWCNT and nanosilica is introduced. The performance of Fe$^{3+}$ nano-composite carbon paste sensor can be greatly improved by using nanosilica, and also by using MWCNTs as enhanced signal transducers. This electrode presented the best response characteristics with a Nernstian behavior (slope of $19.9\pm0.4$ mV per decade) across the Fe$^{3+}$ cations concentration range of $1.0 \times 10^{-9}$–$1.0 \times 10^{-2}$ mol L$^{-1}$ with a detection limit of $8.0 \times 10^{-10}$ mol L$^{-1}$ and a fast response time of 5 s. The constructed sensor worked well in the pH range of 1.6–4.3.
Table 3. Determination of Fe$^{3+}$ ion in presence of metal ions mixture.

<table>
<thead>
<tr>
<th>Fe$^{3+}$ (mol L$^{-1}$)</th>
<th>Added cation (mol L$^{-1}$)</th>
<th>Found$^a$ (mol L$^{-1}$)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Eu(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Er(NO$_3$)$_3$</td>
<td>1.04×10$^{-9}$</td>
<td>104</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Gd(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$) Pr(NO$_3$)$_3$</td>
<td>0.95×10$^{-9}$</td>
<td>95</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)La(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Ho(NO$_3$)$_3$</td>
<td>1.01×10$^{-9}$</td>
<td>101</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Dy(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Yb(NO$_3$)$_3$</td>
<td>0.93×10$^{-9}$</td>
<td>93</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Tb(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Nd(NO$_3$)$_3$</td>
<td>0.95×10$^{-9}$</td>
<td>95</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Pb(NO$_3$)$_2$ &amp; (1.0×10$^{-6}$)Ni(NO$_3$)$_2$</td>
<td>1.03×10$^{-9}$</td>
<td>103</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Cr(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Al(NO$_3$)$_3$</td>
<td>0.96×10$^{-9}$</td>
<td>96</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)K(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Mg(NO$_3$)$_2$</td>
<td>1.03×10$^{-9}$</td>
<td>103</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Na(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Ca(NO$_3$)$_2$</td>
<td>0.93×10$^{-9}$</td>
<td>93</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Pb(NO$_3$)$_2$ &amp; (1.0×10$^{-6}$)Ca(NO$_3$)$_2$ &amp; (1.0×10$^{-6}$)K(NO$_3$)</td>
<td>0.93×10$^{-9}$</td>
<td>93</td>
</tr>
<tr>
<td>1.0×10$^{-9}$</td>
<td>(1.0×10$^{-6}$)Al(NO$_3$)$_3$ &amp; (1.0×10$^{-6}$)Na(NO$_3$) &amp; (1.0×10$^{-6}$)Ca(NO$_3$)$_2$</td>
<td>1.02×10$^{-9}$</td>
<td>102</td>
</tr>
</tbody>
</table>

$^a$Results are based on three measurement

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References


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