



## Determination of titanium in orthodontic with modified graphene paste electrode and ionic liquid by potentiometric method

Sara Sahebnaasagh<sup>1</sup>, Mahmoud Ebrahimi<sup>1\*</sup>, Mohammad Reza Bozorgmehr<sup>1</sup>,  
Mohammad Reza Abedi<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

<sup>2</sup>Department of Applied Chemistry, Quchan Branch, Islamic Azad University, Quchan, Iran

DOI: 10.24896/jrmds.20175314

### ABSTRACT

Two new potentiometric methods for determination of titanium in pure form and in its pharmaceutical form are developed. In the first method, new modified carbon paste electrode based on(SAPD) as a chemical modifier. The construction of carbon paste electrode titanium ion-selective electrode and its use in the potentiometric determination of titanium in pharmaceutical preparations and orthodontic cages is described. The electrode displays a linear log  $[Ti^{3+}]$  versus EMF response over a wide concentration range of  $4.1 \times 10^{-7}$  to  $1.2 \times 10^{-3}$  with nernstian slope of  $19.1 \pm 0.1$  mV/decade with limit of detection  $1.1 \times 10^{-7}$  over the pH range 3.8-7.8; a response time of  $<10$  s; and use for at least 3 months without any significant potential divergence the presence of the complex  $Ti(OH)^{2+}$  ion explains the slope of the response curve. The proposed sensor shows reasonable discrimination ability. The modified electrode was applied as indicator electrode to determine  $Ti(III)$  in aqueous samples with satisfactory results.

**Keywords:** Carbon paste; Potentiometry; 2-AAINH; Titanium, orthodontic cages

**HOW TO CITE THIS ARTICLE:** Sara Sahebnaasagh, Mahmoud Ebrahimi, Mohammad Reza Bozorgmehr, Mohammad Reza Abedi, Determination of titanium in orthodontic with modified graphene paste electrode and ionic liquid by potentiometric method, J Res Med Dent Sci, 2017, 5 (3): 88-92, DOI: 10.24896/jrmds.20175314

**Corresponding author:** Mahmoud Ebrahimi

**e-mail:** m.ebrahimi@mshdiau.ac.ir

**Received:** 12/06/2017

**Accepted:** 21/08/2017

### INTRODUCTION

The paint, pigment, paper and pulp industries discharge very high amount of titanium. Titanium is a metal that has been used in various and varied medical applications for about 40 years. Although many biomaterials have come and gone during this period, titanium is one of the few that has seen its uses and reputation enhanced over the years. There are various methods for the determination of titanium utilizing a number of ligands such as pyridylazoresorcinol [1], 5-bromopyridylazodiethylaminophenol [2] thiazolylazoresorcinol with mordant red 19 [3], solochrome violet relay services (RS), [4] Beryllon (III) and cupferron [5-6].

**Determination of titanium by adsorption voltammetry with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol.**

Carbon nanostructure materials, due to their extremely large surface area and excellent adsorption capacity, have been successfully used as adsorbent in SPE and SPME for trapping or separation of some organic compounds [7]. Graphene (G), which was discovered in 2004, is a relatively new form of carbon made of a single layer of atoms arranged in a honeycomb-shaped lattice and has attracted tremendous attention in recent years [8,9]. It is considered as the basic building block of all the graphitic (including carbon nanotubes, graphite and fullerene C60) [10]. In addition to being the principal component of most carbon based nanomaterials, G also exhibits excellent mechanical, electrical, thermal, optical properties and very high specific surface area. Since the large delocalized electron system of G can form a strong  $\pi$ -stacking interaction with the benzene ring [11,12], it might be also a good candidate as an adsorbent for the extraction of benzenoid form compounds. The introduction of magnetic properties into G would combine the high adsorption capacity of G and the separation convenience of magnetic materials.

On the other hand, the rolled version of graphene, carbonnanotube (CNT) has excellent mechanical, electrical, catalytic and electrocatalytic properties [12]. Enormous amount of work has` nanotubes(SWCNT) for electrochemical applications [13]. Pristine CNTs are highly hydrophobic and as a result it is impossible to prepare its stable aqueous dispersion [14]. Ionic liquid (IL), another material, due to its wide electrochemical windows, high ionic conductivity and good solubility has been widely applied in the fields of analytical chemistry and electrochemical sensors[ 15-17]. The acknowledged advantages of these room temperature ionic liquids (RTILs) include good chemical and thermal stability, almost negligible vapor pressure, good ionic conductivity, and wide electrochemical windows etc [18-22].

In this paper the preparation of a new  $Ti^{+3}$  ion selective electrode was described, based on graphene paste electrode with SAPD as a selector element and ionic liquid as modifier. The modified electrode was successfully used as an indicator for potentiometric determination of  $Ti$  (III) in aqueous sample.

## MATERIALS AND METHODS

The room temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) was acquired from Spectrochem. All analytical reagent grade chemicals and distilled water were used for preparing all aqueous solutions. The reagents in this experiment including  $TiCl_3$ , NaOH and HCl were purchased from Merck. All solutions were prepared from distilled water. (65%, Merck), HCl(37%, Merck) and Ethanol (98%) were used as received.

### Apparatus

An Ag/AgCl electrode (saturated KCl) was used as the counter and reference electrodes respectively. Modified graphene paste electrode (GPE) was applied as a working electrode. All experiments were usually directed at room temperature. A Metrohm model 780 pH-meter (Herisau, Switzerland) with a combined glass electrode was utilized for pH controlling, and also a Heidolph type of stirrer (MR 2000, Kelheim, Germany) was applied for stirring the solutions.

### Electrode Preparation

General procedure to prepare the carbon paste electrode was as follows: Different amounts of nanoparticle with an appropriate amount of graphite powder, ionic liquid, paraffin oil and

plasticizer(DBP) were thoroughly mixed. After homogenization of the mixture, the paste was thoroughly packed into the teflon tube and an electric wire was inserted into the opposite end of the GPE to set up electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 12 h by soaking it in a  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  chromium (VI) solution [23-25].

## RESULTS AND DISCUSSION

### Graphene paste electrode composition

The sensing element of a potentiometric ion-selective electrode has important role in selectivity behavior of the electrode. The influence of the percent of materials in the carbon paste composition was investigated and the results are summarized in Table 1.

### Measuring range and detection limit

The response of the optimal modified  $Ti^{3+}$  carbon paste electrode (no.2) was tested across  $Ti^{3+}$  ion concentration range of  $3.1 \times 10^{-2}$ - $4.9 \times 10^{-10} \text{ mol L}^{-1}$ . The applicable range of the proposed sensor extends from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1} \text{ mol L}^{-1}$  as seen in Table 1.

### pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified  $Cr^{6+}$  sensor (no.6), the potential was measured for a fixed concentration of  $Ti^{3+}$  ion solutions at different pH values. The pH was varied from (1-8) by addition of concentrated  $HNO_3$  or NaOH. The change in potential as a function of pH is shown in Fig.1. The potential was constant and quantitative in the pH range of 1.5-5. At  $pH < 1.5$ , the electrode response increased rather irregularly with increasing analyte acidity. At such high acidic solutions, the observed increase in potential indicates that the protonated titanium possesses a poor response to the  $Ti^{3+}$  ions. The pH dependence of the electrode potential for the sensors is tested in presence of  $4.0 \times 10^{-4} \text{ mol L}^{-1}$  titanium (III) concentration after sensor conditioning. The ionic strength in test solution is maintained constant with  $0.1 \text{ mol L}^{-1} NaNO_3$ .

Table 1. The optimization of the Graphen paste ingredients

NO	Composition of graphene Paste (wt.%)					Dynamic linear range
	Graphene	Ionic liquid	Graphene Powder	Plasticizer	Recovery	
1	12	5	72	11	94.5	$3.1 \times 10^{-3}$ - $4.0 \times 10^{-8}$
2	13	5	71	11	98.3	$3.1 \times 10^{-2}$ - $5.2 \times 10^{-10}$
3	10	8	70	12	94.3	$1.4 \times 10^{-2}$ - $5.3 \times 10^{-8}$
4	10	6	70	14	91.2	$3.0 \times 10^{-3}$ - $5.4 \times 10^{-8}$
5	12	7	71	10	93.1	$5.1 \times 10^{-2}$ - $5.5 \times 10^{-8}$
6	12	6	72	10	98.3	$3.1 \times 10^{-2}$ - $4.9 \times 10^{-10}$
7	13	7	76	4	98	$2.2 \times 10^{-2}$ - $5.5 \times 10^{-6}$
8	15	5	75	5	96.2	$43.0 \times 10^{-2}$ - $2.0 \times 10^{-7}$
9	13	7	74	6	94.4	$3.5 \times 10^{-3}$ - $3.1 \times 10^{-10}$
10	12	5	75	8	94.0	$5.3 \times 10^{-4}$ - $4.2 \times 10^{-6}$

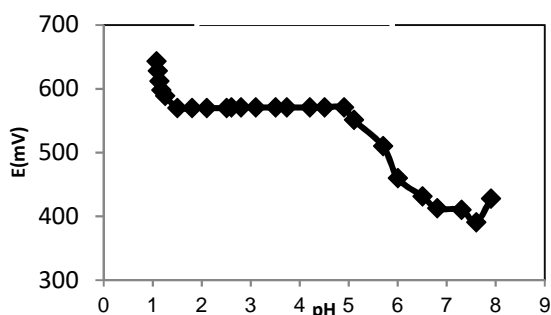


Fig. 1 Effect of pH on the potential response of the Ti<sup>3+</sup> graphene paste electrode in the test solution of Ti<sup>3+</sup> ion (10<sup>-3</sup> mol L<sup>-1</sup>)

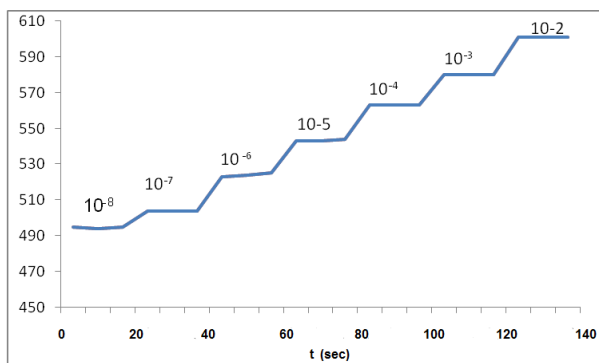


Fig. 2 Dynamic response time of the proposed carbon paste electrode (no.6)

Table 2: Selectivity coefficients of various interfering species for proposed sensor (no.6)

Interfering ions	$K_{ij}^{pot}$	Interfering ions	$K_{ij}^{pot}$
Cu <sup>2+</sup>	$5.1 \times 10^{-3}$	Cd <sup>2+</sup>	$1.3 \times 10^{-3}$
Mg <sup>2+</sup>	$3.2 \times 10^{-3}$	Fe <sup>3+</sup>	$2.1 \times 10^{-2}$
Ca <sup>2+</sup>	$2.5 \times 10^{-2}$	Sr <sup>2+</sup>	$1.1 \times 10^{-3}$

The pH values are adjusted by adding small volumes of diluted nitric acid or sodium hydroxide solutions. The potential value is read and the solution pH is measured when the electrode response is stabilized. The results for solutions containing titanium (III) are shown in Fig. 1. The GPE sensible is pH changes, in presence of Ti(III), with a slope of 19.1mVpH<sup>-1</sup> linear behavior.

**Response time**

Response time is an important factor for any sensor. For electrochemical sensors, this parameter is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. The measurements of potential versus time were carried out with the Ti (III) solutions from lower (1.0×10<sup>-8</sup> M) to

higher ( $1.0 \times 10^{-2}$  M) concentrations (Fig.2). For the proposed modified  $\text{Cr}^{6+}$  sensor, the response time was less than 9s.

### Selectivity

Selectivity is the most important characteristic of any sensor, and describes an ion selective electrode's specificity toward the target ion in the presence of interfering ions, the potentiometric selectivity coefficients of the proposed carbon paste electrode were evaluated by separate solution method (SSM) [26] and the results are depicted in Table 2.

The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with two separate solutions, one containing the ion (i) at the activity  $a_i$ , the other one containing the ion (j) at the same activity  $a_j = a_i$ . If the measured values are  $E_i$  and  $E_j$ , respectively, the value of  $K_{ij}^{pot}$  is calculated from the equation:

$$\log K_{ij}^{pot} = \left[ \frac{Z_i F (E_j - E_i)}{2.303 RT} \right] + \log \left[ \frac{a_i(i)}{a_j(j)^{Z_i/Z_j}} \right]$$

These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

### Analytical applications

The proposed sensor was found to work well under laboratory conditions. It is clear that the amount of Ti(III) ions can be accurately determined using the proposed sensor.

### Determination of mercury in spiked real sample

One gram of the dry and clean orthodontic cages sample was dissolved in minimally concentrated nitric acid and the solution was transferred to a 100 ml of calibrated flask and diluted to the mark with distilled water. The pH of solution was controlled and the measurement was done. With the use of sensor's calibration curve, the nickel content in our sample, obtained from triplicate measurement with electrode. To assess the applicability of the proposed sensor to real samples, Ti(III) was measured in orthodontic cage. Each sample was analyzed in triplicate, using this sensor by the standard addition method. The results, in Table 3, show an average recovery of 92.6% with relative standard deviation (RSD) of 2.43% and indicates the utility of the proposed electrode.

**Table 3. Recovery of copper ions from different water samples**

Sample	Ti <sup>3+</sup> added	Ti <sup>3+</sup> founded	RR%	RSD% (n=3)
Sample 1	$3 \times 10^{-5}$ M	$2.66 \times 10^{-5}$	91.5	3.17
Sample 2	$3 \times 10^{-5}$ M	$2.44 \times 10^{-5}$	92.9	2.91

### CONCLUSION

In this study, a new chemically modified carbon paste electrode based on *N,N*-bis(salicylaldehyde)-phenyldiamine as ionophore and ionic liquid was used for Ti(III) determination. The electrode shows high sensitivity, reasonable selectivity, fast static response, long term stability and applicability over a wide concentration range ( $3.1 \times 10^{-2}$ - $4.9 \times 10^{-10}$ ). The modified electrode was applied as indicator electrode in potentiometric method and successfully used to determine titanium(II) in real samples with satisfactory results.

### REFERENCES

1. E. Grygolowicz-Pawlak, K. Plachecka, Z. Brzozka, E. Malinowska, Sens. Actuators, B 123 (2007) 480-487.
2. J. Zhou, R. Neeb (1990b) J. Anal. Chem., 338: 905.
3. J. Kohn, R.G. Pamela (2008). J. Immunol. Methods, 20: 325.
4. J. Wang, J.S. Mahmoud (1986). J. Electroanal. Chem., 208: 383.
5. X. Zhao, J. Wenrui, W. Xueying (1995) Anal. Chim. Acta, 306: 225.
6. J. Zhou, R. Neeb (1990a). Fresenius J. Anal. Chem., 338: 34
7. L.M. Ravelo-Pérez, A.V. Herrera-Herrera, J. Hernández-Borges, M.A. Odriguez-Delgado, J. Chromatogr. A 1217 (2010) 2618-2641.
8. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306 (2004) 666.
9. M. Farré, J. Sanchis, D. Barcelo, TrAC Trends Anal. Chem. 30 (2011) 517.
10. J.M. Chen, J. Zou, J.B. Zeng, X.H. Song, J.J. Ji, Y.R. Wang, J. Ha, X. Chen, Anal. Chim. Acta 678 (2010) 44.
11. M.J. Allen, V.C. Tung, R.B. Kaner, Chem. Rev. 110 (2010) 132.
12. D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, Chem. Soc. Rev. 39 (2010) 228.
13. J. Wang, Electroanalysis 17 (2005) 7.

14. C.B. Jacobs, M.J. Peairs, B.J. Venton, *Analytica Chimica Acta* 662 (2010)105.
15. L. Vaisman, H.D. Wagner, G. Marom, *Advances in Colloid and Interface Science* 128–130 (2006)37.
16. W. Sun, Y. Duan, Y. Li, H. Gao and K. Jiao, *Talanta*, 2009, 78, 695.
17. J. Peng, C. Hou and X. Hu, *Sens. Actuators, B*, 2012, 169, 81.
18. F. Zhao, X. Wu, M. Wang, Y. Liu, L. Gao and S. Dong, *Anal. Chem.*, 2004, 76, 4960.
19. Y. Liu, J. Li, M. Wang, Z. Li, H. Liu, P. He, X. Yang and J. Li, *Cryst. Growth Des.*, 2005, 5, 1643.
20. Y. Liu, M. Wang, J. Li, Z. Li, P. He, H. Liu and J. Li, *Chem. Commun.*, 2005, 1778.
21. K. Liu, J. Zhang, G. Yang, C. Wang and J.-J. Zhu, *Electrochem. Commun.*, 2010, 12, 402.
22. H. Liu, P. He, Z. Li, C. Sun, L. Shi, Y. Liu, G. Zhu and J. Li, *Electrochem. Commun.*, 2005, 7, 1357.
23. H. Liu, P. He, Z. Li, Y. Liu and J. Li, *Electrochim. Acta*, 2006, 51, 1925.
24. MR. Ganjali, H. Khoshafar, F. Faridbod, A. Shirzadmehr, M. Javanbakht, P. Norouzi 21, 2009; 19:2175.
25. MR. Ganjali, N. Motakef-Kazemi, P. Norouzi, S. Khoei *Int J Electrochem Sci.* 2009;4(7):906.
26. MR. Ganjali, H. Khoshafar, A. Shirzadmehr, M. Javanbakht, *Int J Electrochem Sci.* 2009; 4(3):435.
27. MR. Ganjali, H. Khoshafar, A. Shirzadmehr, M. Javanbakht, F. Faridbod (2009) *Int J Electrochem Sci* 4 (3):435-443.