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Multiwall carbon nanotubes chemically modified carbon paste electrodes for determination of gentamicin sulfate in pharmaceutical preparations and biological fluids

M.M. Khalil *, G.M. Abed El-aziz

[a] Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt

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ABSTRACT

This article focused on the construction and characteristics of novel and sensitive gentamicin carbon paste electrodes which are based on the incorporation of multiwall carbon nanotubes (MWCNTs) which improve the characteristics of the electrodes. The electrodes were constructed based on gentamicin-phosphotungstate (GNS-PTA) called CPE_1, gentamicin-phosphomolybdate (GNS-PMA) called CPE_2, GNS-PTA + MWMCNTs called $MWCPE_1$, and GNS-PMA + MWMCNTs called $MWCPE_2$. The constructed electrodes, at optimum paste composition, exhibited good Nernstian response for determination of gentamicin sulfate (GNS) over a linear concentration range from 2.5×10^{-6} to 1×10^{-2}, 3.0×10^{-6} to 1×10^{-2}, 4.9×10^{-7} to 1×10^{-2} and 5.0×10^{-7} to 1×10^{-2} mol L^{-1}, with lower detection limit 1×10^{-6}, 1×10^{-6}, 1.9×10^{-7} and 2.2×10^{-7} mol L^{-1}, and with slope values of 29.0 ± 0.4, 29.2 ± 0.7, 31.2 ± 0.5 and 31.0 ± 0.6 mV/decade for CPE_1, CPE_2, $MWCPE_1$ and $MWCPE_2$, respectively. The response of electrodes is not affected by pH in the range 3–8 for CPE_1 and CPE_2 and in the range 2.5–8.5 for $MWCPE_1$ and $MWCPE_2$. The results showed fast dynamic response time (about 8–5 s) and long lifetime (more than 2 months) for all electrodes. The sensors showed high selectivity for gentamicin sulfate (GNS) with respect to a large number of interfering species. The constructed electrodes were successfully applied for determination of GNS in pure form, its pharmaceutical preparations and biological fluids using standard addition and potentiometric titration methods with high accuracy and precision.

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1. Introduction

Gentamicin[(3R,4R,5R)-2{[(1S,2S,3R,4S,6R)-4,6-diamino-3-{[(2R,3R,6S)-3-amino-6-[(1R) 1(methylamino)ethyl]oxan-2-yl]oxy}-2hydroxycyclohexyl]oxy}5-methyl-(methylamino)oxane-3,5 diol] sulfate is a lipophilic aminoglycoside derivative which appears as white to off white crystalline powder (Fig. 1). The drug is freely soluble in water [1]. pKa value of GNS is 10.18 [2]. GNS melts at 218–237 °C [3]. Data on reported techniques [4,5] for GNS determination in various objects were mainly based on chromatographic and spectrophotometric techniques. Nevertheless, most of these methods required expensive apparatuses or involving several manipulation steps before reaching the final result of analysis. An interest has been increased for developing reliable rapid and accurate procedures for GNS quantification.

Electrochemical detection of an analyte is a very elegant method in pharmaceutical analysis due to its high sensitivity, rapid response, simple operations and low cost [6]. Potentiometric methods are of choice; since they possess advantages of simplicity, accuracy without the need for separation or pretreatment procedures and common availability of the instrumentation. Ion-selective electrode is a transducer or sensor that converts activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a voltmeter or pH meter. The voltage is theoretically dependent on logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode.

In 1996, Britto et al. [7] demonstrated for the first time use of carbon nanotubes (CNTs) in the study of dopamine detection. The research in the field of sensors based on CNTs is still a hot topic and a number of excellent review articles have been published [8–13]. MWCNTs have very 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 semimetallic behavior and high surface area. The facility of electron transfer between the electroactive species and the electrodes offers great promises for fabricating electrochemical sensors and biosensors. The combination of these characteristics makes MWCNTs unique materials with the potential for diverse applications [14–18].

The present work describes construction and investigation of performance characteristics of novel potentiometric sensors for the determination of GNS in pure form, pharmaceutical preparation and biological fluids.

* Corresponding author.
E-mail addresses: magdy_mmagdy@yahoo.com, mohamed.mahmoud@science.bsu.edu.eg (M.M. Khalil), Gamal_abedelaziz@yahoo.com (G.M. Abed El-aziz).

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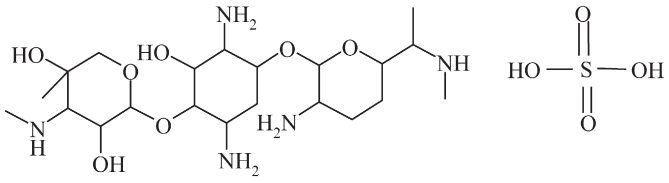

Fig. 1. Chemical structure of gentamicin sulfate.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and double distilled water was used throughout the experiments. Dioctyl sebacate (DOS), tricresyl phosphate (TCP), acetyl tributyl citrate (ATBC), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) were purchased from Merck (Germany). Phosphotungstic acid (PTA) and phosphomolybdic acid (PMA) were obtained from Fluka (USA). The metal salts were provided by BDH Company (UK) as nitrates or chlorides. Spectroscopic graphite powder (1–2 μm, Aldrich) and multi-walled carbon nanotube (supplied by faculty of graduate studies and advanced sciences, Beni-Suef, Egypt) were applied as electrode materials.

Stock solutions of the metal salts were prepared in double distilled water and standardized whenever necessary. In analysis of the biological fluids, human urine and plasma were used; furthermore plasma was obtained from Regional Blood Transfusion Center, Beni-Suef, Egypt and used within 24 h.

Pure-grade GNS ($C_{21}H_{43}N_5O_7 \cdot H_2SO_4$, M · wt = 575.67 g mol^{-1}, assigned to be 99%) was provided by Sigma for pharmaceutical industry, Egypt. The pharmaceutical preparation Epigent® (GNS, 80 mg/2 ml ampoules) was purchased from local drug stores. Standard solution of 10^{-2} mol L^{-1} GNS was freshly prepared by dissolving the accurately weighed amount in double distilled water. Working solutions of the drug (1×10^{-7}–1×10^{-2} mol L^{-1}) were prepared by accurate dilution from the standard solution using double distilled water and kept at 4 °C.

Stock solutions of 10^{-2} mol L^{-1} PTA or PMA were prepared by dissolving the accurately weighed amount of the pure solid in double distilled water. Solutions of sodium hydroxide and hydrochloric acid of concentrations within the range 0.1–1 mol L^{-1} were used for adjusting the pH of the medium.

2.2. Apparatus

Silver-silver chloride double-Junction reference electrode (Metrohm 6.0726.100) in conjugation with different drug ion-selective electrode was used. Potentiometric and pH-measurements were carried out using 702 titroprocessor equipped with a 665 Dosimat (Switzerland) made by Metrohm. An mLw W20 circulator thermostat was used to control temperature of the test solutions. The electrochemical system of the CPEs may be represented as follows: Modified carbon paste electrode/test solution//KCl salt bridge//Ag/AgCl reference electrode

2.3. Procedure

2.3.1. Preparation of the ion-pair compounds

The ion-pair compounds, GNS-PTA and GNS-PMA, were prepared by slow addition of 50 mL of 10^{-2} mol L^{-1} PTA or PMA solution to 75 mL of 10^{-2} mol L^{-1} GNS under stirring for 15 min. The resulting precipitates were left in contact with their mother liquor for 24 h to assure coagulation, Then the precipitates were filtered off through a Whatman Filter Paper no.42, washed with double distilled water several times, left some days to dry at room temperature and ground to fine powder. Composition of the ion-pairs was confirmed by elemental analysis.

2.3.2. Conductometric measurement

Conductometric titrations were followed with a Jenway conductivity meter. 50 mL of 1×10^{-3} mol L^{-1} GNS solution was transferred to the 100-mL cell and the solution was titrated against a 1×10^{-2} mol L^{-1} PTA or a 1×10^{-2} mol L^{-1} PMA solution using a microburette. The conductance of the solution was measured after thorough stirring with each addition (2 min, intervals). Conductance values were corrected through multiplying by the dilution coefficient and plotted versus molar ratio. The titration plot showed a break which corresponds to the stoichiometry of the ion-pair.

Table 1
Optimization of the carbon paste ingredients.

Electrode no.	Composition of membrane% (w/w; mg)				Slope mV/decade	L.R. (mol L^{-1})	LOD (mol L^{-1})	RSD %
	IP	MWCNTs	Graphite	DBP				
CPE_1								
1	1	–	56	43	22.4 ± 2.1	1.0×10^{-5}–1×10^{-2}	1.0×10^{-5}	1.91
2	2	–	56	42	25.7 ± 1.3	7.5×10^{-6}–1×10^{-2}	6.0×10^{-6}	1.75
3	**3**	–	**55**	**42**	**29.0 ± 0.4**	**2.5×10^{-6}–1×10^{-2}**	**1.0×10^{-6}**	**1.51**
4	4	–	54.5	41.5	26.2 ± 0.9	6.0×10^{-6}–1×10^{-2}	5.0×10^{-6}	1.66
5	5	–	54	41	20.4 ± 2.4	1.0×10^{-5}–1×10^{-2}	1.0×10^{-5}	1.81
CPE_2								
6	1	–	56	43	23.7 ± 2.5	1.0×10^{-5}–1×10^{-2}	1.0×10^{-5}	1.85
7	2	–	56	42	26.8 ± 1.0	6.0×10^{-6}–1×10^{-2}	5.0×10^{-6}	1.90
8	**3**	–	**55**	**42**	**29.2 ± 0.7**	**3.0×10^{-6}–1×10^{-2}**	**1.0×10^{-6}**	**1.65**
9	4	–	54.5	41.5	26.1 ± 0.8	8.8×10^{-6}–1×10^{-2}	8.0×10^{-6}	1.72
10	5	–	54	41	24.3 ± 1.9	1.0×10^{-5}–1×10^{-2}	1.0×10^{-5}	1.93
$MWCPE_1$								
11	3	1	54	42	29.4 ± 0.8	1.0×10^{-6}–1×10^{-2}	8.9×10^{-7}	1.80
12	3	3	52	42	30.3 ± 1.0	6.5×10^{-7}–1×10^{-2}	5.5×10^{-7}	1.66
13	**3**	**5**	**50**	**42**	**31.2 ± 0.5**	**4.9×10^{-7}–1×10^{-2}**	**1.9×10^{-7}**	**1.24**
$MWCPE_2$								
14	3	1	54	42	29.5 ± 0.7	8.2×10^{-7}–1×10^{-2}	8.0×10^{-7}	1.45
15	3	3	52	42	30.5 ± 1.3	6.4×10^{-7}–1×10^{-2}	5.6×10^{-7}	1.66
16	**3**	**5**	**50**	**42**	**31.0 ± 0.6**	**5.0×10^{-7}–1×10^{-2}**	**2.2×10^{-7}**	**1.32**

LR: Linear range.
LOD: limit of detection.
RSD: relative standard deviation (four determinations).