Potentiometric Carbon Paste Electrodes for the Determination of Bismuth in Some Pharmaceutical Preparations

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The construction and general performance characteristics of two novel potentiometric membrane sensors responsive to bismuth are described. The sensors are based on the use of ion-association complexes of tetraiodobismate(III) (TIB) anion with polyoxyethylene(10) octyl phenyl ether (**1**) and tris(1,10-phenanthroline)iron(II) (**2**) as exchange sites in a carbon paste matrix. The sensors show fast, stable, and near-Nernstian response for the mono-charged anion of tetraiodobismate(III) over the concentration range 1×10^{-3}–$1 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$ at 25 °C over the pH range 4.0–9.0 and 3.0–8.0 with an anionic slope of 51.5 ± 0.5 and 53.0 ± 0.4 per concentration decade for tetraiodobismate(III)-**1** and -**2** (sensor-**1** and sensor-**2**), respectively. The lower detection limit was 4×10^{-6} and $2 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$ with a response time of 20–40 s for sensor-**1** and sensor-**2** in the same order. The selectivity coefficients for bismuth relative to a number of interfering anions and iodide complexes of some metal ions were investigated. Direct potentiometric determination of 1–200 $\mu\mathrm{g\,cm^{-3}}$ of bismuth in aqueous solution showed an average recovery of 98.4% and a mean relative standard deviation of 1.5% at 80.0 $\mu\mathrm{g\,cm^{-3}}$. The determination of bismuth(III) in suppositories and ointment dosage form in the present study was comparable with the British pharmacopoeia method.

The medical and clinical utilization of bismuth dates back about 70 years, when the element was first introduced in pharmaceutical use for the treatment of syphilis;[1] it is also used for the treatment of hyperacidity, and peptic ulcer and also used in various dermatological preparations. Therefore, there is a necessity for determination of bismuth contents in pharmaceutical formulations.[2]

Several analytical techniques have been reported for the quantitative determination of bismuth, among them spectrophotometry,[3,4] electrothermal atomic absorption spectrometry (ET-AAS),[5,6] hydride-generation atomic-absorption spectrometry (HG-AAS),[7,8] inductively coupled plasma mass spectrometry (ICP-MS),[9] anodic-stripping voltammetry,[10–12] and potentiometry.[13–19] Most of these methods involve several time-consuming manipulation steps and require sophisticated instruments. Potentiometric methods using ion-selective electrodes have found wide application in diverse fields of analysis being of low cost, selective, sensitive, and applicable over a wide range of experimental conditions.[20–22]

Different ion-selective electrodes have been used for determination of bismuth including liquid membrane incorporated trioctylmethylammonium-TIB,[13] trinonyloctylammonium-TIB,[14] and bismuthiol[15] as electroactive material. In another method, Alexander and Joseph have investigated coated wire electrodes based on tricaprylmethylammonium chlorobismuthate[16] as electroactive material. A coated graphite–epoxy ion-selective electrode for bismuth(III) based on the ion-pair between [Biedta]$^-$ anion and tricaprylmethylammonium cation (Aliquot 336 S) incorporated onto PVC matrix has also been reported.[17] The liquid membrane based on the ion-pair between [Biedta]$^-$ with high molecular quaternary ammonium salt (QASs)[18] and tridecylmethylammonium cations[19] as electroactive material has been described. Electrochemical methods based on chemically modified carbon paste electrodes (CMCPEs) have found wide applications[12,23,24] being simple, economical, and applicable over a wide range of conditions. In comparison with ion-selective electrodes based on polymeric membranes, the CMCPEs possess advantages of much lower ohmic resistance, very stable response and easy renewal of its surface. Although considerable attention has been given to the preparation of CMCPEs so far, the application of these CMCPEs mainly has been focused on the field of voltammetric determination[12,24] and only very few of these types of electrodes have been used in potentiometry.[25–27] The aim of the present work was to develop a carbon-paste electrode for potentiometric determination of bismuth in some pharmaceutical formulations. The method was based on formation of ion-associate complexes that can be used as an electroactive site in a carbon paste electrode. This work is based on the same basic principle as was done previously[28,29] in which a chemically modified electrode was constructed by incorporating the ion-associate complex into carbon paste matrix. The sensitivity and stability offered by this simple electrode configuration are high enough to allow accurate determination of low level of bismuth compared to reported methods.[13–16,18,19]

Experimental

Apparatus. All potentiometric measurements were made at 25 ± 1 °C unless otherwise stated using an Orion pH/mV meter (model 330) and a combined Ross glass pH electrode (Orion 81-02) was used for pH measurements. An Orion double junction Ag/AgCl reference electrode (model 90-02) containing

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10% (w/v) potassium nitrate in the outer compartment was used.

Reagents and Materials. All chemicals used were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. *o*-Nitrophenyl octyl ether (*o*-NPOE), potassium iodide, bismuth(III) nitrate pentahydrate, polyoxyethylene(10) octyl phenyl ether (Triton X-100) and 1,10-phenanthroline and graphite powder were obtained from Aldrich Chemical Company. The stock solution of 1×10^{-1} mol dm^{-3} bismuth(III) was prepared by dissolving the appropriate amount of bismuth(III) nitrate pentahydrate in 50 cm^3 of (1 + 3) nitric acid and diluting to exactly 1000 cm^3 with water. Potassium iodide–ascorbic acid reagent was prepared by dissolving an appropriate amount of reagent grade potassium iodide (0.5 mol dm^{-3}) and 1 g of ascorbic acid in distilled water and diluting to 100 cm^3. Phthalate buffer of pH 4.0 and citrate buffer of pH 3.0 were freshly prepared. A standard solution of 1×10^{-2} mol dm^{-3} bismuth(III) as tetraiodobismate(III) was prepared by suitable dilution of the stock solution of 1×10^{-1} mol dm^{-3} bismuth(III) in excess amount of 0.2 mol dm^{-3} KI, acidified $\approx$1 mol dm^{-3} H_2SO_4 in a 100 cm^3 measuring flask and completed to the mark with water. Standard solutions of tetraiodobismate(III) were prepared (1×10^{-2}–1×10^{-5} mol dm^{-3}) by diluting the appropriate amount in double-distilled water. Anusol suppositories and ointment, were obtained from the local pharmacy, which were produce by Alkan Pharma, Egypt.

Preparation of the Bismuth Carbon Paste Electrode. The tetraiodobismate(III) was formed by reaction of bismuth(III) with potassium iodide in acidic medium.[30,31] The potentiometric response characteristic of bismuth sensors are based on the formation of tetraiodobismate(III) anion, which forms when potassium iodide is added to a dilute sulfuric acid solution containing a small amount of bismuth.[32] Upon the addition of 50-mL 1×10^{-2} mol dm^{-3} of bismuth as tetraiodobismate(III) to a 50 cm^3 aliquot of 1×10^{-2} mol dm^{-3} polyoxyethylene(10) octyl phenyl ether or a 25 dm^{-3} aliquot of 1×10^{-2} mol dm^{-3} tris(1,10-phenanthroline)-iron(II), a whitish or red precipitate of tetraiodobismate(III)-**1** or tetraiodobismate(III)-**2** ion exchangers were formed. The precipitates were filtered through Whatman filter paper No. 41, thoroughly washed with doubly distilled water and dried at 50 °C. The dry powders of the formed ion associate have been used for the construction of new chemically modified carbon paste electrodes. The elemental analysis showed that the composition of the complex is 1:1 and 2:1 for tetraiodobismate(III)-**1** and tetraiodobismate(III)-**2**. The sensing electrodes were prepared by mixing two portions of 10 mg of the ion-associate complex with 250 mg graphite powder and 125 µL of NOPE in two separate glass Petri dishes. The resulting paste electrodes were used for sensor construction as previously described.[28,29] Electrode bodies were made from disposable 1 cm^3 polyethylene syringes the tip of which had been cut off with a cutter. These bodies were filled with an approximate amount of such chemical-modified carbon paste (CMCP). Smooth surfaces were obtained by applying manual pressure to the piston while holding the electrode surface against a smooth solid support. A fresh electrode surface was obtained by applying manual pressure to the carbon paste, scraping off the excess against conventional paper and polishing the electrode on a smooth paper to obtain a shiny appearance. The electrical contact to the carbon paste was made with a copper wire. The electrochemical cell used for potential measurements was: Ag/AgCl‖test solution‖CMCPE. The indicator electrode was conditioned by soaking in a 1×10^{-2} mol dm^{-3} aqueous bismuth(III) as tetraiodobismate(III) solution for 1 h and stored in the same solution when not in use.

Procedure. The newly constructed ISEs were calibrated by immersion in conjunction with the reference electrode in a 50 dm^{-3} beaker containing 9.0 dm^{-3} of phthalate or citrate buffer solution of pH 4.0 or 3.0 respectively. Then, a 1.0 cm^3 aliquot of tetraiodobismate(III) solution of concentration ranging from 1×10^{-2} to 1×10^{-5} mol dm^{-3} was added with continuous stirring and the potential was recorded after stabilization to ±0.2 mV. A calibration graph was then constructed by plotting the recorded potentials as a function of $-\log$ [TIB]. The resulting graph was used for subsequent determination of unknown bismuth concentration. Alternatively, the potentials displayed by bismuth test solution before and after the addition of a 1.0 cm^3 aliquot of 1×10^{-2} mol dm^{-3} tetraiodobismate(III) were measured. The change in the potential readings was recorded and used to calculate the unknown bismuth concentration in the test solution using standard addition technique.

Determination of Bismuth in Pharmaceutical Preparations. For the analysis of bismuth in pharmaceutical preparations, the digestion of sample was done as reported.[30] Samples were place in Kjeldahl flasks and to them were added 6.0 cm^3 of concentrated nitric acid followed by 3 cm^3 of 72% perchloric acid. The mixture was warmed gently and the solution was filtered into 100 cm^3 measuring flasks, and diluted to the mark with water. A 10 cm^3 aliquot of filtrate sample was transferred to a 50 cm^3 measuring flask, excess iodide concentration was added to give the final concentration of iodide to 0.2 mol dm^{-3}. The potential of this solution was measured by immersing the proposed sensors in conjunction with an Orion Ag/AgCl double junction reference electrode. The potential of the stirred solution was recorded after stabilization to ±0.2 mV and compared with the previous calibration curve. Alternatively, the potentials displayed by bismuth test solution before and after the addition of a 1.0 cm^3 aliquot of 1×10^{-2} mol dm^{-3} tetraiodobismate(III) to 10 cm^3 of unknown test solution and the change in the potential readings were measured.

Results and Discussion

The performance characteristics of the bismuth ion selective electrodes based on the use of tetraiodobismate(III) with **1** or **2** as ion-exchanger complex or as electroactive material and *o*-NPOE as a solvent mediator in a graphite powder matrix were evaluated according to IUPAC recommendations[33] and the response characteristics of tetraiodobismate(III) sensors based on these complexes are summarized in Table 1. In phthalate buffer of pH 4.0 sensor-**1** exhibits a linear and stable response for bismuth ion over the concentration range of 1×10^{-3}–6×10^{-6} mol dm^{-3} with anionic response of 51 ± 0.2 mV/decade. On the other hand, sensor-**2** exhibited a linear response

Table 1. Response Characteristics of the Modified Carbon Paste Electrodes

Parameter	Value	
	Sensor-**1**	Sensor-**2**
Slope (mV/decade)	-51.0 ± 0.5	-53.0 ± 0.4
Intercept/mV	123.0 ± 0.6	91 ± 0.6
Correlation coefficient (*r*)	0.997	0.998
Detection limit/mol dm^{-3}	4×10^{-6}	2×10^{-6}
Response time for 1×10^{-3} mol dm^{-3} solution/s	20 ± 0.5	15 ± 0.6
Working pH range	4–9	3–8

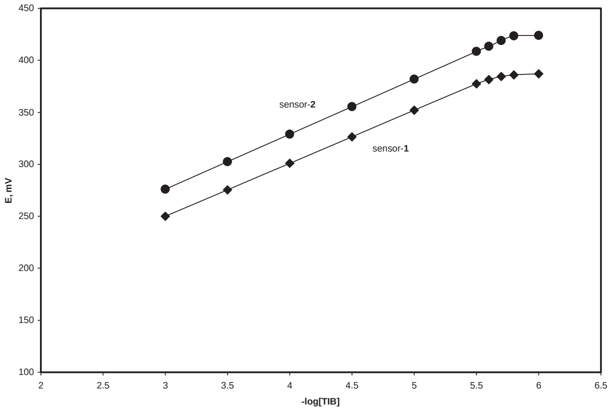

Fig. 1. Calibration graph of sensor-**1** and sensor-**2** using the proposed electrodes.

of 1×10^{-3}–4×10^{-6} mol dm^{-3} in citrate buffer of pH 3.0 with anionic response of 53.0 ± 0.5 mV. The lower limit of detection (LOD) was estimated and confirmed by two criteria, first one is 3σ and the second is relative standard deviation (R.S.D. %) which is not less than 2.5% for five replicates. Also LOD defined as the concentration of bismuth(III) as tetraiodobismate(III) corresponding to the intersection of the extrapolated linear segments of the calibration graph which is 4×10^{-6} mol dm^{-3} (0.85 µg cm^{-3}) and 2×10^{-6} mol dm^{-3} (0.45 µg cm^{-3}) for sensor-**1** and sensor-**2**, respectively. The calibration slopes of the two proposed sensors over the linear response ranges are stable within ±0.55 for at least five weeks. The reproducibility of the proposed method (day to day or intraday) was investigated, the results obtained are with the acceptance range (R.S.D < 2.5%). The calibration graph for both electrodes is shown in Fig. 1. The least-squares equation obtained under these conditions is:

$$E(\text{mV}) = -(51.0 \pm 0.6) \log{[\text{TIB}]} + 123.0 \pm 0.6 \quad \text{for sensor-}\mathbf{1}. \qquad (1)$$

$$E(\text{mV}) = -(53.0 \pm 0.5) \log{[\text{TIB}]} + 91.0 \pm 0.6 \quad \text{for sensor-}\mathbf{2}. \qquad (2)$$

Effect of pH and the Response Time. The effect of pH on the potential of the sensors was checked by recording the emf of both sensors by varying the acidity by the addition of very small volumes of hydrochloric acid and/or sodium hydroxide. The graph presented in Fig. 2 shows linearity in the pH range of 3–9. For pH values less than 3 there is a decrease in the potential of the electrode that may be due to leaching of the ion associate in acidic medium. In the pH range of 3–9, the tetraiodobismate(III) complex does not suffer influence of the medium, which demonstrate that the bismuth(III) complexes with iodide. At pH values higher than 9–12 the potentials change quickly because of precipitation of bismuth as hydroxide.

On the other hand, upon testing different types of buffer solution e.g. citrate, phthalate, phosphate, and borate in the suitable pH range of the proposed membrane sensors, most of the investigated buffer solutions were found to be suitable for measurement. The best buffer solutions are phthalate and citrate of pH 4.0 and 3.0 respectively for sensor-**1** and -**2**, which does not cause change of pH more than 0.15 pH unit for the final concentration of 1×10^{-3}–10^{-6} mol dm^{-3} for both sensors.

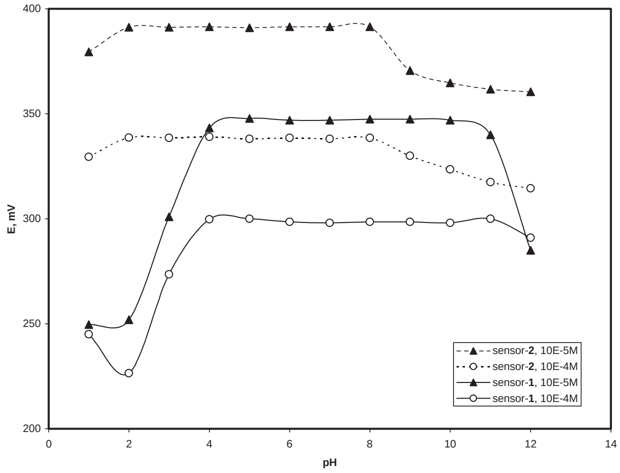

Fig. 2. Effect of pH on the response of sensor-**1** and sensor-**2** using two series of 1×10^{-5} and 1×10^{-4} mol dm^{-3} of tetraiodobismate(III).

The average response time is defined[33] as the time required for the electrode to reach a stable potential within ±0.1 mV of the final equilibrium value, after successive immersion of the electrode in different tetraiodobismate(III) solutions, each having a 10-fold difference in concentration or after rapid 10-fold increases in concentration by addition of tetraiodobismate(III). This time was found to be 20 s for concentration of $\geq 1 \times 10^{-3}$ mol dm^{-3} and 30 s for concentration $\leq 1 \times 10^{-4}$ mol dm^{-3}. The reproducibility of the proposed method (day to day or intraday) was investigated, the results obtained are within the acceptance range (R.S.D < 2.5%). The sensors show that one week has no significant effect on their performance.

Effect of Ion-Exchanger Percentage. It is known that the potentiometric sensitivity and linearity for a given ion exchanger depend significantly on its membrane concentration. In preliminary experiments, it was found that the amounts of ion-exchanger complex exhibit a direct effect on the activity of tetraiodobismate(III) as indicated by the e.m.f response of the sensors towards the tetraiodobismate(III). At high concentration of the ionic exchanger, unsatisfactory potentiometric results have been obtained. The best results (slope, standard error, correlation factor) were obtained at electrodes containing 3.84% (10 mg) for each electrode (sensor-**1** and sensor-**2**). On the other hand, it has been found that, an electrode containing zero percentage of the modifiers showed a negligible response. Therefore, in all incoming studies carbon paste ion selective electrodes were prepared by using a casting solution of the composition 3.84:96.1:0.057% (w/w) ion exchanger, graphite powder, and *o*-NPOE as solvent mediator respectively.

Effect of Potassium Iodide Concentration. The negatively charged tetraiodobismate(III) is formed in acidic solution containing excess iodide. The effect of iodide concentration on the response of the two proposed electrodes was studied, in respect of concentration range and lower limit of detection. The response of the proposed electrodes increased with increasing concentration of iodide solution, 0.1 mol dm^{-3} iodide give a Nernstian slope of about 51.0 ± 0.6 and 53.0 ± 0.5 mV

Table 2. Potentiometric Selectivity Coefficients of Some Common Species, Using the Proposed Modified Carbon Paste Electrodes[a)]

Interferent, J	$K^{\mathrm{Pot}}_{\mathrm{TIB,J}}$		Interferent, J	$K^{\mathrm{Pot}}_{\mathrm{TIB,J}}$	
	Sensor-**1**	Sensor-**2**		Sensor-**1**	Sensor-**2**
Hg^{2+}	0.59	0.5	Phosphate	1.5×10^{-4}	1.4×10^{-4}
Cd^{2+}	0.62	0.60	Citrate	1.2×10^{-4}	1.5×10^{-4}
Sb^{3+}	0.74	0.71	Tartrate	1.2×10^{-3}	1.6×10^{-3}
Cu^{2+}	3×10^{-3}	2×10^{-3}	$Cr_2O_7{}^{2-}$	1.2×10^{-3}	1.2×10^{-3}
Pb^{2+}	3×10^{-3}	2×10^{-3}	$MnO_4{}^{-}$	1.0×10^{-3}	1.0×10^{-3}
Ag^{+}	2×10^{-2}	3×10^{-2}	Ce^{4+}	1.2×10^{-3}	1.2×10^{-3}
Fe^{3+}	1.3×10^{-3}	1.4×10^{-2}	Fe^{2+}	1.1×10^{-3}	1.1×10^{-3}
Zn^{2+}	2.3×10^{-3}	1.3×10^{-3}	Sucrose	1.1×10^{-3}	1.1×10^{-3}
$ClO_4{}^{-}$	1.5×10^{-3}	1.4×10^{-3}	Lactose	1.0×10^{-3}	1.0×10^{-3}
$IO_4{}^{-}$	1.4×10^{-3}	1.6×10^{-3}	Glucose	1.0×10^{-3}	1.0×10^{-3}
F^{-}	1.6×10^{-3}	1.5×10^{-3}	Mg stearate	1.0×10^{-3}	1.1×10^{-3}
Cl^{-}	2.2×10^{-4}	2.2×10^{-4}	Gum accacia	1.1×10^{-3}	1.1×10^{-3}
SCN^{-}	1.2×10^{-3}	1.3×10^{-4}	Cellulose	1.0×10^{-3}	1.0×10^{-3}

a) All metal was tested as metal iodide complex.

for sensor-**1** and sensor-**2** respectively. Again increasing the iodide concentration gave no change in the electrode response until 0.3 mol dm^{-3}, after that concentration the slope began to decrease. Therefore, 0.2 mol dm^{-3} of KI was chosen as the optimum amount of KI.

Interferences Study. The selectivity of a membrane material towards an interfering ion (B) is usually quantified by the so-called selectivity coefficient $K^{\mathrm{Pot}}_{\mathrm{TIB,B}}$ i.e. the ability of an ion-selective electrode to distinguish a particular ion from others. The best selectivity corresponds to very low ($K^{\mathrm{Pot}}_{\mathrm{TIB,B}}$). The selectivity coefficient $K^{\mathrm{pot}}_{\mathrm{A,B}}$ was measured by both separate solution method and mixed solution method.[33,34] The selectivity coefficient measured by separate solution method was calculated from the following equation:

$$E_2 - E_1/S = \log[a_{\mathrm{TIB}} + K^{\mathrm{pot}}_{\mathrm{A,B}}(a_{\mathrm{B}})^{1/z}], \tag{3}$$

where E_1 and E_2 are the potential reading observed after 1 min of exposing the sensor to the same concentration of tetraiodobismate(III) and interfering species (1×10^{-3} mol dm^{-3} each) alternatively. a_{TIB} and a_{B} are the activities or concentration of tetraiodobismate(III) and interfering ions of z and y charges, respectively, and S is the slope of calibration graph (mV/concentration). The selectivity coefficient by mixed solution method was defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. The selectivity coefficient $K^{\mathrm{pot}}_{\mathrm{A,B}}$ measured by mixed solution method was calculated from the following equation:

$$K^{\mathrm{pot}}_{\mathrm{A,B}} = (a'_{\mathrm{A}} - a_{\mathrm{A}})/a_{\mathrm{B}}, \tag{4}$$

where a'_{A} is the known activity of primary ion, a_{A} is the fixed activity of primary ion and a_{B} is the activity of interfering ions. The results obtained in Table 2 show the selectivity coefficient for tetraiodobismate(III) by both sensors with many other common anions and metal iodide. Mercury, cadmium, and antimony are significant interferences due to the formation of the similar structures tetraiodocadmate $[CdI_4]^{2-}$, tetraiodomercurate $[HgI_4]^{2-}$, and tetraiodoantimonate $[SbI_4]^{-}$. There was no response of the proposed sensors to a number of interfering ionic excipients. On the other hand, copper, lead, and silver do not interfere; copper reacts with iodide forming insoluble Cu_2I_2, lead forming insoluble Pb_2I_2, and silver forming insoluble AgI which do not interfere with the tetraiodo complex of bismuth. Some metals e.g. iron(III) oxidize iodide to iodine; also periodate is reduced by iodide to iodine. Their effects can be eliminated by addition of ascorbic acid as reducing agent.

Table 3. Determinations of the Percentage Recovery of Bismuth from Water by Direct Potentiometry Using the Proposed Carbon Paste Electrodes

Added /µg cm^{-3}	Found/µg cm^{-3}		Recovery/%[a)]	
	Sensor-**1**	Sensor-**2**	Sensor-**1**	Sensor-**2**
1.0	0.975	0.975	97.5 ± 1.7	97.5 ± 1.8
10.0	9.75	9.8	97.5 ± 1.7	98.0 ± 1.8
20.0	19.5	19.8	97.5 ± 1.6	99.0 ± 1.7
40.0	39.0	39.5	97.5 ± 1.6	98.75 ± 1.6
80.0	78.5	79.0	98.12 ± 1.5	98.75 ± 1.5
100.0	98.0	99.0	98.0 ± 1.4	99.0 ± 1.5
200.0	198.0	198.0	99.0 ± 1.4	99.2 ± 1.4

a) Average of 5 measurements ± RSD.

Analytical Application. To verify the feasibility of the developed method, the determination of bismuth(III) in water (pure solution) was investigated using the developed electrodes. The analysis of 1–200 µg cm^{-3} of bismuth solutions (in five replicate) by direct potentiometry, an average recovery of 98.12% and 98.7% with a relative standard deviation of 1.5% were obtained with ($n = 5$) at 80 µg/mL for sensor-**1** and -**2** respectively. The results are given in Table 3.

The proposed method was applied for determination of bismuth in suppositories and ointment. Results in Table 4 show an average recovery of 98.25 and 98.75% with a mean standard deviation of ±0.4 and ±0.45 for sensor-**1** and -**2**, respectively. The results were compared with the British Pharmacopoeia method[35] using Na_2H_2edta as titrant and xylenol orange as indicator. The results indicate that the concentration of bismuth in suppositories and ointment is in good agreement with those obtained by the British Pharmacopoeia method.[35] Comparison of the experimental means for the two method was carried out using the null hypothesis of $|t|_2$ for $P = 0.05$ and $n = 5$. It was found that $|t|_2 = 2.3$ and 2.5

Table 4. Determination of Bismuth in Some Pharmaceutical Preparation Using Bismuth Carbon Paste Electrodes

Drug (trade name)	Nominal value of bismuth(III)/%	Bismuth(III) recovery/%		EDTA, method
		Sensor-**1**	Sensor-**2**	
Anusol suppositories	2.95	98.0 ± 0.4	98.5 ± 0.4	98.5 ± 0.5
Anusol ointment	3.125	98.5 ± 0.5	99.0 ± 0.4	98.5 ± 0.6

for sensor-**1** and sensor-**2**, respectively which is less than the tabulated value ($|t|_2 = 3.36$).[36] No significant difference was found between the two methods, which indicate that the proposed method is as accurate as the British pharmacopoeia method. Comparison between the precessions of the proposed method with the British pharmacopoeia method to estimate the random errors of the two sets of data (Table 4) was also carried out using the two-tailed F-test.[36] From this table it is clear that all the experimental $F_{4,4}$ values are 2.5 and 2.7 for both sensor-**1** and sensor-**2**, respectively. These values are obviously less than the tabulated value of $F_{4,4}$ for $P = 0.05$ and $n = 5$ (6.38).[36] This proves that the results obtained by the two methods are not subject to random errors.

Conclusion

The proposed sensors offer the advantages of high stability, fast response over a wide concentration; pH range, low cost, ease of fabrications, and adequate selectivity for quantitative determination of bismuth(III) in some pharmaceutical preparations. In comparison sensor-**2** is slightly better than sensor-**1** with respect to detection limit. The statistical evaluations of the proposed method in comparison with the British Pharmacopoeia method indicate that the method is accurate and precise.

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