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Improved Spectrophotometric Determination of Bismuth (III) with Bromopyrogallol Red in Mixed Surfactants-Application to Waters and Veterinary Preparation

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ABSTRACT

A simple and sensitive spectrophotometric method for the determination of trace amounts of bismuth is established. The method is based on the reaction of bismuth with bromopyrogallol red at pH 3 in the presence of a mixture of cetylpyridinium chloride and triton X-100 surfactants to form a blue coloured complex which shows maximum absorbance
at 644 nm. A plot of absorbance with bismuth concentration gives a straight line indicating that Beer's law has been obeyed over the range 3-150 µg/25 ml, i.e., 0.12-6 ppm with a molar absorptivity of 3.3×10^4 $l.mol^{-1}.cm^{-1}$ and Sandell's sensitivity index of 0.006 $\mu g.cm^{-2}$. The interfering effect of a number of common captions and anions in the presence of comosite mixture (NaF and tartaric acid) and ascorbic acid as masking agents has been studied. The effect of common excipients has also been examined. The method has been applied successfully to the determination of bismuth in water samples and a veterinary preparation.

Keywords: Bismuth, Bromopyrogallol Red, Mixed surfactants, Spectrophotometry.

تحسين طريقة طيفية لتقدير البزموث (III) مع الكاشف بروموبايروكالول الاحمر بوجود مزيج من عوامل الشد السطحي- تطبيق في نماذج مائية وفي مستحضر بيطري

الملخص

تم تثبيت طريقة بسيطة وحساسة لتقدير كميات متناهية في الصغر من البزموث. تعتمد الطريقة على تفاعل البزموث مع الكاشف بروموبايروكالول الاحمر عند دالة حامضية 3 وبوجود مزيج من عوامل الشد السطحي سيتيل كلوريد البريدين والترايتون X-100 لتكوين معقد ازرق اللون اعطى اعلى امتصاص عند الطول الموجي 644 نانوميتر. اظهر منحني الامتصاص مقابل التركيز خطا مستقيما والذي يؤكد على انه يتبع قانون بير عند مدى تراكيز البزموث 3-150 مايكروغرام /25 ملتر اي 0.12- 6 جزء/مليون، وان

الامتصاصية المولارية 3×10^4 لتر.مول$^{-1}$. سم$^{-1}$ ودلالة ساندل للحساسية 0.0063 مايكروغرام .سم$^{-2}$. وقد تم دراسة تأثير العديد من الايونات الموجبة والسالبة الشائعة بوجود عوامل حجب بالإضافة الى دراسة تأثير عدد من المضافات الدوائية. طبقت الطريقة بنجاح في نماذج مائية وفي مستحضر بيطري.

INTRODUCTION

Bismuth is found in the earth's crust up to 0. 0002%. It is least toxic among the heavy metals. Bismuth is used in the form of sub carbonates and sub gullets for the treatment of diarrhea, dysentery and ulcers, and also in the manufacture of low melting alloys, which find application in the fusible elements in automatic sprinklers, special solders, safety plugs in compressed gas cylinders and automatic shutoffs for gas and electric water heating system. (Gaikwad *et al*., 2005). Bismuth and its compounds are used in semiconductors, cosmetic preparations, alloys and metallurgical additives and in the preparation and recycling of uranium nuclear fuels(Thomas, 1991). Bismuth compounds are used orally in human and veterinary medicine for antiacidaction and mildly astringent action in gastrointestinal disorders, including diarrhea, flatulence and ulcerative gastritis and colitis (Demetrius *et al.*, 2001). It has been used in peptic ulcer treatment and tropical dermatological cream. As the use of bismuth in medicine increased, it has spread in the environment and the chance of exposure of organisms to bismuth has been increased. A number of toxic effects in humans have been attributed to bismuth compounds, such as nephrotoxic, neurotoxic, kindeydamhage symptoms nephropthy, osteoarthrapathy, hepatitis and neuropathology (Afkami *et al.*, 2006). Bismuth salts have emerged as efficient lewis acids due to their relatively low toxicity,therefore it used a catalyzed route for the synthesis ofα-aminophosphonates from aldehydes . (Banik *et al*., 2010). Bismuth salt (bismuth nitrate) is used for synthesis and characterization of compounds, using bismuth nitrate pentahydrate in THF adsorbed silica gel/fly ash under microwave method. (Badgjar *et al.*, 2010). The development of analytical techniques for the determination of bismuth at low levels in aquatic sample is significant. So, analytical techniques such as spectrophotometry, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) have been used for its measurement (Oshita *et al.*, 2007). The determination of bismuth in human plasma by ICP-MS and its use in bioequivalence studies has been reported (Shi *et al.*, 2009). Gallacetophenone phenyl hydrazone (GPPH) has been used as an analytical reagent for amperometric determination of bismuth in wood' s alloy (Reddy and Reddy., 2010). Several reagents have been used for the spectrophotometric determination of bismuth such as, dithiozone, diethyldithiocarbamate, xylenol orange, iodide, thiourea and azo reagents, (Marczenko, 2000). Kinetic spectrophotometric determination of Bi (III) has been employed, the method is based on using its catalytic effect on the oxidation of phenylfluorone by hydrogen peroxide in ammonia buffer, the method was confirmed by determining Bi (III) in a stomach ulcer drug (Rancic and Mandic, 2009). Extractive spectrophotometric determination of bismuth (III) in alloy samples using 1-amino-4, 4, 6-trimethyl (1H, 4H) pyrimidine-2-thiol as an analytical reagent has also been reported (Gaikwad *et al.*, 2005).

The present work is devoted to the spectrophotometric study of the coloured complex of bismuth with bromopyrogallolred in the presence of mixture of cetylpyridinum chloride and Triton X-100 surfactants as an attempt to increase the sensitivity and selectivity of bismuth determination.

EXPERIMENTAL

Spectral and absorbance measurements are carried out using Shimadzu UV-Visible computerized double- beam spectrophotometer UV-160. In all measurements, 1-cm matched cells are used. The pH measurements are carried out using (HANNA pH 211).

Reagents

All chemicals used are of highest purity available.

Stock bismuth (III) solution (1000 µg/ ml).

A stock solution is prepared by dissolving 0.2312g of Bi $(NO_3)_3.5H_2O$ (Fluka) in 3 ml 5 M nitric acid and diluting to the mark with distilled water in a 100 ml volumetric flask. (Afkhami, 2006).

Working bismuth solution(100 µg/ml).

It is prepared by diluting 10 ml of the stock solution to 100ml with distilled water in a volumetric flask.

Working bismuth solution(10 µg/ml).

It is prepared by diluting 10 ml of the working solution (100 µg/ml) to 100 ml withdistilled water in a volumetric flask.

Bromopyrogallol Red (BPR) reagent solution (1×10^{-3}M).

It is prepared by dissolving 0.055 g of BPR (BDH) in distilled water and the solution is diluted to 100 ml in a volumetric flask. The solution is transferred to a brown bottle where it remains stable for a least one week.

Buffer solution pH 3

It is prepared by mixing 50 ml of 0.1 M glycine solution with 5.7 ml of 0.2 M HCl solution and diluting the volume to 100 ml with distilled water in a volumetric flask, (Perrin and Dempsey, 1974).

Cetylpyridinium chloride (CPC) solution (2×10^{-3}M)

It is prepared by dissolving 0.179 g of CPC monohydrate (Fluka) in distilled water and the solution is diluted to 250 ml in a volumetric flask.

Triton X-100 solution (4%)

This solution is prepared by diluting 4 ml of Triton X-100 (Scharlau) with hot distilled water and the solution is diluted to 100 ml in a volumetric flask.

Mixed complexing solution

This solution is prepared by dissolving 0.3 g of tartaric acid (BDH) with 0.042g of sodium fluoride) (BDH) in about 80 ml distilled water. The pH of the resulting mixture is adjusted to 3 with 0.1 M HNO_3 solution and the volume is then completed to 100 ml with distilled water.

Ascorbic acid solution (0.01M)

It is prepared by dissolving 0.1761 g of ascorbic acid (BDH) in distilled water. The pH of the solution is adjusted to 3 with nitric acid solution and the volume is completed to 100 ml with distilled water.

Veterinary preparation solution (1000 µg/ml)

The content of 6 sachets of Diaclean containing 2000 mg bismuth subnitrate was weighed. A quantity of powder containing 0.1 mg $Bi^{3+}$is then dissolved in 5 ml of 5 M nitric acid and sufficient amount of distilled water. The solution is shaken thoroughly and then filtered. The filtrate was made up to 100 ml with distilled water in a volumetric flask. The tested solution is prepared by an appropriate dilution.

RESULTS AND DISCUSSION

Preliminary studies of the reaction of bismuth *(*III) with BPR reagent indicate that the reaction proceed immediately after mixing. The violet coloured complex showed an absorption maximum at 597nm in contrast to the reagent blank which shows maximum absorption at 522nm.

Study of the optimum reaction conditions

The effects of various parameters on the absorption intensity of the coloured complex are studied and the reaction conditions are optimised.

Effect of pH

The effect of pH on the colour intensity of the complex is studied with solutions containing 100 µg of Bismuth *(*III) and various volumes of 0.01M HNO_3 and NaOH solutions and 2 ml of (1×10^{-3}M) BPR reagent and the volume is completed to 25ml with distilled water. The absorbance of each coloured solution against its corresponding blank solution and the final pH of the reaction mixtures are both measured. The results indicate that the absorbance is pH dependent, and the maximum absorbance occurred at pH 3 with maximum wavelength 602 nm, therefore it is selected for subsequent experiments.

Effect of buffers

A series of various buffer solutions of pH 3 are prepared and their effects on the absorbance, λ_{max} and the pH of the final reaction mixture are examined. Seven buffer solutions of pH 3 such as tartaric acid- NaOH (B_1), citric acid- NaOH *(*B_2), khphalate -HCl *(*B_3), glycine - HCl *(*B_4) citric acid –sod. citrate *(*B_5),acetic acid – sodium acetate (B_6) and succinic acid - NaOH *(*B_7), (Perrin and Dempsey, 1974) are tested for the purpose. The results are given in Table (1).

Table 1: Effect of buffers.

ml of Buffer solution	Absorbance/ml of Buffer added						
	B_1	B_2	B_3	B_4	B_5	B_6	B_7
1.0	0.034	0.037	0.090	0.138	0.070	0.106	0.099
2.0	0.025	0.036	0.088	0.164	0.058	0.123	0.096
3.0	0.022	0.032	0.099	0.158	0.045	0.121	0.094
4.0	0.020	0.027	0.078	0.151	0.061	0.118	0.092
5.0	0.018	0.021	0.073	0.148	0.035	0.114	0.083
6.0	0.015	0.019	0.071	0.145	0.031	0.112	0.085
7.0	0.011	0.014	0.065	0.142	0.029	0.113	0.082
λ_{max} (nm)	565-585	551-571	550-570	593-608	597-569	600-587	603-596
Final pH of the reaction mixture	3.3-3.1	3.29-3.27	3.3-3.0	3.3-3.0	3.2-3.1	3.3-3.6	3.5-3.7

It can be noticed in Table (1) that buffer solution (B_4) is only useful from the analytical point of view. The other buffers show an un-encouraging results. For the subsequent work, a 2 ml of buffer (B_4) solution has been chosen because it gives the highest sensitivity and good colour contrast.

Effect of surfactants

The effect of the presence of cationic (Cetylpyridinium chloride, CPC, Cetyltrimethylammonium bromide, CTAB), anionic (Sodium dodecyl sulphate, SDS) and non- ionic (Iso-octylphenoxypolyethoxy ethanol, Triton X-100) surfactants on the colour intensity of the complex is examined with different orders of addition. The results are shown in Table (2).

Table 2: Effect of surfactants.

Surfactant solution (3ml)	Absorbance*/order of addition**						λ_{max} (nm)	$\Delta\lambda$ (nm)
	I	II	III	IV	V	VI		
CPC 1×10^{-3}M	0.255	0.296	0.249	0.252	0.231	0.180	638	72
CTAB 1×10^{-3}M	0.181	0.167	0.207	0.201	0.190	0.184	634	57
SDS 1×10^{-3}M	0.144	0.115	0.093	0.105	0.193	0.149	607	70
Triton X-100 1% (v/v)	0.183	0.204	0.204	0.193	0.184	0.120	582	50

* Absorbance without surfactant=0.162

** I=Bismuth ion (M) +B (Buffer) +R (Reagent BPR) +S (Surfactant) .
II=M+S+R+B
III=M+B+S+R
IV=M+S+B+R
V=M+R+B+S
VI=M+R+S+B

The results in Table (2) indicate that CPC solution causes bathochromic shift and increasing in the intensity of absorbance of formed complex with order of addition No.(II). Therefore the effect of different volumes of higher concentration of CPC (2×10^{-3}M) on the intensity of coloured complex has been studied [Table (3)].

Table 3: Effect of CPC amount.

ml of 2×10^{-3} M CPC	Sample	λ_{max} (nm)	Blank
1	0.223	631	0.070
2	0.252	635	0.056
3	0.324	635	0.060
4	0.331	636	0.054
5	0.288	633	0.057

The results obtained in Table (3) indicate that the addition of 4 ml of CPC with order No. (II) [Table (2)] gives maximum absorbance and the lowest blank value, so it has been used in the subsequent experiments.

Effect of mixed surfactants and temperature

It is found that the presence of 4% Triton X-100 solution with 2×10^{-3} M CPC in the reaction mixture, an increase in the absorbance of the coloured complex is observed obviously especially when the reaction mixture is heated. The effect of temperature on the absorbance of the coloured complex is shown in Table (4).

Table 4: Effect of temperature.

Temperature (˚c)	Absorbance*	λ (nm)	Δλ (nm)
20	0.208	630	97
30	0.331	636	103
40	0.496	639	106
45	0.556	640	107
50	0.592	644	111
55	0.590	644	99

*Using 1 ml of Triton X-100

From the results in Table 4, it is observed that maximum absorbance and a good colour contrast are obtained at 50C˚.The effect of heating time on the absorbance of the coloured complex is then studied and the experimental results showed that a heating time of 5-7 min, was enough for the completion of the reaction.

Effect of the amount of Triton X-100

The effect of different volumes of 4%Triton X-100 on the intensity of the formed complex has next been studied. The experimental results showed that 1 ml of 4%Triton X-100 was optimum.

Effect of reagent amount

Different volumes of 1×10^{-3} M BPR solution are added to 10-125 µg of bismuth while other conditions being kept constant. A 2 ml of the reagent solution has been found to be optimum volume since the linearity (correlation coefficient) is good and the sensitivity of the colour reaction is fair.

Effect of masking agents

The presence of tartaric acid, NaF and ascorbic acid in the reaction mixture is essential because they increase the selectivity of the method by masking cations from their reactions with BPR. Other complexons such as EDTA, EGTA and NTA decrease the absorbance owing to their complexons action with bismuth. Therefore, a composite masking solution has been prepared containing 0.01M NaF and 0.02M tartaric acid. Since the solution of ascorbic acid is unstable, it is added separately. The effect of composite complexing solution (with different volumes of 0.01M ascorbic acid) on the absorbance of coloured complex is examined. The results are given in Table (5)

Table 5: Effect of composite mixture with different volumes of ascorbic acid.

Amount of composite complexing solution (ml)	Absorbance/ml of (0.01 M) ascorbic acid			
	0	**1**	**2**	**3**
1	0.587	0.589	0.603	0.601
2	0.623	0.635	0.645	0.615
3	0.569	0.544	0.533	0.516
4	0.551	0.536	0.534	0.533
5	0.511	0.496	0.452	0.432

The results indicate that 2 ml of both mixed complexing solution and ascorbic acid are desired for subsequent experiments because of the highest sensitivity.

Effect of order addition

The orders of addition of solution are examined and the results are shown in Table (6)

Table 6 : Effect of order addition.

Reaction components*	Order number	Absorbance
M+CM+AA+S_1+S_2+R+B	I	0.578
M+CM+AA+B+S_1+S_2+R	II	0.653
M+B+S_1+S_2+CM+AA+R	III	0.073
M+S_1+S_2+B+CM+AA+R	IV	0.545
M+B+R+CM+AA+S_1+S_2	V	0.079
M+B+CM+AA+R+S_1+S_2	VI	0.137
M+R+CM+AA+B+S_1+S_2	VII	0.474
M+S_1+S_2+CM+AA+B+R	VIII	0.528

*Bismuth (M) ,buffer solution (B) , CPC (S_1) , Triton X-100 (S_2) , BPR reagent(R) , CM=Composite mixture, AA=Ascorbic acid.

From the results above, order (II) has been used for a subsequent experiment, due to the highest sensitivity.

Effect of time

A study of the time effect on the absorbance of the final reaction mixture shows that the maximum absorbance is obtained after 20 minutes and remains stable for at least 1 hour.

Final absorption spectra

Under the above established conditions, absorption spectra of a blue complex of bismuth-BPR-CPC-Triton X-100 and of its reagent blank are recorded and are shown in Fig. (1). The coloured complex exhibits maximum absorbance at 644 nm in contrast with the reagent blank which shows maximum absorbance at 533 nm.

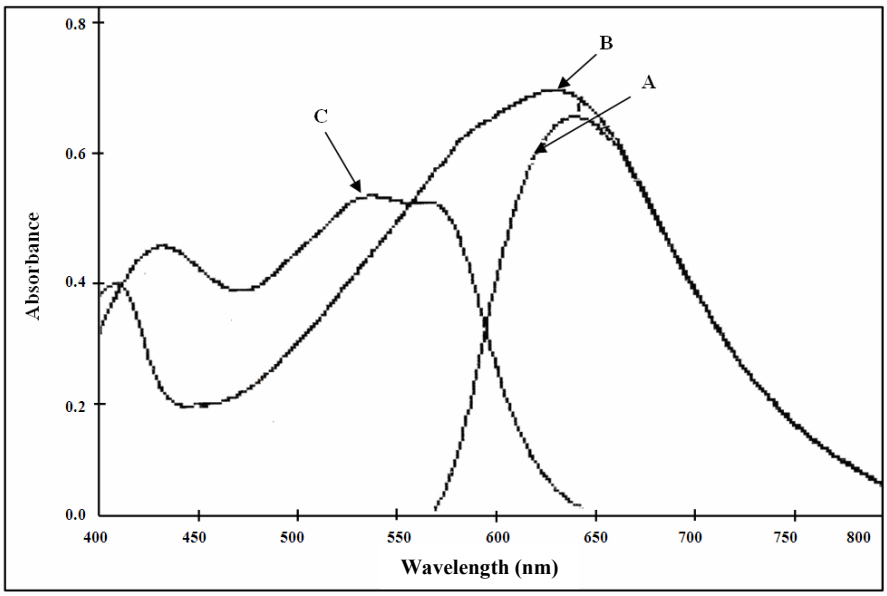


Fig. 1: Absorption spectra of 100 µg Bi (III) /25ml measured against (A) blank, (B) distilled water and (C) blank against distilled water.

Recommended procedure and calibration Graph

Sample aliquots containing 3-250 µg of bismuth solution are placed into 25-ml volumetric flasks. To each bismuth solution, 2ml of mixed complex solution (0.01M NaF and 0.02M tartaric acid), 2ml of 0.01M ascorbic acid, 2ml of buffer pH 3, 4ml of 2×10^{-3}M CPC, 1ml of 4% Triton X- 100, and 2 ml of 1×10^{-3}M BPR are added. The solution is mixed and diluted to the mark with distilled water and heated to 50 C° for about 5 min in water bath. After about 10 min, the absorbance of each coloured solution at 644 nm is measured against the reagent blank, prepared in the same manner but without bismuth. Beer 's law is obeyed within the range (3-150) µg of Bi (III) in a final volume of 25 ml (i.e., 0.12-6 ppm) [Fig. (2)]. The molar absorptivity and Sandell's sensitivity are 3.3×10^{4} l.mol^{-1}.cm^{-1}and 0.006 µg.cm^{-2}, respectively.

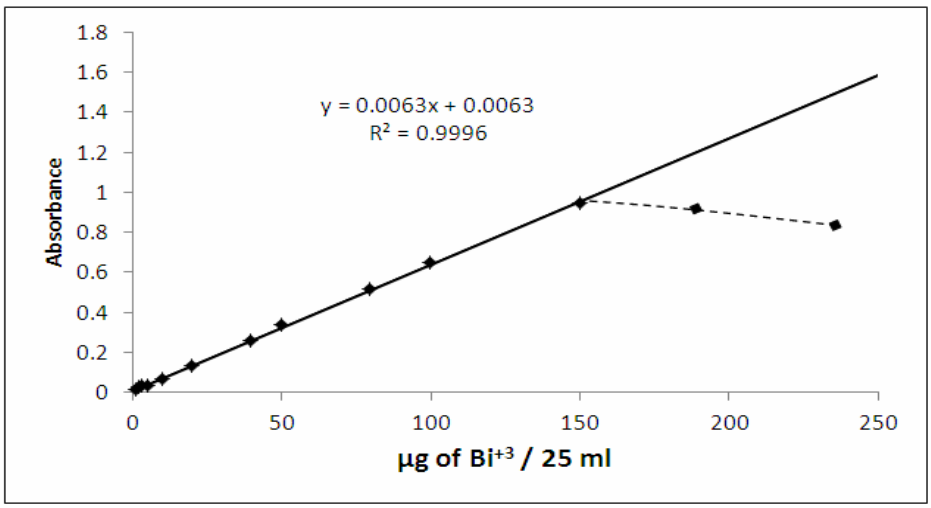


Fig. 2: Calibration graph for Bi $^{3+}$ determination using the proposed method.

Accuracy and precision

To check the accuracy and precision of the cribration graph, bismuth (III) is determined at three different concentrations. The results shown in Table (7) indicate that the method is satisfactory.

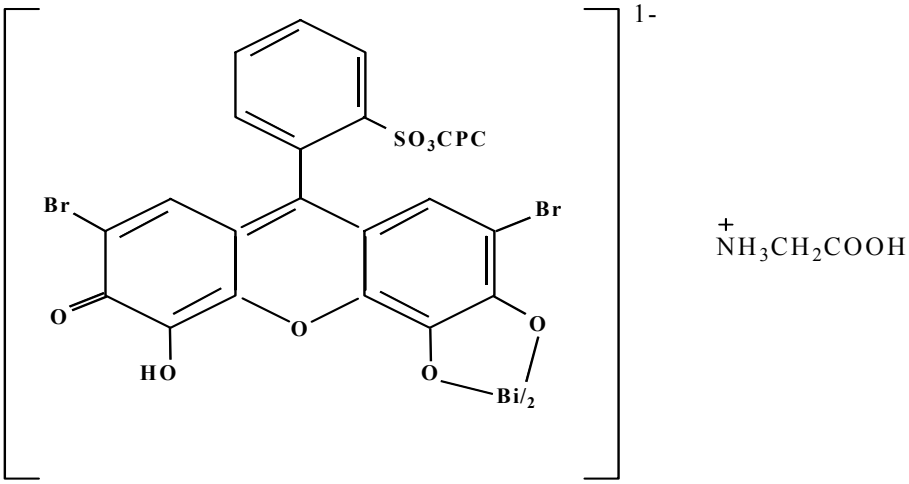
Table 7: Accuracy and precision.

Amount of bismuth taken, µg	Recovery* (%)	RSD (%)
25	100.5	± 0.543
50	98.03	± 1.752
100	99.9	± 0.398

*Average of five determinations.

Nature of the complex

The stoichiometry of the complex has been studied by both Job's method of continuous variations and mole-ratio method (Delevie, 1997). The results reveal that the combination ratio of bismuth (III) with BPR is (1:2). Both methods are used to study the proportion of CPC in the complex and the results obtained do not give the expected proportion, as the colour of the solution changes with the addition of different amounts of CPC. The average of the stability constant of the coloured complex is found to be (4.3×10^{11}) M^{-2} (Hargis, 1988). The empirical formula of the chelate can be written as follows.



Bi(III)-Bromopyrogallol Red-CPC Complex

Effect of Interference

The influence of diverse ions on the determination of bismuth is examined under the conditions of standard procedure. The diverse ions are added, individually, to solutions containing 100 µg of bismuth. The results are summarised in Table (8), from which it can be concluded that the method seems to be selective except towards Al^{3+}, Fe^{2+}, Mn^{2+}, Ni^{2+} and Zr^{4+}ions.

Table 8: Effect of interference (1).

Foreign ion	Form added	Error %/µg of interference added		
		50	100	300
Al^{3+}	$AlCl_3.6H_2O$	-49.3	-66.46	-70.12
Ag^{+}	$AgNO_3$	-2.81	-4.21	-3.12
Ba^{2+}	$BaCl_2.2H_2O$	0.91	-4.42	-14.32
Be^{2+}	$BeSO_4.4H_2O$	+2.51	+3.31	3.29
Ca^{2+}	$Ca(NO_3)_2$	-2.5	-3.2	-4.5
Cd^{2+}	$Cd(CH3COO)_2.H_2O$	-3.6	-2.43	+1.22
Co^{2+}	$Co(NO_3)_2.6H_2O$	-0.30	-2.91	-3.31
Cs_2	CS_2CrO_4	+1.3	+2.13	5.0+
Cu^{2+}	$CuCl_2$	+0.150	+0.60	+0.91
Fe^{2+}	$FeSO_4(NH_4)_2SO_4.6H_2O$	-14.7	-34.4	-50.76
Fe^{3+}*	$Fe(NO_3)_3.9H_2O$	0.30	-3.20	-3.81
Hg^{2+}	$Hg(NO_3)_2$	0.0	-0.15	2.3+
K^{+}	KBr	+0.15	-2.83	-4.44
Mg^{2+}	$MgCl_2.6H_2O$	-0.59	-0.45	+2.39
Mn^{2+}	$MnCl_2$	-39.6	-57.62	-66.76
Na^{+}	NaCl	+0.14	+0.25	0.37+
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	-84.75	-87.80	89.93-
Pb^{2+}	$Pb(NO_3)_2$	-3.20	-4.11	-4.50
Zn^{2+}	$Zn(Ac)_2.2H_2O$	+2.59	3.81+	+4.42
Zr^{4+}	$ZrOCl_2.8H_2O$	-35.21	-39.02	-64.02
Br^{-}	KBr	+0.15	-3.65	-4.72
Se^{4+}	SeO_2	+1.98	-1.06	-1.82
$S_2O_3^{2-}$	$Na_2S_2O_3.5H_2O$	-2.61	-3.21	-3.86
SO_3^{2-}	Na_2SO_3	+3.72	+4.58	+5.02
SO_4^{2-}	Na_2SO_4	+3.21	+3.42	+4.35
CO_3^{2-}	Na_2CO_3	+2.51	+3.25	+4.26
HCO^{3-}	$NaHCO_3$	-2.13	-2.59	-3.20
NO_2^{2-}	$NaNO_2$	-1.37	-2.82	-3.65
PO_4^{3-}	$NaH_2PO_4.2H_2O$	+2.59	+0.152	-3.50
BO_3^{3-}	H_3BO_3	+0.91	-3.20	-4.72
$C_2O_4^{2-}$	$Na_2C_2O_4$	+0.35	+0.932	+1.45

*Without ascorbic acid.

Also, the effect of foreign compounds that may be present in dosage form were studied by adding different amounts of foreign substances to 100 µg Bi^{3+}/25ml.It was observed that the studied foreign species did not interfere in the present method Table (9).

Table 9: Effect of interference (2).

Interferences	Recovery(%) of 100 µg Bi (III) / µg of Interferences		
	100	**500**	**1000**
Starch	98.6	97.0	96.0
Glucose	97.5	100.0	98.1
Lactose	103.6	100.7	101.6
Gum Arabic	101.5	98.6	100.0

Application of the method

Determination of Bi (III) in waters

The proposed method has been applied to the determination of bismuth *(*III) in various water samples, the results are shown in Table (10).

Table 10: Determination of Bi (III) in water samples.

Amount of sample(ml)	Sample	Bi *(*III) added *(*µg)	Recovery(%)
1	Tap water	25	103.8
		50	104.2
		100	104.9
3		25	101.0
		50	93.6
		100	105.2
5		25	105.4
		50	106.0
		100	101.3
1	Riverwater[a]	25	95.0
		50	107.8
		100	95
3		25	107.1
		50	96.3
		100	95.8
5		25	103.2
		50	93.3
		100	101.3
1	Well water[b]	25	103.2
		50	102.7
		100	96.8
3		25	95.6
		50	102.4
		100	97.6
5		25	103.8
		50	102.4
		100	100.4
1	Natural spring water[c]	25	97.8
		50	95
		100	103.7
3		25	101.0
		50	104.8
		100	103.5

Amount of sample(ml)	Sample	Bi (III) added (µg)	Recovery(%)
5		25	101.6
		50	97.5
		100	98.7
1	Rashidia water[d]	25	93.0
		50	106.0
		100	95.8
3		25	95.6
		50	90.3
		100	93.6
5		25	103.2
		50	96.3
		100	102.4
1	Bekhaal fallwater[e]	25	106.0
		50	103.0
		100	100.9
3		25	105.4
		50	95
		100	100.3
5		25	104.3
		50	92.7
		100	101.0

a=River water from Tigris river in Mosul city.
b=Well water from Algubba near Mosul city
c=Natural spring water from life company.
d=River water from Al Rashidia region north Mosul city.
e=From Bekhaal region in Erbil city.

The results listed in Table (10) show that the method is successful for determining Bi (III) in the above water sample.

Determination of Bi (III) in a veterinary preparation

The proposed method has also been applied to the determination of Bi (III) in veterinary preparation. The results are listed in Table (11).

Table 11: Determination of Bi (III) in a veterinary preparation.

Veterinary preparation	Bi^{3+} (µg)	Recovery*%
Diaclean , 2000 mg $Bi_5O(OH)_9(NO_3)_4$ / Sachet, AVICO, Jordan	25	99.3
	50	102.2
	100	98.3

- Average of five determinations.

The above results reveal that the method is suitable for determining bismuth in the above sample with satisfactory recovery. Both the present method and the literature method (Marczenko, 2000) have been applied at the same time to t-test (Christian, 2004) and the value compared with the statistical tables for eight degrees of freedom at 95% validation

level. The results in Table (12) show that there is no real difference between the two methods.

Table 12: The result of t-test.

Veterinary preparation	Bi^{3+} (µg)	Recovery%*		t. exp
		Present method	Literature method (Marczenko,2000)	
Diaclean 2000 mg$Bi_5O(OH)_9(NO_3)_4$/Sachet	25	99.3	99.6	0.032
	50	102.2	100.2	0.060
	100	98.3	96.4	0.83

* Average of five determinations.

Comparison of methods

Table (13) shows the comparison between the analytical variables of the present method with those of other methods for bismuth determination.

Table 13: Comparison of method.

Analytical Parameter	Present Method	Literature Method* (Afkami *et al.*, 2006)	Literature Method** (Gaikwad *et al.*, 2005)
Reagent	Bromopyrogallol Red	Bromopyrogallol Red	1-amino-4,4,6-trimethyl (1H,4H)pyrimidine-2-thiol
Surfactant	CPC + Triton X-100	Triton X-114	-
pH	3	3.8	-
Buffer	Glycine – HCl	Acetic acid – acetate buffer	-
λ_{max}(nm)	644	542	470
Beer's law rang	0.12-6 ppm	4.60-120.0ppb	7-24ppm
Molar absorptivity ($l.mol^{-1}.cm^{-1}$)	3.3×10^4	-	6.501×10^3
Determination coefficient (R^2)	0.999	0.998	-
LOD	0.0462 µg/ ml	2.0 ng/ ml	-
LOQ µg/ ml	0.0573	-	-
Application of the method	Determination of bismuth in water, and veterinary preparation	Determination of bismuth in human urine sample	Determination of bismuth in alloy samples

*Involves flash point extraction.

**Involves extraction in chloroform.

Comparatively, the present method is simple, sensitive and applicable to waters and veterinary preparation.

CONCLUSION

The proposed spectrophotometric method is simple, sensitive and low cost, it does not involve solvent extraction steps and gives precise and accurate results. The method has been applied successfully to the determination of bismuth in water samples and a veterinary preparation.

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