

Spectrophotometric Determination of Bismuth with Alizarin Red S and Cetylpyridinium Chloride - Application to Water Samples, Urine and Veterinary Preparation

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(Received 14 / 10 / 2012 ; Accepted 7 / 1 / 2013)

ABSTRACT

A simple, accurate, sensitive and reliable method for spectrophotometric determination of Bismuth(III) is developed. The method is based on the reaction of bismuth (III) with alizarin red S (ARS) and cetylpyridinium chloride (CPC) in the presence of Triton X-100 at pH 3 to form a pink, water soluble ternary complex which shows maximum absorption at 507 nm with a molar absorptivity of $1.4 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$. The calibration curve is linear in the concentration range 5– 150 μg of bismuth (III) in a final volume of 20ml (i.e. $0.25\text{-}7.5 \mu\text{g ml}^{-1}$) with a determination coefficient of (R^2) (0.9974). The limit of detection (LOD) and the limit of quantification (LOQ) are 0.0671 and $0.2235 \mu\text{g.mL}^{-1}$, respectively. Under optimum conditions, the stoichiometry of the reaction between bismuth (III), alizarin red S and cetylpyridinium chloride is found to be 1:3:6, respectively. The recoveries are obtained in the range of 98.8- 102.1% and a relative standard deviation (RSD) of ± 0.93 to $\pm 3.07\%$ depending on the concentration level. The proposed method has been applied successfully to the determination of bismuth (III) in various samples such as, natural waters, urine and veterinary preparation.

Keywords: Bismuth(III) determination, Alizarin red S, Cetylpyridinium chloride, Spectrophotometry.

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.(III)

↓

(pH 3)

100-X

$10^4 \times 1.4$

507

20

(III)

150 -5

(LOD)	.0.9974	(¹⁻	7.5 – 0.25)
	¹⁻	0.2235	0.0671	(LOQ)
±0.93	(RSD)	%102.1	98.8	
	(III)			±3.07%
		6:3:1		!
			!	(III) :

INTRODUCTION

Bismuth is found in the earth's crust up to 0.0002%. It is widely used in the form of oxides, carbonates and sulfides in nature (Didi *et al.*, 2011). It is used in producing malleable iron and as a catalyst for making acrylic fibers. The metal is also used as a thermo coupling material and has found application as a carrier for U²³⁵ or U²³³ fuel in nuclear reactors (Chandrashekhar and Mansing, 2008). Bismuth and its compounds are used in semiconductors, cosmetic preparations, alloys and metallurgical additives (Afkhami *et al.*, 2006 ; Yamini *et al.*, 2002). Bismuth compounds have been used in medicine for more than 200 years in a variety of gastrointestinal disorders, because of their demulcent properties. Bismuth and its compounds are used in the treatment of syphilis and gastric disorders especially for colitis, diarrhea and peptic ulcers. They were and still are used for burn bandage dressings, antiseptic powders, and in the treatment of venereal diseases (Yamini *et al.*, 2002 ; Barakat, 2002). A number of toxic effects in humans have been attributed to bismuth compounds, such as nephrotoxic, neurotoxic, kidney damage symptoms nephropathy, osteoarthrapathy, hepatitis and neuropathology. As the uses of bismuth in medicine increases, it has spread in the environment and the chance of exposure of organisms to bismuth has been increased, therefore, the determination of bismuth in the environmental and biological samples is important (Afkhami *et al.*, 2006). Various analytical techniques, such as chemiluminometric method (Al-Hakeem and Shakir, 2008), derivative spectrophotometry (Gumus *et al.*, 2005), resonance light scattering (Cui *et al.*, 2007), potentiometric stripping analysis (Nayan *et al.*, 2010), hydride generation-atomic fluorescence spectrometry (HG-AFS) (Ling *et al.*, 2005), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Araki *et al.*, 2008), stripping voltammetry (Amir and Karel, 2012), graphite furnace atomic absorption spectrometry (GFAAS) (Yamini *et al.*, 2002), square wave voltammetry (SWV) (Hasdemir and Karaboduk, 2010) and amperometry (Reddy and Reddy, 2010) were used for its measurement. Many spectrophotometric methods have also been used for the determination of bismuth in various samples due to their simplicity, rapidity and wide applications, for this purpose widely used reagents such as xylenol orange (Jeronimo *et al.*, 2004), 1,2-diaminocyclohexaneN,N,N,N-tetraacetic acid(DACT) (Jan *et al.*, 2007), 4-(2-benzothiolylazo)-2,2-biphenyl diol (BTABD) (Amin, 2011), di-(hydrogenated tallow alkyl)dimethylammonium chloride (Barakat, 2002), 1-amino-4,4,6-trimethyl(1H,4H) pyrimidine-2-thiol (Gaikwad *et*

al., 2005), bromopyrogallol red in the presence of Triton X-114 (Afkhami *et al.*, 2006), methyl thymol blue (Tzanavaras *et al.*, 2004), and pyrocatechol violet (PCV) (Honova *et al.*, 1988) were proposed some of these methods suffer from several disadvantages, such as, the use of heating step, low range of determination, critical working conditions, no applications, time consuming and poor selectivity. Other methods are typically less sensitive, relatively complicated, or require ion exchange, solvent extraction and expensive instrumentation. In this work, a detailed investigation of the bismuth (III)-ARS reaction has been carried out in the presence of cetylpyridinium chloride and Triton X-100 to increase the sensitivity of the method and to explore its applicability.

EXPERIMENTAL

Apparatus

All absorption spectra and absorbance measurements were carried out by a Shimadzu UV-160 double beam UV-visible spectrophotometer (Japan) with matched 1-cm quartz cells. While all pH measurements were recorded by using HANNA 211 pH meter.

Reagents

All chemicals used are of highest purity available.

Stock bismuth (III) solution (1000 $\mu\text{g}\cdot\text{ml}^{-1}$). This solution is prepared by dissolving 0.2312 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Fluka) in 3 ml of 5 M nitric acid and diluted to the mark with distilled water in a 100-ml volumetric flask .

Working bismuth solution(100 $\mu\text{g}\cdot\text{ml}^{-1}$). It is prepared by diluting 10 ml of the stock solution of bismuth to 100 ml with distilled water in a volumetric flask.

Alizarin red S (ARS) ($1 \times 10^{-3}\text{M}$). This reagent is prepared by dissolving 0.0342 g of ARS (Fluka) in 100 ml distilled water using a volumetric flask. The solution is then transferred to a brown bottle and remained stable for at least one week.

Buffer solution (pH 3). It is prepared by mixing 50 ml of 0.1 M potassium hydrogen phthalate with 22.3 ml of 0.1M HCl and the volume is diluted to 100 ml with distilled water (Perrin and Dempsey, 1974) using a volumetric flask.

Composite mixture solution. This solution is prepared by dissolving 0.8805 g of ascorbic acid (BDH) with 0.0210 g of sodium fluoride (Fluka) in about 40 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 50 ml with distilled water using a volumetric flask. This solution is freshly prepared.

Cetylpyridinium chloride (CPC) solution ($1 \times 10^{-3}\text{M}$). It is prepared by dissolving 0.0895 g of CPC (Koch-Light) in 250 ml distilled water.

Solution of triton X-100 (1%). This is also prepared by dissolving 1 g of Triton x-100 (Fluka) in 100 ml distilled water.

Recommended procedure and calibration graph

A suitable aliquot containing 5 – 200 μg of Bi(III) was transferred into 20-ml calibrated flask and mixed with 2 ml of $1 \times 10^{-3}\text{M}$ ARS reagent, 5 ml of $1 \times 10^{-3}\text{M}$ CPC solution, 1 ml of buffer solution pH 3, 2 ml of composite mixture solution and 0.5 ml of 1% Triton x-100 solution. The mixture is mixed and completed to the mark with distilled water and its absorbance is measured at 507 nm against a blank solution prepared in the same manner but without bismuth.

Procedure for human urine

The sample of urine is digested as follows (Afkhami *et al.*, 2006). In a 100 ml beaker, 25 ml of urine sample accurately measured, then treated with a mixture of 5 ml H_2O_2 and 2.5 ml of concentrated HNO_3 , and is placed on a hot plate. The sample is moderately heated and evaporated almost to dryness. Thereafter, fresh portion of 2.5 ml of concentrated HNO_3 is added to the residue and heated to dryness. The residue is dissolved in 2.5 ml of 1 M HCl and the pH of the resulting solution is adjusted to 3.0 with 0.1 M NaOH and diluted to 25 ml with distilled water. A suitable aliquot of this solution is pipeted out into a 20 ml calibrated flask and the bismuth content is determined as in the recommended procedure.

Procedure for dosage form (veterinary sample)

The content of 3 sachets of Diaclean containing 2000 mg bismuth subnitrate are weighed. A quantity of powder equivalent to 0.01 g of bismuth is weighed and dissolved in 10 ml of 2.5 M nitric acid. The solution is then shaken thoroughly, filtered and diluted with distilled water to 100 ml in a volumetric flask. An aliquot of the diluted drug solution is then treated as done in the recommended procedure.

RESULTS AND DISCUSSION

The preliminary investigation showed that on mixing 100 μg of bismuth (III) with excess of $1 \times 10^{-3}\text{M}$ ARS reagent, 1 ml of $1 \times 10^{-3}\text{M}$ CPC solution, 2 ml of 1% Triton X-100 solution and distilled water in a 20-ml calibrated flask, a red ternary water soluble complex [Bi(III)-ARS-CPC] is observed and showed a maximum absorption at 501 nm against the corresponding reagent blank solution. This observation led us to the development of a sensitive method for the determination of bismuth based on a ternary complex formation. The effect of various parameters on the absorption intensity of the coloured complex is studied and reaction conditions have been optimized.

Effect of pH

The colour intensity of [Bi(III)-ARS-CPC] complex showed pH dependent absorption maximum at 507 nm, whereas the reagent blank solution showed maximum absorption at 426 nm. The optimum pH range for complex formation is 2.92-3.09 (Fig.1). pH 3 is considered the optimum because of the high absorbance intensity and good colour contrast ($\Delta\lambda=83\text{nm}$). Therefore, a 1 ml of (potassium hydrogen phthalate – HCl) buffer solution of pH 3 is selected.

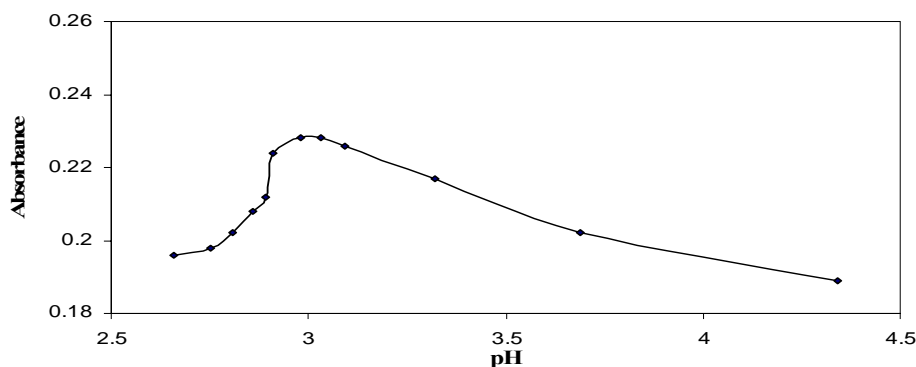


Fig. 1: Effect of pH on absorbance of [Bi(III)-ARS-CPC] complex.**Effect of reagent amount**

The influence of different amounts of the ARS reagent in the presence of CPC with respect to bismuth (III) on the formation of ternary complex is investigated. The experimental results indicated that a 2 ml of 1×10^{-3} M ARS reagent can be considered optimum because of its highest colour sensitivity and lowest corresponding blank value.

Effect of CPC and triton X-100 amounts

The presence of Triton X-100 in the reaction mixture has been necessary in removing the slight turbidity formed in its absence. The effect of different amounts of various surfactants [cationic (CPC) and neutral (Triton X-100)] are studied for this purpose. The results listed in Table (1) show that 5 ml of 1×10^{-3} M CPC and 0.5 ml of 1% Triton X-100 solutions have been considered the optimum amounts and used for the subsequent experiments for the following: (i) turbidity of solution was disappeared and (ii) the colour contrast of the Bi(III)-ARS reaction is improved. The experimental data reveal that cetyltrimethyl-ammonium bromide (CTAB) can also be used instead of CPC. Also, other neutral surfactants such as, between 20 has been tried but the results obtained were not as useful as those with Triton X-100.

Table 1: Effect of surfactants on absorbance.

Triton X-100	mL of 1%	Absorbance		λ_{\max} (nm)	$\Delta\lambda^*$ (nm)
		Sample	Blank		
0.5	1	Turbid	-	-	-
0.5	2	Turbid	-	-	-
0.5	3	Turbid	-	-	-
0.5	4	0.321	0.056	510	80
0.5	5	0.334	0.034	507	80
1.0	1	0.303	0.038	507	75
1.0	2	0.327	0.043	507	77
1.0	3	0.322	0.057	509	74
1.0	4	0.317	0.050	508	76
1.0	5	0.319	0.051	509	75
1.5	1	0.308	0.033	505	70
1.5	2	0.286	0.036	507	69
1.5	3	0.285	0.036	505	72
1.5	4	0.287	0.039	504	70
1.5	5	0.283	0.044	505	72

* $\Delta\lambda$: is the colour contrast = $\lambda_{\max} S - \lambda_{\max} B$, where S= sample, B= blank.

Effect of Masking agent on absorbance

To evaluate the applicability of ARS reagent to the determination of bismuth, the effect of various masking agents which are usually used for interfering metal ions are studied. The results are shown in Table (2).

Table 2: Effect of masking agent on absorbance of 100 µg/20ml Bi(III)

Masking agents*	Absorbance/ml. of masking agent			
	0.0	0.5	1.0	2.0
Ascorbic acid (0.1M)	0.332	0.328	0.329	0.319
Tartaric acid (0.01M)		0.301	0.275	0.216
Succinic acid (0.01M)		turbid	turbid	turbid
5-Sulphosalicylic acid (0.01M)		turbid	turbid	turbid
NaF (0.01M)		0.334	0.341	0.336
EDTA (0.01M)		0.018	0.007	0.009
Nitrilotriacetic acid(NTA) (0.01M)		0.009	0.006	0.005

- The pH of solutions are adjusted to 3.0.

The results in Table (2) indicate that ascorbic acid and NaF solutions have no effect on the absorbance of [Bi(III)-ARS-CPC] complex, while other masking agents exhibit decreasing in the absorbance owing to their complexing action with bismuth. Therefore, composite mixture solution containing (ascorbic acid(0.1M) + NaF(0.01M)) is prepared and its effect on the absorbance of coloured complex is then examined. The experimental results showed that 2 ml of the composite mixture solution is optimum and it was recommended for the subsequent experiment. The order of addition on the absorbance is also investigated. The experiments showed that the order of (Bi(III) + ARS + CPC + buffer solution + composite mixture solution + Triton X-100) at 507 nm is the optimum because of its high absorbance value.

Effect of time on colour development

To test the effect of time on the absorbance of the coloured complex at 507 nm, the Bi(III) complex has been prepared from different amounts (50 and 100 µg) of Bi(III) under the optimal experimental conditions, the absorbance is measured at different time intervals up to 60 min. Table (3) indicates that the colour of the complex develops immediately and the absorbance remains maximum and constant for at least 40 minutes.

Table 3: Effect of time on colour development of Bi(III) complex.

Bi(III) (µg)	Absorbance / min.										
	0	5	10	15	20	25	30	35	40	50	60
50	0.177	0.181	0.190	0.192	0.197	0.199	0.194	0.186	0.183	0.178	0.176
100	0.347	0.349	0.349	0.347	0.341	0.334	0.330	0.326	0.328	0.318	0.319

Validity of Beer's law and reproducibility

Under the optimum operating conditions, a linear calibration graph is obtained for 5-150 μg of Bi(III) in a final volume of 20 ml (i.e., $0.25 - 7.5 \mu\text{g} \cdot \text{ml}^{-1}$). Higher concentrations show a negative deviation from Beer's law (Fig. 2). The apparent molar absorptivity of the ternary Bi-ARS-CPC complex is $1.4 \times 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, which corresponds to Sandell's sensitivity index of $0.01492 \mu\text{g} \cdot \text{cm}^{-2}$ of Bi(III). The limit of detection (LOD) is $0.0671 \mu\text{g} \cdot \text{ml}^{-1}$ and the limit of quantification (LOQ) is $0.2235 \mu\text{g} \cdot \text{ml}^{-1}$. The reproducibility of the procedure is studied by the analysis of three series of solutions (five identical samples for each series) having final bismuth concentration of 1.5, 5 and $7.5 \mu\text{g} \cdot \text{ml}^{-1}$. The results showed a relative standard deviation of 3.07, 0.94 and 0.93 %, respectively.

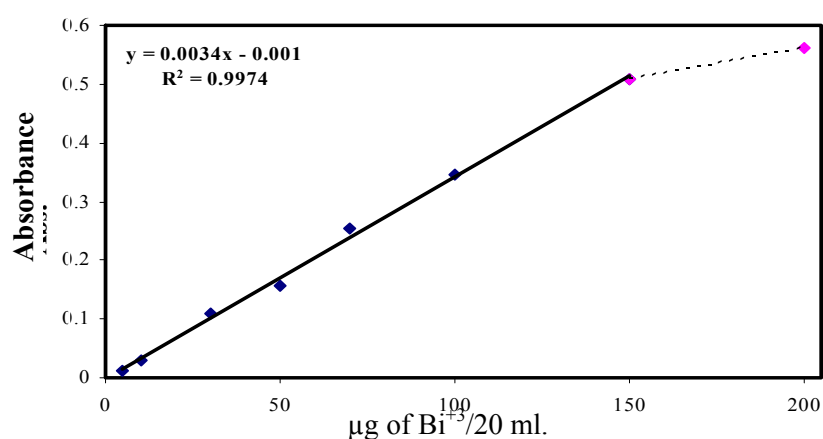


Fig. 2: Calibration graph for bismuth determination using the proposed method

Final absorption spectra

Under the above established optimized conditions, bismuth ion forms a red water soluble ternary complex with ARS and CPC at pH 3 in the presence of composite mixture solution. The coloured complex exhibits one maximum absorption located at 507 nm against the reagent blank solution (Fig. 3).

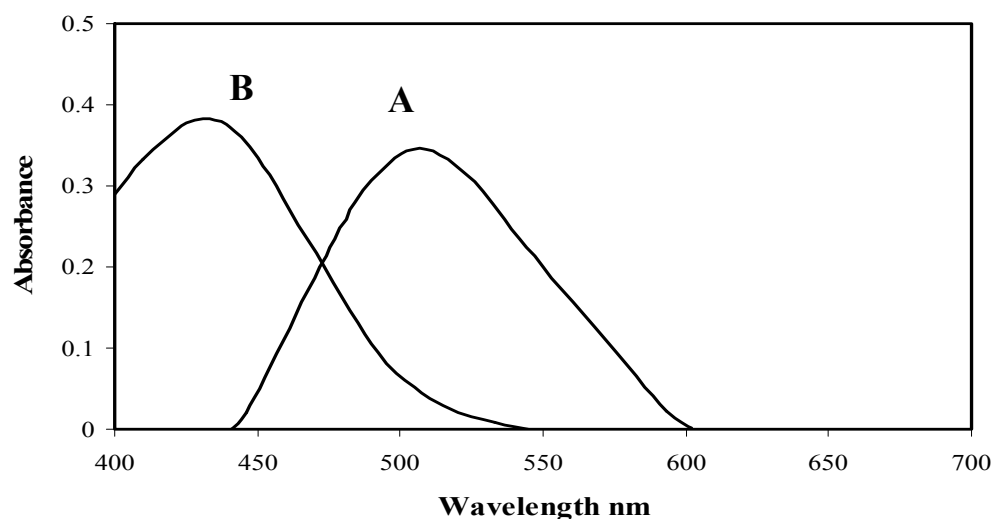


Fig. 3: The absorption spectra of 100 μg Bi(III) /20 ml (A) against blank and (B) blank against distilled water.

Composition of the complex

The stoichiometry of the complex is studied under the established conditions by applying the continuous variations method (Job's method) and mole-ratio method (Delevic, 1997). The experimental results in both methods (Fig. 4) show that the molar ratio of Bi(III) to ARS in the complex is found to be 1:3. The molar ratio of the Bi-ARS to CPC in the presence of Triton X-100 is also estimated and it was found to be 1:3:6, respectively. The stability constant of the coloured complex is also studied (Hargis, 1988) and it was found to be $2.47 \times 10^{13} \text{M}^{-2}$.

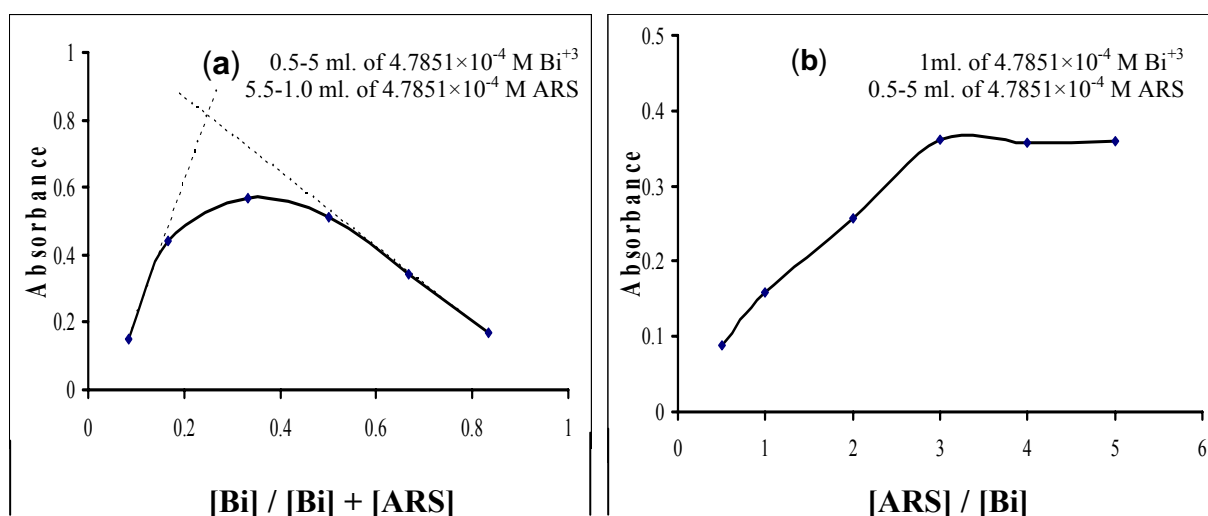


Fig. 4: (a) Continuous variations and (b) mole-ratio plots for Bi(III) – ARS complex.

Effect of Interference

The effect of interfering species on the determination of 100 μg /20 ml bismuth was studied under optimum conditions with proposed method. As shown in Table 4, the largest interfering species are found to be Al^{3+} , Cr^{3+} , Fe^{3+} , Fe^{2+} , Cd^{2+} , Ni^{2+} , Zr^{4+} and PO_4^{-3} ions.

Table 4: Individual tolerance limit of foreign ions on the determination of 100 μg of Bi(III)

Foreign ions added	Tolerance limit, μg
Na^+ , NO_3^-	1000
Pb^{2+} , Ag^+ , Cl^- , Br^-	750
Ba^{2+} , Zn^{2+} , Cu^+ , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-}	500
Co^{2+} , La^{3+} , Cu^{2+} , Ca^{2+} , Mn^{2+} , SO_3^{2-}	250
Hg^{2+} , NH_4^+	150
Zr^{4+} , Fe^{2+}	150
Fe^{3+} , Cd^{2+} , Ni^{2+} , PO_4^{-3}	50
Al^{3+} , Cr^{3+}	25
	<10

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Also the effect of some foreign substances (e.g., glucose, lactose, starch and gum Arabic), that usually present in dosage forms are studied by adding different amounts of foreign substances to 100 μg of bismuth. It is observed that the studied foreign species did not show any interference with the proposed method, Table (5).

Table 5 : Effect of additives and percipients on the determination of 100 μg of Bi(III)

Interferences	Recovery (%) of 100 μg Bi (III)/ μg of interferences		
	250	500	1000
Glucose	97.3	95.9	103.2
Lactose	99.4	103.5	102.9
Starch	101.2	103.5	103.5
Gum Arabic	106.8	Turbid	Turbid

APPLICATIONS

Determination of Bi (III) in water and urine samples

The proposed method has been successfully applied to the determination of bismuth(III) at two different concentrations added to appropriate volumes of tap, river, sea water and urine samples. The results are compiled in Table 6 and show that the proposed method is suitable for determining bismuth with satisfactory recovery.

Table 6 : Determination of Bi (III) in water and urine samples

Sample	ml of sample	Bi(III) added (μg)	Recovery* (%)
Tap water	2	50	98.1
		100	101.3
	6	50	101.5
		100	100.7
River water (Tigris river)	2	50	104.4
		100	102.9
	6	50	100.9
		100	102.0

Sea water**	2	50	101.0
		100	102.3
	6	50	101.9
		100	103.9
Urine	2	50	97.1
		100	104.2
	6	50	96.8
		100	97.5

*Average of three determinations

** The Mediterranean sea (Turkey)

Determination of Bi (III) in a veterinary preparation

The present method has also been applied to the determination of Bi (III) in veterinary preparation. The results are listed in Table 7, from which it can be concluded that the method is suitable for determining bismuth in the veterinary preparation sample with satisfactory recovery.

Table 7 : Determination of Bi (III) in veterinary preparation

Veterinary preparation	Bi(III) amount (μg)	Recovery, (%)*
Diaclean 2000 mg $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ /Sachet Avico, Jordan	50	95.3
	100	98.9
	150	96.5

*Average of five determinations.

The performance of the proposed method was assessed by calculating the student's t-test compared with the literature method (Marczenko and Baleczak, 2000). The results in Table 8 show that the calculated values of "t" do not exceed the theoretical values at the 95% confidence level (Christian, 2004) indicating that there is no significant difference in the precision between the proposed method and the reported method.

Table 8: Determination of bismuth by the proposed and literature methods

Veterinary preparation	Bismuth amount, μg	Recovery, %*		t. exp**
		Present method	Reported Method [#]	
Diaclean 2000 mg $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ /Sachet Avico, Jordan	50	95.3	98.6	1.29
	100	98.9	99.3	0.13
	150	96.5	98.9	0.69

*Average of five determinations.

**Tabulated t-value at 95% confidence level and eight degree of freedom is 2.31 for (n= 10),

(Marczenko and Baleczak, 2004)

CONCLUSION

A simple, sensitive and accurate spectrophotometric method has been developed for the determination of bismuth(III) in aqueous solution, using alizarin red S (ARS) as

chelating agent in the presence of CPC at pH 3. The method has been applied successfully to the determination of Bi(III) in natural water, urine and in a veterinary preparation.

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