Quantitative Analysis of Bismuth (III) Ion by Coupling Turbidy Method with Cloud Point Extraction Mode

Dr. Ahmed Fadhil Khudhair[1], Shaymaa Ibrahim Saeed[2]

[1, 2]Chemistry Department, College of Science, University of Kerbala, Kerbala, Iraq

Abstract: *A new turbidimetric method is described for the determination of bismuth(III) ion .This method is based reaction between Bi(III) ion with fuchsine reagent and Sodium dodecyl sulfate (SDS) as a surfactant compound in aqueous medium to form red ion-pair complex as turbid phase .The product was determined by using batch turbidimatric method.. All optimization parameters were studied. The calibration graph was linear in the range of $(0.05 -25)\mu g.mL^{-1}$, with correlation coefficient r =0.9973 and limit of detection (0.047 $\mu g.mL^{-1}$).A comparison was made between the newly developed method analysis with classical method using standards addition method via the use of t-test it was noticed that there was no significant difference between two methods at %95 confidence level.*

Keywords: Bismuth, Turbidity, Cloud point extraction

1. Introduction

Bismuth presents in two oxidation state three and five, its compounds are not exist in solution and are very important in view of analytical chemistry [1].Although bismuth was not known as a metal, it was used as a beauty treatment during[2]. Bismuth and its compound are also used in semiconductors cosmetic preparations, alloys and metallurgical additives and in the preparation and recycling of uranium nuclear fuels[3]. The development of analytical techniques for the determination of bismuth at low levels by analytical techniques such as spectrophotometry [4-7], graphite furnace atomic absorption spectrometry [8,9], voltammetry [10,11] and inductively coupled plasma mass spectrometry[12] have been used for its measurement. Several procedure have been developed for the separation and preconcentration of contaminants from environmental matrices such as liquid –liquid extraction [13], co-precipitation [14], solid phase extraction [15]. Cloud point extraction is one of the method that used for the extraction of metal chelates, flame atomic adsorption spectrometry is used for analytical detection[16], in addition that cloud point extraction used to extract hydrocarbons content of river sediments by a solvent containing metal ion to form complex and addition surfactant with heating to form a precipitate to be measured the turbidity to solid product and the same time transfer the hydrocarbon to the water phase[17]. The aim of this work is to describe a simple and sensitive turbidimetric method which is based on the formation of ion-pair complex in aqueous medium by coupling with cloud point extraction mode to determine the bismuth(III) ion in pure and pharmaceutical preparation samples.

2. Materials and Methods

Chemicals

All chemicals were used of analytical reagent grade while distilled water was used to prepare the solutions. Stock Bismuth nitrate solution $(Bi(NO_3)_3.5H_2O$,Merck, 1.0 mg.mL^{-1}) was prepared by dissolving 0.2312 g in 3mL of 5mol.L^{-1} nitric acid and diluted to mark in a100mL volumetric flask. A Basic Fuchsine in aqueous solution (4-[(4-Aminophenyl)-(4-imino-1-cyclohexa-2, 5dienylidene) methyl] aniline hydrochloride, $C_{20}H_{19}N_3 \cdot HCl$, 337.86 g mol^{-1} , 1mmol.L^{-1})by dissolving 0.3378g in 100mL,. Sodium dodecyl sulfate stock solution (SDS, 288.3 g mol^{-1}, 4% w/v) was prepared by dissolving 4.0000g in 100 mL of distilled water, sodium hydroxide solution (NaOH, Fluka, 1.0 mol L^{-1}) was prepared by dissolving 40.0000 g in 1.00 L (standardized with HCl solution).

Apparatus

A Loviband tubidimeter (Germany) with 1cm glass cell where it is calibrated with graduated concentration for formazine solutions from 10 to 1000NTU. UV-Vis absorbance spectra were recorded on a Shimadzu 160A UV-Vis spectrophotometer using 1cm quartz cells. A Bench Top pH meter with a combined glass electrode was used for pH measurements. A water bath with a good temperature control was used to achieve and accelerate the phase separation process.

Cloud Point Extraction Procedure

The pink precipitate formation by the following steps: 10mL solution contain 25µg.mL^{-1} Bi(III) ions added to 0.5 ml of 1mmol.L^{-1} for Fuchsin then mixed with 0.5 mL from 0.4 % w/v SDS was adjusted to related pH 8.0 , the mixture shaken for 1min and left to stand in a thermostatic bath at 85C$^{°}$for 20 min, high viscosity Cloud point formed ,the bulk aqueous phase was readily evaluated by turbidimeter to measure the attenuation of incident light, the chemical reaction was illustrated in Scheme 1.
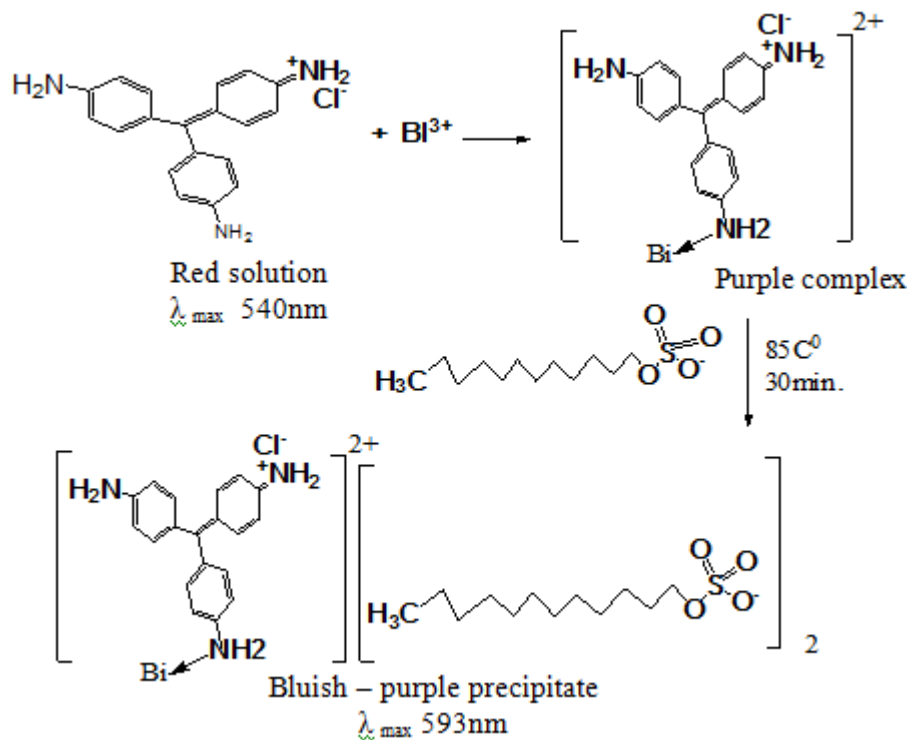
Scheme 1: Probable proposed mechanism to form the viscose aqueous phase Bi-fuchsin-SDS

3. Results and Discussion

The chemical as well as physical parameters (mainly concentration and pH of the reaction medium, temperature of complex formation, time of heating, stability of product, and interferences effect) were studied.

Effect of Fuchsine Concentration

A series of the Fuchsin reagent (0.005- 0.1 mmol.L^{-1}) were prepared. A 25µg m$L^{-1}$of Bi(III) ion was used. The influence of Fuchsin concentration on CPE of Bi(III) was found to be quantitative hence, this concentration of Fuchsin was used for other experiments. The total results were illustrated in Fig. 1. It can be seen that an increase in concentration of Fuchsin causes an attenuation of incident light due to accumulation and compactness of the precipitated particles causing obstruction of the incident light which led to increase of attenuation of the incident light, up to 0.05 mmol.L^{-1} Fuchsin concentration was chosen as the optimum concentration that used for further experiments. The concentration of Fuchsin larger than 0.05 mmol L^{-1} cause to decrease of attenuation of incident light. It is probable that it could be due to the restriction of the passage of incident light due to the accumulation of precipitate particles in front of the detector.
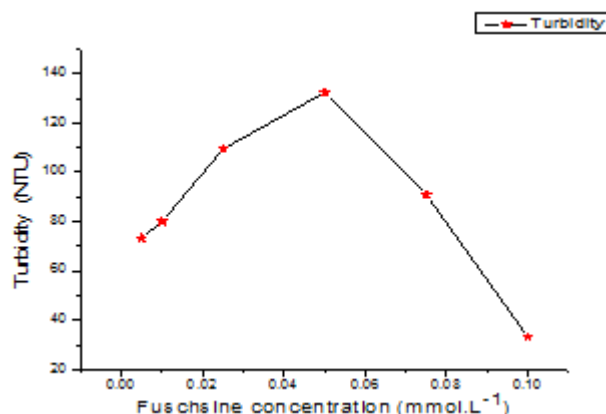
Figure 1: Effect of concentration o f Fuchsin on the measurement of Turbidity. [Bi(III) 25µg mL^{-1} , 0.5 mL of 4% (w/v) SDS]

Variable Concentration of SDS

The effect of surfactant concentration on CPE is important. In this study, SDS was used as a surfactant agent. The variation in CPE extraction efficiency of Bi(III) within the SDS concentration range of 0.04 -0.40% (*w/v*) was examined, and the results are shown in Figure 2. As can be seen, the recovery increased with the increase of SDS concentration up to 0.2 % (*w/v*), which is considered as complete extraction. SO, a concentration of 0.2% (*w/v*) was chosen as the optimum surfactant concentration. The preconcentration and enhancement factor decreased at higher concentrations due to an increase in the volume of the surfactant-rich phase. For this reason, the measured turbidity decreased because of its sensitivity. At lower concentrations, the extraction efficiency of the complex was low, probably because of the inadequacy of assemblies to entrap the hydrophobic complex quantitatively. The results were tabulated in Table 1.

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Table 1: Effect of SDS concentration on the measurement of attenuation of incident light

| Volume of SDS (mL)	Concentration of SDS(w/v)%	Turbidity $\bar{y}_i \pm t_{0.05/2}\sigma_{n-1}/\sqrt{n}$ (n=3)(NTU)
0.2	0.08	41.0± 1.02
0.3	0.12	57.5±1.32
0.4	0.16	98.0±0.00
0.5	0.20	238.0±0.97
0.6	0.24	136.0±0.76
0.8	0.32	119.5±0.05
1.0	0.40	124.0±0.06

To a cretin of the selectivity of the SDS surfactant, compared the results with Triton x-100 surfactant as shown in Table 2.

Table 2: Influence surfactant type on the attenuation of incident light

| Type of surfactant	Turbidity $\bar{y}_i \pm t_{0.05/2}\,\sigma_{n-1}/\sqrt{n}$ (n=3) (NTU)
Triton x-100	2.8±0.27
SDS	196.0±2.87

Effect of pH

The influence of pH in CPE procedure is deemed the crucial step to ensure the reaction between metal ions and chelating molecules with sufficient hydrophobicity and subsequent extraction into the small volume of surfactant-rich phase. So, pH plays an incomparable role in complex formation and its extraction into micellemediated solvent to obtain the desired preconcentration by CPE ,The effect of pH on turbidity for the turbid solution formation of the Bi(III)-Fuchsin complex in SDS medium was studied by varying the pH from (2.2 -12.5) using different pH buffer solutions. As shown in Figure 3 that the turbidity first decrease sharply with increasing pH indicating decrease extraction efficiency was achieved because of partial dissociation of the complexes at higher pH, which may result in an incomplete extraction of complex. Therefore, pH 2.2 was chosen as the optimum working pH for complete formation of complex and hence a good extractability.
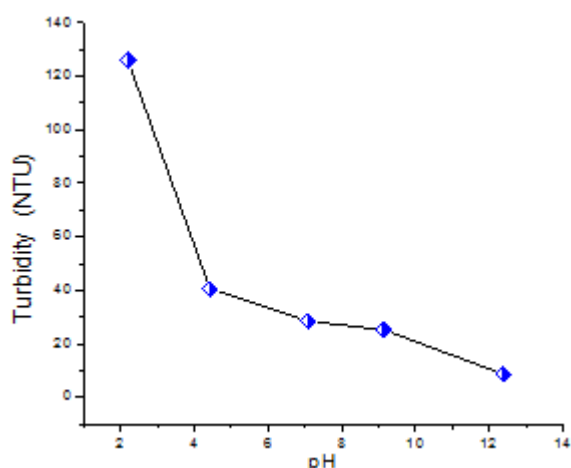
Figure 3: Effect of pH on the formation of Bi(III)- Fuchsin complex .[Bi(III) 25 µg mL^{-1} , 0.05 mmol.L^{-1} Fuchsin, 0.5 mL of 4 % (w/v)SDS]

Temperature and Time of Heating

It is desirable to have the shortest incubation time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of the phases. The effect of the equilibration temperature and time was studied with a range of 25–100°C and 5–45 min, respectively. It was found that an equilibration temperature of 80°C and a time of 15 min were adequate to achieve quantitative extraction. The maximum signals were presented between 75–85°C. Therefore, 80°C was selected as the working equilibration temperature. Figure 4 show effect of temperature and time of heating on the measurement of attenuation of incident light for Bi(III)-Fuchsin –SDS complex. The stability of the complex that study by measuring with time leaving, which is showed the complex is stable for long time.

A

B
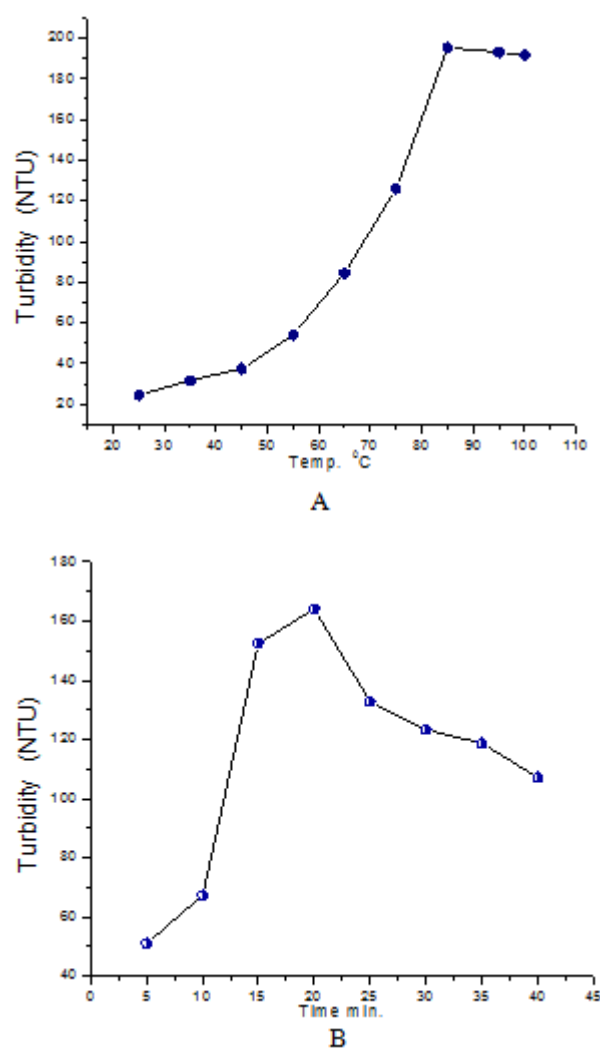
Figure 4: Effect of temperature and time of heating on the measurement of attenuation of incident light for Bi(III)-Fuchsine –SDS complex .[Bi(III) = 25 µg.mL^{-1} , 0.05 mmol.L^{-1} Fuchsine, 0.5 mL of 4 % (w/v)SDS, pH 2.2] , (A) temperature influence, (B) Effect of the time

Interferences Effect

The effect of foreign ions on the determination of bismuth by the proposed method was investigated by measuring the turbidity of the solutions containing 25 µg mL^{-1} of bismuth.

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The maximum tolerances of the investigated cations and anions are given in Table 3. According to the results, Bi(III) recovery was nearly quantitative in the presence of other ions.

Table 3: Effect of divers ions on the measurement of attenuation of incident light signal of Bi(III)

Interference ion	Turbidity measurement $\bar{y}_i \pm t_{0.05/2}\,\sigma_{n-1}/\sqrt{n}$ (n=3)(NTU)	Erel(%)
Cr	203.0±4.97	-02.53%
Pb	153.0±2.49	22.73%
Fe	113.0±2.49	42.93%
Hg	33.4±0.99	83.13%
Ba	301.0±4.97	-52.02%
Cu	255.0±4.97	-28.79%
Ni	252.0±2.49	-27.27%
Cd	261.0±2.49	-31.82%
Without interfere	198.0±4.97	00.00%

Scatter Plot Calibration Curve

Under the established optimum conditions, the calibration curves of attenuation of incident light method were estimated. A series 1-25 μg mL^{-1} Bi(III) solution was prepared. Table 4 depicts all the results obtained using linear regression analysis.

Table 4: Summary of results for linear regression analysis using turbidity method

Range of [Bi] μg.mL^{-1}	$\hat{Y}_i = a \pm s_a t + b \pm s_b t[\text{Bi}]$ at confidence level 95%,n-2	r r^2 %r^2	t$_{tab}$ at 95%, n-2	$t_{cal} = \frac{|r|\sqrt{n-2}}{\sqrt{1-r^2}}$
0.05 - 25.00	y =6.3115x + 1.3663	0.9973 0.9947 99.47%	2.776 << 30.631	

Limit of Detection

A study was carried out to calculate the limit of detection of Bi(III)-Fuchsin-SDS through two method .Gradual dilution of low concentration in the calibration graph or based on the numerical value of slope . The results tabulated in Table 5.

Table 5: Limit of detection for Bi(III) ion at optimum parameters .

Practically based on the gradual dilution for the minimum concentration (0.05 µg.mL^{-1})	Theoretical based on the value of slope x=3S$_B$/slope for n=10
0.01	0.047

x= value of L.O.D. based on slope , S$_B$= standard deviation of blank repeated for 10 times

Repeatability

The value of the relative standard deviation (RSD %) for bismuth 25 mg L^{-1} was tabulated in Table 6. The percentage relative standard deviation less than 1.5 % was obtained indicating a reliable measurement can be achieved using this method.

Table 6: Repeatability of Bi (III) at optimum parameters

[Bi] μg.mL^{-1}	Average response $\bar{y}i$ (mV) n*=8	RSD %	Confidence interval at 95% $\bar{y}i \pm t_{0.05/2,n-1}\,\sigma_{n-1}/\sqrt{n}$
25	199.5	1.28	199.5±2.14

n* =Number of repeated measure, t $_{0.05/2,7}$= 2.365

Analysis of Pharmaceutical Formulations

Turbidity method achieved in this work was used for the analysis of bismuth ion in pharmaceutical preparations (Bismuth subsalicylate , 350 mg / 15mL) and was compared by spectrophotometric method. The standard additions method for the turbidity method was applied by preparing a series of solution of pharmaceutical drug to the six volumetric flask, followed by the addition graduated volume standard solution of Bi(III) in order to have the concentration range from 0.0-20 mg.L^{-1}. The results of linear part of the scatter plot diagram by standard additions method were illustrated in Tables 7. While the result of sample estimation showed in Table 8.

Table 7: Summary of linear regression equation of turbidity method for the estimation of Bi(III) ion by standards additions method).

y$^{\wedge}$(mV)=a± S$_a$t+ b± S$_b$t[x] at confidence level 95%, n-2	r r^2 %r^2	t$_{tab}$ at 95% confidence level, n-2	$t_{cal} = \frac{|r|\sqrt{n-2}}{\sqrt{1-r^2}}$
y = 6.7552x + 15.178	0.9968 0.9936 99.36%	3.182<<24.9825	

y$^{\wedge}$: Estimated response (NTU) for (n=3), [x] : Bi(III) (mg.L^{-1}), r: correlation coefficient, r$^{2:}$ coefficient of determination, r^2%: linearity percentage, t$_{tab}$: t $_{0.05/2,\ n-2}$ at 95% confidence level.

Table 8: Bi (III) determination in pharmaceutical sample using turbidity method by standard additions method

Information of pharmaceutical drug	Theoretical calculation	Practical calculation	Recovery %
Bismuth subsalicylate (350mg/15mL)	35 mg mL^{-1}	29.9mg/ml	85.43%

In classical spectrophotometric method [18] via the measurement of λ$_{max}$ at 465nm , linear calibration curve was obtained for the concentration range of 0.00478 - 0.033 mmol L^{-1}, correlation coefficient was of 0.9881 and limit of detection was of 0.003 mmol L^{-1}. The preparation of standard additions calibration plot to spectrophotometric method was prepared by different aliquots of 0 , 0.4, 0.8, 1.2, 1.6 and 2.0 mL of 0.1195 mmol L^{-1} standard solution of Bi(III) in order to have a concentration range of 0- 0.0239 mmol L^{-1}. These solutions were transferred into a series of 10 mL volumetric flasks and to each flask 0.4 mL of drug 0.1195 mmol L^{-1} Bi (III), 1.0 ml of 1:5 v/v sulfuric acid and 5.0 mL of 20% potassium iodide solutions were added, mixed well and diluted to mark with water and mixed. The absorbance of each solution was measured at 465 nm against water blank after 5 min. All the results were illustrated in Table 9.

Table 9: Summary of linear regression equations for the estimation of Bi(III) ion by UV-Vis-spectrophotometric method.

Range of [Bi(III)] mmol L^{-1}	$\hat{y}= a\pm S_a t+ b\pm S_b t[x]$ at confidence level 95%, n-2	r $r^2\%$	t_{tab} at 95% confidence level, n-2	$t_{cal} = \dfrac{\lvert r\rvert\sqrt{n-2}}{\sqrt{1-r^2}}$.
0.0 - 0.0239	0.1769±0.050+42.978±3.48[x]	0.9971 99.42	2.778<<12.338	

y^: Estimated response (absorbance) for (n=3), [x]: [Bi(III)] (mmol L^{-1}), r: correlation coefficient, $r^2\%$: linearity percentage, t_{tab}: $t_{0.05/2, n-2}$ at 95% confidence level.

Paired t-test was used in order to compare the new turbidity method with the classical spectrophotometric method. The obtained results as shown in Table 10. indicated clearly that there were no significant differences between newly turbidity method and the spectrophotometric method at 95% confidence interval as the calculated t-value is less than critical t-value.

Table 10: Paired t-test for the new proposed method and the spectrophotometric method for the determination of Bi(III) in pharmaceutical drugs by standard additions method.

	Theoretical [Bi(III)] mg mL^{-1}	Practical [Bi(III)] mg mL^{-1}	Mean	σ_{n-1}	P- value
Proposed method	35.00	29.90	31.8	2.68	0.3388
Spec. Method	35.00	33.68			

4. Conclusion

A simple, accurate and sensitive turbidimetric method proposed. The new method can be used to determine of Bi(III) in pure and pharmaceutical preparation. Bluish – purple precipitate formed to measure and did not show significant differences in analytical performance when compared with other methods as shown in table (10). Therefore. It can be regarded as an alternative reliable determination method for the drug discussed in this research.

References

[1] A. S. Bashammakh, Extractive Spectrophotometric Determination of Bismuth(III) in Water Using some Ion Pairing Reagent, *E-Journal of Chemistry*, 8(3), 1462-1471, 2011.

[2] S. A. Barakat, Flow Injection Extraction-Spectrophotometric Determination of Bismuth with Di-(hydrogenated tallow alkyl) dimethylammonium Chloride, *Turk J Chem,* 26, 345-349, 2002.

[3] A. Afkhami, T. Madrakian , H. Siampour, Cloud point Extraction Spectrophotometric Determination of Trace Quantities, *J. Braz. Chem. Soc.*, 17(4), 797-802, 2006.

[4] A. Abbaspour and L. Baramakeh, Simultaneous determination of antimony and bismuth by beta-correction spectrophotometry and an artificial neural network algorithm , *Talanta*, 65, 692–699, 2005.

[5] T. Madrakian , A. Afkhami and A. Esmaeili, Spectrophotometric determination of bismuth in water samples after preconcentration of its thiourea - bromide ternary complex on activated carbon, *Talanta* , 60, 831-838, 2003.

[6] Z. Nan, "Direct Microspectrophotometric Determination of Bismuth in Silver with Semi-Xylenol Orange",Microchim. Acta, 146, 43-47, 2004.

[7] A. Bashammakh, Extractive Spectrophotometric Determination of Bismuth(III) in Water Using Some Ion Pairing Reagents , *E-Journal of Chemistry*, 8(3), 1462-1471, 2011.

[8] N. Tokman and S. Akman , Determination of bismuth and cadmium after solid-phase extraction with chromosorb-107 in a syringe, *Analytica Chimica Acta*, 519, 87–91, 2004.

[9] K. M. Elsherif and H. M. Kuss, Simultaneous Multi-Element Determination of Bismuth (Bi), Antimony (Sb), and Selenium (Se), *Advances in Applied Science Research*, 3 (4), 2402-2412, 2012.

[10] H. Guoa, Y. Li , P. Xiao and N. Hea, Determination of trace amount of bismuth(III) by adsorptive anodic stripping voltammetry at carbon paste electrode, *Analytica Chimica Acta*, 534,143–147, 2005.

[11] E. Hasdemir and K. Karaboduk, Simultaneous Determination of Bismuth and Copper by Square Wave Voltammetry in The Presence of Ethylenediaminetetraacedic Acid, *G.U. Journal of Science*, 23(1), 33-39, 2010.

[12] K. Norisuye and Y. Sohrin, Determination of bismuth in open ocean waters by inductively coupled plasma sector-field mass spectrometry after chelating resin column preconcentration, *Analytica Chimica Acta*, 727 ,71-77, 2012.

[13] A. N. Anthemirani, D.G.Themelis, J.A. Stratis, *Talanta* 54, 37(2011) .

[14] G. Doner, A. Ege, *Anal.Chim. Acta* 547, 14, 2004.

[15] A. M. Starvin, T. Prasada Rao, *J. Hazard. Mat.* B113, 75, 2004.

[16] A. Moghimi, Extraction of Ultra Trace Amounts Bismuth in Water Samples Using Cloud point Extraction with 2-Amino-Cyclopentene-1-Dithiocarboxylic Acid", *Journal of Chemical Health Risks*, 2(1), 23-30, 2012.

[17] M. M. Barbooti, Turbidimetric Determination of Hydrocarbon Contamination in Passaic River Sediments and Refinery Polluted Soils , *Journal of Environmental Protection*, 2, 915-922, 2011.

[18] Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood Ltd, Chichester , 149, 1986.

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