



# Cloud point extraction – Microvolume spectrophotometry for extraction and determination of bismuth in waters and roadside soil

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## ABSTRACT

The authors, in the present work, described a new microvolume spectrophotometric method for extraction, preconcentration and determination of extremely low quantities of bismuth in waters and roadside soil. The strategy of method is based on the formation of an ionic pair between  $[\text{BiL}_4]^-$  and trioctylamine  $[\text{TOA}]^+$  in aqueous phase and extraction of this ion associate by cloud point extraction technique (CPE) using Triton X-100. The influence of different empirical parameters e.g. pH of aqueous phase, surfactant concentration, equilibrium time and temperature on performance efficiency of developed method was studied and then optimized. On the optimum conditions, the absorbance of Triton X-100 – rich phase measured at 342 nm was linear with bismuth quantity in aqueous phase in the range of 10–1250  $\mu\text{g L}^{-1}$  with  $R = 0.996$ ,  $n = 7$ . The limit of detection (LOD), quantitation (LOQ), and preconcentration factor ( $C_F$ ) were calculated to be 2.86 and 9.54  $\mu\text{g L}^{-1}$ , and 40, respectively. The evaluation of method was performed by monitoring bismuth in sea, and tap waters and roadside soil, where, the recovery percentage obtained (>96%) proved the precision of our method. On the other hand, thermodynamic characteristics in terms of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  of extraction process were studied and the numerical values of these parameters were calculated and discussed in details.

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## 1. Introduction

Bismuth compounds, either inorganic or organic, have become essential in various applications of our daily life. They have been used as medicines for therapy of some disorders e.g. flatulence, diarrhea, colitis and gastritis [1]. In industrial field, bismuth compounds may be used in the synthesis processes of cosmetics, semiconductors, alloys, and uranium nuclear fuel [2–6]. As a result of that, bismuth may diffuse into the environment causing some risks to the human and organisms [7]. For example, some recent studies have indicated that large doses may cause a mild kidney damage, serious exodermatitis, and feeling of bodily discomfort [8,9].

In recent years, several analytical procedures have been progressed for bismuth estimation. Although, spectrophotometry is low cost technique and widely employed [10], its sensitivity is highly low, therefore, it is inappropriate for monitoring ultra – trace levels of bismuth in real samples. For this reason, highly sensitive and selective techniques e.g. hydride generation technique combined with either atomic absorption spectrometry (HG – AAS) [11], inductively coupled plasma optical

emission spectrometry (HG-ICP – OES) [12], or atomic fluorescence spectrometry (HG-AFS) [13], were introduced. Other sensitive methods, not dependent on hydride generation technique, were also developed like electro thermal coupled atomic absorption spectrometry (ET – AAS) [14], cathodic and anodic stripping voltammetry [15–17], atomic absorption spectrometry (AAS) [18,19], inductively coupled plasma mass spectrometry (ICP-MS) [20], inductively coupled plasma optical emission spectrometry (ICP – OES) [21] and a fluorescence quenching [22]. However, because bismuth concentrations in soils and sea water are on the order of 0.12–0.91  $\text{mg kg}^{-1}$ , and 0.02–0.11  $\mu\text{g L}^{-1}$ , respectively [23], and due to the high cost of the above techniques, the separation and preconcentration steps become necessary prior to the application of traditional low-cost technologies like spectrophotometry for bismuth determination in such samples. So that, several techniques for preconcentration of bismuth have been reported including preconcentration by electrodeposition using Mg–W cell [24] a flow injection/on-line preconcentration [25–27], dispersive liquid–liquid microextraction [28,29], solid phase extraction [30–34], on – line preconcentration followed by flame atomic absorption spectrometry (FAAS) [35], trap hydride generation – AAS [36] and cloud point extraction [37–41].

The trend in analytical chemistry is to reduce the use of toxic organic solvents, therefore, novel Eco friendly extraction methods e.g. ionic

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liquid–liquid extraction (ILLE) [42–44], homogeneous liquid–liquid extraction (HLE) [45–47], and cloud point extraction (CPE) [37–41, 48–53] have been developed. CPE, a type of micellar systems, has received a great deal of attention because it is agreement with the green chemistry rules [54]. The principles of CPE technique were explained in details by Watanabe and Tanaka [55]. Concisely, the nonionic surfactant solution becomes hazy at a specific temperature namely the cloud point temperature (CPT), and over this point, the aqueous solution will be separated into two phases, one of them is a surfactant rich phase (SRP) with tiny volume which contains the analyte enclosed by micelle structures, while, the other phase is diluted aqueous phase (AQ) [56,57]. The nonionic surfactants solutions have clouding phenomena which is most likely attributed to the attraction between the polyethylene glycol slices and ethyl oxide in the micelles at high temperatures, whereas, lacking such attraction at low temperature [58–60]. It is important to note that, the number of scientific papers devoted to the analysis of bismuth in soil collected from roadsides is limited until now, on the other hand, CPE is a low cost, and efficient method for separating and determining wide selection of organic and inorganic pollutants in different environmental samples [61–66]. Therefore, the present study provides a highly sensitive and selective method for microextraction and determination of bismuth in water and roadsides soil samples using CPE coupled to microspectrophotometry. It is well known that the thermodynamic characteristics of solubilization process in surfactant – rich phase have a strong impact on the efficiency of any analytical method based upon CPE technique, therefore, such characteristics were investigated and discussed in details in the present paper.

## 2. Experimental

### 2.1. Reagents solvents

The reagents and solvents used in this work were highly purity in agreement with specifications of committee of analytical reagents of the American chemical society.  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Aldrich Chemical Co Ltd., Milwaukee, WC, USA) was employed for preparing stock solution of Bi(III) ions ( $1000 \mu\text{g mL}^{-1}$ ) by dissolving 0.232 g of salt in deionized water (100 mL) and adding drops of dilute  $\text{HNO}_3$ . The standard solutions at concentration levels of 10–1250  $\mu\text{g L}^{-1}$  were prepared by suitable dilution of the stock solution using deionized water. Triton X – 100 (Aldrich Chemical Co., USA) solution at concentration level of  $0.5 \text{ mol L}^{-1}$  was prepared by mixing 64.88 g of surfactant with a sufficient amount of deionized water. Potassium iodide solution (1% w/v) was prepared using 1 g of KI in 100 mL deionized water. 3 mL of trioctylamine (TOA) (Aldrich Chemical Co., USA) was added to 100 mL of the solution containing drops of concentrated nitric acid to obtain 3% v/v. Mixture of  $0.5 \text{ mol L}^{-1}$  of both  $\text{H}_2\text{SO}_4$  and NaOH was used to adjust pH of the aqueous phase in the range of 0.5–8.

### 2.2. Apparatus

Perkin-Elmer (model Lambda 25, USA) spectrophotometer and a quartz micro cell with internal capacity of 500  $\mu\text{L}$  were used for recording the electronic spectra in the range of 190–1100 nm. The pH meter from an Orion (model EA 940) and micropipette model Volac were employed for pH measurements and the preparation of solutions, respectively. Centrifuge (Clay Adams) with 5000 rpm was employed for collection of fine droplets scattered in aqueous phase and achieving phases – separation. Thermostat water bath (Precision Scientific, USA) was kept at the required temperature for production cloudy solution. Milli – Q Plus system (Millipore, USA) was used for obtaining deionized water. The type of ICP – MS instrument used as a reference procedure and its operational parameters are explained in details in [29].

### 2.3. Cloud point extraction procedure

In a glass centrifuge tube (10 mL), known concentrations of bismuth (III) ions ( $10\text{--}1250 \mu\text{g L}^{-1}$ ), certain volumes of both KI (1 mL, 1% w/v), and sulfuric acid (1 mL,  $5 \text{ mol L}^{-1}$ ) were mixed with TOA (1 mL, 3% v/v) and Triton X – 100 (0.4 mL,  $0.5 \text{ mol L}^{-1}$ ). The solution was completed by deionized water to 10 mL and then blended by the vortex mixer to 1 min and put in a water bath at  $70^\circ\text{C}$  for ten min. The analyte dispersed in aqueous phase was collected by centrifugation at 2500 rpm for 3 min. After separation phases, glass tube containing the solution was inserted to the an ice bath for 15 min, and the coacervate layer was separated out and diluted by acetone to final volume of 250  $\mu\text{L}$  prior to measurement at  $\lambda_{\text{max}}$  342 nm. Extraction percentage was calculated by using Eq. (1):

$$\% \text{Extraction percentage} = \frac{C_{\text{initial}} - C_{\text{diluted}}}{C_{\text{initial}}} \times 100 \quad (1)$$

where,  $C_{\text{initial}}$  and  $C_{\text{diluted}}$  are the bismuth concentrations in aqueous phase before and after CPE respectively.  $C_{\text{diluted}}$  was calculated from an appropriate calibration curve. The partition coefficient (D) of CPE was calculated using the equation mentioned in [50].

### 2.4. The pretreatment of samples

Two water samples (Tap, and marine waters) and two samples of soil taken from roadsides, Makkah city, KSA were employed for the validation of the developed method and the samples were treated prior to the application of the proposed method as the follows:

#### 2.4.1. Water samples

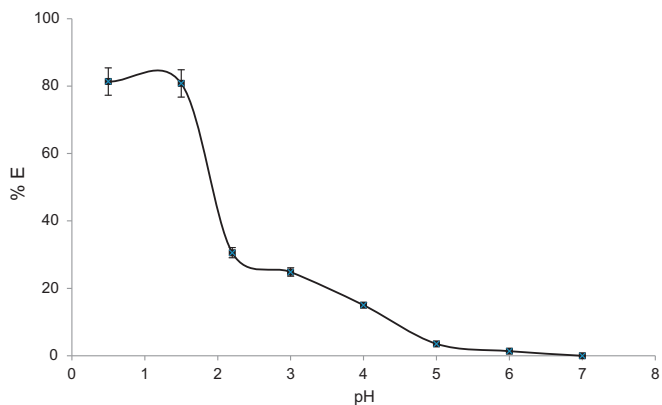
Sea water was collected from Red Sea (Jeddah City, KSA), whereas, Tap water was taken from the laboratories of Chemistry Department (University College, Umm Al-Qura University, Al-Jamoum, KSA). The filtration through cellulose membrane filter (0.45  $\mu\text{m}$ ) was used for removing suspended particulate matter and then all water samples were stored at  $4^\circ\text{C}$  in the dark. To defeat potential interferences of  $\text{Cd}^{2+}$  and  $\text{Fe}^{3+}$ , few quantities of KCN & NaF with concentration of 0.1% m/v were mixed with all samples. Then recommended procedure was applied.

#### 2.4.2. Soil samples

Soil samples were taken from different roadsides in Makkah city, KSA. The sampled soils were dried in air, grounded, and finally passed through a 2 mm sieve. 5 g of soil samples was refluxed with 20 mL of  $\text{HNO}_3$  ( $5 \text{ mol L}^{-1}$ ) for 1 h, and clear supernatant was then filtered into a 100 – mL measuring flask. An aliquot of sample solution diluted to 100 mL by deionized water was chosen for applying CPE procedure mentioned above.

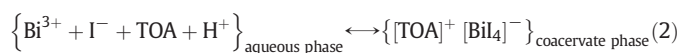
## 3. Results and discussions

Tetraiodobismuthate (III) complex,  $[\text{BiI}_4]^-$ , is one of the most famous bismuth complexes and widely employed in extraction processes of bismuth from different samples [67]. For example, our research group has effectively used this complex which has  $\lambda_{\text{max}}$  at 342 nm for extraction of bismuth from aqueous media by multi – walled carbon nanotubes [68]. However, the negative charge on the complex of  $[\text{BiI}_4]^-$  may make it able to form ion – pair with any bulky cation like  $[\text{TOA}]^+$ . Thus,  $[\text{TOA}]^+$  was mixed well with Bi(III) and excess of iodide ions, and the orange – yellow colored species was then extracted by CPE. In the absence of  $[\text{TOA}]^+$ , tetraiodobismuthate (III) complex did not transfer into surfactant – rich phase, therefore, the presence of  $[\text{TOA}]^+$  plays an important role in extraction process by CPE. Moreover, the stoichiometry of the ion – pair extracted in surfactant – rich phase was determined by Job's continuous variation method at  $\lambda_{\text{max}}$  342 nm. The molar ratio of  $[\text{TOA}]^+$  to  $[\text{BiI}_4]^-$ , and the formation constant of complex calculated by the equation reported in [28] were 1:1, and  $5.8 \pm 0.05 \times 10^4$ ,



**Fig. 1.** The pH influence of the aqueous phase on % E of bismuth(III) ions:  $\text{Bi}^{3+} = 1250 \mu\text{g L}^{-1}$ ;  $\text{KI} = 1\%$ , Triton X - 100 =  $0.02 \text{ mol L}^{-1}$ ; TOA =  $0.3 \text{ v/v}$ ; temperature =  $70 \text{ }^\circ\text{C}$ ; and 10 min standing time.

respectively. Therefore, the extraction of Bi(III) ions by CPE in the presence of TOA and iodide ions may occur according to the following:

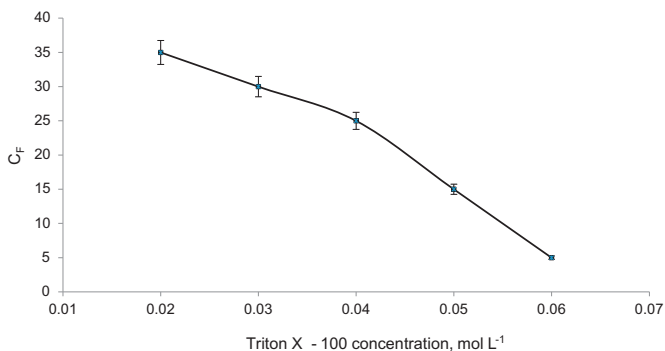


3.1. The optimization of CPE

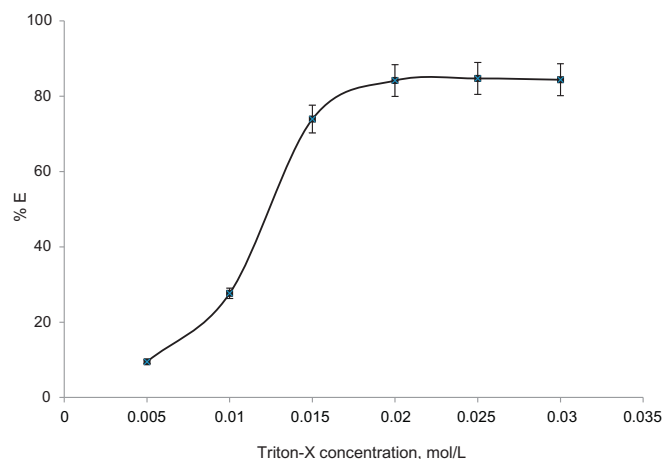
The influence of different experimental parameters on the efficiency of proposed CPE method was systematically studied as follows:

3.1.1. The effect of sample pH

Fig. 1 illustrates the extraction percentage (%E) of  $\text{Bi}^{3+}$  ions as function of pH of aqueous phase at experimental conditions shown below Fig. 1. The results indicated that %E of bismuth (III) ions decreases clearly with increasing the pH, and the maximum uptake was accomplished at pH ~ zero. The fact is that TOA is in the cationic form ( $[\text{TOA}]^+$ ) in very strong acidic media [50], therefore, it is ready to form an ion – pair species with  $[\text{BiI}_4]^-$ . The ion – pair of  $[\text{TOA}]^+ \cdot [\text{BiI}_4]^-$  formed in aqueous phase is extractable in phases which are rich with surfactant. Thus, the lower the value of pH, the greater the efficiency of extraction. At  $\text{pH} > 5$ , the extraction efficiency was dramatically decreased, probably because of bismuth hydroxide formation in the form of precipitation. However, the absorbance of coacervate phase was sensitive to the kind of mineral acid used to adjust acidity of aqueous phase where this absorbance was higher when using  $\text{H}_2\text{SO}_4$  compared with other acids tested ( $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{CH}_3\text{COOH}$ ). Thus, all subsequent investigations were executed at  $\text{pH} \sim \text{zero}$  by using  $\text{H}_2\text{SO}_4$  ( $0.5 \text{ mol L}^{-1}$ ).



**Fig. 2.** The relationship between preconcentration factor and Triton X - 100 concentration.  $\text{Bi}^{3+} = 1250 \mu\text{g L}^{-1}$ ;  $\text{KI} = 1\%$ , TOA =  $0.3 \text{ v/v}$ ; sulfuric acid =  $0.5 \text{ mol L}^{-1}$ ; temperature =  $70 \text{ }^\circ\text{C}$ ; and 10 min standing time.



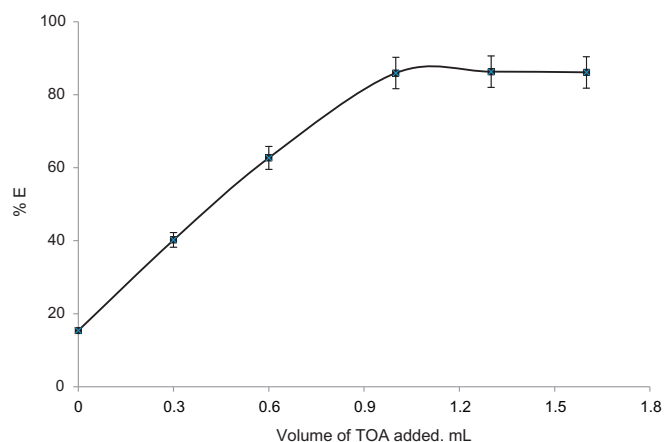
**Fig. 3.** The influence of neutral surfactant concentration on % E of bismuth(III) ions.  $\text{Bi}^{3+} = 1250 \mu\text{g L}^{-1}$ ;  $\text{KI} = 1\%$ , TOA =  $0.3 \text{ v/v}$ ; sulfuric acid =  $0.5 \text{ mol L}^{-1}$ ; temperature =  $70 \text{ }^\circ\text{C}$ ; and 10 min standing time.

3.1.2. The influence of surfactant concentration

The surfactant concentration plays an important rule for the success of the extraction by cloud point technique. Mathematically, preconcentration factor ( $C_F$ ) of CPE decreases with increasing surfactant concentration at a fixed volume of aqueous phase as shown in Eq. (2) [51]:

$$C_F = \frac{\%E V_0}{100V_s} \quad (3)$$

where,  $V_0$  and  $V_s$  are the volumes of aqueous and surfactant – rich phases, respectively. The plot in Fig. 2 illustrates that the values of  $C_F$  decreased when concentration of Triton X - 100 increased and the maximum value of  $C_F$  was obtained at concentration level of  $0.02 \text{ mol L}^{-1}$ . However, reducing surfactant concentration will lead to incomplete extraction of bismuth due to the insufficient amounts of Triton X - 100 in the coacervate phase, thus, the ion associate will not be entrapped well in the micellar media, and hence extraction is less efficient [69]. The plot of the %E of  $\text{Bi}^{3+}$  ions extraction by CPE against Triton X - 100 concentration is demonstrated in Fig. 3. Maximum %E ( $\approx 85$ ) was obtained at  $0.02 \text{ mol L}^{-1}$  in an excellent agreement with the findings of preconcentration factor. Thus, in all subsequent experiments, the concentration of surfactant (Triton X - 100) was optimized at the level of  $0.02 \text{ mol L}^{-1}$ .



**Fig. 4.** The influence of TOA volume on extraction of bismuth(III) ions.  $\text{Bi}^{3+} = 1250 \mu\text{g L}^{-1}$ ;  $\text{KI} = 1\%$ ;  $\text{H}_2\text{SO}_4 = 0.5 \text{ mol L}^{-1}$ ; temperature =  $70 \text{ }^\circ\text{C}$ ; and 10 min standing time.

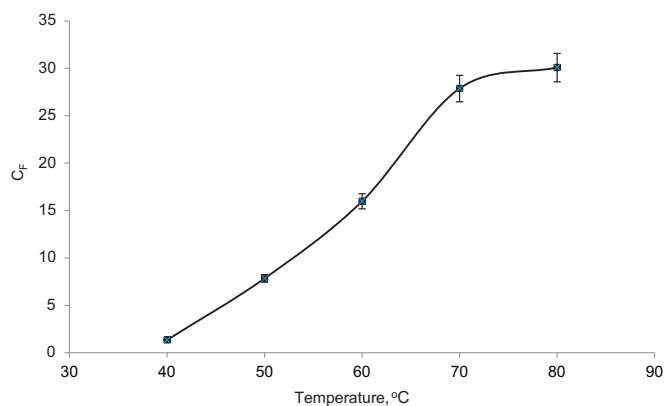


Fig. 5. The variations of preconcentration factor ( $C_F$ ) as a function of temperature at the optimal conditions.

### 3.1.3. Effects of trioctylamine volume

The extraction efficiency in the developed method is based upon the interaction between  $[\text{BiL}_4]^-$ ,  $[\text{TOA}]^+$  and micelles formed in the test solution. Consequently, the plot of the %E vs. the added volume of TOA (3% v/v) shown in Fig. 4 indicates that the maximum %E was at concentration level of 0.3% v/v at the constant concentration of Triton X – 100.

### 3.1.4. Optimization of CPE temperature and time

The relation between extraction efficiency and equilibrium temperature and time was investigated in ranges of 40–80 °C and 2–30 min, respectively. The results exhibited that the temperature of 70 °C and the time of 10 min were satisfactory to achieve a quantitative extraction of bismuth. Therefore, these values were used in subsequent studies. However, the time of 10 min is much shorter than that required for solid adsorbents providing an additional advantage of CPE compared with solid phase extraction techniques. Moreover, the variations of  $C_F$  vs. temperature were also investigated in the range between 40 and 80 °C. As shown in Fig. 5, the value of  $C_F$  increases with temperature increase until 70 °C then the variation become approximately constant. The fact is that, the increase of temperature increases the micellar aggregation number [70]; therefore, the repulsive micellar interaction forces become attractive [71]; therefore, dehydration will happen on the external surface of ethoxy groups present in surfactant, thus, the water is a poor solvent for the molecules of surfactant [72], and hence, the phases separation is enhanced and concentration of micelle in coacervate phase increases. On the other hand, the partition coefficient (D) which can be defined as the ratio between the concentration of analyte in the surfactant – rich and aqueous phases, declines with rising

temperature according to equation:

$$D = e^{\frac{\Delta H^0 - T\Delta S^0}{RT}} \quad (4)$$

where,  $\Delta H^0$ ,  $\Delta S^0$ , T, and R are standard enthalpy, and entropy changes, temperature in Kelvin and gas constant ( $8.315 \text{ J K}^{-1} \text{ mol}^{-1}$ ), respectively. However, the plot (not shown) of D as a function of surfactant concentration at different temperatures (65, 67, 70, 72, and 75 °C) revealed that the maximum value of D was achieved at  $0.02 \text{ mol L}^{-1}$  of surfactant and a temperature of 70 °C. Therefore, to maximize extraction efficiency, temperature should not be increased over 70 °C.

### 3.2. Thermodynamic characteristics

The thermodynamic parameters,  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$ , were carefully investigated to explain the influence of temperature variation on CPE system over equilibration temperature (CPT). Over CPT, the aqueous solution of Triton X – 100 is separated into two phases, coacervate and aqueous phases. Coacervate layer contains high concentrations of surfactant and analyte, while aqueous phase contains low concentration of surfactant and ultra – traces levels of analyte. Thus, influence of temperature on extraction efficiency of bismuth (III) ions using CPE was investigated at optimized conditions and in the range of temperatures from 313 to 353 K.  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  were calculated using the following equations [50]:

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303 R} + \frac{-\Delta H^0}{2.303 R} \left(\frac{1}{T}\right) \quad (5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

where, the ratio of  $\frac{q_e}{C_e}$  is called the affinity of solubilization,  $q_e$  is the amount of  $[\text{BiL}_4]^-$ ,  $[\text{TOA}]^+$  in mole solubilized in one mole of surfactant,  $C_e$  is the concentration of bismuth ions ( $\text{mol L}^{-1}$ ) at equilibrium before the completion of phases separation. However, the plot of  $\log \frac{q_e}{C_e}$  vs.  $1/T$  was linear as shown in (Fig. 6) with  $R^2 = 0.984$ . From the data of slope and intercept, the values of  $\Delta H^0$  and  $\Delta S^0$  were  $14.78 \pm 1.12 \text{ kJ mol}^{-1}$  and  $48.38 \pm 1.73 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. On the other hand, the value of  $\Delta G^0$  increased from  $-0.365$  to  $-2.3112 \text{ kJ mol}^{-1}$  when temperature were raised from 313 to 353 K. Here, the negative value of  $\Delta G^0$  indicates that the bismuth extraction process by CPE technique is spontaneous and thermodynamically favorable. Whereas, the positive value of  $\Delta H^0$  confirms that the extraction process is endothermic. Thus, the hydrophobic micelles number in the coacervate phase was turn into more [73].

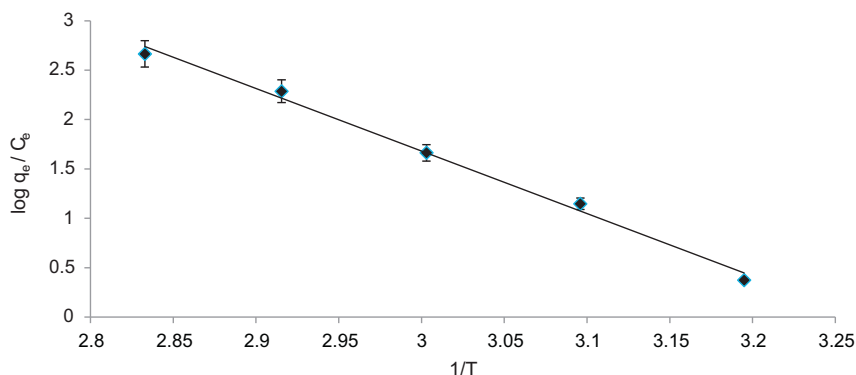


Fig. 6. Effect of  $\log q_e/C_e$  of bismuth ions extracted against  $1/T$  from the aqueous solution at the optimal conditions.

**Table 1**  
The influence of overlapping ions on bismuth estimation by the proposed CPE method.

Foreign ion	Tolerable level
Ca <sup>2+</sup> , NH <sub>4</sub> <sup>+</sup> , PO <sub>4</sub> <sup>3-</sup> , Ag <sup>+</sup> , As <sup>3+</sup> , SO <sub>4</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup> , CN <sup>-</sup> , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> , F <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	1500
Mn <sup>2+</sup> , Ca <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Cr <sup>3+</sup> , NO <sub>2</sub> <sup>-</sup> , Hg <sup>2+</sup> , Cu <sup>2+</sup> , Cl <sup>-</sup>	500
Mg <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup> ,	200
Cd <sup>2+</sup> , Fe <sup>3+</sup> , Al <sup>3+</sup>	10

### 3.3. Interferences study

The effect of overlapping ions was examined in the presence of different variety of ions (cations and anions) including ions commonly found in soil e.g. Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, in addition to cations forming stable complexes with iodide ion e.g. zinc, and lead. An error of less than ±5% in the absorbance of surfactant – rich phase after dilution by acetone of standard solution containing 100 µg mL<sup>-1</sup> of bismuth was considered tolerable and the results are tabulated in Table 1. However, most ions did not interfere even when they are existing in 500 – fold excess over the bismuth. Fe<sup>3+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup> ions have serious interferences. However, such interferences were quantitatively removed by the addition of few drops of NaF & KCN (0.1% *m/v*) into samples solutions. It should be taken into the account added of KCN, where the large concentration of KCN may cause the generation of harmful HCN.

### 3.4. Characteristics of the method

The analytical performance of the new procedure was examined by estimation of dynamic linear range, molar absorptivity ( $\epsilon$ ) at  $\lambda_{\max}$  = 342 nm, LOD, LOQ and the analytical figure of merits of proposed CPE – spectrophotometry are summarized in Table 2. The dynamic linear range was from 10 to 1250 µg L<sup>-1</sup> according to the following linear equation:

$$A = 0.298C + 0.017 \quad (r^2 = 0.992, n = 10) \quad (7)$$

where, A is the absorbance of [BiI<sub>4</sub>]<sup>-</sup>.[TOA]<sup>+</sup> complex in surfactant – rich phase; C is initial bismuth (III) ions concentration, µg L<sup>-1</sup>. The proposed method accuracy was assessed by seven independent measurements for the determination of Bi<sup>3+</sup> ions at level of 60 µg L<sup>-1</sup> and the relative error and relative standard deviation of the proposed procedure were 1.74% and 2.42, respectively. The LOD and LOQ were calculated with the aid of the equations reported in [74,75] and their numerical values are present in Table 2. Enrichment factor was calculated at optimized conditions to be 40 indicating that our method is more sensitive for estimation of bismuth [50]. On the other hand, the presented CPE – spectrophotometry was compared with the other literature reported techniques for the bismuth determination [34–39]. Our method offered higher dynamic linear range and low detection limit as given in Table 3 with the simplicity and economy of the used detection technique (spectrophotometry).

**Table 2**  
Analytical characteristics of the proposed CPE method for bismuth determination.

Parameters	Analytical features
Linear range (µg L <sup>-1</sup> )	10–1250
Molar absorptivity ( $\epsilon$ ) (L mol <sup>-1</sup> cm <sup>-1</sup> )	$1.3 \times 10^5$
Correlation coefficient (R)	0.996
Slope	0.298
LOD (µg L <sup>-1</sup> )	2.86
LOQ (µg L <sup>-1</sup> )	9.54
Extraction efficiency (%)	90 ± 0.8
Enrichment factor	40 ± 1.1

**Table 3**  
The comparison between suggested method and some methods previously published for bismuth determination.

Preconcentration method	Detection technique	LOD, µL <sup>-1</sup>	Linear range, µL <sup>-1</sup>	RSD%	Reference
Solid-phase extraction	UV–Vis	31	100–7500	1.65	34
On-line preconcentration	FAAS	2.75	0.1–20	3	35
W-coil	HG-AAS	25	0.1–10	5.2	36
CPE	FAAS	4	>1200	4.2	37
CPE	FI-ICP-OES <sup>a</sup>	0.12		2.3	38
CPE	TS-FF-AAS <sup>b</sup>	8	20–1000	3.8	39
CPE	UV–Vis	2.86	10–1250	2.42	Present work

<sup>a</sup> FI-ICP-OES, Flow Injection combined with Inductively Coupled Plasma Optical Emission Spectrometry.

<sup>b</sup> TS-FF-AAS, Thermo Spray coupled to Flame Furnace Atomic Absorption Spectrometric.

### 3.5. The evaluation of developed method

The new method was assessed by determination of bismuth content in both a standard reference material (SRM – 3106) and real samples (waters and roadside soil). Before the application of the developed method to analyze the bismuth in the real samples, the accuracy of this method should be firstly tested using a certified reference material. The concentration of bismuth in SRM – 3106 and previously employed in our works [28,29] was determined by CPE – spectrophotometry. The source and the substrates of SRM 3106 is described in detail in [28]. The concentration of bismuth determined by the developed method was 10.11 ± 0.25 mg/g with a slight difference from certified value (10.00 mg/g). However, the statistical evaluation involving student's *t*-test revealed that no a significant difference between two values (found and certified) at the 95% confidence level where the calculated value of *t* (2.45) is less than the tabulated *t* – value (3.18) for four replicate measurements. Therefore, the method submitted in the present work provides a satisfactory accuracy level. Thus, the bismuth concentration in real samples can be analyzed using the proposed procedure. The bismuth content in two water samples (red sea, and tap waters) and two samples of soil collected from different roadsides in Makkah City, KSA was analyzed with the assistance of the standard addition method and the direct calibration curve and the results are listed in Table 4. The precision and accuracy of the developed method are analytically acceptable, therefore our method is suitable for bismuth determination in real samples with complex matrices like sea water and soil.

## 4. Conclusion

An approach based upon cloud point extraction coupled to spectrophotometry has been developed in the present study for the preconcentration and determination of bismuth in water and soil using KI and TOA. The depth investigation of the experimental results obtained in the present study leads to the following conclusions:

- The CPE efficiency powerfully depends on the aqueous phase pH, temperature and concentrations of Triton X – 100, and TOA.
- Preconcentration factor ( $C_F$ ) is obviously influenced by the amount of neutral surfactant in aqueous medium and temperature since the values of  $C_F$  increased with decreasing the surfactant concentration and increasing temperature.
- The KI/TOA/Triton X – 100 extraction system affords high extraction percentage of Bi<sup>3+</sup> (%E over 90) and good values of LOD and LOQ, therefore, this system provides good efficiency for the analysis of bismuth in some real samples.
- $\Delta G^0$  was negative indicating that CPE process is spontaneous in nature.



**Table 4**  
The analysis of bismuth in some real samples by the developed CPE – spectrophotometry and standard method (ICP – MS).

Sample	Concentration		Relative error, (%) <sup>b</sup>
	Spiked	Found <sup>a</sup>	
		$\chi \pm \frac{ts}{\sqrt{n}}$	
Sea water, $\mu\text{g L}^{-1}$	–	ND (0.01 $\pm$ 0.002)	
	80	78.58 $\pm$ 1.3(80 $\pm$ 0.5)	–1.7
	100	96.19 $\pm$ 4.4(99.8 $\pm$ 0.4)	–3.81
Tap water, $\mu\text{g L}^{-1}$	–	ND (ND)	
	20	18.86 $\pm$ 2.4 (20 $\pm$ 1.5)	–5.7
	50	51.65 $\pm$ 1.9 (50 $\pm$ 0.85)	3.3
Soil (1), $\mu\text{g g}^{-1}$	–	ND (2.00 $\pm$ 0.3)	
	5	7.2 $\pm$ 1.00 (8.02 $\pm$ 1.2)	2.8
	10	11.8 $\pm$ 1.10 (12.02 $\pm$ 0.2)	–1.67
Soil (2), $\mu\text{g g}^{-1}$	–	4.85 $\pm$ 0.91 (5.00 $\pm$ 1.32)	
	15	20.15 $\pm$ 2.10 (21.00 $\pm$ 1.75)	0.75

<sup>a</sup> Mean of seven replicate measurements with 95% confidence level, the values between brackets represent the concentration of bismuth determined by ICP – MS.

<sup>b</sup> Relative error(%) is calculated only for the developed method.

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