



# Determination of trace bismuth in human serum by cloud point extraction coupled flow injection inductively coupled plasma optical emission spectrometry

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## ABSTRACT

A cloud point extraction method for the preconcentration of ultra-trace bismuth in human serum prior to its determination by inductively coupled plasma optical emission spectrometry had been developed in this paper. The cloud point extraction method was based on the complex of Bi(III) with 8-hydroxyquinoline and Triton X-114 was used as non-ionic surfactant. The main factors affecting cloud point extraction efficiency, such as pH of solution, concentration of complexing agent, concentration of non-ionic surfactant, equilibration temperature and time were investigated in detail. An enrichment factor of 81 was obtained for the preconcentration of Bi(III) with 25 mL solution. Under the optimal conditions, the detection limit of Bi(III) is  $0.12 \mu\text{g L}^{-1}$ . The relative standard deviation ( $n=7$ ) of determination was 2.3%, values of recovery of bismuth were from 92.3% to 94.7% for three samples. This method is simple, accurate, sensitive and can be applied to the determination trace bismuth in human serum.

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## 1. Introduction

Bismuth-containing pharmaceuticals have been long used for different medical purposes, especially for the treatment of gastrointestinal tract disturbances, such as gastritis and peptic ulcer [1,2]. Despite the medicinal interest, the metabolism of bismuth drugs is still not well understood. This is partially due to the lack of suitable techniques to detect bismuth at trace or ultra-trace levels ( $\text{sub-}\mu\text{g L}^{-1}$ ) [3].

The determination of extremely low concentrations of bismuth in biological samples requires powerful techniques and only few of them have sufficient sensitivity. Inductively coupled plasma mass spectrometry (ICP-MS) [4,5] has been used for the determination of bismuth but the cost of the required instruments may be prohibitive to many laboratories.

Although, electrothermal atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry (ICP-OES) are the most used techniques in the determination of trace level metals, the bismuth concentration in human serum is not compatible with the detection limit of such techniques. In order to achieve accurate, reliable and sensitive results, a preconcentration step is essential.

Cloud point extraction (CPE) is an impressive alternative to conventional solvent extraction because it produces a high pre-

concentration factor when an analyte passes from a large volume of matrix solution to a reduced micellar phase volume [6]. It is based on the behavior of non-ionic surfactant aqueous solutions, that exhibit a phase separation by changing the temperature. To date, CPE has been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes, then the complex in the surfactant-rich phase is determined by different spectrometric methods [7].

ICP-OES could, in this sense, combine all the benefits associated with cloud point extraction to a sensitive instrumental technique. CPE coupled with ICP-OES could obtain lower detection limit. In recent years, cloud point extraction as an extraction technique prior to the ICP-OES determination of Pb [8,9], Hg [10,11], V [12], Ce [13], Ga [14], Al [15], Dy [16], Sb [17], Cr [18], rare earth elements [19], Pt [20] and Pd [20] had been widely studied. However, the research work on bismuth has not reported at present.

In the present work, a CPE method based on the complex of Bi(III) with 8-hydroxyquinoline (8-HQ) and using Triton X-114 as non-ion surfactant was proposed for separation and preconcentration of Bi(III) prior to its determination by a simple flow injection (FI) system coupled with ICP-OES. FI coupled with ICP-OES offered many advantages including lower sampling volume requirement, lower the viscosity of sample and lower effect about surfactant preconcentration phase on plasma discharging. Several experimental variables affecting the method sensitivity and stability were investigated in detail. The proposed method has been successfully applied for determination of trace Bi(III) in human serum samples and certified human hair biological standard reference material

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**Table 1**  
ICP instrumental and FI system parameters for bismuth determination.

Instrumental parameters	Value
Analytical line (nm)	223.061
RF generator power (W)	1300
Frequency of RF generator (MHz)	40.68
Plasma gas flow rate (L min <sup>-1</sup> )	15
Auxiliary gas flow rate (L min <sup>-1</sup> )	0.2
Nebulizer gas flow rate (L min <sup>-1</sup> )	0.8
Plasma view	Axial
Viewing distance (mm)	15.0
Integration time (s)	0.1
Delay time (s)	20
The number of measurements	3
Sample flow rate (mL min <sup>-1</sup> )	1.5
Sample loop volume (μL)	100

(SRM) with satisfactory result. The simplicity, high efficiency and low-cost of performance are the other features of the proposed method.

## 2. Experimental

### 2.1. Apparatus

A PerkinElmer Optima 7300DV inductively coupled plasma optical emission spectrometer including the PerkinElmer FIAS 400 flow injection system was used. The optimized operating conditions for ICP-OES and flow injection system were listed in Table 1. A HH-S11-2 thermostated bath (Xiamen Medical Treatment Electronic Instrument Co. Ltd., China) was maintained at the desired temperature and phase separation was assisted using a centrifuge (TDL-50B, Shanghai Anting Scientific instrument Co. Ltd., China). Milli Q water purification system (Millipore Corp., Bedford, MA, USA).

### 2.2. Reagents

All reagents used in this work were of analytical purity grade at least. Ultra-pure water with a resistivity of 18.2 MΩ cm was prepared by Milli Q water purification system. HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HClO<sub>4</sub> (MOS grade, Tianjing Fengchuan Chemical Reagent Science and Technology Co., Ltd., China).

Bismuth standard working solutions were prepared from the 100 μg mL<sup>-1</sup> GBW(E)080571 bismuth stock solution (National Institute of Metrology, China) by serial dilutions with ultra-pure water; 1 × 10<sup>-4</sup> mol L<sup>-1</sup> 8-hydroxyquinoline (Shanghai Chemicals Co., China) was prepared by dissolution in ethanol; The nonionic surfactant Triton X-114 (Belgium, USA); Certified human hair national standard reference material (National Institute of Metrology, PR China).

Vessels used for trace analysis were kept in 50% (v/v) nitric acid for at least 24 h and were subsequently washed several times with distilled water, deionized water and ultra-pure water.

### 2.3. Procedures

For the cloud point extraction, an analytical solution contained 25 mL sample solution or standard solution, 0.3 mL 2% (v/v) Triton X-114, 0.2 mL of 1 × 10<sup>-2</sup> mol L<sup>-1</sup> 8-HQ and 1.5 mL buffer solution (pH 7.0) was kept in the thermostatic bath maintained at 50 °C for 20 min. Separation of the two phases was accelerated by centrifugation for 10 min at 4000 rpm. After cooled in an ice–NaCl mixture bath for 15 min, the surfactant-rich phase became viscous and retained at the bottom of the tube. The aqueous phase then was readily separated by inverting the tubes. To decrease the viscosity of the extract, a 0.25 mL of dilution agent solution containing 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> in 10% (v/v) ethanol was added to the surfactant-

rich phase. Calibration was performed against aqueous standards submitted to the same cloud point extraction procedure. A blank submitted to the same procedure was measured parallel to the samples and calibration solutions.

### 2.4. Collection and preparation of samples

In this work, many healthy volunteers were involved for the pharmacokinetic test of bismuth in the form of Ranitidine bismuth citrate (RBC). After administrated oral dose, the blood samples were collected in a certain period. The serum samples were made by centrifugation. Then these serum samples were saved in the refrigerator at –20 °C till they would be digested.

The standard biological reference material and real human serum samples were digested according to the following procedure. The 0.5 g or 1.0 mL of each sample was transferred into glass cup, 3 mL HNO<sub>3</sub> and 0.25 mL HClO<sub>4</sub> were added to the cups, then the cups were covered and placed on a heating plate in clean room at the temperature of 80 °C for refluxing. After the solution became clear, the temperature was increased to 150 °C for HClO<sub>4</sub> to oxidize the organic residuals. Then the digested solutions were vaporized to be nearly dry. Finally, the residual solids of samples were dissolved and diluted to 25 mL with ultra-pure water. An aliquot of 25 mL of sample solution would be subjected to the CPE-FI-ICP-OES methodology as described above.

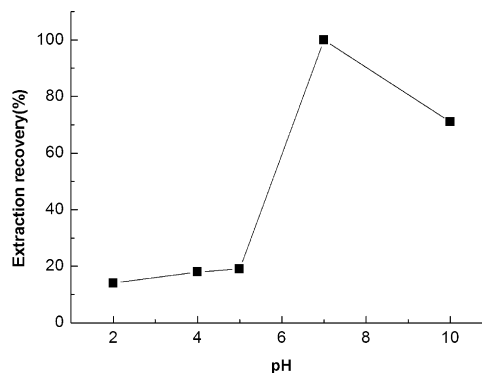
## 3. Results and discussion

### 3.1. Effect of pH

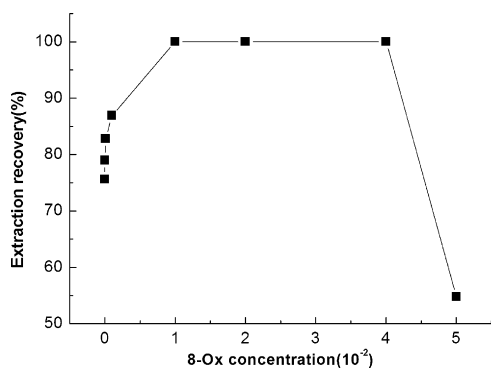
The formation of metal–chelate and its chemical stability are two important influence factors for CPE. The pH, which plays a unique role on formation of the complex and subsequent extraction, is proved to be a main parameter for CPE. Fig. 1 shows the effect of pH on the extraction of Bi(III). It can be seen that extraction efficiency was the highest for Bi(III) in the pH 7.0 when the volume of buffer solution was kept constant at 1.5 mL, so a pH of 7.0 was chosen for the subsequent work.

### 3.2. Effect of complexing agent concentration

The extraction recovery as a function of the 8-HQ concentration is shown in Fig. 2. For this study, 25 mL of a solution containing 0.01 μg mL<sup>-1</sup> bismuth in 0.25 mL of 2% (v/v) Triton X-114 with various amounts of 8-HQ was subjected to the cloud point preconcentration process. It could be seen that the extraction efficiency was the highest when 1 × 10<sup>-2</sup> mol L<sup>-1</sup> 8-HQ was used and the volume of 8-HQ was kept constant at 0.2 mL. So 0.2 mL of



**Fig. 1.** Effect of pH on cloud point extraction efficiency of bismuth. CPE condition: 0.01 μg mL<sup>-1</sup> Bi(III), 0.25 mL of 2% (v/v) Triton X-114, 0.20 mL of 1 × 10<sup>-2</sup> mol L<sup>-1</sup> 8-Ox.



**Fig. 2.** Effect of 8-Ox concentration on the extraction of bismuth. CPE condition:  $0.01 \mu\text{g mL}^{-1}$  Bi(III), 0.25 mL of 2% (v/v) Triton X-114, pH 7.0.

$1 \times 10^{-2} \text{ mol L}^{-1}$  8-HQ solution was chosen for subsequent experiments.

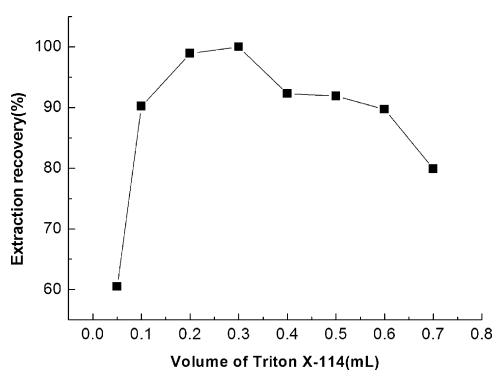
### 3.3. Effect of Triton X-114 concentration

A successful cloud point extraction should be able to maximize the extraction efficiency through minimizing the phase volume ratio ( $V_{\text{surfactant-rich phase}}/V_{\text{aqueous phase}}$ ), so as to improve the pre-concentration factor. Triton X-114 was chosen as the nonionic surfactant due to its lower cloud point temperature ( $22\text{--}25^\circ\text{C}$ ) [21], which facilitates phase separation by centrifugation.

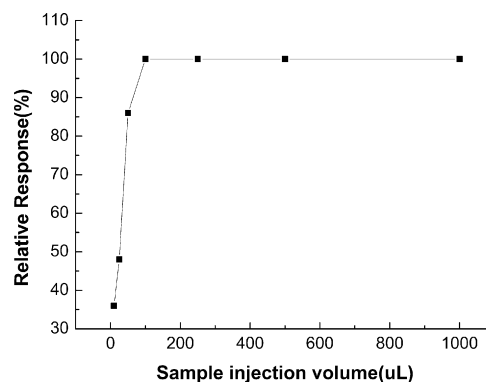
The variations of the analytical signal as a function of the volume of Triton X-114 in the range 0.05–0.7 mL were investigated when the concentration of Triton X-114 was always kept at 2% (v/v). According to the results (Fig. 3), Triton X-114 was found to have higher extraction efficiency for Bi(III) at surfactant volume above 0.10% (v/v). However, the extraction efficiency decreases when the volume of Triton X-114 is higher than 0.6 mL, which is resulting from the increase in phase volume ratio. So a 0.3 mL of 2% (v/v) Triton X-114 was chosen as the optimum surfactant concentration in order to obtain the highest possible extraction efficiency.

### 3.4. Effects of equilibration temperature and time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction recovery upon equilibration temperature and time were studied with a range  $30\text{--}60^\circ\text{C}$  and 5–30 min, respectively. The optimal temperature was found to be in the range of  $50\text{--}60^\circ\text{C}$ . Therefore, an equilibration temperature of  $50^\circ\text{C}$  was chosen for further experiments.



**Fig. 3.** Effect of Triton X-114 concentration on the extraction of bismuth. CPE condition:  $0.01 \mu\text{g mL}^{-1}$  Bi(III), 0.2 mL of  $1 \times 10^{-2} \text{ mol L}^{-1}$  8-Ox, pH 7.0.



**Fig. 4.** Effect of sample injection volume on the response of bismuth. CPE condition:  $0.01 \mu\text{g mL}^{-1}$  Bi(III), 0.2 mL of  $1 \times 10^{-2} \text{ mol L}^{-1}$  8-Ox, 0.3 mL of 2% (v/v) Triton X-114, pH 7.0.

The effect of equilibration time was examined in the range of 5–30 min at  $50^\circ\text{C}$  equilibration temperature. An equilibration time of 20 min was selected as optimum since complete separation occurred at this time and no appreciable improvements were observed for longer times.

### 3.5. Effects of sample injection volume

Effect of flow injection sample injection volume on the response of bismuth was studied. A 100  $\mu\text{L}$  of injection volume was chosen because it is the minimum volume for which a higher sensibility is obtained (Fig. 4).

### 3.6. Interferences

The competitive effect for majority elements naturally occurring in the hair matrix was assessed. Bi(III) recovery was almost quantitative in the presence of other species with tolerance limits (error < 5%) indicated in Table 2. It can be seen that bismuth recoveries were essentially quantitative in the presence of foreign cations.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  could be tolerated up to at least  $10 \text{ mg L}^{-1}$ , since at the working pH (7.0), these elements do not form complexes. In addition, the preconcentration system proposed in this paper allows the elimination of great part of the saline content in the sample—principally sodium and potassium because a limited tendency to form 8-hydroxyquinoline complexes is shown by these elements [22]. Therefore these ions produce no interference in the cloud point extraction of Bi(III).

### 3.7. Figures of merit and analytical performance

The calibration graphs of Bi(III) was obtained by preconcentrating 50 mL of standard solutions containing known amounts of the analytes in the presence of 8-HQ and Triton X-114 in a medium

**Table 2**  
Tolerance limits of interfering species in the determination of  $10 \text{ ng mL}^{-1}$  of Bi(III).

Ion	Ion/Bi ratio	Extraction recovery (%)
Na	5000	98.6
K	5000	98.2
Ca	1000	96.4
P	1000	97.2
Mg	1000	96.3
Zn	1000	95.5
Cu	200	99.2
Mn	200	101.4
Hg	200	98.8
Al	100	98.1
Fe	100	95.2

**Table 3**  
Comparison of the published methods with the proposed method in this work.

Separation method	Detection method	Enrichment factor	Relative standard deviation	Detection limit	Type of analyzed samples	References
Solid phase preconcentration CPE	FI-HG-ICP-AES	37	3.5%	0.02 ng mL <sup>-1</sup>	Human urine	[22]
	ET-AAS	196	<5%	0.02 ng mL <sup>-1</sup>	Water samples and biological samples (urine and hair)	[24]
In situ trapping	HG-FAAS	175	8.2%	1.4 µg g <sup>-1</sup>	Stream sediment and Human hair certified reference material	[25]
Ion flotation separation and concentration	ICP-AES	500	–	0.28 ng mL <sup>-1</sup>	Aqueous solution	[26]
Electrothermal vaporization	ICP-MS	–	3.8%	0.13 pg	Aqueous solution and certified orchard leaves samples	[27]
CPE	FI-ICP-AES	81	2.3%	0.12 ng mL <sup>-1</sup>	Human serum	Present work

**Table 4**  
Recovery test.

Sample	Base value (µg L <sup>-1</sup> )	Quantity of Bi added (µg L <sup>-1</sup> )	Bi found (µg L <sup>-1</sup> )	Recovery <sup>a</sup> (%)
1	1.25	5.00	6.17	93.6
2	3.04	5.00	7.88	94.7
3	2.86	5.00	7.64	92.3

<sup>a</sup> 100[(found-base)/added].

buffered at pH 7.0 for CPE. Under the optimal experimental conditions, the calibration curve for Bi(III) is linear up to 50 ng mL<sup>-1</sup> with a correlation coefficient (*r*) of 0.9996. The precision calculated as the relative standard deviation for seven replicate determinations of a sample solution was 2.3%. The enhancement factor [23], calculated as the ratio of slope of preconcentrated sample to that obtained without preconcentration, were 81 for bismuth. The limit of detection (LOD) calculated as five times the standard deviation of the blank signal, was 0.12 µg L<sup>-1</sup>.

Table 3 compares the characteristic data of the present method for bismuth with those reported in literatures. Generally, the enrichment factor and the detection limit obtained by the present method are comparable to those reported methods, and the relative standard deviation is better than most of them. It should be mentioned that the enrichment factor of our method can be improved using larger volumes of initial solution and using less volumes of dilution solution.

### 3.8. Recovery study

In order to estimate the accuracy of the procedure, different amounts of bismuth(III) ions were added to human serum samples. The resulting solutions were submitted to the procedure given in Section 2.3. The results are shown in Table 4. A good agreement was obtained between the added and measured analyte amounts of bismuth. The recovery values calculated for the added standards were ranged from 92.3% to 94.7%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed preconcentration method.

### 3.9. Application to real samples

#### 3.9.1. Analysis of SRMS

In order to validate the method for accuracy, the contents of bismuth in certified reference material of human hair (GBW07601, PR China) were determined by the proposed method. The determined value ( $0.33 \pm 0.02 \mu\text{g g}^{-1}$ ,  $n = 3$ ) was not significantly different from certified value ( $0.34 \pm 0.02 \mu\text{g g}^{-1}$ ,  $n = 3$ ).

#### 3.9.2. Analysis of human serum samples

The developed method was applied to the determination of Bi(III) in different human serum samples. The analyzed results were

**Table 5**  
Analytical results of bismuth in human serum samples ( $n = 3$ )  $\rho/(\mu\text{g L}^{-1})$ .

Samples	Bi(III)
1	2.15 ± 0.05
2	2.05 ± 0.08
3	5.12 ± 0.06
4	6.04 ± 0.05
5	1.95 ± 0.06
6	0.89 ± 0.09

showed in Table 5. It can be seen that the content values of bismuth in some human serum samples are very low.

## 4. Conclusions

In this work, the use of new micellar system as an alternative method to other methods about preconcentration of trace bismuth in human serum before detection by a simple flow injection system, which was easily coupled to ICP-OES with pneumatic nebulization. The method offers several advantages including inexpensive, rapid, safe, lower-toxicity, high sensitivity, high recovery, low sample consumption and low contamination, low LOD, good reproducibility and accuracy. Triton X-114 was chosen for the formation of the surfactant-rich phase due to its excellent physicochemical characteristics: lower cloud point and higher density, which are easy to phase separation. The results of this study demonstrate the possibility of using the Quinolin-8-ol-Triton X-114 system for preconcentration of trace bismuth in human serum samples with complicated matrices.

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