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Determination of Ultra-trace Cobalt in Water Samples by Graphite Furnace Atomic Absorption Spectrometry after Cloud Point Extraction Using 2-(5-Bromo-2-pyridylazo)-5-dimethylaminoaniline as Chelating Agent

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A new method for the determination of ultra-trace cobalt in water sample by graphite furnace atomic absorption spectrometry after cloud point extraction using 2-(5-bromo-2-pyridylazo)-5-di methylaminoaniline (5-Br-PADMA) as a chelating agent and TritonX-114 as extractant was established. The main parameters affecting extraction, such as pH, concentration, chelating agent and surfactant, equilibrium temperature and time, were investigated in detail. The optimized CPE conditions were as follows: pH=5.5 HAc-NaAc buffer solution, 80 μL 5×10^{-4} mol L^{-1} 5-Br-PADMA, 0.6 mL 1.0 % (w/v) Triton X-114, and heat-assisted at 60℃ for 10 min. Under optimum conditions, the analytical curve was linear in the range of 0.05~1.0 ng/mL and the detection limit was 0.004 ng mL^{-1} for cobalt，the relative standard deviation was 3.3 % (c=0.5 ng mL^{-1}, n=6), and the recovery were 96.7 %~104.0%．The method was applied to the determination of ultra-trace cobalt in water with satisfactory results．

Introduction

As a component of vitamin B12, cobalt is an essential element with various important physiological functions for human beings, animals, and plants. The deficiency of cobalt in humans and animals usually results in different types of anemia, while excess amounts of cobalt lead to toxic effects.[1] It is clear that the determination of trace amounts of cobalt is important in the field of environmental analysis.

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The determination of trace cobalt in natural waters and environmental samples is difficult due to its low concentrations and matrix effects. Although several methods for the determination of trace cobalt have been reported, such as graphite furnace atomic absorption spectrometry (GAAS),[2-4] neutron activation analysis (NAA),[5,6] inductively coupled plasma-atomic emission spectrometry(ICP-AES),[7-9] and inductively coupled plasma-mass spectrometry(ICP-MS),[10,11] an analyte preconcentra- tion and/or matrix separation step is required prior to most analytical techniques. The widely used techniques for separation and preconcentration of trace amounts of cobalt are liquid–liquid extraction,[12] high performance chromatography[5] and solid-phase extraction with various adsorbents such as Amberlite XAD resins,[13,14] polymeric beads[15] and other sorbents.[16] However, the liquid–liquid extraction is laborious and may cause contamination. The technique of chromatography often suffers from several drawbacks: incomplete derivatization, being time-consuming and complicated operating procedures. The solid-phase extraction has the disadvantage of low selectivity or low reversibility of sorption-desorption processes.[17]

Cloud point extraction (CPE), based on surfactant-mediated phase separation, is now an attractive method for the separation and preconcentration of trace metal ions because it has several important advantages. These advantages

includes: low cost, safety, convenience, simplicity, higher extraction and preconcentration factors.[11,18] CPE as a preconcentration step in connection with GFAAS for the determination of trace metals have been reported.[19-25] Yan et al [25] proposed a method for the determination of trace level of cobalt in water sample by GFAAS coupled with CPE using 1-(2-pyridylazo)-2-naphthol (PAN) as a chelating agent and TritonX-100 as extractant. However, the method is rather time-consuming, and it takes 2 h (equilibration time) at 70 ℃ to complete the quantitative extraction of cobalt.

The purpose of this research paper is to combine CPE with GFAAS and developed a new simple method for the determination of trace cobalt in water samples. In the developed method, 2-(5-bromo-2-pyridylazo)-5-dimethylaminoaniline (5-Br-PADMA)[26] was chosen as the chelating agent. We chose this particularly because it was a good chromogenic reagent for spectrophotometric determination of cobalt. The structure of the cobalt complex is shown in Scheme 1. In addition, Triton X-114 was used as the extractant because it has a convenient cloud point (in the range of 23-25℃) and a high density of the surfactant-rich phase which facilitates phase separation by centrifugation. The experimental parameters affecting the CPE efficiency were investigated in detail. The proposed method is not only sensitive but also facile, rapid and convenient.
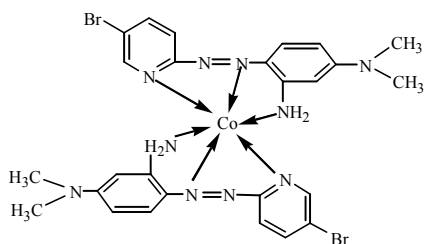
Scheme 1 The structure of Co(II)-5-Br-PADMA complex

Experimental

Apparatus and Reagents

A model TAS-990 atomic absorption spectrophotometer (Purkinge General Instrument Co. Ltd., Beijing, China) with a deuterium background correction was used for the Co measurements. A cobalt hollow cathode lamp was used as radiation source. The pH values of the solutions were measured by a model PB-10 pH meter (Sartoris Scientific Instrument Co. Ltd., Beijing). A model HH-2 thermostatic bath, maintained at the desired temperature, for cloud point temperature experiments (Kewei Yongxing Instrument Co. LTD., Beijing). A model 800-1 centrifuge (Pudong Physical Instruments Factory, Shanghai, China) was used to accelerate the phase separation. The optimized conditions for GFAAS are given in Table 1.

Table 1 Optimum operating conditions for GFAAS

Parameters	
Wavelength/nm	240.7
Slit/nm	0.2
HCL. Current/mA	8
Dry temp/℃	120 (ramp 15 s, hold 20 s)
Ashing temp/℃	1100 (ramp 5 s, hold 30 s)
Atomization temp/℃	2100 (ramp 0 s, hold 3 s)
Cleaning temp/℃	2300 (ramp 1 s, hold 3 s)
Pressure (Ar)/ Mpa	0.6
Filter coefficient	0.10
Injected volume/μL	20

Double distilled water was used throughout the experimental work. All the chemicals were analytical reagent grade, unless it was stated otherwise. Cobalt standard stock solution: 1000 mg L^{-1} prepared by $Co(NO_3)_6 \cdot 6H_2O$. Working solutions were obtained by step-wise dilution of this solution. 5×10^{-4} mol L^{-1} 5-Br-PADMA (laboratory-synthesized [20]) ethanol solution. 1 % (*w/v*) Triton X-114 (Sigma-Aldrich, Milwaukee, USA) solution. Buffer solution of pH 5.5 was prepared from 0.2 mol L^{-1} HAc and 0.2 mol L^{-1} NaAc solution, correct by pH meter. The 0.1 mol L^{-1} HNO_3-Methanol solution was prepared by mixing of 0.2

mol L^{-1} HNO_3 and methanol with equal volume.

Procedure

For CPE, an aliquot of working standard cobalt or sample solution, 2.0 mL of acetate buffer solution (pH 5.5), 80 μL of $5.0×10^{-4}$ mol L^{-1} 5-Br-PADMA, 0.6 mL of 1 % (*w/v*) Triton X-114 were placed in a 10-mL graduated conical centrifuge tube. The mixture was diluted to 10 mL with water. The resultant solution was kept at 60℃ for 10 min in the thermostatic bath for equilibration. Following this step, it was then separated into two phases, which was achieved by centrifugation for 5 min at 3500 rpm. After cooling in an ice-bath for 10 min, the surfactant-rich phase became viscous and was retained at the bottom of the tube. The bulk aqueous phase was easily decanted by simply inverting the tube. The surfactant-rich phase was heated in water bath at 100 ℃ to remove the remaining water. 20 μL 0.1 mol L^{-1} HNO_3-Methanol solution was added to the remaining phase. The final solution was introduced by conventional aspiration into the furnace for GFAAS determination.

Results and Discussion

Effect of pH

The chelating agent 5-Br-PADMA exists in the solution in four species H_3L^{3+}, H_2L^{2+}, HL^+ and L, with protonation of the ring nitrogen and the two amino group nitrogen atoms. The concentration distribution of the four species is determined by the acidity; therefore, the pH value affects not only the formation, but also the hydrophobicity of the chelate, and is one of the critical parameters. The effect of pH on the extraction of Co was studied within the pH range 3.5-9.0 (Fig.1). As seen in Fig.1, the optimum pH for the extraction of Co is within the range of 5.0 ~ 7.0. In

the subsequent experiments, a pH of 5.5 was chosen.

Effect of the Amount of 5-Br-PADMA

The effect the amount of 5-Br-PADMA on the analytical responses was studied. As seen in Fig.2, the absorbance increased significantly with the increasing amounts of 5-Br-PADMA, and then kept stable within the range of 60 ~ 100 μL of 5-Br-PADMA. However, the signal decreased gradually when the amount of 5-Br-PADMA was above 100 μL. This was due to the fact that 5-Br-PADMA had strong hydrophobicity. In addition, there was more 5-Br-PADMA and less complex in the surfactant-rich phase with the further increasing of amounts of 5-Br-PADMA. Therefore, 80 μL of $5×10^{-4}$ mol L^{-1} 5-Br-PADMA solution was chosen.

Effect of the Amount of Triton X-114

The amount of Triton X-114 affected the extraction efficiency as well as the volume of surfactant-rich phase. The variation in the extraction efficiency affected by the amount of Triton X-114 solution was then investigated. The results are shown in Fig. 3. As can be seen, the absorbance significantly increased with the amount of 1.0 % (*w/v*) Triton X-114 up to a volume of 0.6 mL, then almost kept stable between 0.6 and 1.2 mL, and finally above 1.2 mL, absorbance decreased. Considering that the increase of the surfactant amount also increased the volume, as well as the viscosity of the surfactant-rich phase obtained after centrifugation of the samples, 0.6 mL of 1.0 % Triton X-114 (*w/v*) was used in subsequent experiments.

Effect of the ionic strength

In cloud point extraction, surfactants with too low or too high cloud points are not convenient and suitable for the separation and preconcentration of trace metals. The appropriate cloud point

temperature avoids back extraction during centrifugation. The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects).[27,28] In this study, Triton X-114 was chosen as the extractant due to its convenient cloud point temperature (23-25 □) as compared to other surfactants and high density of the surfactant-rich phase which facilitates phase separation by centrifugation. The influence of the ionic strength on performance of CPE was investigated in the NaCl concentration range of 0-0.2 mol L^{-1}. The results showed that ionic strength has no significant effect on the extraction efficiency or the sensitivity up to 0.1 mol L^{-1} NaCl. This is in agreement with the results reported in the literature, which show that an increase in the ionic strength in micelle-mediated systems does not seriously alter the extraction efficiency of the analyte.[29, 30]

Effect of Equilibration Temperature and Time

The effect of equilibration temperature and incubation time was investigated. It is desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromised completion of the reaction and efficient separation of the phases. The dependence of absorbance upon equilibration temperature and time was studied within the range of 40-80℃ and 5-30 min, respectively. The results showed that an equilibrium temperature of 60℃ and equilibrium time of 10 min was adequate to achieve quantitative extraction.

Interferences

The effect of foreign ions on the determination of 5 ng mL^{-1} cobalt by the proposed method was studied. An ion

was considered to interfere when its presence produced a variation in the absorbance of the sample of more than ± 5 %. The results showed that 2500-fold amounts of K^+, Na^+, Ca^{2+} and Sr^{2+}，2500-fold amounts of Sr^{2+} and Ca^{2+}, 2000-fold amounts of Pb^{2+}, NO_3^-, 1000-fold amounts of Mg^{2+}, Zn^{2+} and Cu^{2+}，500-fold amounts of Fe^{3+}, Al^{3+}, F^-, Br^- and I^-，400-fold amounts of La^{3+}, As(V) and Mo(□), 200-fold amounts of SO_4^{2-} and Cd^{2+}, 100-fold amounts of W(□), 50-fold amounts of Cr^{3+}, Ir^{3+} and Mn^{2+}, 40-fold amounts of Ag^+, 20-fold amounts of Pd^{2+}, Ce(Ⅳ), Bi^{3+}, Hg^{2+}, and Ni^{2+}, and 10-fold amounts of Pt(Ⅳ) did not interfere with the measurements.

Calibration Curve, Detection Limit and Precision

Under the optimal experimental conditions for preconcentration of cobalt, the calibration graph was linear over the range of 0.05-1.0 ng mL^{-1} cobalt. The linear equation was $A=0.06685+0.5344c$, where A is the absorbance and c is the cobalt concentration in solution (ng mL^{-1}), and the correlate coefficient was $R=0.9969$. The detection limit, calculated as three times the standard deviation of the blank, was 4.0×10^{-3} ng/mL (3σ). The relative standard deviation (RSD) was 3.3% ($n=11$, $c=0.2$ ng·mL^{-1}). In order to determine the preconcentration factor, an analytical curve was prepared without the preconcentration step for cobalt in the range of 20-500 ng mL^{-1}. The calibration equation obtained was $A=0.0085+1.157 \times 10^{-3}c$. Enrichment factor (EF) calculated as the ratio of the slopes of the calibration graphs obtained with and without preconcentration was 462.

The developed method in this study was compared with the reported methods concerning with cobalt preconcentration by CPE in the existing

literature in terms of detection limits and instruments employed (Table 2). As seen from the table, the detection limit of this method is much better than those given in the table except the literature 25. However, the literature method[25] is rather time-consuming, and it takes more than 2 h (equilibration time, 2 h at 70 □) to complete the quantitative extraction of cobalt. The this method has comparable detection limit with the literature method,[25] but it present has a much shorter analytical time, and is facile, rapid and convenient.

Table 2 Comparison of the present method with reported methods for the preconcentration and CPE of cobalt

Reagent	Surfactant	Technique	DL	Ref.
2-amino-cyclopentene-1-dithiocarboxylic acid	Triton X-114	SP	7.5 µg L^{-1}	31
1-(2-pyridylazo)-2-naphthol	Triton X-114	SP	0.2 µg L^{-1}	32
1-nitroso-naphthol	PONPE 7.5	FAAS	1.22 µg L^{-1}	33
1-(2-thiazolylazo)-2-naththol	Triton X-114	FAAS	0.24 µg L^{-1}	34
2-[(2-mercaptophenylimino)methyl]phenol	Triton X-114	FAAS	0.21 µg L^{-1}	35
methyl-2-pyridylketone oxime	Triton X-114	FAAS	2.1 ng mL^{-1}	36
1-phenylthiosemicarbazide	Triton X-114	FAAS	1.00 µg L^{-1}	37
ammonium pyrrolidinedithiocarbamate	Triton X-114	FAAS	5 µg L^{-1}	38
2-[2′-(6-methyl-benzothiazolylazo)]-4-bromophenol	Triton X-114	FAAS	0.9 µg L^{-1}	39
1-(2-pyridylazo)-2-naphthol	Triton X-114	FAAS	0.38 µg L^{-1}	40
1-(2-pyridylazo)-2-naphthol	Triton X-114	TLS	0.03 ng mL^{-1}	41
8-hydroxyquinoline	Triton X-114	ICP-OES	0.04 µg L^{-1}	42
2-(pyridine-2-yl)-N-p-chlorohydrazinecarbothioamide	Triton X-114	GFAAS	0.0165 ng L^{-1}	24
1-(2-pyridylazo)-2-naphthol	Triton X-100	GFAAS	0.003 ng L^{-1}	25
2-(5-bromo-2-pyridylazo)-5-dimethylaminoaniline	Triton X-114	GFAAS	0.004 ng L^{-1}	This work

Determination of Water Samples

Under the recommended experimental conditions, the proposed method was applied to the determination of cobalt in tap and well water samples. In addition, recovery tests were performed, and the results are shown in Table 3. The recoveries are within the range of 96.7 ~ 104 %. These results demonstrated the accuracy and applicability of this method to the analysis of these samples.

Table 3 Analytical results of cobalt in water samples and recovery

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})			Average (ng mL^{-1})	RSD (%)	Recovery (%)
Tap water	-	0.288	0.272	0.275	0.280	3.2	-
		0.270	0.286	0.290			
	0.30	0.615	0.573	0.610	0.592	3.4	104.0
		0.564	0.590	0.601			
	0.60	0.856	0.860	0.882	0.865	2.3	97.5
		0.846	0.896	0.850			
Well water	-	0.228	0.216	0.221	0.220	2.4	-
		0.225	0.215	0.216			
	0.30	0.515	0.540	0.532	0.526	1.9	102.0
		0.515	0.528	0.525			
	0.60	0.775	0.790	0.838	0.800	3.0	96.7
		0.785	0.820	0.792			

Conclusion

We have proposed a new method for the determination of cobalt through the combination of CPE with GFAAS using 5-Br-PADAM as chelating reagent and the nonionic surfactant of Triton X-114 as extractant. CPE is a simple, rapid, economical and eco-friendly method for preconcentration and separation of trace metals from aqueous solutions to low volume surfactant-rich phase. GFAAS as a very sensitive spectrometry method is suitable for analysis of low volume of the remained phase after CPE. Triton X-114 was chosen as the extractant due to its convenient cloud point temperature

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(23-25 ℃) and high density of the surfactant-rich phase, which separates easily by centrifugation. The results showed that 5-Br-PADMA is a suitable chelating agent for the extraction of cobalt using CPE. The new method gave a highly selective, very sensitive, low cost, and is easily applied to the determination of traces of cobalt in real water samples.

Acknowledgements

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Fig. 1 Effect of pH on absorbance. 0.08 mL 5×10^{-4} mol L^{-1} 5-Br-PADMA; 0.60 mL 1.0 % (*w/v*) Triton X-114; temperature：60℃；heating time：10 min；5 ng Co
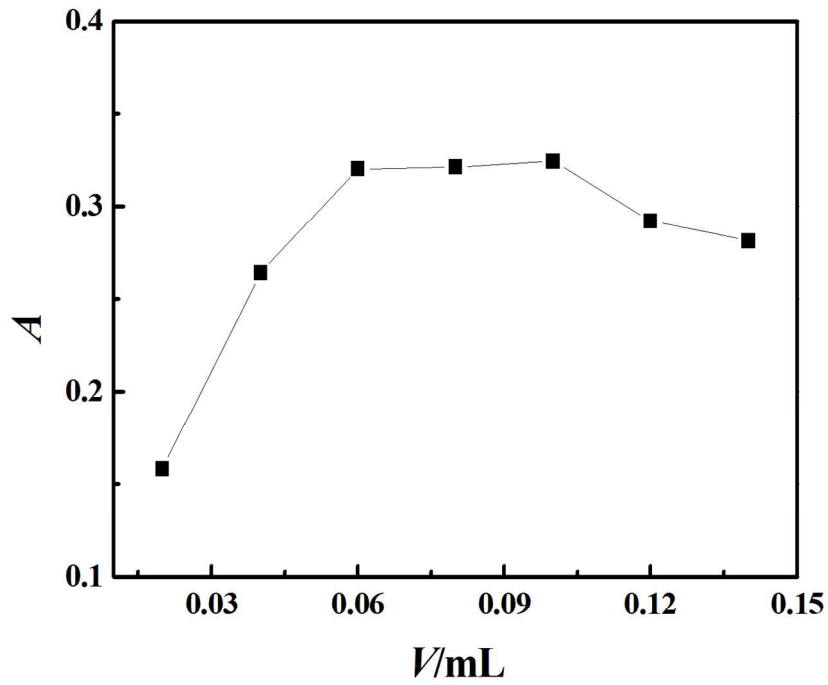
Fig.2 Effect of the amount of 5-Br-PADAM on absorbance. 0.6 mL 1.0 %(m/v) Triton X-114；temperature：60℃；heating time：10 min；pH=5.5；5 ng Co

Fig. 3 Effect of the amount of Trition X-114 on absorbance. 0.08 mL 5×10^{-4} mol L^{-1} 5-Br-PADMA; temperature：60 ℃；heating time：10 min；pH = 5.5；5 ng Co。
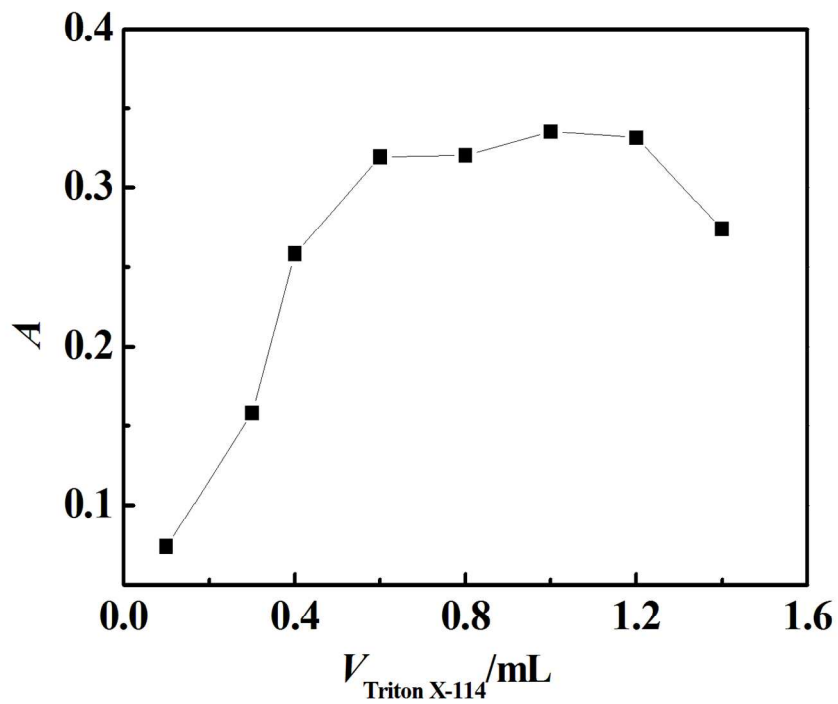
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