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Flame Atomic Absorption Spectrometric Determination of Trace Amounts of Cobalt after Cloud Point Extraction as 2-[(2-Mercaptophenylimino)methyl]phenol Complex

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Um procedimento de extração no ponto nuvem (CPE) foi desenvolvido para a separação e pré-concentração de baixas concentrações de cobalto previamente à determinação por espectrometria de absorção atômica em chama (FAAS). O procedimento é baseado na formação do complexo de Co(II) com 2-[(2-mercaptofenilimino)metil]fenol (MPMP), seguido pela extração em fase rica em surfactante Triton X-114. Alguns parâmetros importantes que afetam a complexação e extração, tais como pH, concentrações do agente quelante e do surfactante, temperatura e tempo de equilíbrio, foram otimizados. Sob condições ótimas, a pré-concentração de um volume de 25 mL da amostra resultou em um limite de detecção de 0,21 µg L^{-1}, um fator de enriquecimento de 97 e um desvio padrão relativo de 1,2% (n = 8, 60 µg L^{-1}) para a determinação de Co(II) por FI-FAAS. O método foi aplicado com sucesso para amostras de água, vitamina B$_{12}$ e ampolas de complexo B. A exatidão do método foi comprovada por experimentos de adição-recuperação, análise independente por espectrometria de absorção atômica com forno de grafite e determinação de Co em material de referência certificado.

A cloud point extraction (CPE) procedure was developed for the separation and preconcentration of trace amounts of cobalt prior to its determination by flame atomic absorption spectrometry (FAAS). The procedure is based on the formation of Co(II) complex with 2-[(2-mercaptophenylimino) methyl]phenol (MPMP) followed by its extraction into a Triton X-114 surfactant-rich phase. Some important parameters affecting both complexation and extraction, such as pH, concentrations of chelating agent and surfactant, temperature, and time of equilibration, were optimized. Under optimum conditions, the preconcentration of a volume of 25 mL of sample resulted in a limit of detection of 0.21 µg L^{-1}, an enhancement factor of 97, and a relative standard deviation of 1.2 % (n = 8, 60 µg L^{-1}) for the determination of Co(II) by FI-FAAS. This procedure was successfully applied to water, vitamin B$_{12}$ and B-complex samples. The accuracy was assessed employing addition-recovery experiments, independent analysis by graphite furnace atomic absorption spectrometry and by using a certified reference material.

Keywords: cloud point extraction, cobalt, flame atomic absorption spectroscopy, Triton X-114, 2-[(2-mercaptophenylimino)methyl]phenol

Introduction

Cobalt is an essential trace element present in most body tissues, with the highest concentrations typically found in the liver. It is a component of vitamin B$_{12}$ (cyanocobalamin), which is involved in the production of the blood red cells and the prevention of pernicious anemia.[1,2] Cobalt toxicity is quite low compared to many other metals. However high exposure to this element can cause several health problems such as asthma and skin irritation.[3,4] Therefore, quantitative determination of cobalt at low concentrations plays an important role in different fields such as environmental analysis, process control and medicine.

Several analytical techniques including Graphite Furnace Atomic Absorption Spectrometry (GFAAS),[5] Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES),[6] Inductively Coupled Plasma Mass Spectrometry (ICP-MS),[7] and Flame Atomic Absorption Spectrometry (FAAS)[8] have been used for the determination of cobalt in different matrixes. Despite the development of new, more sensitive analytical methods, the determination of cobalt in natural samples still remains a challenge. In many cases, the analytical instrumentation available does not present the sensitivity requirements necessary to analyze this type of sample. Thus, several procedures have been developed

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for the separation and preconcentration of cobalt, including liquid-liquid extraction,[9,10] solid phase extraction,[11,12] coprecipitation,[13] and flotation.[14]

In recent years, cloud point extraction (CPE) has become one of the most popular methods used in the separation and enrichment of metal ions.[15-18] The main advantages of cloud point extraction to other techniques of separation are low cost, simplicity, safety, high capacity for preconcentration of wide variety of analytes and high enrichment factor with good recoveries. Non-ionic surfactant solutions become turbid above a certain temperature, called "cloud point temperature". When the cloud point temperature is reached, the micellar solution separates into two phases; a surfactant-rich phase and an essentially bulk aqueous phase. Metal ions can be extracted from the aqueous solution into the small-volume surfactant-rich phase after reacting with a suitable ligand and forming an aqueous low solubility complex. The principles and applications of CPE have been discussed in various interesting reviews.[19-21]

Shift bases derived from salicylaldehyde (salens) are polydentate ligands that play an important role in the development of coordination chemistry as they readily form strong complexes with a wide number of transition metal ions.[22,23] In analytical chemistry, these ligands have been used as ion carriers in construction of membrane electrodes[24,25] and as chelating agents in solid phase extraction.[26-28]

This work presents a cloud point extraction procedure for the separation and preconcentration of cobalt (II) ions based on the formation of a hydrophobic complex with 2-[(2-mercaptophenylimino)methyl]phenol (MPMP) (Figure 1). Octylphenoxypolyethoxyethanol (Triton X-114) was used as surfactant and the metallic complex extracted into the surfactant-rich phase was determined by FI-FAAS.
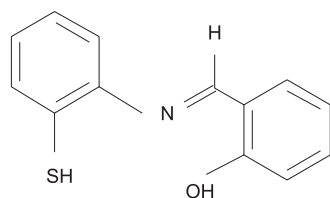

Figure 1. Chemical structure of MPMP.

Experimental

Apparatus

A Buck Scientific atomic absorption spectrometer (model 210 VCP, East Norwalk, CT, USA), equipped with a cobalt hollow cathode lamp and an air-acetylene flame atomizer, was used for in all determinations. The wavelength, lamp current and spectral bandwidth used, were 240.7 nm, 10 mA and 0.2 nm, respectively. A single line flow injection system consisted of a peristaltic pump (Ismatic, MS-REGLO/8-100, Zurich, Switzerland) and a rotary injection valve (Rheodyne, Rohnert Park, CA, USA) was used for effective control of the amount of sample and repeatability of the measurements. The pH measurements were carried out with a Metrohm pH meter (model 691, Herisau, Switzerland) using a combined glass calomel electrode. A centrifuge was used to accelerate the phase separation process (Hittich, Universal 320, Tuttingen, Germany). A thermostated water-bath (Shimi Fann, model S.57, Tehran, Iran) maintained at the desired temperature, was used in the cloud point extraction experiments.

Reagents

All chemicals used were of analytical reagent grade, unless otherwise stated. Doubly distilled, deionized water was used in all experiments. The stock solution of 1000 mg L^{-1} cobalt was prepared by dissolving 0.4770 g of $CoSO_4.7H_2O$ (E. Merck, Darmstadt, Germany) with distilled deionized water into a 100 mL flask, and diluting it to the mark. Working solutions were prepared from the stock solution by serial dilution with distilled deionized water. The non-ionic surfactant Triton X-114 (Fluka, Chemie AG, Buchs, Switzerland) was used without further purification. The stock solution (2.5% v/v) was prepared by dissolving 2.5 mL of the concentrated solution in 100 mL of hot distilled water. A 0.2 mol L^{-1} stock buffer solution was prepared by dissolving an appropriate amount of boric acid (E. Merck) in distilled water and adjusting the pH to 8.0 by adding diluted NaOH. The ligand, 2-[(2-mercaptophenylimino)methyl]phenol was synthesized and purified according to the literature.[29,30] The MPMP solution (0.02 mol L^{-1}) was prepared by dissolving a proper amount of the ligand in ethanol.

The vessels and pipettes used for trace analysis were kept in 10% (m/v) nitric acid for at least 24 h and subsequently washed four times with doubly distilled water.

Recommended procedure

An aliquot of the sample or standard solution (25 mL) containing cobalt(II) in the range of 1-120 μg L^{-1}, Triton X-114 (0.1% v/v), MPMP (1.8×10^{-3} mol L^{-1}), and borate buffer with pH 8.0 (8.0×10^{-3} mol L^{-1}) were mixed and kept in a thermostated water-bath at 50 ºC for 10 min. The separation into two phases was accelerated by centrifugations at 3500 rpm for 10 min. The mixture was then cooled in an ice bath for 5 min in order to increase

the viscosity of the surfactant-rich phase and facilitate the removal of the aqueous phase. A volume of 200 μL of a HNO$_3$ 0.1 mol L^{-1} methanolic solution was added to the remaining surfactant-rich phase to reduce its viscosity before Co determination by FAAS. Finally, in order to effectively control the repeatability of the measurements, an aliquot of 100 μL of the resultant solution was introduced into the FAAS system by a single line flow injection (Figure 2).
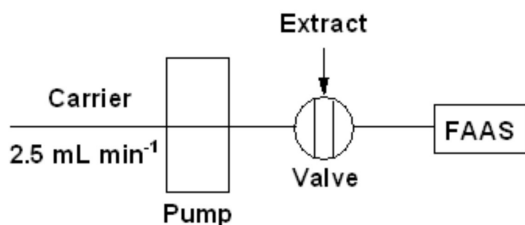

Figure 2. FI-FAAS manifold used for the injection and determination of cobalt.

Sample preparation

Water samples were filtered with a Millipore 0.45 μm pore size membrane (Millipore) into previously cleaned polyethylene bottles. The samples were analyzed within 6 h of collection according to the recommended procedure.

The content of 2 mL B-complex or 1 mL vitamin B$_{12}$ ampoules was transferred to a 100 mL flask and 10 mL of a mixture of nitric acid and sulfuric acid (10:1 v/v) were added to the sample. The resultant solution was heated to near dryness on a hot plate. The final residue was neutralized with a diluted solution of sodium hydroxide and diluted to 100 mL with distilled deionized water.

To 0.01 g of the certified ore, 2 mL of concentrated nitric acid was added and the sample was heated on a water bath for a few min, then 2 mL of hydrogen peroxide was added and the mixture was heated for another 5 min. The sample was then filtered through a Millipore filter, the pH was adjusted to approximately 8, diluted to the 50 mL, and was treated according to the recommended procedure.

Results and Discussion

In order to achieve the best performance for the cloud point extraction procedure, the effects of several parameters such as pH, concentrations of ligand and surfactant, temperature, and time of equilibration on the analytical signal were evaluated and optimized.

Separation and preconcentration of metal ions by cloud point extraction involve previous formation of a metallic complex, which needs to present sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase. The pH is a critical factor affecting both the reaction between metal ions and ligand molecules, and the metallic complex extractability into the surfactant-rich phase. Thus, the effect of pH on the cloud point extraction, and ultimately on the cobalt analytical signal, was studied in the range of 2-11. As it can be seen in Figure 3, the maximum Co absorbance was obtained in the pH range of 7-9. The decrease in absorbance at pH > 9 is probably due to the precipitation of cobalt ions as hydroxides, and the signal decrease at pH < 7 may be due to competition between hydronium and cobalt ions for complexation with MPMP.
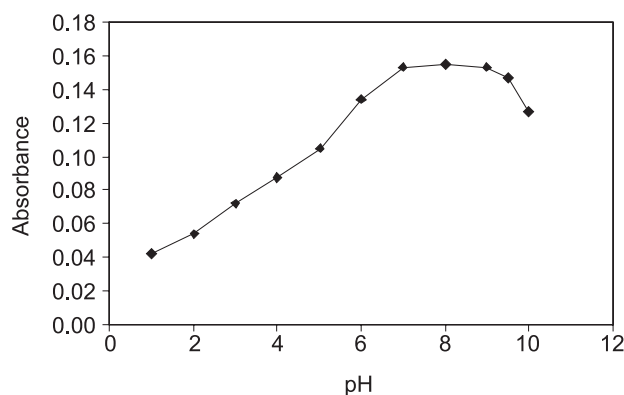

Figure 3. Effect of pH on the analytical signal of cobalt. Conditions: 60 μg L^{-1} Co, 2 × 10^{-3} mol L^{-1} MPMP, and 0.15% (v/v) Triton X-114.

The variation of the analytical signal as a function of the concentration of ligand is shown in Figure 4. As it is seen, the extraction of cobalt increases up to a MPMP concentration of 1.5 × 10^{-3} mol L^{-1}, when it reaches a plateau. At this MPMP concentration the extraction of 60 μg L^{-1} of Co can be considered complete. The MPMP concentration of 1.8 × 10^{-3} mol L^{-1} was chosen as the optimum condition.
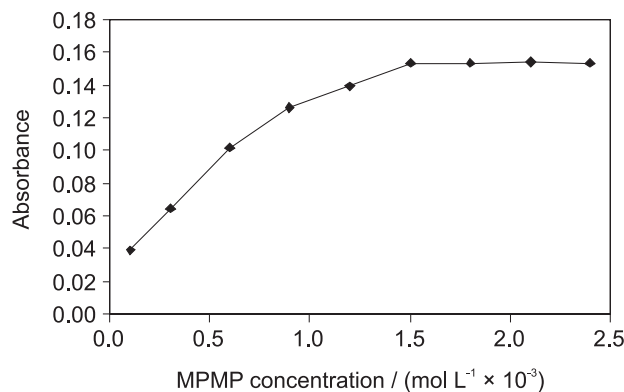

Figure 4. Effect of MPMP concentration on the analytical signal of cobalt. Conditions: 60 μg L^{-1} Co, 0.15% (v/v) Triton X-114, and pH 8.

Triton X-114 was chosen as non-ionic surfactant in the cloud point extraction procedure due to its commercial availability, low toxicity, high density, and low cloud point temperature.[31,32] The effect of the Triton X-114 concentration on cobalt extraction was evaluated by varying the surfactant concentration in the range of 0.04-0.2% (v/v). As it can be seen in Figure 5, Co absorbance increases as surfactant concentration is increased up to 0.08% (v/v). Above this Triton X-114 concentration, the analytical signal remains constant. At low concentration of Triton X-114, the extraction efficiency of complex is decreased probably due to the inadequacy of the surfactant assemblies to entrap the hydrophobic complex quantitatively. A Triton X-114 concentration of 0.10% (v/v) was employed in all further studies.
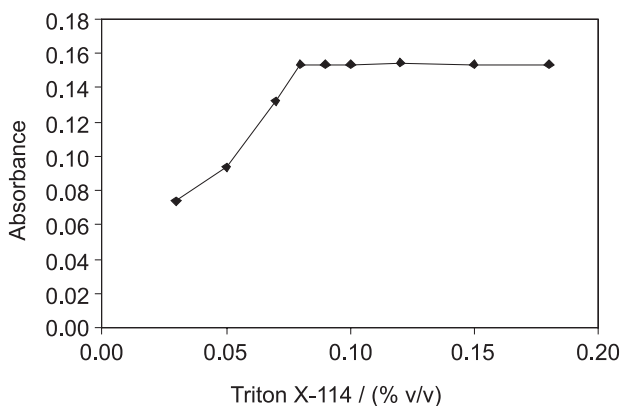

Figure 5. Effect of Triton X-114 concentration on the analytical signal of cobalt. Conditions: 60 µg L^{-1} Co, MPMP = 1.8 × 10^{-3} mol L^{-1} and pH 8.

Ionic strength of the aqueous phase can affect the efficiency of extraction by salting out effect. So, the influence of the ionic strength on metal extraction and consequently on the analytical signal was investigated by applying the CPE procedure to cobalt (60 µg L^{-1}) standard solutions presenting NaCl concentrations varying from 0.1-0.6 mol L^{-1}. It was observed that ionic strength had no significant effect on the cloud point extraction efficiency.

It is desirable a CPE procedure which employs the shortest incubation time and the lowest equilibration temperature possible, considering the compromise between the completion of the reaction and efficiency of the extraction and phase separation. The influence of the equilibration temperature on the cloud point extraction of cobalt was investigated within the range of 25-85 °C. The results showed that the maximum signal intensity for Co (II) was obtained at temperatures between of 45 and 60 °C. A further increase in temperature resulted in a decrease of the absorbance signal. This may be due to the thermal instability of the Co complex formed with MPMP. So, an equilibration temperature of 50 °C was used in further experiments. Studies on the effect of the incubation time

on the analytical signal were carried out in the range of 5-30 min. Results showed that an incubation time of 10 min is adequate to obtain quantitative Co extraction and that a further increase in the incubation time would have no significant effect on the extraction efficiency.

The effect of centrifugation time on phase separation was studied in the range of 2-20 min at 3500 rpm. The results showed that a centrifugation of 10 min is the most adequate to achieve a complete phase separation.

Analytical performance

A calibration curve was constructed by collecting the analytical signals of different Co standard solutions submitted to the method proposed. Under the optimum experimental conditions, the calibration curve for Co(II) was linear from 1 to 120 µg L^{-1}.

The enhancement factor of about 97 was obtained as the ratio between the angular coefficients of the calibration curves for the preconcentrated samples (25 mL) and the ones not submitted to preconcentration. Limit of detection and limit of quantification defined as 3S$_b$/m, and 10S$_b$/m (where S$_b$ is the standard deviation of the blank and m is the slope of the calibration curve) were 0.21 µg L^{-1} and 0.70 µg L^{-1}, respectively. The relative standard deviation (RSD) for 8 replicate measurements of 60 µg L^{-1} of cobalt was 1.2%. Table 1 presents the analytical figures of merit for the proposed method.

Table 1. CPE-FI-FAAS figures of merit

Parameters	Analytical parameter
Equation for the calibration curve, C / (µg L^{-1})	A = 2.3 × 10^{-3} C$_{Co}$ + 0.012
Correlation coefficient	0.9994
Linear range / (µg L^{-1})	1-120
Enhancement factor	97
Limit of detection / (µg L^{-1})	0.21
RSD, % (n=8)	1.2

Interferences

The effect of different cations and anions on the determination of 50 µg L^{-1} of cobalt (II) ions at mol ratio of 1000 by the proposed method was evaluated. An ion was considered to be an interferent when it caused an error greater than ±5% in the determination of cobalt. When the error was greater than ±5%, the amount of interferent ion was lowered. The results are given in Table 2. At the given mole ratio no interference was observed and the recovery of cobalt was quantitative in the presence of all foreign ions studied. Those results indicate the efficiency of the method proposed and its potential for real sample applications.

Application

The feasibility of the method proposed for cobalt determination in different matrixes was investigated. The method was applied to water samples and vitamin ampoules. The accuracy was checked by spiking the

Table 2. Effect of foreign ions

Ions	Mole ratio (ion/ Co^{2+})	Recovery / (%)
NO_3^-	1000	100
SO_4^{2-}	1000	95.3
Cd^{2+}	1000	98.5
Mg^{2+}	1000	96.6
Mn^{2+}	1000	95.3
Al^{3+}	1000	95.4
Ag^+	1000	97.3
Pb^{2+}	1000	99.9
K^+	1000	98.4
Hg^+	1000	96.6
Na^+	1000	101
Cl^-	1000	99.7
Br^-	1000	99.1
Ca^{2+}	500	96.5
Sr^{2+}	500	98.4
Fe^{2+}	500	97.2
PO_4^{3-}	250	98.6
Zn^{2+}	250	99.7
Cu^{2+}	100	96.5
Ag^+	100	95.3
Cr^{3+}	50	98.3
Ni^{2+}	50	99.0
Fe^{3+}	50	99.2

samples with different concentrations of Co and comparing the values obtained with the method proposed with data from direct analysis by graphite furnace atomic absorption spectrometry (GFAAS). The results given in Tables 3 and 4 show recoveries greater than 97% and satisfactory agreement between the values determined by both methods, at a 95% confidence limit. Those results suggest that the proposed method is suitable for the sample types examined. To additionally validate the accuracy of the method, cobalt was determined in a certified nickel-copper-cobalt reference ore SU-1a (Canadian Certified Reference Materials Project). The concentration of cobalt determined by the method proposed presented no significant difference from the value certified in a 95% level of confidence (Table 3). Thus, the method proposed can be considered reliable for Co determination in a wide range of samples.

Conclusions

A simple, fast, inexpensive and sensitive cloud point extraction method has been developed for the determination of trace amounts of cobalt in aqueous samples by FI-FAAS. A sensitivity improvement has been achieved by the method proposed when compared to previously reported works using CPE and FAAS (Table 5). The method proposed can be applied to the determination of cobalt in different water samples, vitamin B_{12}, and B-complex ampoules.

Table 3. Determination of cobalt in water samples and a certified nickel-copper-cobalt reference ore (SU-1a)

Samples	Added / (µg L⁻¹)	Found[a] / (µg L⁻¹)	Recovery / (%)	ETAAS[a] / (µg L⁻¹)
	0.0	1.62 ± 0.04		1.72 ± 0.11
Well water	10.0	11.4 ± 0.2	97.8	
	20.0	21.5 ± 0.2	99.4	
	0.0	4.61± 0.13		4.71 ± 0.23
River water	10.0	14.5 ± 0.3	98.9	
	20.0	24.4 ± 0.4	99.0	
	0.0	n.d.[b]		n.d.
Tap water	10.0	9.72 ± 0.21	97.2	
	20.0	19.8 ± 0.4	99.0	
SU-1a[c]		0.040 ± 0.001 (%)	97.6	

[a]Mean and standard deviation related to three determinations. [b]Not detected. [c]Composition: Ni = 1.233 ± 0.008%, Cu = 0.967 ± 0.005%, Co = 0.041 ± 0.001%, Ag = 4.3 ± 0.3 µg g⁻¹, Pt = 0.41 ± 0.06 µg g⁻¹, and Pd = 0.37 ± 0.03 µg g⁻¹.

Table 4. Determination of cobalt in vitamin ampoules

Samples	Added / µg	Found[c] / µg	Recovery / %	GFAAS[c] / µg
B Complex[a]	0.0	0.35 ± 0.01		0.34 ± 0.02
	2	2.30 ± 0.04	97.5	
B_{12}[b]	0.0	4.46 ± 0.09		4.48 ± 0.07
	2	6.44 ± 0.12	99.0	

[a]Lorestan Co. Iran: Each ampoule (2 mL) contains: vitamin B_{12} (8 µg) equivalent to 0.35 µg Co, vitamin B_2 (4 mg), vitamin B_6 (4 mg), vitamin B_1 (10 mg), Dexpanthenol (6 mg), Nicotinamide (40 mg). [b]Zahravi Pharm. Co. Iran: Each ampoule (1 mL) contains: vitamin B12 (100 µg) equivalent to 4.35 µg Co. [c]Mean and standard deviation of three determinations.

Table 5. Procedure using cloud point extraction prior cobalt determination by FAAS

Reagent	Surfactant	Sample volume / mL	EF[a]	LOD[b] / (µg L^{-1})	Reference
ammonium pyrrolidinedithiocarbamate	Triton X-114	10	20	5	33
1-(2-thiazolylazo)-2-naphthol	Triton X-114	50	57	0.24	34
1-(2-pyridylazo)-2-naphthol	Triton X-114	10	115	0.38	35
2-(5-bromo-2-pyridylazo)-5-diethylaminophenol	Triton X-100, SDS	12.5	28.5[c]	1.06[c]	36
			21.7[d]	1.58[d]	
1-nitroso-2-naphthol	PONPE 7.5	10	27	1.22	37
2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol	Triton X-114	10	28	0.9	38
Methyl-2-pyridylketone oxime	Triton X-114	15	67	2.1	39
2-[(2-mercaptophenylimino)methl]phenol	Triton X-114	25	97	0.21	This work

[a]Enhancement factor, [b]limit of detection, [c]in presence of hydrochloric acid, [d]in presence of sodium chloride.

Acknowledgment

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