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Original Article

CLOUD POINT EXTRACTION, PRECONCENRATION AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT IN WATER SAMPLES

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ABSTRACT

Objective: A new cloud point extraction (CPE) method was developed for pre concentration of trace cobalt (II) in water samples.

Methods: The method is based on the complexation reaction of Co (II) with 2-(benzothiazolyl azo)-4-nitrophenol reagent (BTANP) at pH 7.0 and micelle-mediated extraction using the nonionic surfactant Triton X-114 of the complex.

Results: The enriched analyte in the surfactant-rich phase was diluted with methanol and the cobalt content was determined by spectrophotometry at 549 nm. The optimum conditions (e. g. pH, reagent and surfactant concentrations, and temperature and centrifugation times) were evaluated and optimized. The proposed CPE method showed linear calibration within the range 10–300 ng/ml of Co(II) and the limit of detection of the method was 1.5 ng/ml with a pre concentration factor of 50. The relative standard deviation (RSD) was found to be 1.20% (*N* = 6). The interference effect of some cations and anions was also studied.

Conclusion: The proposed method has been successfully applied to the determination of Co(II) in water samples with a recovery from spiked samples in the range of 96.60–98.70%.

Keywords: Cloud point extraction, Cobalt(II), Spectrophotometry, BTANP, Water samples.

INTRODUCTION

Heavy metal pollution is and will be a public health problem. Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals. It is an essential micronutrient required for the growth of both plants and animals. Cobalt is an essential element for humans because it is a component of Vitamin B_{12}. However, the metal can also be harmful, because exposure to high levels of cobalt can result in lung and heart effects and dermatitis and its deficiency can lead to pernicious anemia. Thus, monitoring of the nutritional and toxicological aspects of foods by determination of trace elements, such as cobalt, plays an important role. Finally, it is also necessary for the synthesis of a number of hormones, neuro-transmitters, and other compounds, such as bile acids and DNA. The human organism is supplied with cobalt through food and water, therefore it is necessary to determine and control its concentration in both [1-3].

There are many spectrophotometric methods have been developed for the determination of Co(II) [4-26] [Table 1]. Most of spectrophotometric methods developed for the determination of cobalt are, unfortunately, not practically usable due to poor sensitivity and partly poor selectivity. Routine spectrophotometric methods are often not sensitive enough to determine low concentrations of cobalt ions in environmental samples only at the µg/l level. Consequently, a pre concentration step is usually required.

Table 1: Comparison of the reported spectrophotometric methods for determination of Co (II)

Reagent	λ_{max} (nm)	Beer's law (µg/ml)	ε x 10^4 L/mol. cm	Medium pH	Reference
Ninhydrin	395			8.2	[4]
MBTAQ	655		11.5		[5]
2-PYAINH	346		7.1	9.0	[6]
HNAHBH	425	0.12–3.54	2.3	5.0	[7]
Sodium isoamyl xanthate	400	3.0–35	1.92	4.5–9.0	[8]
2-Pyridine carboxalde hydeisonicotinyl-hydrazine	346	0.01–2.7	7.1	9.0	[9]
2-Hydroxy-1-naphthalidene salicyloyl hydrazone	430	0–10	0.16	8.0-9.0	[10]
Pyridine-2-acetaldehyde salicyloyl hydrazone Extraction	415	0.5–7.0	1.04	1.0–6.0	[11]
Bis-4-phenyl-3-thiosemicarbazone	400	0.6–6.0	2.2	4	[12]
2-(2-Quinolynylazo)-5-dimethylamino aniline	625	0.01–0.6	4.3	5.5	[13]
2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone	390	0.06–2.35	2.74	6	[14]
2',4'-dinitro APTPT	490	2.5-15	0.1109	9.5-10.2	[15]
Vanillilfluorone/Zephiramine	575	0.024-0.470	13.5		[16]
QADMAB	625	0.01-0.32	12.8	3.2-5.2	[17]
Cyanex 923	635	58.9-589	0.0679		[18]
Alpha-benzilmonoxime	380	0.05-1.50	3.72	9.0	[19]
Cyanex-272	635	0.295-2.36	0.0307		[20]
BSOPD	458	0.1-15	1.109		[21]
HIMH	400	0.1-5.0	1.135		[22]
PAN	639		27.21	Triton X-100	[23]

N,N-Bis(2-aminobenzoyl) ethylenediamine	470		1.10	Aqueous	[24]
TAN	572		262	Immobilized on C18 bonded silica	[25]
BTAHQ	658	0.01–0.38	24.2	Isopentyl alcohol	[26]
BTANP	518	0.4-6.0	0.2425	7.0	Proposed method

Abbreviations: MBTAQ: 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline; 2-PYAINH: 2-pyridine carboxaldehyde isonicotinyl hydrazone; HNAHBH: 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone; 2',4'-dinitro APTPT: 1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol; QADMAB: 2-(2-Quinolinylazo)-5-dimethylaminobenzoic acid; BSOPD: Bis(salicylaldehyde) orthophenylenediamine; HIMH: isonitroso-5-methyl-2-hexanone; PAN: 1-(2-Pyridylazo)2-naphthol; TAN: 1-(2-Thiazolylazo)-2-naphthol; BTAHQ: 5-(2-Benzothiazolylazo)-8-hydroxy-quinolene.

In spite of recent advances in instrumental analysis, a direct determination of trace elements in complex matrices, such as environmental, biological, mineral, ore and high purity materials, seems still to be difficult because of insufficient sensitivity and selectivity of the methods. Thus, enrichment and separation of the analytes are important for the determination of Co(II), because of its extremely low concentration in natural water. Cobalt determination at trace levels in real samples has been frequently difficult because of low concentration of the metal and matrix interferences. In this manner, the determination generally is associated to the preliminary step for enrichment and the elimination of interfering species. Several enrichment procedures have been developed for the determination of Co (II), involving different analytical techniques such as coprecipitation [27, 28], liquid–liquid [29] and solid-phase extractions (SPE) [26, 30-34].

The use of micellar systems such as CPE for separation and pre concentration has attracted considerable attention in the last few years, mainly because it is in agreement with the "green chemistry" principles. Green chemistry can be defined as those procedures for decreasing or eliminating the use or generation of toxic substances for human health and for the environment [35]. CPE is a green method for the following reasons: (a) it uses as an extractor media diluted solutions of the surfactants that are inexpensive, resulting in the economy of reagents and generation of few laboratory residues; and (b) surfactants are not toxic, not volatile, and not easily flammable, unlike organic solvents used in liquid–liquid extraction [36-38].

CPE consists of three simple steps: (1) solubilization of the analytes in the micellar aggregates; (2) clouding; (3) phase separation for analysis. When a surfactant solution is heated over a critical temperature, the solution easily separates into two distinct phases: one contains a surfactant at a concentration below, or equal to, a critical micelle concentration; the other is a surfactant-rich phase. The hydrophobic compounds initially present in the solution and bound to the micelles are extracted to the surfactant-rich phase. This phenomenon is observed, in particular, for polyoxyethylene surfactants and can be attributed to the two ethylene oxide segments in the micelle that repel each other at low temperature when they are hydrated and attract each other when the temperature increases owing to the dehydration.

The concentration of the surfactant-rich phase is the critical micellar concentration. CPE methodologies are based on this property. The use of CPE in procedures for separation and pre concentration of metal ions has been centered on the extraction of these metallic substances as sparingly water-soluble chelate complexes.

Many cloud-point extraction (CPE) methods for pre concentration and determination of Co (II) in various samples have been developed involving several chelating agents [39-64]. The proposed method was compared to a variety of other CPE separation/ pre concentration methods for determination of Co (II) reported recently in the literature. The distinct characteristics are summarized in table 2.

Table 2: Comparision of the reported methods using cloud point extraction of Co(II)

Reagent	Micellar system	SRP diluting agent	Detection system	DL ng ml^{-1}	Linearity ng ml^{-1}	PF	Matrix	Reference
5-Br-PADAP	TritonX-100 and SDS/HCl(1) or NaCl(2)	0.1 mol/l HCl in ethanol	FAAS	1.06 (1) 1.58 (2)	25–200	28.5 (1) 21.7 (2)	Tablets	[39]
5-Br-PADAP	TritonX-114	HNO_3 (1:1)	GFAAS	12	0.25–5.0	41	Vegetal leaves of orange tree (Citrus sinensis), alfalfa (Medicago sativa L.), apple tree leaves	[40]
PAN 5-Br-PADAP	TritonX-114	HNO_3	ICP-OES	4.6 4.3	15-300	13	Dolomite and bone ash	[41]
PAN	TritonX-114	Methanol	FAAS	0.38	1.0-120	115	Urine samples	[42]
PAN	Triton X-114	Ethanol	S		5.0–250	20	Tap water and urine	[43]
PAN	TritonX-114	Carbon tetrachloride	TLS	0.03	0.2–40	470	Tap, river and seawater	[44]
PAN	TritonX-114	Ethanol	FO-LADS	0.2	0.6–30	198	Tap, river, dispenser water, serum	[45]
TAN	Triton X-114	HNO_3 (0.1 mol/l) in methanol	FAAS	0.24	0–120	57	Tap, river and sea water	[46]
Me-BTABr	Tritorn X-114	1.0 mol/l HNO_3 in methanol	FAAS	0.9	0.9–100	28	Spinach leaves river, tap and well water	[47]
Br-TACl	TritonX-114	1.0 mol/l HNO_3 in	FAAS	2.8	10–100	25	Tablets: cyanocobalamin, hydroxycobalaminchloridrat	[48]

		ethanol					e, 5-deoxyadenosylcobalamin	
APDC	TritonX-114	Methanolic solution of 70 g/l HCl containing 1 g/l KCl and 50 g/l8-HQ	FAAS	5.0	Upto200	20	Sea, river, tap and wastewater, red wine, settled sewage	[49]
1-Phenyl thiosemi-carbazide	TritonX-114	1.0 mol/l HNO_3 in methanol	FAAS	1.0	0.25–5	25	Tap,springandseawater,cannedfish,blackandgreen tea, tomatosauceandhoney	[50]
8-HQ	Triton X-114	1.0 mol/l HNO_3 in methanol	FAAS	4.5	2.5–4500	100	Lake, waste and distilled water	[51]
8-HQ	Triton X-114		ICP-OES	0.0 4	0.08–0.32	9.95	River water	[52]
8-HQ	Triton X-114	0.1 mol/l HNO_3 in ethanol	FAAS	0.26	5.0–20	70	Canal and waste water	[53]
N,N'-bis[(1R)-1-ethyl-2-hydroxyethyl]ethane-diamide-DAD1	Triton X-114	1.0 mol/l HNO_3 in methanol	FAAS	1.25		18	Tap and waste water	[54]
N(2-thiophenyl)-1-(2-hydroxyphenyl)imine	Triton X-114	1.0 mol/l HNO_3 in methanol	FAAS	6.0	0.007–0.33	30	Tap and well water, chocolate, honey	[55]
Thenoyltrifluoracetone	TritonX-114	0.5 mol/l HNO_3 in propanol	ICP-OES	0.3	0.5–100	97	Tap, well, sea and mineral water	[56]
ACDA	TritonX-114	DMF	Spectrophotometry	7.5	20–200		Tap, river, sea and waste water	[57]
Calcon carboxylic acid	TritonX-114	Acetonitrile	FAAS	0.20	0.7–100	60	Fortified, drinking and tap water, beer, wine	[58]
5-Br-PADAP	TritonX-114	1.0 mol/l HNO_3 in ethanol.	FAAS	2.4	1.0-100	25	Water samples	[59]
1-Nitroso-2-naphthol	PONPE 7.5	0.25 ml methanol	FAAS	1.22		27	Tap, river, sea and waste water	[60]
MPKO	Triton X-114	1.0 mol/l HNO_3	FAAS	2.1		30	Biological, natural and wastewater, soil and blood samples.	[61]
MPMP	Triton X-114	0.1 mol/l HNO_3 in methanol	FAAS	0.21	1.0-120	97	Water, vitamin B12 and B-complex samples	[62]
2-guanidinobenzimidazole	Triton X-114	HNO_3 in ethanol	FAAS	7.8	77.8-2000 7.8-2000	15	Ni-Cd and Co filter cakes	[63]
MOSDAA	TritonX-114	0.1 mol/l HNO_3	FAAS	0.47	2.0–1200	19	Water samples	[64]
BTANP	TritonX-114	Methanol	S	1.5	10-300	50	Water samples	Proposed work

Abbreviations: DL: detection limit; SRP: surfactant rich phase; PF: pre concentration factor; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; PAN: 1-(2-pyridylazo)-2-naphthol; TAN: 1-(2-thiazoly-lazo)-2-naphthol; Me-BTABr: 2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol; Br-TACl: 2-(5-bromothiazolylazo)-4-chlorophenol; APDC, ammonium pyrrolidine dithiocarbamate; 8-HQ: 8-hydroxyquinoline; ACDA: 2-amino-cyclopentene-1-dithiocarboxylic acid; MPKO: Methyl-2-pyridylketone oxime; MPMP: 2-[(2-Mercaptophenylimino) methyl]phenol; MOSDAA: 4-methoxy-2-sulfobenzenediazo-aminoazobenzene; FAAS: flame atomic absorption spectrometry; GFAAS: graphite furnace atomic absorption spectrometry; ICP-OES: inductively coupled plasma optical emission spectrometry; TLS: thermal lens spectrometry; FO-LADS: fiber optic-linear array detection spectrophotometry; S: Spectrophotometry.

Thiazolyle azo and benzothiazolyl azo dyes have attracted much attention as they are sensitive chromogenic reagents in addition to being important complexing agents. These azo dyes have been applied to a cloud point extraction method for determinations of many metal ions due to its good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesize and purify. Nevertheless, for conventional spectrophotometric analysis in aqueous solution, the low solubility of these azo compounds and their complexes is a significant drawback, that can be overcome by adding organic solvents or surfactants [65].

In the present work, 2-(benzothiazolyl azo)-4-nitrophenol reagent (BTANP) was used for the first time as a chromogenic reagent for the cloud point extraction (CPE) pre concentration of Co(II) after the formation of a complex and spectrophotometric determination using Triton X-114.

The factors influencing the efficiency of CPE extraction and spectrophotometric determination were systematically studied. The proposed CPE method was simple, selective and sensitive for the accurate determination of trace amount of Co (II) in water samples with satisfactory results.

MATERIALS AND METHODS

Apparatus

All absorption spectra were made using Varian UV–Vis spectrophotometer (Cary 100 Conc., Australia) equipped with a 5.0 mm quartz cell were used for absorbance measurements. This spectrophotometer has a wavelength accuracy of±0.2 nm with a scanning speed of 200 nm/min and a bandwidth of 2.0 nm in the wavelength range of 200–900 nm. Hanna pH-meter instrument equipped with a combined glass-calomel electrode (Portugal) (HI: 9321) was used for checking the pH of prepared buffer solutions. A centrifuge with 25 ml calibrated centrifuge tubes (Isolab, Germany) was used to accelerate the phase separation process. A thermo stated water bath with good temperature control was used for the CPE experiments. In order to characterize the new reagents, the IR spectra were recorded as KBr discs using Matson FTIR spectrophotometer in the 4000–200 cm^{-1} range. The ^{1}H-NMR spectrum of the reagent was performed using a varian EM 390-90 NMR spectrometer in d^6-DMSO as solvent using tetramethyl silane (TME) as an internal standard. The Microanalysis of C, H and N of this compound was performed in the Micro analytical Center.

Chemicals and reagents

All chemicals were of analytical reagent grade unless otherwise stated. Ultra pure deionised water was used throughout the work. All the plastic and glassware were cleaned by soaking in 5.0% (v/v) HNO_3 solution for 24h and then rinsed with bi distilled water at least three times prior to use.

The stock solution (1000 µg/ml) of Co (II) ion was prepared from high purity $Co(NO_3)_2.6H_2O$, supplied by (Merck, Darmstadt, Germany). The working standard solutions were prepared daily by diluting stock standard solutions. The standard solution (200 µg/ml) used for the calibration procedures was prepared before use by dilution of the stock solution with 1.0 mol/l HNO_3.

The pH of the solutions was adjusted using buffer solutions. Phosphate buffer solutions at pH 2.0 and 3.0 were prepared by mixing appropriate volumes of 1.0 mol/l sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$) and phosphoric acid (*o*-H_3PO_4) solutions. Acetate buffer solution (CH_3COONa/CH_3COOH) at pH (4.0 and 5.0) was prepared by mixing appropriate volumes of 1.0 mol/l acetic acid and 1.0 mol/l sodium acetate solutions. For pH 6.0 and 7.0, phosphate buffer solutions (NaH_2PO_4/Na_2HPO_4) were prepared by mixing appropriate volumes of 1.0 mol/l sodium dihydrogen phosphate and 1.0 mol/l sodium hydrogen phosphate. Ammoniacal buffer (NH_3/NH_4Cl) solutions at pH (8.0-10) were prepared by mixing appropriate amounts of 1.0 mol/lammonia and 1.0 mol/l ammonium chloride solutions [66].

Triton X-114 (tertoctylphenoxy poly (oxyethylene) ethanol) (Fluka, Buches, Switzerland) was used as the non-ionic surfactant without further purification. Aqueous 0.2 % (v/v) solution of Triton X-114 was prepared by dissolving 0.2 ml of Triton X-114 in 100 ml of bidistilled water in 100 ml volumetric flask with stirring.

Nitric acid solutions were prepared by direct dilution with deionized water from the concentrated solutions. Methanol, acetone, and ethanol (Merck) were used to decrease the viscosity of surfactant-rich phase. The solutions of various cations and anions used for the interference study were obtained from the respective high purity inorganic salts (Sigma-Aldrich, USA) by proper dilution in bidistilled water.

Synthesis of 2-(benzothiazolyl azo)-4-nitrophenol reagent (BTANP)

A solution of 2-amino benzothiazole (7.5 g) (Sigma-Aldrich) was dissolved in 10 ml concentrated hydrochloric acid, and then 15 ml of ice water was added. To this solution, a cold solution of sodium nitrite (Merck) (1.75 g) dissolved in 20 ml of water at 0–2°C was added drop wise and the mixture was stirred for 1.0 h in an ice bath at-5.0°C. 4-nitrophenol (6.95 g) was dissolved in small amounts of 10 ml ethanol, then add 5.0 g sodium acetate dissolved in 20 ml water and cooled in ice to 0–2°C. The solution was added drop wise to the above diazotized solution with vigorous stirring. The mixture was stirred for an additional 2.0 h in an ice-bath at-5.0°C and allowed to stand overnight. The precipitate formed was filtered off, washed with water, air dried and first purified by base-acid recrystallization method and further purified by recrystallization from ethanol, then dried in the oven at 70 °C for several hrs [67].

A stock solution (1.0×10^{-3} mol/l) of BTANP was prepared by dissolving an appropriate amount of the reagent in a minimum amount of absolute ethanol and diluting the mixture to 100 ml with ethanol in a 100 ml measuring flask. The working solution was prepared by its appropriate dilution with the same solvent.

CPE Procedure

An aliquot of Co(II) standard solution was transferred to a 25 ml centrifuge tube, 1.0 ml of the $1.0{\times}10^{-3}$ mol/l BTANP solution and 3.0 ml of phosphate buffer solution (pH 7.0) were added. After that, 1.0 ml of (0.2% v/v) Triton X-114 solution was added. This system was heated in a water bath at 40ºC for 10 min. To separate the two phases, the mixture was centrifuged for 10 min at 4000 rpm. Then, it was cooled in an ice-bath for 5.0 min. The surfactant-rich phase became a viscous phase, which could then be separated by inverting the tubes to discard the aqueous phase. A volume of 0.5 ml methanol was added to the surfactant-rich phase to reduce its viscosity and to facilitate sample handling prior to spectrophotomeric assay at 549 nm. The pre concentration factor was 50 for standard solutions during calibration. Calibration was performed by using different standard solutions of Co(II), submitted to the same pre-concentration and determination procedures. Blank solution was also submitted to a similar procedure and measured in parallel to the sample solutions.

Applications in water samples

The proposed method was applied to different water samples, including tap, river, sea and mineral water samples. The tap and mineral water samples were collected from Zagazig city and Nile river water samples were collected from Shobra Al-Keima, Egypt and seawater samples from Red Sea, Egypt, and the samples stored in polyethylene bottles. The samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size and acidified with 1.0 % nitric acid and were subsequently stored at 4.0 °C in a refrigerator. The organic content of the water samples was oxidized in the presence of 1.0% H_2O_2 and by the addition of concentrated nitric acid. The pH of the samples was adjusted to 7.0 with a buffer solution. Then the pre concentration CPE procedure given above was applied to understudy water samples. The analyte concentrations in the samples were determined by spectrophotometry.

RESULTS

Characteristic infrared and ^{1}H-NMR spectra of BTANP

The elemental analysis of the synthesized brown BTANP ($C_{13}H_8N_4SO_3$; M. Wt. 300.29), (%): C, 52.0; H, 2.69; N, 18.66 and Found: C, 52.03; H, 2.68; N, 18.65 with Yield: (82%) and melting point 122 ºC. The infrared spectra of the free ligand (BTANP) are given in fig. 1. The spectrum of azo ligand (BTANP) shows an absorption band around 3351 cm^{-1}due to the υ(O—H) group. This suggests a strong intermolecular hydrogen bonding. The weak bands which observed at 3081 cm^{-1} in the ligand spectrum is due to υ(C—H) aromatic. The spectrum of ligand shows an absorption band at 1662 cm^{-1} due to υ(C=N) of the thiazole ring.

The azo group (N═N) appears at 1590 cm^{-1} in the ligand spectrum. The band at 1239 cm^{-1} has also been appeared in the ligand spectrum, which is due to υ(C—S) of the thiazole ring. The IR spectra indicate that azo ligand (BTANP) behaves as a tridentate chelating agent coordinated through phenolic oxygen, nitrogen of azo group and thiazole ring nitrogen [68].

The different types of signals for the hydrogen, which are expected for the BTANP compound and the chemical shift of different types of protons take the integration value which gives evidence and helps to assign the peaks. The peak is lying at δ = 5.17 ppm for the BTANP reagent are referred to the hydrogen of OH group which are attached to the aromatic system of 4-nitrophenol. Multiple peaks at ranges δ = 7.55-8.2 ppm which is due to these protons of aromatic rings.

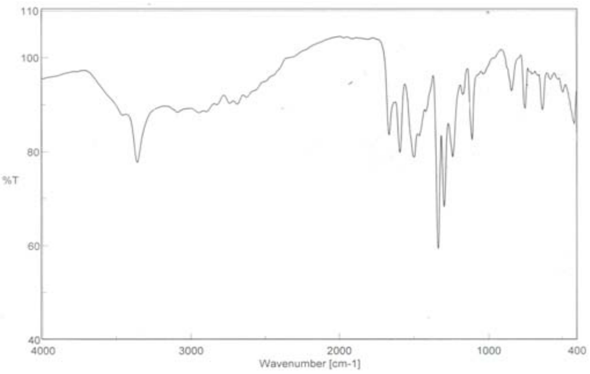

Fig. 1: FTIR spectrum of the new reagent 2-(benzothiazolylazo)-4-nitrophenol (BTANP)

Fig. 2. shows the absorption spectra of a standard solution of Co(II) complex with BTANP which extracted by CPE at pH=7.0 and has a maximum absorbance at 549 nm in surfactant-rich phase and the complex formed without CPE was measured at 549 nm against a reagent blank.

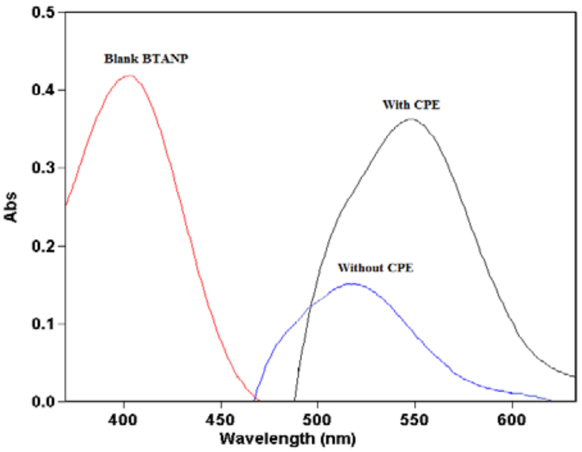

Fig. 2: Absorption spectrum of Co (II)-BTANP complex with and without CPE procedure against BTANP reagent blank

Optimization of the experimental conditions

Effect of pH

Cloud point extraction of Co(II) was carried out in buffer solutions at different pH. The extraction yield depends on the pH at which complex formation is carried out. fig. 3. Shows the effect of pH on the absorbance of Co(II) complex. It is seen that the absorbance increases with an increase in pH up to 7.0. Hence, pH 7.0 (phosphate buffer) was chosen as the optimum pH value for further experiments. In addition, the influence of the buffer amount was assessed, while the other experimental variables remained constant. The results have shown that if 3.0 ml or larger volumes of buffer solution were added in 25 ml solution, no obvious variation took place in the absorbance. Therefore, it was concluded that 3.0 ml of phosphate buffer solution was chosen as the optimum volume.

Effect of BTANP concentration

Twenty five milliliters of a solution containing 2.5 µg of Co(II), 0.2% Triton X-114 and at a medium buffer of pH 7.0 containing various amounts of BTANP were subjected to the cloud point pre concentration process. In order to study the influence of BTANP concentration on the extraction and determination of Co(II) complex different concentrations of the chelating reagent in the range of 2.0 x 10^{-5}–2.0 x 10^{-4} mol/l was used, and the general procedure was applied. Fig. 4. Shown that the absorbance increased up to a BTANP concentration of 1.0 × 10^{-4} mol/l which was selected as the optimum concentration for the CPE of Co(II).

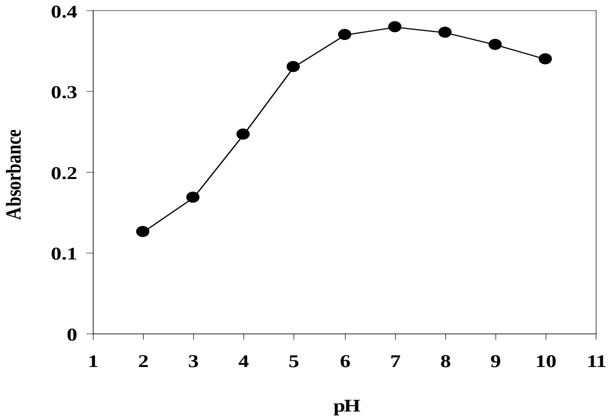

Fig. 3: Effect of pH on the absorbance after CPE. Conditions: Co (II), 200 ng/ml; BTANP, (1.0 × 10^{-4} mol/l) and Triton X-114, 0.2% (v/v). Other experimental conditions are described under procedures

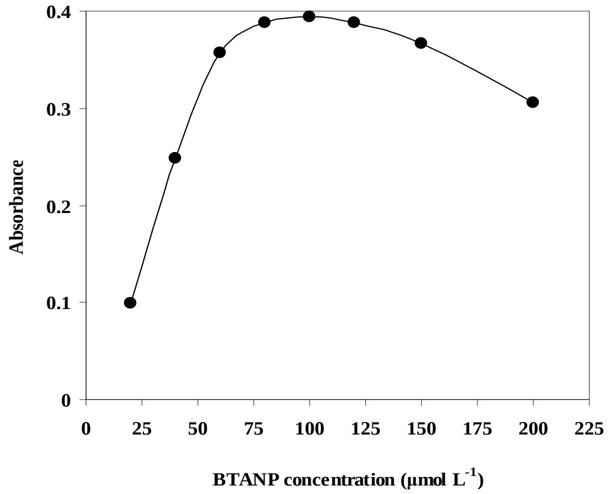

Fig. 4: Effect of BTANP concentration on the absorbance after CPE. Conditions: Co (II), 100 ng/ml; Triton X-114, 0.2% (v/v) and pH 7.0. Other experimental conditions are described under procedures

Effect of Triton X-114 concentration

Triton X-114 is one of the non-ionic surfactant extensively used in CPE. This is due to its advantages such as commercial availability with high purity, relatively low cloud point temperature, low toxicity and cost and high density of the surfactant-rich phase which facilitates phase separation by centrifugation.

Fig. 5. Shows the effect of non-ionic surfactant concentration within the Triton X-114 concentration range from 0.05–0.5% (v/v), on the CPE efficiency of Co(II) ions. The absorbance of the complex was increased by increasing the Triton X-114 concentration up to 0.2% (v/v).

A considerable decrease in the absorbance is observed with increasing surfactant amounts higher than 0.2% (v/v). This can be attributed to an increase in volume and viscosity of the micellar phase. At concentrations below this value, the extraction efficiency of complexes was low because there are few molecules of the surfactant to entrap the BTANP complexes quantitatively. Thus, Triton X-114 concentration of 0.2% (v/v) was selected for subsequent experiments.

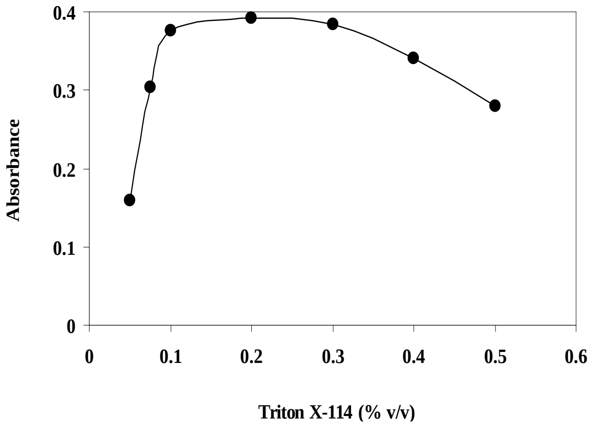

Fig. 5: Effect of Triton X-114 surfactant concentration on the absorbance after CPE. Conditions: Co(II), 100 ng/ml; BTANP, (1.0×10^{-4} mol/l) and pH 7.0. Other experimental conditions are described under procedures

Effects of incubation time and temperature

In order to achieve easy phase separation and efficient pre concentration in cloud point extraction processes, it is imperative to optimize the incubation time and temperature. It was desirable to employ the shortest incubation time and the lowest possible incubation temperature, as a compromise between completion of extraction and efficient separation of phases.

The influence of incubation time and temperature was investigated in the ranges 5.0-20 and from 30-60 °C. The results demonstrate that in the incubation time of 10 min and the temperature of 40 °C were chosen for further experiments. The extraction efficiency for the Co(II)–BTANP complex was constant.

Therefore, an incubation temperature of 40 °C was chosen for the separation process. Higher temperatures lead to the decomposition of BTANP and the reduction of extraction yield. A centrifuge time period of 10 min at 4000 rpm was selected as optimum, as complete separation occurred within this time and no appreciable improvements were observed for longer periods.

Effects of diluents

In order to decrease the viscosity of the surfactant-rich phase a diluting agent was used. For the spectrophotometric method, the addition of a diluent into the surfactant-rich phase is often needed to obtain a homogeneous solution with compatible viscosity. Methanol, ethanol, acetone and acetonitrile were tested as diluent solvents. Surfactant-rich phase was found to be freely soluble in methanol. Therefore, methanol was chosen in order to have an appropriate amount of sample for transferring and measurement of the absorbance of the sample and also a suitable pre concentration factor. Hence the surfactant-rich phase was completed to 500 μl by methanol. Therefore, the pre concentration factor which defined as the ratio of the initial solution volume to the volume of surfactant rich phase was 50 using the proposed method.

Interference studies

In view of the high selectivity provided by spectrophotometry at the characteristic absorption wavelength of 549 nm, the only interference may be attributed to the pre concentration step. The effect of foreign ions on the absorbance of cobalt was tested. Different amounts of common ions were added to the test solution containing 300 ng/ml of cobalt and the developed procedure was applied. The tolerance limits were determined for a maximum error of±5.0% and the results are given in table 3. These results demonstrate that the common coexisting ions did not have a significant effect on the separation and determination of Co(II). BTANP method was observed to be fairly selective for Co(II) ions at pH 7.0. Since commonly present ions in water samples did not affect significantly the recovery of Co(II), the method can therefore be applied to determination of Co(II) in water samples.

Table 3: Effect of interferent ions on pre concentration and recoveries of 300 ng/ml Co(II) (n=3)

Ions	Added as	Maximum amount tolerable (mg/l)	Recovery (%)±SD[a]
K^+	KCl	5.0	96.0±3.0
Na^+	NaCl	12	97.0±2.0
Al^{3+}	$Al(NO_3)_3$	1.0	98.0±2.0
Cr^{3+}	$Cr(NO_3)_3$	1.0	99.0±3.0
Fe^{3+}	$FeCl_3$	1.0	96.0±2.0
Ca^{2+}	$CaCl_2$	2.0	95.0±3.0
Mg^{2+}	$MgCl_2$	1.0	96.0±2.0
Zn^{2+}	$ZnSO_4$	1.0	97.0±3.0
Pb^{2+}	$Pb(NO_3)_2$	0.8	97.0±3.0
Mn^{2+}	$Mn(NO_3)_2$	1.0	96.0±2.0
Ni^{2+}	$NiSO_4$	0.7	95.0±2.0
Cd^{2+}	$Cd(NO_3)_2$	0.8	97.0±3.0
Cu^{2+}	$CuSO_4$	0.5	98.0±3.0
NO_{3-}	KNO_3	5.0	96.0±2.0
SO_4^{2-}	Na_2SO_4	5.0	97.0±2.0
Cl-	NaCl	5.0	95.0±3.0
F^-	NaF	5.0	95.0±2.0

[a] mean±standard deviation.

Analytical characteristics

The calibration graphs were linear in the range 10–300 ng/l between the absorbance measured and the concentration of the metal in solution was obtained under the optimum conditions of the general procedure. table 4. summarizes the analytical characteristics such as the regression equation, linear range, limits of detection and quantification, reproducibility and pre concentration and enhancement factors. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively) was 1.5 ng/ml.

The enhancement factor was calculated as the ratio of the slope of the calibration graph with pre concentration CPE procedure to the slope of the calibration graph without CPE was also approximately 43. The consumptive index is defined as the sample volume, in milliliters, consumed to reach a unit of enrichment factor (EF): CI = Vs (ml)/EF were found to be 0.58, where Vs is the sample volume.

The precision of the procedure was determined as the relative standard deviation (RSD) and relative error for six replicate measurements carried out in solutions containing 200 ng/ml of Co(II) was found to be 1.20% and 1.26%, respectively.

Table 4: Optimum conditions and analytical characteristics of the proposed method for determination of Co(II) with and without CPE

Parameters	With CPE	Without CPE
λ max (nm)	549	518
Calibration range (ng/ml)	10–300	400–6000
Molar absorptivity (L/mol. cm)	9.91 x 10^7	2.425 x 10^3
Sandell sensitivity (ng/cm^2)	5.95 x 10^{-4}	24.30
Regression equation (*n*=6)[a]		
Slope	0.0013	0.00003
Intercept	0.0082	0.0146
Correlation coefficient (*r*)	0.9997	0.9985
Limit of detection (ng/ml)	1.50	120
Limit of quantification, (ng/ml)	5.0	400
Reproducibility (RSD, %) (*n*=6)	1.20 (200 ng mL^{-1})	2.20 (5000 ng mL^{-1})
Pre concentration factor	50	-
Enrichment factor	43	-
Consumptive index	0.58	-

[a] A = a+bC, where C is the concentration of Co(II) in ng/ml

Table 5: Determination of Co(II) in water samples using the proposed method (N=3)

Samples	Added	Found±SD (ng/ml)	Recovery[a] (%)
Tap water	-	1.82±0.10	-
	100	100.50±0.90	98.70
	200	198.50±1.20	98.35
River water	-	2.24±0.11	-
	100	100.0±1.20	97.80
	200	197.0±1.40	97.40
Sea water	-	5.60±0.10	-
	100	102.0±1.10	96.60
	200	200.20±1.30	97.37
Mineral water	-	1.25±0.10	-
	100	98.00±0.8	96.80
	200	19700±1.60	97.89

[a] Average of three determinations with 95% confidence level.

Determination of Co(II) in water samples

In order to test the reliability of the proposed method, it was applied to the determination of Co(II) from different water samples (tap, river, sea and mineral). The results are described in table 5. For calibration purposes, the working standard solutions were subjected to the same pre concentration procedure as used for the analyte solutions. In addition, the recovery experiments of different amounts of Co(II) were carried out, and the results are also shown in table 5. The percentage recovery (R) was calculated by using the equation:

$$R\ \%= \{(C_m - C_0)/m\} \times 100.$$

Where C_m is a value of the metal in a spiked sample, C_0 is a value of metal in a sample and m is the amount of metal spiked. The results indicated that recoveries were reasonable for trace analysis, in a range of 96.60–98.70% and confirm the validity and efficiency of the proposed method.

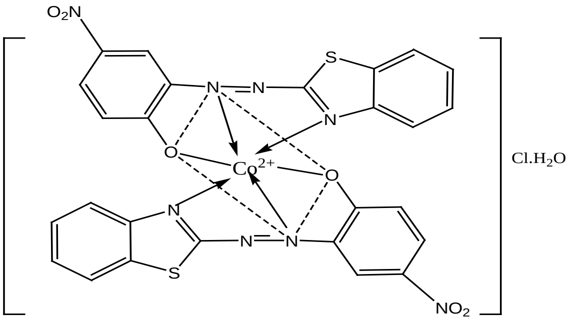

Fig. 6: The structural formula of Co-BTANP complex

DISCUSSION

The separation of metal ions by CPE methods involves prior formation of a metal complex by an appropriate complexing agent, with sufficiently hydrophobic character, and subsequent extraction into a small volume of surfactant-rich phase. The required hydrophobic character of the extracted copper complexes is guaranteed by the high lipophilic nature of the complexing agent (BTANP) used. In the present work, this characteristic was confirmed by the application of BTANP as a complexing agent in a cloud point extraction for separation and pre-concentration of Co(II) ions in water samples. The Co(II) might react with BTANP [69] and form the ML_2 chelate as shown in fig. 6.

CONCLUSION

The proposed cloud point extraction was successfully applied for pre concentration and determination of trace amounts of Co(II) in water samples using BTANP as a selective complexing reagent and spectrophotometric detection. This study allowed the development of a new, fast, easy to use, sensitive, and safe environmentally friendly methodology. The procedure is inexpensive, because it consists of many low equipment and running costs, such as spectrophotometry which is available in most laboratories. Table 2. shows a comparison of the proposed method with other CPE procedures for cobalt using several reagents. From the table, it was observed that the proposed procedure presents analytical characteristics comparable to that reported in the literature. Finally, further work is being carried out in the application of thiazolylazo reagents in the determination of several species by cloud point methodologies in our laboratory.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests

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