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ORIGINAL ARTICLE

Study on the solid phase extraction and spectrophotometric determination of cobalt with 5-(2-benzothiazolylazo)-8-hydroxyquinolene

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Abstract A highly sensitive, selective and rapid method for the determination of cobalt based on the rapid reaction of cobalt(II) with 5-(2-benzothiazolylazo)-8-hydroxyquinolene BTAHQ and the solid phase extraction of the Co(II)-BTAHQ complex with C18 membrane disks were developed. In the presence of pH = 6.4 buffer solution and cetylpyridenium chloride (CPC) medium, BTAHQ reacts with cobalt to form a deep violet complex with a molar ratio of 1:1 (cobalt to BTAHQ). This complex was enriched by the solid phase extraction with C18 membrane disks. An enrichment factor of 100 was obtained by elution of the complex from the disks with a minimal amount of isopentyl alcohol. In isopentyl alcohol medium, the molar absorptivity of the complex is 2.42×10^5 L mol^{-1} cm^{-1} at 658 nm. Beer's law is obeyed in the range of 0.01–0.38 μg mL^{-1} in the measured solution. The relative standard deviation for 11 replicate samples of 0.20 μg mL^{-1} level is 1.37%. The detection and quantification limits reach 3.1 and 9.7 ng mL^{-1} in the original samples. This method was applied for the determination of cobalt in biological, water, soil and pharmaceutical preparation samples with good results.

1. Introduction

Cobalt is an essential element for the functioning of many vital processes. It is extremely important in the processes of blood formation, stimulation of hemoglobin synthesis, and the functioning of vitamins, enzymes and hormones. This metal has a very positive influence on the metabolism of vitamins, such as ascorbic acid and vitamin B_{12}. Cobalt is an essential element in the human body as a component of vitamin B_{12} and it is clear that the monitoring of body fluids for cobalt is important for the control of nutritional deficiencies and, perhaps, the prevention of its toxic effect in cases of occupational exposure. Finally, it is also necessary for the synthesis of a number of

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hormones, neurotransmitters, and other compounds, such as bile acids and DNA (Vucetic and Krstic, 2000; Jeredic and Vucetic, 1982). The human organism is supplied with cobalt through food and water, therefore it is necessary to determine and control its concentration in both.

Thiazole azo compounds have been applied for spectrophotometric determinations 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. However, the low solubility of these compounds can become an advantage when the solid phase spectrophotometry (SPS) technique is applied because the reagent can be immobilized through physical sorption on a proper support (Amin, 2001).

There are many methods such as spectrophotometric methods reported for the determination of trace amounts of cobalt owing to the advantages of simplicity and inexpensive instrumentation. The main chromogenic reagents include 2,2-dipyridyl-2-pyridylhydrazone (Vasilikiotis et al., 1973; Themelis et al., 1995), 1-(2-pyridylazo)-2-naphthol (Wei et al., 1994), bis(2,4,4,-trimethylpentyl) phosphinic acid (Reddy and Sarma, 1994), 2-(8-quinolylazo)-5-N,N-dimethylamino-benzoic acid (Shen et al., 1995), 4,4-diazobenzenediazo aminoazobenzene (Jin et al., 1997), 2-(2-imidazolyl-azo)phenyl-4-sulfonic acid (Zhao et al., 1997) and 2-(2-quinolinylazo)-5-dimethylaminobenzoic acid (Li et al., 2002). Most of spectrophotometric methods developed for the determination of cobalt are, unfortunately, not practically usable due to poor sensitivity and partly poor selectivity.

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 cobalt, because of its extremely low concentration in natural water. Among a wide variety of methods proposed and used for preconcentration of cobalt, solvent extraction and column extraction using various sorbents have been most frequently used. The latter is superior to the former in its ability to treat a large volume of samples in a closed system free from contamination, with a high concentration factor.

Routine spectrophotometric methods are often not sensitive enough to determine low concentrations of cobalt ions in environmental samples only at the $\mu g\,L^{-1}$ level. Consequently, a preconcentration step is usually required. Solid phase extraction is an attractive technique because of its notable advantages (Garg et al., 1999; Pyrzynska and Trojanowicz, 1999; Urasa et al., 1997; Yang et al., 2003). In this paper, BTAHQ was first used as a chromogenic reagent for cobalt. Based on the color reaction of BTAHQ with cobalt and the solid phase extraction of the colored complex with C18 disks, a highly sensitive, selective and rapid method for the determination of cobalt in environmental samples was developed. The method was applied for the determination of cobalt in biological, water, soil and pharmaceutical preparation samples with satisfactory results.

2. Experimental

2.1. Apparatus

A Perkin Elmer Lambda 12 UV-Visible spectrophotometer with a 1.0 cm quartz cell was used for all spectral measurements. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. The extraction was performed on a Waters Solid Phase Extraction (SPE) device (that can prepare 20 samples simultaneously), and Zorbax C18 membrane disks [47 mm (diameter) × 0.5 mm (thickness), 8 μm, 50 mg] (Agilent Technologies, USA) were used. The samples were passed through the disks in a forward direction and the retained complex was eluted from the disks in a reverse direction. A Perkin Elmer atomic absorption spectrometry model A Analyst 300 was used for all GFAAS measurements.

2.2. Reagents

All chemicals used were of analytical grade unless otherwise stated. All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Isopentyl alcohol (Fisher Corporation, USA) was used. BTAHQ used in the present investigation was prepared according to the procedure described previously (Amin and Ibrahim, 2001). A stock 1×10^{-3} M solution of BTAHQ was prepared by dissolving an appropriate weight of the reagent in a minimum amount of pure ethanol and brought to 100 mL in a measuring flask with ethanol.

A stock standard solution of cobalt chloride (1×10^{-3} M) was prepared by dissolving an accurate weight in water and completed to 100 mL in a 100 mL measuring flask which had been standardized gravimetrically.

The buffer solution of 0.5 M acetic acid-sodium acetate (containing 5.0% of Zn-EGTA and 5.0% of NaF) was prepared by dissolving 30 g of acetic acid, 50 g of sodium fluoride and 50 g of glycoletherdiamine tetraacetic acid zinc salt (Zn-EGTA) in 600 mL of water. The pH was adjusted to 6.4 with sodium hydroxide solution and diluted this solution to a volume of 1000 mL with water. Cetyl pyridenium chloride (CPC) solution (2.0%) was prepared by dissolving the CPC with 10% ethanol.

2.3. General procedure

To a standard or sample solution containing no more than 1.9 μg of Co(II) in a 100 mL calibrated flask, 5.0 mL of 0.5 M acetic acid-sodium acetate buffer solution (containing 5% Zn-EGTA and 5% NaF) at pH 6.4, 5.0 mL of 1×10^{-3} M BTAHQ solution and 3.0 mL of 2.0% CPC solution were added. The mixture was diluted to a volume of 100 mL and mixed well. After 5.0 min, the solution was passed through the C18 disks at a flow rate of 20 mL min^{-1}. After the enrichment had finished, the retained complex was eluted from the disks with 4.0 mL of isopentyl alcohol at a flow rate of 5.0 mL min^{-1}. The eluent was adjusted to the accurate volume of 5.0 mL in a 5.0 mL calibrated flask by isopentyl alcohol. The absorbance of the eluant was measured in a 1.0 cm cell at 658 nm against a reagent blank prepared in a similar way without cobalt.

2.4. Procedure for water samples

A 100 mL of water sample was acidified with hydrochloric acid and filtrated by 0.45 μm filter. The cobalt contents were analyzed according to the general procedure described above.

2.5. Procedure for human hair samples

The 2.0 g of sample was weighed accurately into a Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). Then 2.5 mL of concentrated nitric acid and 2.5 mL of 30% hydrogen peroxide were added to dissolve, oxidize and decompose the organic component in the hair samples. The bombs were sealed tightly and then positioned on the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 1.0% HCl acid, and the cobalt contents were analyzed according to the general procedure.

2.6. Procedure for pharmaceutical preparations

Four vitamin B_{12} ampoules were placed into a dry flask and then the flask was shaken well. The 1.0 mL of this vitamin B_{12} sample solution was transferred to a 50-mL flask, to which 8.0 mL of HNO_3 (1:1) was added before it was heated until almost dry. Then, 8.0 mL of HCl (1:1) was added, heated to near dryness, cooled, and the residue was dissolved by adding an appropriate amount of water. Then it was transferred to a 50-mL flask and diluted to the mark with water.

2.7. Procedure for soil samples

An exact weight of finely ground soil sample was dried at 110 °C and treated with 15 mL of concentrated nitric acid and evaporated to dryness. The residue was decomposed by heating with 60 mL of sulphuric acid (1 + 1) to near dryness. Then 20 mL of 0.1 M sulphuric acid and 100 mL of boiling water were added. The suspension was digested for 30 min at 60 °C and the silica was then filtered off. The paper and residue were washed with water; the filtrate and washings were made up to approximately 200 mL with water. The solution was then neutralized with sodium hydroxide pellets and made up to volume in a 250-mL standard flask with water. Suitable aliquots of solution were taken and analyzed by the general procedure.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of BTAHQ and its Co(II) complex in isopentyl alcohol medium are shown in Fig. 1. The absorption bands of BTAHQ and its complex are located at 495 and 658 nm.

3.2. Effect of acidity

The results showed that the optimal pH for the reaction of Co(II) with BTAHQ is 6.0–6.8. A pH 6.4 acetic acid-sodium acetate buffer solution was recommended to control the pH

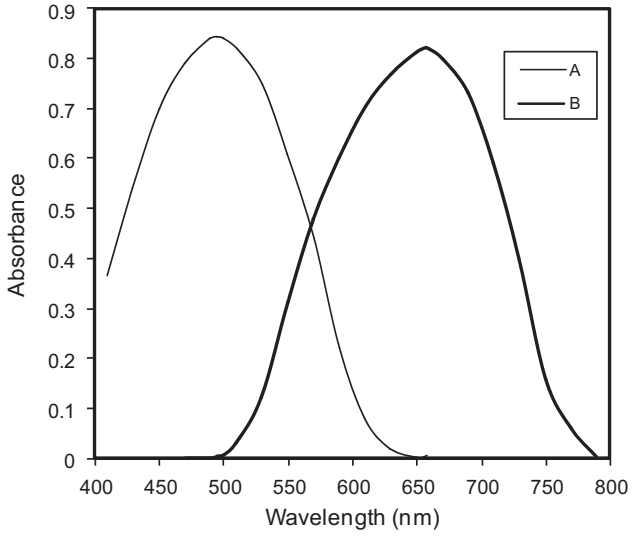

Figure 1 Absorption spectra of BTAHQ and its Co(II) complex: A-BTAHQ-CPC blank against water; B-BTAHQ-Co(II)-CPC complex against reagent blank.

(Fig. 2). The use of 3.5–7.5 mL of buffer solution per 100 mL was found to give a maximum and constant absorbance. Therefore, 5.0 mL of buffer solution was recommended, since the results are highly concordant. In this work, the routine ions Ni(II), Cu(II), and Fe(III) react with BTAHQ to cause serious positive interference. According to the literature (Zhang and Zheng, 1989), in the determination of cobalt with pyridylazo reagent, the interference of Fe(III) can be masked by NaF, and the interference Ni(II) and Cu(II), can be masked by Zn-EGTA. Therefore, experiments containing an appropriate amount of Zn-EGTA and NaF in buffer solution to mask Ni(II), Cu(II) and Fe(III) ions were performed. The results showed that levels of 4.0–6.0% Zn-EGTA and 3.0–10% NaF in buffer solution can greatly enhance the tolerance limits of Ni(II), Cu(II) and Fe(III) and

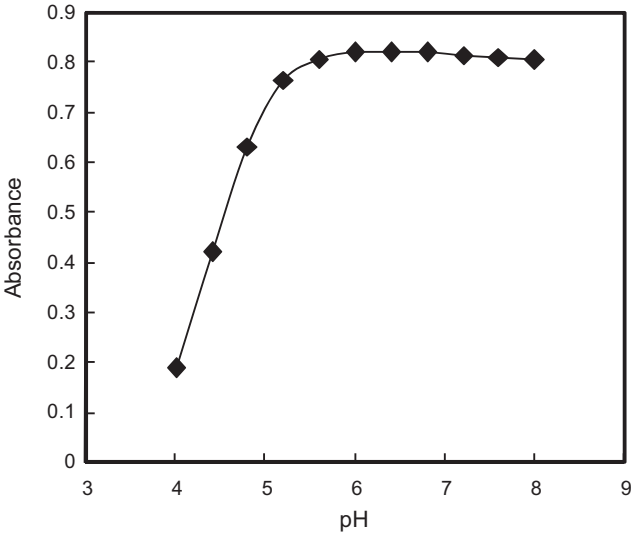

Figure 2 Effect of pH on the formation of 0.2 μg mL^{-1} Co(II) complex; other conditions as in the general procedure.

do not affect the sensitivity of this method. Levels of 5.0% Zn-EGTA and 5.0% NaF in the buffer solution were recommended to mask the Ni(II), Cu(II) and Fe(III) ions.

3.3. Effect of surfactants

The Co-BTAHQ complex has poor solubility in water solution. It is required to add a suitable amount of surfactants to enhance the solubility of the complex. The experiments showed that all the anionic, nonionic and cationic surfactants are effective in enhancing solubility. In addition to enhancing solubility, in the nonionic and cationic surfactants medium, the sensitivity of the Co-BTAHQ complex was also increased markedly. The effect of the nonionic and cationic surfactants on improving sensitivity is recorded in Table 1. The results showed that CPC was the best additive surfactant and that the use of 2.0–4.0 mL of 2.0% CPC gave constant and maximum absorbance (Fig. 3). Accordingly, 3.0 mL of 2.0% CPC solution was recommended.

3.4. Effect of reagent concentration

For up to 1.9 μg of Co(II), the use of about 4.0–6.0 mL of 10^{-3} M of BTAHQ solution was found to be sufficient for a complete color enhancement. Accordingly, 5.0 mL of BTAHQ solution was added in all further measurements.

3.5. Stability of the chromogenic system

After mixing the components, the absorbance reached its maximum within 5.0 min at room temperature and remained stable for 9.0 h in aqueous solution. The complex was stable for at least 24 h when extracted into the isopentyl alcohol medium.

3.6. Solid phase extraction

Both the enrichment and the elution were carried out on a Waters SPE device (capable of preparing 20 samples simultaneously). The flow rate was set to 50 mL min^{-1} when enriching and 5.0 mL min^{-1} when eluting. Some experiments were carried out in order to investigate the retention of BTAHQ and its Co(II) complex on the disks. It was determined that the BTAHQ and its Co(II) complex were retained on the disks quantitatively when they passed the disks as an aqueous solution. The capacity of the disks for BTAHQ was 29 mg and that for its Co(II)-complex was 23 mg in 100 mL of solution. In this experiment, the disks were of sufficient capacity to enrich the Co(II)-BTAHQ complex and the excessive BTAHQ.

In order to choose a proper eluant for the retained BTAHQ and its Co(II) complex, various organic solvents were studied. The effect of the various organic solvents was in the following sequence: isopentyl alcohol > DMF > dioxane > acetonitrile > acetone > ethanol > methanol. Isopentyl alcohol was therefore selected as the eluant. The experiment showed that it was easier to elute the retained BTAHQ and its Co(II) complex in a reverse direction than in a forward direction, and it is necessary to upturning the disks when eluting. In addition, 4.0 mL of isopentyl alcohol was sufficient to elute the BTAHQ and its Co(II) complex from the disks at a flow rate of 5.0 mL min^{-1}.

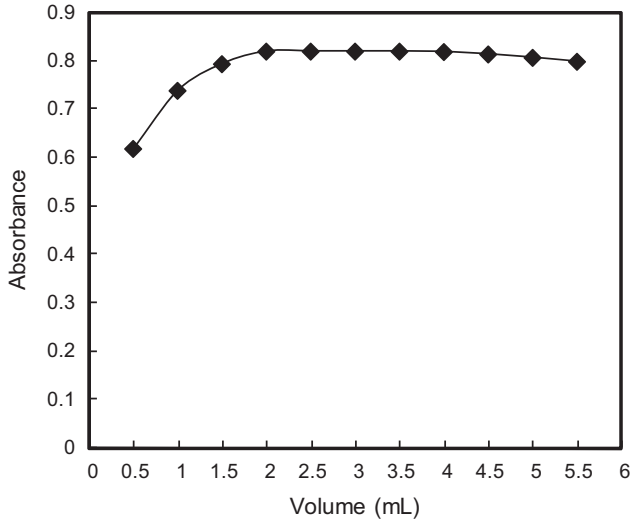

Figure 3 Effect of 2.0% CPC on the formation of 0.2 μg mL^{-1} complex with BTAHQ; other conditions as reported in the general procedure.

3.7. Calibration curve and sensitivity

The calibration curve shows that Beer's law is obeyed in the concentration range of 0.01–0.38 μg Co(II) per mL in the final solution. Ringbom optimum concentration ranges were obtained by plotting the logarithmic value of the concentration of Co(II) against the transmittance percentage and the result is recorded in Table 2. The linear regression equation obtained was

$$A = 4.105\,\mathrm{C}(\mu\mathrm{g\,mL^{-1}}) + 0.0067,\ (r = 0.9994)$$

The molar absorptivity and Sandell sensitivity were calculated to be 2.42×10^5 L mol^{-1} cm^{-1} and 0.0244 ng cm^{-2} at 658 nm. The standard deviations of the absorbance measurements were calculated from a series of 13 blank solutions. The limits of detection ($K = 3$) and of quantification ($K = 10$) of the method were established (IUPAC, 1978) and recorded in Table 2, according to the IUPAC definitions ($C_1 = KS_o/s$) where C_1 is the limit of detection, S_o is the standard error of blank, s is the slope of the standard curve and K is the constant related to the confidence interval. The relative standard deviation was 1.37% obtained from a series of 11 standards each containing 0.2 μg mL^{-1} of Co(II) in the final assay solution.

Table 1 The effect of surfactants on the Co-BTAHQ chromogenic system.

Surfactant	Absence	Triton X-100	Emulsifier-OP	Tween-80	Tween-60	CTMAB	CPB	CPC
λ_{max} (nm)	617	625	633	636	635	647	650	658
Molar absorptivity L mol^{-1} cm^{-1} $\times 10^4$	0.652	0.836	0.941	0.980	0.997	1.12	1.56	2.42

Table 2 Analytical parameters.

Parameter	Value	Parameter	Value
Beer's law limit (μg mL^{-1})	0.01–0.38	Regression equation[a]	
Ringbom optimum range (μg mL^{-1})	0.03–0.36	Slope (*b*)	4.105
Molar absorptivity (L mol^{-1} cm^{-1})	2.42×10^5	Intercept (*a*)	0.0067
Sandell sensitivity (ng cm^{-2})	0.0244	Correlation coefficient (*r*)	0.9994
Detection limit (ng mL^{-1})	3.1	RSD (%)	1.37
Quantification limit (ng mL^{-1})	9.7	Stoichiometric ratio (M:L)	1:1

[a] $A = a + bC$, where C is the concentration of iron in μg L^{-1}.

Table 3 Comparison of the sensitivity for spectrophotometric determination of Co(II).

Reagent	λ_{max} (nm)	$\varepsilon \times 10^4$ (L mol^{-1} cm^{-1})	Medium	Ref.
2-(2-Quinolylazo)-5-diethylamino-aniline	625	14.3	Isopentyl alcohol	Hu et al., 2004
Nitroso R(sodium-l-nitroso-2-hydroxynaphthalene-3,6-disulfonate)	550		Aqueous	Zhang and Terada, 1994
1-(2-Pyridylazo)2-naphthol	639	2.72	Triton X-100	Afkhami and Bahram, 2004
2-Diethylamino-5-nitroso-1,4,5,6-tetrahydropyrimidine-4,6-dione	385	6.3	Acidic	Tsuchiya and Iwanami, 1992
2-(2-Thiazolylazo)-4-methyl-5-(sulfomethylamino)benzoic acid	655	11.3	Aqueous	Wada et al., 1983
2-Acetyl-6-methyl pyridine oxime	357	1.4	Aqueous	Beaupr and Holland, 1984
Di-2-pyridyl Ketoxime	388	2.0	Aqueous	Beaupr and Holland, 1984
2-Pyridyl-2-thienyl-ZKetoxime	412	2.0	Aqueous	Beaupr and Holland, 1984
Indane-l,2,3-trionetrioxime	320	5.32	Aqueous	Rao et al., 1987
[2-(3,5-Dibromopyridyl)azo]-5-dimethylaminobenzoic acid	673	15.5	Extraction	Katami et al., 1983
2,2′-Dipyridyl-2-benzothiazolyl hydrazone	530	3.43	Extraction	Singh et al., 1984
Potassium tetrahydrofuryl xanthate	350	1.65	Aqueous	Hussain et al., 1985
Morpholine-4-carbodithioate	365	1.39	Molten naphthalene	Sethi et al., 1983
2,2′-Dipyridyl-2-primidyl-hydrazone	440	3.15	Aqueous	Singh et al., 1979
Bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone)	390	3.28	Aqueous	Balairon et al., 1979
Nitroso-R salt	415	3.5	Heating	Marczenko, 1976
N,N–bis(2-aminobenzoyl) ethylenediamine	470	1.10	Aqueous	Kumar and Muthuselvi, 2001
1-(2-Thiazolylazo)-2-naphthol	572	262	Immobilized on C18 bonded silica	Teixeira1 et al., 2001
5-(2-Benzothiazolylazo)-8-hydroxy-quinolene	658	24.2	Isopentyl alcohol	This work

The sensitivity expressed as molar absorptivity of the proposed method is compared with those of published spectrophotometric methods (Table 3). Although the solid phase spectrophotometric method depending on the reaction with a chromogenic reagent 1-(2-thiazolylazo)-2-naphthol which immobilized on C18 bonded silica (Teixeira1 et al., 2001) gave a higher sensitivity (2.62×10^6 L mol^{-1} cm^{-1}) compared with the proposed method, it was suffering from positive interferences of Cu(II), Fe(II), Ni(II) and Zn(II) at all concentration levels. The higher sensitivity of the proposed method is notable, greater even than that of the SPE (Hu et al., 2004) that used 2-(2-quinolylazo)-5-diethylaminoaniline. Also, the proposed method is more sensitive than other method (Zhang and Terada, 1994; Afkhami and Bahram, 2004; Tsuchiya and Iwanami, 1992; Wada et al., 1983; Beaupr and Holland, 1984; Rao et al., 1987; Katami et al., 1983; Singh et al., 1984; Hussain et al., 1985; Sethi et al., 1983; Singh et al., 1979; Balairon et al., 1979; Marczenko, 1976; Kumar and Muthuselvi, 2001; Teixeira1 et al., 2001) that based on spectrophotometry (Table 3).

3.8. Nature of the complex

The nature of the complex was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of BTAHQ to Au(III), obtained by varying the BTAHQ concentration, showed inflection at molar ratio 1.0, indicating presence of three DCHNAQ molecules in the formed complex. Moreover, the Job method showed a ratio of BTAHQ to Au(III) = 1.0. Consequently, the results indicated that the stoichiometric ratio was (1:1) (Au(III):BTAHQ). The conditional formation constant (log *K*), calculated using

Table 4 Tolerance limits in the determination of 0.2 μg of Co(II) with BTAHQ (relative error ± 5.0%).

Foreign ions	Tolerance limit μg
Na^+, K^+, Li^+, CH_3COO^-	20,000
Cl^-, ClO_4^-, PO_4^{3-}, NO_3^-, thiourea	15,000
Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, SO_4^{2-}, SiO_3^{2-}	11,000
Mn^{2+}, Ce^{4+}, SnO_3^{2-}, tartrate	7500
WO_4^{2-}, MoO_4^{2-}, UO_4^{2-}	5000
Ti^{4+}, Bi^{3+}, VO_3^-, CrO_4^{2-}, F^-	3500
Cr^{3+}, Al^{3+}, Ru^{3+}, Ag^+, Br^-	2500
Ir^{4+}, Rh^{3+}, Pd^{2+}, Pt^{4+},I^-	1200
OsO_5^{2-}, SeO_3^{2-}, TeO_3^{2-}	850
Hg^{2+},CN^-, SCN^-	600
Pb^{2+}, Ru^{3+}, Bi^{3+}, Sb^{3+}, Th^{4+}	350
La^{3+}, Sm^{3+}, Gd^{3+}	200
Be^{2+}, Sc^{3+}, Fe^{2+}, Cd^{2+}, Zn^{2+}	80
Fe^{3+}, Cu^{2+}, Ni^{2+}	35

Harvey and Manning equation applying the data obtained from the above two methods, was found to be 6.88, whereas the true constant was 6.60.

3.9. Interference

A systematic study of the effect of potentially interfering species on the cobalt determination was undertaken. This study was carried out by adding a known amount of foreign species to a cobalt solution of 0.2 μg mL^{-1}. The tolerance limit was taken as ±5.0% change in absorbance. The results are listed in Table 4 showing that most common ions do not interfere with the determination suggesting the highly selectivity of the proposed method.

3.10. Application

In order to assess the applicability of the proposed method to real samples, this method was successfully applied for the determination of cobalt in water (tap, river, sea water and waste water), soil, biological (human hair), and pharmaceutical preparation samples. The Co(II) contents were analyzed according to the general procedure. The accuracy was further validated by comparison of the results obtained by the proposed method with those obtained by the GFAAS (Goswami and Singh, 2002) as a reference method.

The performance of the proposed method was assessed by calculation of the *t*-value (for accuracy) and *F*-test (for precision) compared with GFAAS method (Goswami and Singh, 2002). The mean values were obtained in a student's *t*- and *F*-tests at 95% confidence limits for five degrees of freedom (Miller and Miller, 2005). The results showed that the calculated values (Tables 5 and 6) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other method.

4. Conclusion

In this study, a highly sensitive and selective reagent BTAHQ for cobalt determination was used. The experiment showed that the molar absorptivity of the Co(II)-BTAHQ-CPC chelate reaches 2.42×10^5 L mol^{-1} cm^{-1} in the measured solution. By solid phase extraction with C18 disks, an enrichment factor of 100 was achieved. The detection and quantification limits reached 3.1 and 9.7 ng L^{-1} in the original samples, and low concentrations of cobalt in samples can be determined with

Table 5 Determination of μg L^{-1} Co(II) in water samples.

Sample	Added (μg L^{-1})	Found[a] (μg L^{-1})					
		Proposed method			GFAAS method		
		Co(II)	*t*-Value[b]	*F*-test[b]	RSD (%)	Co(II)	RSD (%)
River Nile water	–	8.7	1.17	2.78	1.46	8.65	1.68
	4.0	12.75	1.29	3.13	1.79	12.60	1.43
	8.0	16.65	1.32	3.27	1.32	16.70	1.59
Well water	–	5.6	1.34	3.46	1.56	5.55	1.75
	5.0	10.50	1.08	2.58	1.81	10.60	1.54
	10.0	15.55	1.20	2.93	1.38	15.50	1.66
Sea water	–	14.5	1.44	3.69	1.74	14.45	1.92
	6.0	20.40	1.30	3.25	1.31	20.40	1.54
	12.0	26.60	1.26	3.07	1.62	26.50	1.78
Waste water	–	17.20	1.19	2.85	1.88	17.25	1.56
	5.0	22.30	1.40	3.73	1.73	22.30	1.87
	10.0	27.25	1.52	3.98	1.62	27.20	1.72
Lake water	–	38.10	1.69	4.17	1.83	38.00	1.35
	6.0	44.20	1.28	3.27	1.92	44.05	1.54
	12.0	50.39	1.23	2.91	1.73	2.38	1.44
Tap water	–	1.53	1.65	4.11	1.95	1.54	1.76
	0.5	2.03	1.43	3.65	1.63	2.02	1.28
	1.0	2.52	1.37	3.52	1.57	2.53	1.39

[a] Average of six determinations.
[b] Theoretical values for *t*-and *F*-values at 95% confidence level for five degrees of freedom are 2.57 and 5.05, respectively.

Table 6 Determination of Co(II) in biological and pharmaceutical samples.

Sample	Added Co(II)	Proposed method[a]				GFAAS method	
		Co(II)	*t*-Value[b]	*F*-test[b]	RSD (%)	Co(II)	RSD (%)
Human hair	–	0.525	1.63	4.11	1.95	0.530	1.76
	0.5	1.03	1.44	3.65	1.63	1.035	1.28
	1.0	1.52	1.37	3.49	1.57	1.054	1.39
Vitamin-B12	–	3.267	1.34	3.46	1.56	3.255	1.75
Amp[c]	2.5	5.260	1.08	2.61	1.81	5.770	1.54
	5.0	8.265	1.20	2.93	1.38	8.280	1.66

[a] Average of six determinations.
[b] Theoretical values for *t*- and *F*-values at 95% confidence level for five degrees of freedom are 2.57 and 5.05, respectively.
[c] Adco company, Egypt (1 g mL^{-1} Co(II) vitamin B12).

good results. The consumption of organic solvents in this method is much lower than that in the liquid–liquid extraction method. By using a Waters SPE device, 20 samples can be prepared simultaneously. This method is a rapid means of simultaneously preparing large amounts of sample.

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