

Third Derivative Spectrophotometric Determination of Trace Amounts of Cobalt after Separation and Preconcentration onto Amberlite

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Abstract

A simple, rapid, sensitive third-derivative spectrophotometric method has been developed for the determination of trace amount of cobalt in various samples after separation and preconcentration onto Amberlite XAD-4 loaded with 2-[1-(2-hydroxy-5-sulforphenyl)-3-phenyl-5-formazano]-benzoic acid monosodium salt (Zincon) in the pH range of 5.0 to 9.0. The cobalt that was retained on the resin was recovered with 5.0 mL of dimethylformamide and was then determined by third derivative spectrometry. Linearity was observed within a concentration range of 0.1 and 5.0 $\mu\text{g/mL}$ in the final solution, with a correlation coefficient of 0.9996. Seven measurements of 5.0 mg of cobalt in the final solution gave a mean $d^3A/d\lambda^3$ (peak-to-peak signal between $\lambda_1 = 649$ and $\lambda_2 = 680$ nm) of 0.352 with a relative standard deviation of 1.2%. The sensitivity of the method ($d^3A/d\lambda^3$) was 0.3016 mL/ μg , which was found from the slope of the calibration curve. Various parameters such as pH, flow rate of sample and eluent, and interference by a large number of ions on the determination of cobalt were studied in detail to optimize the conditions for determination of cobalt in various samples.

Keywords: Solid-phase extraction, cobalt determination, derivative spectrophotometry, Amberlite XAD-4, Zincon

Résumé

Nous avons développé une méthode spectrophotométrique simple, rapide, et sensible à la troisième dérivée pour la détermination de quantités traces de cobalt dans divers échantillons, après séparation et préconcentration sur Amberlite XAD-4,

elle-même pré-chargée avec le sel monosodique de l'acide benzoïque-2-(1-(2-hydroxy-5-sulforphényl)-3-phényl-5-formazano] ou Zincon, dans la gamme de pH range de 5.0 à 9.0. Nous pouvons déterminer la substance à analyser retenue sur la résine et récupérée par 5.0 mL de diméthylformamide; on obtient alors la valeur du cobalt par spectrométrie de troisième dérivée. La linéarité est maintenue dans la gamme de concentration de 0.1-5.0 $\mu\text{g mL}^{-1}$ pour la solution finale avec un coefficient de corrélation de 0.9996. La détermination de sept mesures répétées de 5.0 mg de cobalt dans la solution finale a donné une moyenne $d^3A/d\lambda^3$ (signal pic-sur-pic entre $\lambda_1 = 649$ et $\lambda_2 = 680$ nm) de 0.352, avec un écart-type relatif de 1.2%. La sensibilité de la méthode ($d^3A/d\lambda^3$) est de 0.3016 mL/ μg tel que trouvée à partir de la pente de la droite de calibration. Nous avons étudié en détail divers paramètres comme l'effet du pH, du débit de l'échantillon et de l'éluent ainsi que les interférences par un grand nombre d'ions afin d'optimiser les conditions pour la détermination du cobalt dans des échantillons divers.

Introduction

Dissolved cobalt is present in the environment at concentrations ranging from 0.5 to 12 $\mu\text{g/L}$ in sea water up to 100 $\mu\text{g/L}$ in waste water (1). Calculation of the inorganic complexation of cobalt using an ion-pairing model and stability constants (2) show that it is weakly coordinated by inorganic ligands, the predominant inorganic species being Co(II) and its chloride complexes. On the other hand, there is evidence that cobalt is strongly complexed by organic ligands and they are especially found in burdened waters and solids (3,4).

High sensitivity procedures for the determination of cobalt generally use graphite furnace atomic absorption spectrometry (GFAAS) followed by a preconcentration step, which usually involves risk of sample contamina-

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tion and analyte loss (1,5-9). Voltammetric techniques seem to overcome most problems, proving to be very useful even at low levels of cobalt (10,11). However, they suffer from interferences from various electroactive compounds present in real samples, which are co-oxidized at the applied potential. On the other hand, spectrophotometric (12-18) and spectrofluorimetric techniques (19) have been extensively used. Most of the complexing reagents are either non-selective for cobalt, interfered by nickel or iron, sensitive at extreme pH ranges (21-23), long in extraction and color development time (24), or the products become water insoluble. When they become insoluble, extraction (13,20), separation (16,18) or even a computational (12,14,17) step for the determination of each species are required. Zincon is a photometric reagent for Cu, Zn (25) and Ga (26) and soluble in water and alcohol. Proton dissociation constants are reported to be $pK_{a1} = 7.9$, $pK_{a2} = 8.3$, and $pK_{a3} = 13 - 14$. The aqueous solution of Zincon is yellow or orange-yellow under weak alkaline conditions. The structure of Zincon is given in Figure 1.

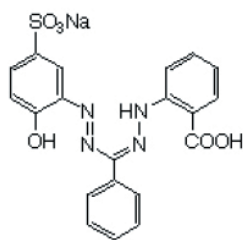


Figure 1. Structure of Zincon.

Derivative spectrophotometry, which involves the differentiation of a normal spectrum, offers a useful means for improving the resolution of mixtures because it enhances the detectability of minor spectral features. Derivative spectrophotometry is an analytical technique used to obtain both qualitative and quantitative information from spectra composed of unresolved bands by using the first or higher derivatives of absorbance with respect to wavelength. It tends to emphasize subtle spectral features, allowing the resolution of multi-component elements, by reducing the effect of spectral background interferences. This technique offers an alternative approach to the enhancement of sensitivity and specificity in mixture analysis. It involves calculating and plotting one of the mathematical derivatives of a spectral curve. The derivative transformation of a spectrum permits

discrimination against broad band interferences that may arise from turbidity or non-specific matrix absorption. Derivative spectrophotometry has been extensively used in analytical chemistry (27-30).

In the present communication, we have developed a simple, rapid, sensitive third derivative spectrophotometric method for the trace determination of Co[II] following its complexation with Zincon, which was loaded onto Amberlite XAD-4 resin, and its subsequent desorption with 5.0 mL of dimethylformamide (DMF).

Experimental

Apparatus

In the present work a Shimadzu UV 160 spectrophotometer (Shimadzu, Japan, Model no. 160) with 1.0 cm quartz cell was used. A Beckman pH meter was employed for pH measurements. A funnel-tipped glass tube (60 × 6 mm) was used as a column for preconcentration. All glassware and columns were kept overnight in a mixture of concentrated sulfuric and nitric acids (1:1) before use.

Reagents

All the reagents were of analytical reagent grade. Cobalt(II) nitrate was dissolved in deionized water and standardized complexometrically (31). A 2.0 mg/mL solution of cobalt was prepared by appropriate dilution of the standard solution. A 0.1% solution of 2-[1-(2-hydroxy-5-sulforphenyl)-3-phenyl-5-formazano]-benzoic acid monosodium salt (Zincon) in ethanol was prepared. Buffer solution of pH ~7.0 was prepared by mixing appropriate ratios of 0.5 M Na_2HPO_4 and 0.5 M KH_2PO_4 solutions.

Preparation of Amberlite XAD-4 column loaded with Zincon

Amberlite XAD-4 was treated overnight with a mixture of 95% ethanol: 1 M of hydrochloric acid: deionized water (2:1:1) solution. The resin was rinsed with 50 mL of deionized water. Packing of the column must be done using ethanol as eluent. The resin was then saturated with the reagent by passing 2 mL of a 0.1% Zincon solution in ethanol at a flow rate of 1 mL/min. Afterwards it was washed with 10 mL of deionized water until the excess reagent was eliminated from the resin. All experiments were done in a funnel-tipped glass tube (60 × 6 mm), which was used as a column for preconcentration. It

was plugged with polypropylene fibers and then filled with the XAD-4. The column must be preconditioned by passing 3 mL of buffer solution before the sample is loaded. The column can be reused repeatedly for at least ten times.

Procedure for the sorption of cobalt on the column

An aliquot of cobalt solution (containing 0.5 to 25 μg) was placed in a 100 mL beaker and to it was added 3.0 mL buffer solution pH ~ 7.0 , and then it was diluted to ~ 30 mL with deionized water. This solution was passed through the column at a flow rate 3.0 mL/min. Then, the column was eluted with 5.0 mL of deionized water. The adsorbed cobalt (II) on the column was eluted with 5.0 mL of DMF at a flow rate 0.5 mL/min. The third derivative absorption spectra were recorded against a blank solution in the same way from 500 to 800 nm. The $d^3A/d\lambda^3$ was measured between $\lambda_1 = 649$ and $\lambda_2 = 680$ nm. A calibration curve was prepared by taking various known amounts of cobalt under the conditions given above.

Determination of cobalt in pepperbush and pond sediment samples

The accuracy and applicability of the proposed method was applied to the determination of cobalt in National Institute for Environment Studies (NIES) No. 1 pepperbush and NIES No. 2 pond sediment. A 0.5 g sample was added to a beaker and dissolved in concentrated nitric acid (~ 5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was increased

to 100 mL with distilled water in a calibrated flask. An aliquot of the sample solution was taken individually and cobalt was determined by the general procedure. The results are given in Table 1 and they were in good agreement with the certified value.

Determination of cobalt in synthetic samples

The accuracy and applicability of the proposed method was applied to the determination of cobalt in synthetic samples. The appropriate amounts of metal salts were prepared in 10 mL of concentrated hydrochloric acid and nitric acid (1:1). The solution was filtered (if needed), and the solution was diluted to 100 mL in a 100-mL volumetric flask. An aliquot of the sample solution was analyzed by the general procedure and the results are given in Table 2.

Determination of cobalt in water samples

The same method was employed for the determination of cobalt in well, river and spring water. A 100 mL water sample was adjusted to pH 1.5 with nitric acid and filtered to remove suspended material and the general procedure was applied. In order to compare the proposed method, the actual water samples were analyzed by direct FAAS (using standard addition method). The results are given in Table 3.

Results and Discussion

In order to determine the optimum conditions for

Table 1. Determination of Pepperbush and Pond sediment for cobalt

Sample	Composition	Found ^a $\mu\text{g/g}$	% Recovery
NIES, No. 1 Pepperbush	K, 1.51 ± 0.06 ; Mn, 0.203 ± 0.17 ; Ca, 1.38 ± 0.07 Mg, $0.408 \pm 0.020\%$ Cd, 6.7 ± 0.5 ; Ni, 8.7 ± 0.6 ; Cu, 12 ± 1 ; Cs, 1.2; Tl, 0.13; Fe, 205 ± 17 ; Co, 23.0 ± 3.0 ; Pb, 5.5 ± 0.8 ; P, 1100; As, 2.3 ± 0.3 ; Rb, 75 ± 4 ; Na, 106 ± 13 ; Hg, 0.05; Cr, 1.3; Zn, 340 ± 20 ; Ba, 165 ± 10 ; Sr, $36 \pm 4 \mu\text{g g}^{-1}$	23.6 ± 0.5	102.6
NIES No. 2 Pond sediment	Al, 10.6 ± 0.5 ; Fe, 6.53 ± 0.35 ; Ca, 0.81% Zn, 343; Cu, 210; Pb, 105; Cd, 0.82; Ni, 40; Cr, 75; Co, $27 \mu\text{g g}^{-1}$	26.6 ± 0.5	98.5

^a Average of five determinations, \pm standard deviation

NIES: National Institute of Environmental Studies. Reference materials

Conditions: buffer, 3 mL; flow rate of sample, 3 mL min^{-1} ; final solution, 5.0 mL of dimethylformamide; flow rate of solvent, 1.0 mL min^{-1} ; reference, reagent blank

Determination by third derivative spectrophotometry from signal peak to peak measurements between $\lambda_1=649$ and $\lambda_2=680$ nm with $\Delta\lambda = 9$ nm.

Table 2. Determination of cobalt in synthetic samples

Composition of synthetic sample ($\mu\text{g/g}$)	Expected value ($\mu\text{g/g}$)	Amount found by the present method ^a ($\mu\text{g/g}$)	% Recovery
Cr, 50; Ir, 100; Cd, 20; Cu, 5; Al, 20; Ca, 300; Fe, 20; Ni, 20; Mn, 10.0; Hg, 20; Mg, 600; Pb, 20; Zn, 5; Tl, 30	10.0	10.0 \pm 0.1	100
Fe, 20; Mn, 10; Pb, 20; Cr, 50; Ni, 10; Hg, 15; Al, 10; Zn, 6; Sr, 200; Mg, 250; Ce, 200; Cd, 20; Pd, 8.0; Cu, 6	5.0	4.95 \pm 0.10	99
Pb, 20; Ni, 10; Fe, 20; Zn, 10; Ca, 500; Ir, 100; Al, 10; Hg, 10; Mg, 300; Mn, 10; Tl, 20; Pd, 16; Cd, 20; Cr, 50	7.5	7.55 \pm 0.07	100.7

^a Average of five determinations, \pm standard deviation
Conditions were the same as in Table 1.

the quantitative extraction of cobalt by using amberlite XAD-4 resin with Zincon complex, several parameters were assessed.

Spectral Characteristics

The absorption spectra of the Co-Zincon complex in DMF versus that of a blank prepared under the similar conditions were recorded (Figure 2). The first, second and third derivative spectra are shown in Figure 3 were given. As shown in Figure 3, third derivative leads to sharper and higher signals in the resulting spectra. Preliminary observations revealed that the best result were obtained from the third derivative with wavelength interval $\Delta\lambda = 9$ nm. In the present work, a peak-to-peak method between $\lambda_1 = 649$ and $\lambda_2 = 680$ nm was applied.

Reaction Conditions

Reaction conditions were established by using 5.0 μg of cobalt. The adsorption of cobalt on this absorbent was found to be maximum in the pH range of 5.0 to 9.0 (Figure 4). In a subsequent study, the pH was maintained at pH \sim 7.0. Addition of 1.0-5.0 mL of the buffer (pH \sim 7.0) did not affect the retention of cobalt and the use of 3.0 mL was recommended.

The flow rate of sample was varied from 0.5-10 mL/

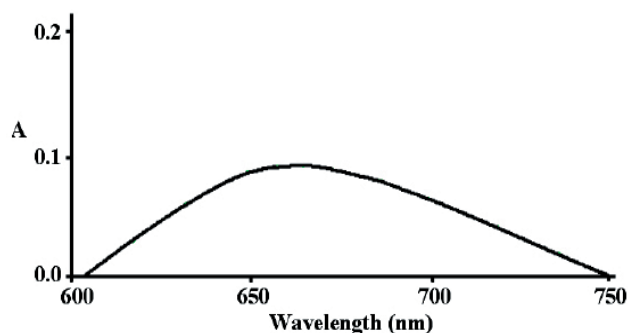


Figure 2. Spectra of the Co-Zincon complex. Conditions: Cobalt, 5.0 μg in final solution; final solution, 5.0 mL of DMF; buffer, 3 mL; flow rate of sample, 3 mL/min; flow rate eluent, 1.0 mL/min; reference, reagent blank.

min. It was found that a flow rate 0.5-6.0 mL/min did not affect adsorption. A flow rate of 3 mL/min is recommended in all experiments. The flow rate of eluent was varied from 0.5-4.0 mL/min. It was found that a flow rate 0.5-1.5 mL/min did not affect the adsorption. A flow rate of 1.0 mL/min is recommended.

The volume of the aqueous phase was varied in the range of 20-1200 mL under optimum conditions, keeping the other variable constant. It was observed that the adsorption was almost constant up to 1000 mL (preconcentration factor of 200). However, for convenience, all

Table 3. Determination of Cobalt in Water Samples

Sample	FAAS ^a (ng/mL)	Recommended Procedure ^b (ng/mL)	% Recovery
Spring water	7.4 \pm 0.2	7.3 \pm 0.2	98.6
River water of Rayen in Kerman	10.0 \pm 0.3	10.1 \pm 0.2	101.0
River water of Kohpayeh in Kerman	9.6 \pm 0.2	9.8 \pm 0.3	102.1
Well water	8.2 \pm 0.3	8.4 \pm 0.3	102.4

^aDirect FAAS using the method of standard additions

^bAverage of five determinations, \pm standard deviation

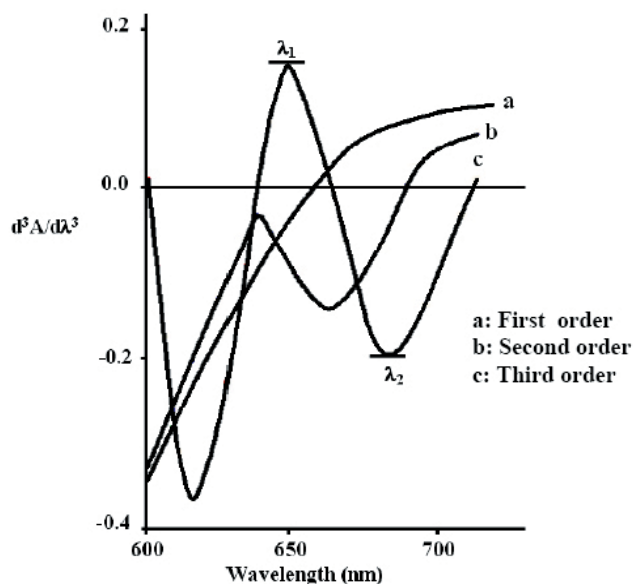


Figure 3. The first, second and third derivative spectra of the Co-Zincon complex. Conditions were the same as Figure 2.

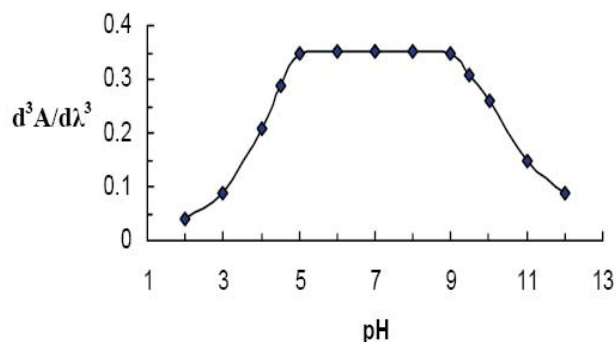


Figure 4. Effect of pH on adsorption of cobalt complex. Determination by third derivative spectrophotometry from signal peak to peak measurements between $\lambda_1=649$ and $\lambda_2=680$ nm with $\Delta\lambda = 9$ nm. Conditions were the same as Figure 2.

the experiments were carried out with 30 mL of aqueous phase.

A number of solvent were tried in an effort to dissolve the metal complex. DMF was preferred because of the high solubility and stability of metal complexes. It was found that 2-3 mL of this solvent was sufficient to dissolve the entire complex, thus further enhancing the sensitivity of the method. Therefore, 5 mL of DMF was used in the present work.

Sorption capacity of resin for cobalt

The sorption capacity of Amberlite XAD-4 for the

cobalt complex with Zincon was also evaluated. The Amberlite XAD-4 was found to have a sorption capacity of 0.05 mg per gram of resin for cobalt.

Calibration

The calibration curve (Figure 5) for the determination of cobalt was prepared according to the general procedure under above developed the optimum condition. The detection limit was 35 ng/mL for cobalt at the minimum instrumental setting (signal-to-noise ratio = 3). The linearity was maintained in the concentration range of 0.1-5.0 $\mu\text{g/mL}$ cobalt in final DMF solution with a regression equation $Y = 0.0184 + 0.3016X$ with a correlation factor 0.9996. Seven replicate determinations of 5.0 μg of cobalt in final solution gave a mean $d^3A/d\lambda^3$ of 0.352 with a relative standard deviation of 1.2%. The sensitivity of the method ($d^3A/d\lambda^3$) is 0.302 mL/ μg was found from the slope of the calibration curve.

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 5.0 μg of cobalt and the general procedure was applied. The tolerance limit was set at the ion concentration required to cause a $\pm 3\%$ error in the determination of cobalt. The results obtained are given in Table 4. Among the anions examined, most could tolerate up to milligram levels except for EDTA, which interfered significantly because of the higher formation constants of Co-EDTA complexes than of the Co-Zincon complexes. Of the metal ions examined, many did not interfere up to mg levels except for Cu (II) and Zn (II).

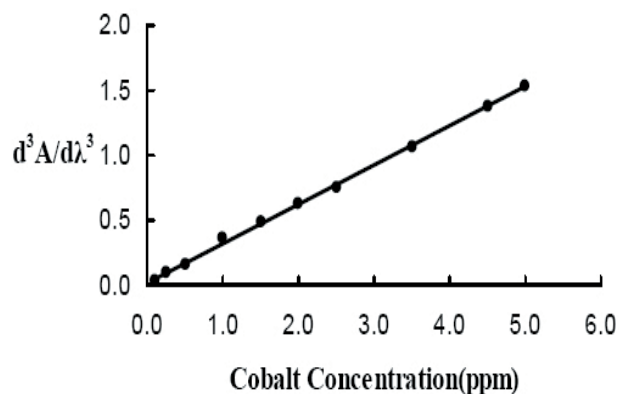


Figure 5. Calibration curve for cobalt by third derivative spectrophotometry from signal peak to peak measurements between $\lambda_1=649$ and $\lambda_2=680$ nm with $\Delta\lambda = 9$ nm. Conditions were the same as Figure 2.

Table 4. Effect of diverse salts and metal ions on the cobalt determination

Salt or ion	Tolerance limit/mg
Thiourea	25
KSCN	45
Sodium potassium tartrate	10
K ₂ S ₂ O ₃	20
K ₂ SO ₄	25
K ₂ CO ₃	40
Na ₂ EDTA	0.050
Ni(II), Tl(I), Mn(II), Ag(I)	1
Ca(II), Ce(IV), Sr(II)	3
NaF	10
Mg(II), Ir(III)	7
Pb(II), Cr(III)	0.75
Hg(II), Fe(III)	1.3
Al(III)	2.0
Cd(II)	0.3
Zn(II), Cu(II)	0.1

Conditions were the same as Table 1.

Conclusion

The proposed method is more sensitive and selective than the reported methods for the spectrophotometric determination of microgram amounts of cobalt. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference. It has been successfully applied to the determination of cobalt at trace level in standard and synthetic samples. The RSD value for real samples analysis is less than 1.5%, proving the versatility of the developed method.

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