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# Flame Atomic Absorption Spectrometric Determination of Cobalt(II) after Extraction and Preconcentration on to Modified Analcime Loaded with Zincon

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A simple, rapid, sensitive flame atomic absorption spectrometry method has been developed for the determination of trace amount of cobalt(II) in various samples after adsorption of its 2-[1-(2-hydroxy-5-sulfophenyl)-3-phenyl-5-formazano] benzoic acid monosodium salt (zincon) complex on modified Analcime by column method in the pH range 5–9 at flow rate 3 mL $min^{-1}$. The retained analyte on the analcime with recovered with 10.0 mL of 2 M hydrochloric acid solution and determined by flame atomic absorption spectrometry. Detection limit is 8 ng $mL^{-1}$ and calibration curve is linear in the range of 0.02–3.8 μg $mL^{-1}$ in final solution with correlation coefficient of 0.9997. Eight replicate determinations of 1.5 μg $mL^{-1}$ cobalt in final solution give absorbance of 0.140, with relative standard deviation of ±1.2%. The interference of a large number of anions and cations has been studied and the proposed method was used for determination of cobalt in various water and standard samples. Determination of cobalt in standard samples indicated that the proposed method has good accuracy.

**Key Words: Cobalt, Preconcentration, Zeolites, Flame atomic absorption spectrometry**

## INTRODUCTION

The significance of cobalt as a transition metal lies in its wide spectrum of applications covering many frontier areas of study, particularly in medicine. Even though cobalt is not considered to be toxic as most of the heavy metals, it is an equally harmful element. Hence owing to the significance of cobalt, its determination from associated elements has been of considerable importance. Dissolved cobalt occurs in the environment at concentrations ranging from 0.5 to 12 μg $L^{-1}$ in sea waters up to 100 μg $L^{-1}$ in waste water[1, 2]. High sensitivity procedures for the determination of cobalt generally use graphite furnace atomic absorption spectrometry after a preconcentration step, which usually involves the risk of sample contamination and analyte loss[1, 3–7]. Voltammetric techniques seem to overcome most problems, proving to be very useful even at low levels of cobalt[8, 9]. However, they suffer from interferences various electroactive compounds present in real samples, which are co-oxidized at the applied potential.

Zeolites are high crystalline alumino-silicate frameworks comprising $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral units. The atoms (Si, Al) are joined by an oxygen bridge. Introduction of an overall negative surface charge requires counter ions, *e.g.*, $Na^+$, $K^+$ and $Ca^{2+}$. Due to the charged nature of the framework and its ability

to form Bronsted acid sites, zeolites are useful catalysts for many applications[10]. Zeolites have been used in purification processes like gas swetting and air decontamination as well as in separation processes and it is believed that the attitude may be attributed to the absorption of cationic surfactants on to zeolite surface[11]. The potential of synthetic zeolites for the enrichment of metallic trace has been investigated[12]. Nevertheless, the potential of natural Analcime zeolite as useful material for the enrichment of metallic traces has not been investigated yet. Natural Analcime zeolite was collected from Torfeh, Shahr Babak area, Kerman region in Iran[13].

In the present work, the potential of analcime modified as adsorptive material for preconcentration of cobalt traces, by formation of its complex with zincon has been investigated. The method is economical (all reagents are cheap), rapid and sensitive.

## EXPERIMENTAL

A Varian model Spectra AA 220 atomic absorption spectrometer was used in the following conditions: wavelength, 240.7 nm; lamp current, 7.0 mA; slit width, 0.2 nm; acetylene flow, 1 L $min^{-1}$; air flow, 4 L $min^{-1}$. A Beckman pH-meter was employed for pH measurements. A funnel-tipped glass tube (80 × 10 mm) was used as a column for preconcentration. All glassware and columns were washed with a mixture of concentrated hydrochloric acid and concentrated nitric acid (1 : 1) before use. All reagents were of analytical reagent grade. A standard cobalt solution was prepared from cobalt(II) chloride in a standard flask and standardized by known methods[14]. A 0.1% solution of zincon in ethanol was prepared. A 0.5% solution of benzyl dimethyl tetradecyl ammonium chloride-dihydrate in water was prepared. Buffer solutions of pH 3–6, 6–8 and 8–11 were prepared by mixing appropriate ratios of 0.5 M acetic acid and 0.5 M sodium acetate solutions, 0.1 M potassium dihydrogen phosphate solution and 0.1 M disodium hydrogen phosphate solution, and 0.5 M ammonia solution and 0.5 M ammonium acetate solution, respectively. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations, respectively.

**Preparation of Analcime zeolite:** After purification of analcime, the zeolite was sieved to obtain a particle size < 150 μm (200 mesh). 20 mL hydrochloric acid (4 M) was added to 20 g zeolite for removal of the cation exit in Analcime and then washed with 100 mL distilled water. The adsorbent in this form was dried at 110°C in an oven and stored in a calcium chloride desiccator until used.

**Preparation and loading of column with zincon:** 1 g of the Analcime zeolite was added to a funnel tipped glass tube and 2 mL 0.5% solution of benzyl dimethyl tetradecyl ammonium chloride-dihydrate in water passed through the column. Then, the analcime was saturated with the reagent by passing 2 mL of a 0.1% zincon solution in ethanol at a flow rate 0.5 mL $min^{-1}$. Afterwards, it was washed with water until reagent excess was eliminated from the column. All experiments were done in a funnel-tipped glass tube (80 × 10 mm) as a column for preconcentration. Before sample loading, the column must be preconditioned by passing a buffer solution. Then, the column could be used repeatedly for ten

times at least. A 0.5% solution of benzyl dimethyl tetradecyl ammonium chloride-dihydrate in water was prepared.

**Procedure for the sorption of cobalt by column:** An aliquot of the solution containing 0.2–38.0 μg of cobalt was taken in a 50 mL beaker and 3 mL of buffer pH *ca.* 7.0 added to it, then diluted to *ca.* 30 mL with distilled water. Then, this solution was passed through the column at a flow rate 3 mL $min^{-1}$. After passing this solution, the column was eluted with 5 mL of distilled water. The adsorbed cobalt on the column was eluted with 10.0 mL of hydrochloric acid 2 M. The eluent was collected in a 10.0 mL volumetric flask and cobalt was determined by flame atomic absorption spectrometry.

## RESULTS AND DISCUSSION

**Reaction conditions:** The reaction conditions were investigated with 15 μg of cobalt. The sorption of cobalt on the column was found to be a maximum in the pH range of 5–9 (Fig. 1). In subsequent studies, the pH was maintained at approximately 7.

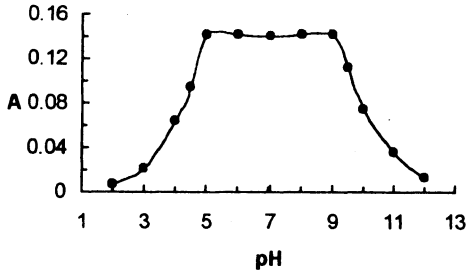


Fig. 1. Effect of pH on adsorption of cobalt complex. Conditions: Cobalt, 15.0 μg in final solution; buffer, 3 mL; flow rate of sample, 3 mL $min^{-1}$; final solution, 10.0 mL of 2 M HCl solution; flow rate eluent, 0.5 mL $min^{-1}$; reference, reagent blank. Instrumental setting: Wavelength, 240.7 nm; current lamp, 7 mA; slit width, 0.2 nm; acetylene flow, 1 L $min^{-1}$; air flow, 4 L $min^{-1}$.

Addition of 1–5 mL of buffer did not have any effect on the adsorption. Therefore, 3.0 mL of the buffer, pH *ca.* 7, was used in all subsequent experiments.

The flow rate of sample solution varied from 1–10 mL $min^{-1}$. It was found that a flow rate of 1–6 mL $min^{-1}$ did not affect adsorption. A flow rate of 3 mL $min^{-1}$ was recommended in all experiments.

The flow rate of eluent solution was varied from 0.2–2 mL $min^{-1}$. It was found that a flow rate of 0.2–1.0 mL $min^{-1}$ did not affect adsorption. A flow rate of 0.5 mL $min^{-1}$ was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10–1000 mL under the optimum conditions, keeping the other variables constant. It was observed that the absorption was almost constant up to 700 mL. However, for convenience, all the experiments were carried out with 30 mL of the aqueous phase.

A number of eluents are tried to desorb cobalt from the column. Organic solvents can be used as eluent but remove the zincon reagent from the column. If acid solutions as eluent are used, the reagent is retained on the column and therefore allows using the column several times. Preliminary observations indicated that 2 M HCl better than 2 M $HNO_3$ and $H_2SO_4$ desorbed cobalt. For further enhancing the sensitivity and the preconcentration factor of the method minimum volume of eluent must be used. Hence, 10.0 mL of hydrochloric acid 2 M was used in the present work.

**Sorption capacity of analcime for ligand and cobalt:** The sorption capacity of the Analcime zeolite for ligand and cobalt was also evaluated. Analcime has sorption capacities of 1.5 and 0.06 mg per g of Analcime for ligand and cobalt, respectively.

**Calibration and sensitivity:** Detection limit is 8 ng $mL^{-1}$ and calibration curve is linear in the range of 0.02–3.8 μg $mL^{-1}$ in final solution with correlation coefficient of 0.9997 (Fig. 2). Eight replicate determinations of 1.5 μg $mL^{-1}$ cobalt in final solution give absorbance of 0.140, with relative standard deviation of ±1.2%. Sensitivity for 1% absorbance was 0.049 μg $mL^{-1}$.

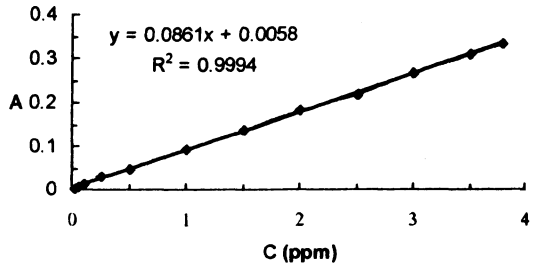


Fig. 2. Calibration curve for cobalt. Conditions and instrumental setting were same as Fig. 1.

**Effect of diverse ions:** Various salts and metal ions were added individually to a solution of containing 15 μg of cobalt and the general procedure was applied. The tolerance limit was set as the concentration of the diverse ion required to cause ±3% error in the determination of cobalt. The results obtained are given in Table-1. Among the salts examined, most could be tolerated up to gram or milligram levels except EDTA. Of the metal ions examined, many did not interfere up to mg levels. Thus, the proposed method is selective and can be used for the determination of cobalt in various samples without any prior separation.

**Analysis of cobalt in water samples:** The method has been employed for determination cobalt in well water, river water and drinking water of several cities. A 100 mL water sample was adjusted to pH 1.5 with nitric acid, 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 flame atomic absorption spectrometry (using standard addition method). The results are given in Table-2.

TABLE-1
EFFECT OF DIVERSE SALTS AND METAL IONS ON COBALT DETERMINATION

| Salt or ion | Tolerance limit (mg) |
|---|---|
| Thiourea | 25 |
| KSCN | 45 |
| Sodium potassium tartrate | 10 |
| $K_2S_2O_3$ | 20 |
| $K_2SO_4$ | 25 |
| $K_2CO_3$ | 40 |
| $Na_2EDTA$ | 50 μg |
| 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) | 1.2 |
| Fe(III) | 0.5 |
| Al(III), Cd(II) | 0.3 |
| Zn(II), Cu(II) | 0.1 |

Conditions: Cobalt, 15.0 μg in final solution; buffer, 3 mL; flow rate of sample, 3 mL $min^{-1}$; final solution, 10.0 mL of 2 M HCl solution; flow rate of eluent, 0.5 mL $min^{-1}$; reference, reagent blank. Instrumental settings: Wavelength, 240.7 nm; current lamp, 7 mA; slit width, 0.2 nm; acetylene flow, 1 L $min^{-1}$; air flow, 4 L $min^{-1}$.

TABLE-2
ANALYSIS OF COBALT IN WATER SAMPLES

| Sample | Recommended procedure[a] (ng $mL^{-1}$) | FAAS[b] (ng $mL^{-1}$) |
|---|---|---|
| Spring water | 15.8 ± 0.3 | 16.0 ± 0.4 |
| River water of Rayen in Kerman | 24.1 ± 0.4 | 24.5 ± 0.5 |
| Tehran drinking water | 7.5 ± 0.2 | 7.8 ± 0.5 |
| Kerman drinking water | 9.1 ± 0.3 | 9.0 ± 0.4 |

[a]Average of five determinations, ±standard deviation.
[b]Direct FAAS using the method of standard additions.
Conditions and instrumental settings were same as in Table-1.

**Analysis of cobalt in pepperbush and pond sediment samples:** The accuracy and applicability of the proposed method has been applied to the determination of cobalt in National Institute for Environment Studies (NIES) No. 1 pepperbush and NIES No. 2 pond sediment. A 0.1 g sample was taken in a beaker and dissolved in concentrated nitric acid (*ca.* 5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made 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-3 which is in good agreement with the certified value.

TABLE-3
ANALYSIS OF PEPPERBUSH AND POND SEDIMENT FOR COBALT

| Sample | Composition | Found[a] |
|---|---|---|
| NIES, No. 1 Pepperbush | K, 1.51 ± 0.06; Mn, 0.203 ± 0.17; Ca, 1.38 ± 0.07; Mg, 0.408 ± 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; Cr, 1.3; Zn, 340 ± 20; Ba, 165 ± 10; Sr, 36 ± 4; As, 0.3 ± 0.3; Rb, 75 ± 4; Na, 106 ± 13; Hg, 0.05 μg $g^{-1}$ | 23.6 ± 0.5 |
| 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 μg $g^{-1}$ | 26.6 ± 0.5 |

[a] Average of five determinations, ±standard deviation.
Conditions and instrumental settings were same as in Table-1.
NIES: National Institute of Environmental Studies reference materials.

**Analysis of cobalt in synthetic samples:** The accuracy and applicability of the proposed method has been 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 volume was made to 100 mL in a standard flask. An aliquot of the sample solution was analyzed by the general procedure and the results are given in Table-4.

TABLE-4
ANALYSIS OF COBALT IN SYNTHETIC SAMPLES

| Composition of synthetic sample (μg/g) | Expected value (μg/g) | Amount found by the present method[a] (μg/g) |
|---|---|---|
| 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 ± 0.1 |
| 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 ± 0.10 |
| 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 ± 0.07 |

[a] Average of five determinations, ±standard deviation.
Conditions and instrumental setting were same as in Table-1.

## Conclusion

The aim of this study was to develop a suitable method for preconcentration and determination of Co(II) by flame atomic absorption spectrometry in biological samples with precision better than 1.5% and a recovery rate better than 95% of the expected concentration. The results of our study indicate that the procedure proposed, consisting of preconcentration of Co(II) followed by flame atomic absorption spectrometry measurement in the aqueous phase, can accurately determine Co(II) in various samples. The main advantages of this procedure are: (I) natural analcime is very cheap; (II) the preparation of the extractor system is simple and fast; (III) during cobalt desorption, the zincon reagent remains in the column, that allows using the column several times; (IV) a good enrichment factor (70) can be achieved.

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