



Solid Phase Extraction and Flame Atomic Absorption Spectrometry for the Determination of Cobalt

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A solid phase extraction and flame atomic absorption spectrometry for the determination of cobalt with SEPABEADS SP825 resin as sorbent was studied. Cobalt complexed with 2-ethylhexyl benzimidazolyl sulfide (EHBMS) was preconcentrated on a nonpolar resin SEPABEADS SP825 and 2-methoxyethanol was used as eluent. The effects of various parameters such as acidity, flow rate of sample and eluent, type of eluent, amount of adsorbent and interfering ions have been studied. The cobalt in 300 mL solution can be concentrated to 5.0 mL, representing an enrichment factor of 60 was achieved. The detection limit for 300 mL of sample was $0.16 \mu\text{g L}^{-1}$ using flame atomic absorption spectrometry. The analytical result for the certified reference sample (GBW07301a) was in a good agreement with the certified value. The relative standard deviation for ten replicate measurements of $10 \mu\text{g L}^{-1}$ cobalt was 2.9 %. The method was successfully applied to the determination of trace amount cobalt in water samples.

Key Words: Solid phase extraction, Cobalt, 2-Ethylhexyl benzimidazolyl sulfide, Flame atomic absorption spectrometry.

INTRODUCTION

Cobalt is an important element, not only for industry but also for biological systems. Cobalt is one of the heavy metals and exists in the vast majority of industrial effluents and waste waters, such as mining effluents, etching or pickling baths, dilute leaching solutions generated during hydrometallurgy, electroplating rinse liquors, *etc.*¹. As an essential biochemical element, cobalt is mainly stored in red blood cells with smaller amounts in kidney, liver pancreas and spleen. Cobalt is an essential micronutrient for man, animals and plants for a range of metabolic processes. Insufficient natural levels of cobalt in feed cause co-deficiency diseases characterized by anemia, loss of weight, or retarded growth². However, in larger amounts it is toxic and has been reported to produce pulmonary disorders, dermatitis, nausea, vomiting, diarrhea, blood pressure, slowed respiration, giddiness cardiomyopathy, hyperglycemia and enlargement of the thyroid gland³.

Many methods have been reported for the determination of ultratrace amounts of cobalt, including neutron activation analysis, graphite furnace atomic absorption spectrometry, wavelength dispersive X-ray spectrometry, inductively coupled plasma (ICP) atomic emission spectrometry, ICP-mass spectrometry and high performance liquid chromatography⁴⁻¹⁵. However, the analysis of samples by readily available and low cost flame atomic absorption spectrometry demands the use of

preconcentration procedures in view of its insufficient sensitivity and matrix interference.

The aim of this work is to combine solid phase extraction (SPE) with flame atomic absorption spectrometry (FAAS) and develop a new method for the determination of cobalt. In this method 2-ethylhexyl benzimidazolyl sulfide (EHBMS), which reacts with Co(II) forming a stable Co(II)-EHBMS complex. Subsequently, water sample containing Co(II)-EHBMS complex was passed through SEPABEADS SP825 resin. Cobalt complexed with EHBMS were preconcentrated on a non-polar resin SEPABEADS SP825. The Co(II)-EHBMS complex adsorbed on SEPABEADS SP825 resin was eluted with 2-methoxyethanol. The levels of analyte ions in the samples were determined by flame atomic absorption spectrometry. The optimum analytical conditions for the quantitative recoveries of cobalt on SEPABEADS SP825 adsorption resin were investigated.

EXPERIMENTAL

Synthesis of 2-ethylhexyl benzimidazolyl sulfide (EHBMS): Synthesis of 2-ethylhexyl benzimidazolyl sulfide was synthesized according to the following procedure: 2-mercaptobenzimidazole (0.1 mol), acetone (150 mL) and KOH (0.1 mol) were put in a round-bottom fitted with a mechanical stirrer and condenser and the mixture was heated for about 20 min. 2-Ethylhexyl bromide (0.1 mol) was then added gradually with stirring through a dropping funnel and

the reaction mixture was refluxed for 3 h. The residual solid was filtered after cooling down and the acetone was removed by distillation. The organic phase was diluted with ether (50 mL), washed with water two times and dried with anhydrous Na_2SO_4 . The ether was evaporated and EHBMS was obtained. The precipitate was re-crystallized from ethyl acetate to give a yield of 75 %. Melting point of the obtained product was 76–78 °C. Its structure (Fig. 1) was verified by elemental analysis, ^1H NMR, ^{13}C NMR and mass spectra. The results of elemental analysis are listed below: $\text{C}_{15}\text{H}_{22}\text{N}_2\text{S}$, calcd. (%) (found), C 68.66 (68.76), H 8.46 (8.26), N 10.68 (10.62); ^1H NMR (500 MHz, CDCl_3) δ 7.55–7.53 (m, 2H), 7.18–7.17 (m, 2H), 3.40–3.36 (m, 2H), 1.67–1.64 (m, 1H), 1.40–1.30 (m, 4H), 1.18–1.17 (m, 4H), 0.81–0.78 (m, 6H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 151.81, 139.48, 122.13, 114.22, 39.13, 37.13, 32.26, 28.65, 25.50, 22.90, 13.98, 10.65 ppm; HRMS(ESI) m/z , calcd. (%): 263.1576 (M + H)⁺; found (%): 263.1569 (M + H)⁺.

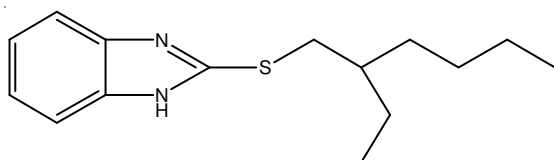


Fig. 1. Structure of 2-ethylhexyl benzimidazolyl sulfide (EHBMS)

Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan) was used to measure the concentration of Co(II). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Co 240.7 nm. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China). A peristaltic pump mode FIA-3110 (Titan Instruments Co., Ltd. Beijing, China) was used in the solid phase extraction process.

SEPABEADS SP825 resin was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). SEPABEADS SP825 resin is an aromatic type adsorbent (75–150 μm particle size). It is based on crosslinked polystyrenic matrix. SEPABEADS SP825 is widely used in different industrial fields^{16,17}.

A 0.5 % (w/v) solution of EHBMS was prepared by dissolving an appropriate amount of EHBMS in ethanol. All other reagents used were of the highest available purity and of at least analytical reagent grade. Ultra-pure water of resistivity 18 MO cm obtained from a UPHW purification device (Ulupure Co. Shanghai, China) was used to prepare all the solutions.

All glass and plastic material were thoroughly cleaned and kept into 10 % (m m^{-1}) nitric acid for at least 48 h. The material was then rinsed three times with ultra-pure water before being used. Standard stock solutions of Co(II) (1000 mg L^{-1}) was obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution.

Solid phase extraction: The stopcock of the glass column (80 mm in length and 8 mm in diameter) was covered with a fritted glass disc. A total of 500 mg of SEPABEADS SP825 resin was poured into the column. A small amount of glass wool was placed on the disc to prevent loss of the resin beads during sample loading. It was washed successively with

methanol, water, 1.0 mol L^{-1} HNO_3 in acetone, water, 1.0 mol L^{-1} NaOH and water, sequentially. The solution containing Co(II) was passed through the column at a flow rate of 8 mL min^{-1} (controlled by a peristaltic pump) after adjusting pH 5.0. The metal ions were stripped from the resin bed by using 5 mL 2-methoxyethanol and determined by FAAS. A blank solution was also run under the same conditions without adding the analytes.

Sample preparation: For sediment reference material (GBW 07301a China), 200 mg of the sediment sample was accurately weighed into a 100 mL beaker and aqua regia (15 mL concentrated hydrochloric acid and 5.0 mL of concentrated nitric acid) was added to the sample. The beaker was covered with a watch glass and the mixture was evaporated on a hot plate at 100 °C almost to dryness. Then 20.0 mL of aqua regia was added to the residue and the mixture was again evaporated to dryness. After cooling, resulting mixture was filtered using whatman No. 1 filter paper (pore size, 11 μm). The filtrate was diluted to 100 mL with distilled water and was analyzed by the preconcentration procedure given above.

For water samples, river water sample was collected from Tanglang chuan River (Kumming, P.R. China). Tap water sample was freshly collected from our laboratory. All water samples were immediately acidified by adding several drops of nitric acid and filtrated with 0.45 μm filter. Then the preconcentration procedure given above was applied to the samples.

Flame atomic absorption spectrometric analysis: The FAAS analysis condition is listed in Table-1. The atomic absorption signals were measured with the Zeeman background corrector in operation. The measurement was repeated 3 times and the obtained signals were averaged.

TABLE-1
SETTING OF ANALYTICAL CONDITIONS

Analytical condition	Cobalt
Calculation mode	Integral
Wavelength (nm)	240.7
Slit width (nm)	0.2
Lamp current (mA)	12.5
Burner height (mm)	7.5
Fuel gas flow rate L min^{-1}	2.0

RESULTS AND DISCUSSION

Effect of pH: The acidity of the sample solution is one of the important factors affecting the formation of Co(II)-complex and the subsequent solid phase extraction. According to the results (Fig. 2), quantitative recoveries (> 95 %) for analytes were obtained. The optimum pH range is 4.0–6.0. The pH was adjusted to the desired value with aqueous ammonia and diluted HNO_3 . Therefore, to obtain the maximum extraction efficiency, pH of the sample solution should be carefully adjusted at pH 5.

Influences of ligand amount: In order to determine the amounts of EHBMS required for quantitative recovery for Co(II), the proposed method was applied. Changing the EHBMS amounts (0.5 % solution) at the range of 1–10 mL. The results showed that the recovery values of the analyte Co(II) were increased with increasing amounts of EHBMS

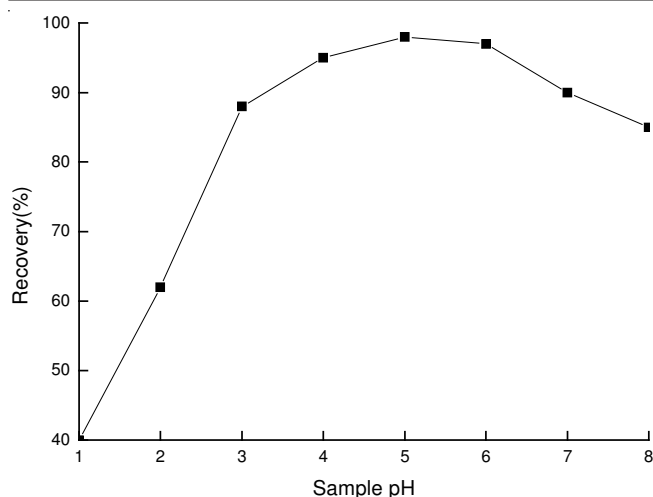


Fig. 2. Influences of acidity on the recovery of cobalt. Conditions: sample volume: 300 mL; flow rate: 8 mL min⁻¹; amount of the resin: 500 mg

added. The recovery reaches a constant value with at least 3.0 mL of 0.5 % EHBMS solution used. On this basis, studies were carried out at EHBMS amounts of 5.0 mL. This amount of EHBMS is enough for the separation and preconcentration procedure because of the low level of the investigated Co(II) concentrations in real samples.

Effects of the amount of resin: The amounts of solid phase extraction material are another important factor on the column studies for the quantitative recoveries of metal complexes. The effect of the amount of SEPABEADS SP825 resin on the sorption of metal ions was examined in the range of 200-800 mg. The results demonstrated that, quantitative recoveries (> 95 %) of cobalt was observed in the range of 500-800 mg. Above 800 mg the recoveries were below 95 % with 5.0 mL of the eluent. Therefore, in the proposed procedure, 500 mg of SEPABEADS SP825 resin is recommended.

Effect of flow rate of sample solution and eluent: The influence of flow rate on the adsorption of Co(II)-EHBMS complex was also studied. Flow rate in the range of 1-10 mL min⁻¹ had no significant effect on the recoveries of Co(II). Therefore, in the proposed procedure, 8 mL min⁻¹ flow rate is recommended.

Among several media investigated as eluent (ethanol, methanol acetone, pentanol, thiourea, ethyl acetate, 2-methoxyethanol), only 2-methoxyethanol showed satisfactory elution characteristics. 5.0 mL 2-methoxyethanol provided quantitative recovery (> 95 %) and reproducibility. The flow rate of eluent solution was examined in the range of 0.5-2.0 mL min⁻¹. Maximum recoveries for cobalt was obtained in the range of 0.5-1.5 mL min⁻¹. The flow rate of 1.0 mL min⁻¹ was chosen as optimum value.

Loading capacity: To 0.1 g resin was placed in the conical flasks. Stock solution of Co(II) and EHBMS were added to the flask. Acidity of the solution was adjusted to pH 5 using aqueous ammonia and diluted HNO₃. After shaking for 4 h, the mixture was filtered. Concentration of Co(II) was measured by FAAS. The loading capacity of SEPABEADS SP825 resin was 80 µg g⁻¹ for cobalt.

Maximum sample volume and enrichment factor: The enrichment factor was studied following recommended column

procedure by increasing volume of Co(II) solution and keeping the total amount of loaded Co(II) constant to 6.0 µg. For this purpose, 100, 150, 200, 250, 300, 350 and 400 mL of sample solutions containing 6.0 µg Co(II) were passed through the column at the optimum flow rate. The results showed that the maximum sample volume could be up to 300 mL with the recovery > 95 %. Therefore, 300 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. And a high enrichment factor of 60 was obtained.

Limit of detection: Using the optimized conditions of preconcentration, calibration curve was prepared for Co(II). The limit of detection (LOD) value (blank + 3σ)^{18,19}, where σ is standard deviation of blank determination (n = 10), were found to be 0.16 µg L⁻¹. The relative standard deviation for ten replicate measurements of 10 µg L⁻¹ cobalt was 2.9 %. SEPABEADS SP825 resin can be reused at least 80 times.

Effect of neutral electrolytes and coexisting metal ions: Various neutral electrolytes, viz., NaCl, NaNO₃, Na₂SO₄, CaCl₂ and MgCl₂ at 0.2 mol L⁻¹ level and 800 µg of coexisting metal ions, viz., Cd, Cu, Zn and Ni do not have any deleterious effect on the enrichment of 6 µg cobalt present in 300 mL of aqueous solution during enrichment with 500 mg of SEPABEADS SP825 resin.

Applications of the presented procedure: In order to establish the validity of the proposed procedure, the method has been applied to the determination of Co in sediment reference material (GBW 07301a China). The results are given in Table-2.

TABLE-2
DETERMINATION OF COBALT (µg g⁻¹) IN THE CERTIFIED REFERENCE MATERIALS AFTER APPLICATION OF THE PRESENTED PROCEDURE (n = 5)

Sample	Certified value (µg g ⁻¹)	Present value (µg g ⁻¹)
GBW07301a	20.0 ± 2.0	20.5 ± 1.2

The proposed method was applied to determine of Co in water samples. The results for water samples were given in Table-3. The results indicate that the recoveries in the range of 94.0-101.0 % are reasonable well for trace analysis.

TABLE-3
DETERMINATION OF Co (µg L⁻¹) IN WATER SAMPLES (n = 5)

Samples	Added	Found* by present method	Recovery (%)
River water	0	4.2 ± 0.1	–
	10	14.3 ± 0.2	101
	15	19.0 ± 0.5	98.7
Tap water	0	BDL	–
	10	9.4 ± 0.2	94.0
	15	14.6 ± 0.3	97.3

–: Not determined; BDL: below the detection limit. *Mean ± SD.

Conclusion

A new method of solid phase extraction combined with flame atomic absorption spectrometry has been proposed for the determination of cobalt in water sample. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of SEPABEADS SP825 resin was as high as greater than 80 cycles without any loss in its sorption behaviour. The tolerance limits of interfering ions on the recovery of

cobalt ions are quite high. The results acquired from the analyses of the certified reference sample confirmed the reliability of the method. The method suitable for the determination of trace amount of cobalt in water samples

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