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Determination of ultra-trace cobalt ion by ET-AAS after preconcentration by pyridine-functionalized magnetic nanoparticles

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Abstract : We present a study on the application of magnetic nanoparticles (MNPs) prepared from Fe₃O₄ and functionalized with pyridine as an adsorbent for the solid-phase extraction of trace quantities of Co(II) ion. The pyridine group was immobilized on the surface of the MNPs by covalent bonding of isonicotinamide. The modified MNPs can be readily separated from an aqueous solution by applying an external magnetic field. Effects of pH, the amount of functionalized MNPs, type and quantity of eluent, desorption time on the extraction efficiency were optimized. The amount of Co (II)

was then determined using Electrothermal Atomic Absorption Spectroscopy (ETAAS). Under the optimized conditions, the detection limit and preconcentration factor are 0.11 µg L⁻¹ and 200, respectively, and the relative standard deviation (at 10 µg L⁻¹; for n=5) is 3.5 %. The method had a linear analytical range from 0.10 to 80 µg L⁻¹ and was applied to determine Co (II) in water samples. © Global Scientific Inc.

Keywords : Cobalt; Atomic absorption spectroscopy; Pyridine; Nanoparticles magnetic.

INTRODUCTION

Cobalt is a natural element found throughout the environment and used to make super alloys (alloys that maintain their strength at high temperatures approaching their melting points) and in pigment manufacture. It can benefit or harm human health. In general, heavy metal ions are toxic, non-biodegradable, and tend to be accumulated in vital human organs, where they can

act progressively over a long period through food chains. The determination of trace heavy metal ions in environmental samples has received increasing attention. Some trace elements are essential to man, whose daily requirement is only a few milligrams. However, if ingested in high levels, this can be harmful to human health. Thus, the elemental composition is essential to ensure food quality^[1]. Cobalt is an essential trace element that has an important role in many bodily functions. It is toxic in

large amounts and chronic ingestion of Co in the daily diet can cause toxic effects^[2]. Toxicological effects of cobalt include vasodilatation, flushing and cardiomyopathy in humans and animals^[3]. There is great interest in the determination of trace levels of Co (II) in environmental investigations because cobalt affects living species as complexed Vitamin B12.

The quantification of metal species in various matrices has been performed by different techniques, including flame atomic absorption spectrometry (FAAS)^[4], graphite furnace atomic absorption spectrometry (GFAAS)^[5] and inductively coupled plasma optical emission spectrometry (ICP-OES)^[6], among others. However, these techniques do not have adequate sensitivity and selectivity for some analyses. Thus, procedures of separation or preconcentration may be required to purify the sample and remove matrix interference before the determination of trace elements. In recent decades the developments of preconcentration steps prior to analytical determinations of trace level compounds have been explored in considerable depth. In this way, a number of accurate and reliable methods have been developed for Co (II) determination^[7-12]. In addition, the preconcentration and determination of cobalt (II) have been studied by various extraction methods such as: liquid-liquid extraction (LLE), flow injection extraction (FIE), cloud point extraction (CPE), solid phase extraction (SPE), and dispersive liquid-liquid microextraction (DLLME). New (LLE) methods based on liquid membranes^[13,14] and hollow fiber contactors^[15] were used for extraction and preconcentration of cobalt. However, these methods are time-consuming and tedious. Also the use of large amounts of high purity expensive solvents is inevitable. The continuous quest for novel sample preparation procedures has led to the development of new methods, which have main advantages such as rapidity and reduction of solvents consumption. Initial efforts to address the problem of large solvent consumption have led to the development of the (FIE) method. Some of these methods have been applied for cobalt extraction^[16-27].

EXPERIMENTAL

All analytical grade reagents were purchased from

Merck (Darmstadt, Germany) or from Fluka (Buchs SG, Switzerland) and used without further purification. The following buffer solutions were used for various pHs: pH 1 and 2, KCl/HCl, pH 4–6 CH₃COOH/CH₃COONH₄, pH 6–8 Na₂HPO₄/NaH₂PO₄ and pH 8–10 NH₃/NH₄Cl. The standard solution of Cobalt (II), 1000 mg L⁻¹, 3-aminopropyltriethoxysilane, oxalyl chloride and 4-pyridine carboxylic acid were purchased from Merck. All solutions were prepared using deionized water.

Cobalt concentration was determined by ET-AAS 5100 (PERKIN ELMER) electrothermal atomic absorption spectrometer (ET-AAS), according to the user's manual, provided by the manufacturer. Cobalt hollow cathode lamp was used as the radiation source with wavelength of 240.73 nm. The pH was measured at 25±1 °C with a digital WTW pH (Germany). A vacuum pump was obtained from Leybold (Cologne, Germany) and an adjustable vacuum gauge and controller were obtained from Analytichem International (Harber City, CA).

Fe₃O₄ nanoparticles were synthesized according to the previously reported procedure^[28] and Preparation of pyridine functionalizing agent (N-3-(triethoxysilyl)propyl)isonicotinamide according to the previously reported procedure^[29,30].

Pyridine functionalized Fe₃O₄ nanoparticles were synthesized according to the previously reported procedure^[31]. In a typical reaction, 1.0 g of Fe₃O₄ nanoparticles was suspended in 70 mL of toluene, afterward 1.0 g of TPI was added and the mixture was refluxed for 24 h. The solid phase was filtered from the solvent and washed 3 times with 50 mL of ethanol in order to remove any impurities and then dried at room temperature. Functionalization of pyridine functionalized Fe₃O₄ nanoparticles was confirmed by XRD pattern (Figure 1), IR spectroscopy, thermal and elemental analyses.

The sample was digested in a mixture of concentrated nitric acid and hydrogen peroxide, using a microwave oven to dissolve the Co (II). Rapid digestion procedure for HNO₃ with hydrogen peroxide (H₂O₂) digestion of plant material by using a closed-vessel, microwave-digestion system (Anton paar). The proposed method consists of two stages: (1) the predigested (overnight) sample and HNO₃ mix is heated at 75°C for 10

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min, followed by 109°C for 15 min; (2) after cooling for 10 min, 1 mL of H₂O₂ is added to each vessel through the ventilation hole and the sample mix is heated at 110°C for a further 15 min. The analytical results were statistically analyzed by using linear regression, linear correlation, and two independent means tests to determine analytical precision and accuracy of the proposed digestion method.

A portion of sample solution containing the studied ions was transferred to a 500 mL beaker, the pH values was adjusted to desired value with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NH₃·H₂O, and the final volume was diluted to desired volume. Then, 15 mg of adsorbent was added, and the solution was shaken for 3 min to facilitate adsorption of the Co (II) onto the modified MNP. Then the magnetic adsorbent was separated readily by using a strong flat permanent magnet and the supernatants were decanted directly, washed with 5 mL deionized water and then decanted directly. Finally, 2.5 mL of 0.5 mol L⁻¹ thiourea in 0.4 mol L⁻¹ HCl was added as eluent and shaken for 3 min and the eluted ions were determined by ETAAS.

RESULT AND DISCUSSION

Extraction and preconcentration of cobalt ions on Py-Fe₃O₄ NPs were highly dependent on the different parameters such as pH of the sample, extraction time, type, volume and concentration of eluent, desorption time, sample volume and concentration of coexisting ions. In this context, the procedure was optimized for the various analytical parameters.

To study the effect of pH on the extraction, the pH of 25 mL of different sample solutions containing 3 μg L⁻¹ cobalt was adjusted in the range of 1–10. The obtained results in Figure 2 indicate that the Co (II) ions could be retained quantitatively on functionalized Fe₃O₄ NPs in the pH range of 2–6.

The results suggest that adsorption has two mechanisms: ion pair and coordination ability. Therefore, pH 3.0 was chosen as the optimum pH for further studies.

Compared to conventional sorbents (microsized adsorbents), NPs offer a significantly higher surface area-to volume ratio and a short diffusion route, which results in high extraction capacity, rapid extraction dynamics and high extraction efficiencies. Also, MNPs

can be rapidly collected from sample solution by applying magnetically assisted separation, thus shorter extraction times can be achieved. Therefore, satisfactory results can be obtained with fewer amounts of these adsorbents. For the optimization of the amount of adsorbent, 5, 10, 15, 20, 25, and 30 mg of the MNP were tested (Figure 3).

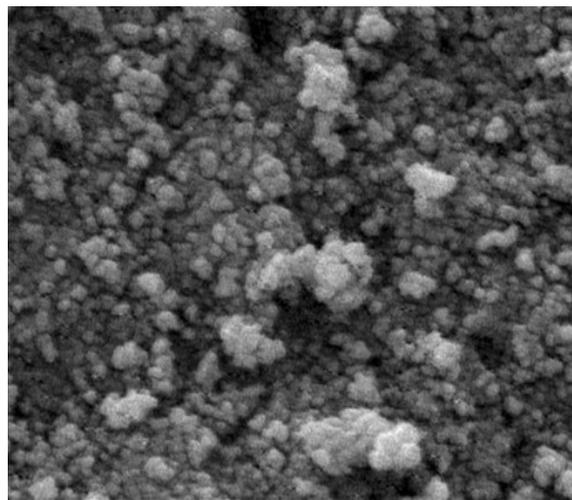


Figure 1 : SEM micrograph pyridine - functionalized Fe₃O₄ nanoparticles

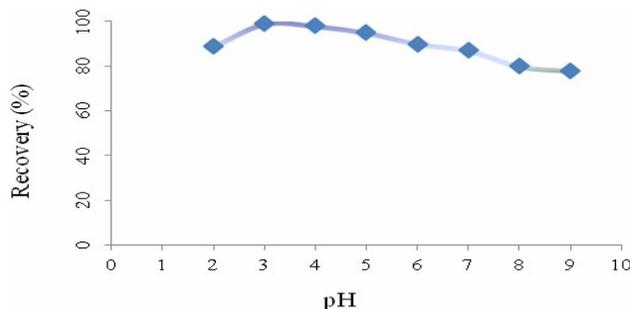


Figure 2 : Effect of sample pH on recovery of Co(II) ions on the Pyridine- Fe₃O₄ NPs (Condition: 5 μg L⁻¹ of cobalt, shaking time : 3 min and room temperature)

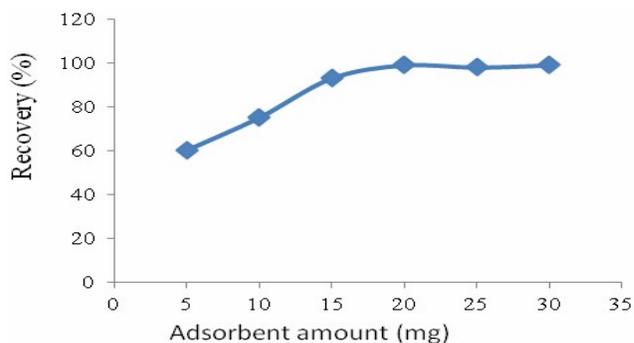


Figure 3 : Effect of adsorbent amount recovery Co(II) ions on the Pyridine- Fe₃O₄ NPs (Condition: 5 μg L⁻¹ of cobalt, Shaking time : 3 min and room temperature, pH: 3)

In the present work, by increasing amounts of the Py-Fe₃O₄ NPs due to increase in the surface area and accessible sites to the adsorption of the analytes, the extraction efficiency increased. Quantitative extraction of the cobalt ions was achieved using only 20 mg of the Py-Fe₃O₄ NPs. At higher amounts of the adsorbent, the extraction efficiency was almost constant.

In order to investigate the effect of shaking time on the extraction efficiency, extraction experiments were carried out at 1, 2, 3, 4, 7, 12, and 20 min time intervals. According to the results, an equilibration time of about 3 min was required for quantitative extraction of the analyte from solution into solid phase. Thus, the mixtures have been shaken for 3 min to reach equilibrium in the subsequent experiments.

As the surface of Fe₃O₄ nano-particles coated with a silica layer, this composite is stable in high concentrations of acids without any leak of Fe³⁺ or Fe²⁺ in solution. So a series of selected eluent solutions, including HNO₃, HCl, HCl/thiourea, HNO₃/thiourea and CH₃COOH were used for elution of cobalt ions from Py-Fe₃O₄ NPs. The results show that 0.4 mol L⁻¹ thiourea in 0.4 mol L⁻¹ HCl is a suitable and effective eluent to elute cobalt ions from Py-Fe₃O₄ NPs. Also the results show, quantitative recovery could be obtained with 2.0 mL of 0.4 mol L⁻¹ thiourea in 0.4 mol L⁻¹ HCl. Therefore, a 2.0 mL volume of eluent for desorption of cobalt ions was used in the following experiments. Desorption times were evaluated in the range of 1–15 min. The results showed that the time of 3 min is sufficient for quantitative desorption of the cobalt ions by 2.0 mL of the 0.4 mol L⁻¹ thiourea in 0.4 mol L⁻¹ HCl.

Due to the low concentrations of trace metals in real samples, by using samples with large volumes, the trace metals in these volumes should be taken into smaller volumes for high preconcentration factor. Hence, the maximum sample volume was optimized by the investigation of the recovery of cobalt ion in various real samples, volumes in the range of 5–100 mL containing 0.01 mg of cobalt was used to study. In the optimization of the sample volume, 15 mg of the sorbent was used. The recovery of Co (II) ion from different volumes of aqueous solutions was shown in Electronic Supplementary Material. The recovery was found to be stable until 25 mL and was chosen as the largest sample volume to work (TABLE 1).

TABLE 1 : Results obtained for analysis of the target compounds in different dust samples.

Sample	Concentration (µg L ⁻¹)	Co ⁺²
Tap Water (10.0 µg L ⁻¹ added)	Concentration (µg L ⁻¹)	ND*
	Found (µg L ⁻¹)	9.6
	Recovery (%)	96
	RSD% (n = 10)	3.4
Rain Water (20.0 µg L ⁻¹ added)	Concentration (µg L ⁻¹)	ND
	Found (µg L ⁻¹)	20.4
	Recovery (%)	102
	RSD% (n = 10)	3.3
Towhid tunnel (25.0 µg L ⁻¹ added)	Concentration (µg L ⁻¹)	ND
	Found (µg L ⁻¹)	26.1
	Recovery (%)	104
	RSD% (n = 10)	2.7
Potato sample (50.0 µg L ⁻¹ added)	Concentration (µg L ⁻¹)	ND
	Found (µg L ⁻¹)	52.5
	Recovery (%)	105
	RSD% (n = 10)	3.9

Because of the presence of other elements in real samples, the determination and preconcentration of cobalt ion is difficult. So, the effects of common coexisting cations and anions on the adsorption of cobalt ions on the Py-Fe₃O₄ NPs were investigated. In these experiments, 25 mL of solution containing 0.01 mg cobalt ions were added to interfering cations and anions and treated according to the recommended procedure. The results in TABLE 2 show that majority of transition, alkaline, and earth alkaline metals do not interfere at environmentally relevant concentrations. This is due

TABLE 2 : The tolerance limit of various ions on the determination of Cobalt (condition: sample pH = 3.0, sample volume=25 ml, 0.01 µg L⁻¹ of Cobalt ion, Shaking time: 3 min, eluent 2 mL of 0.5 mol L⁻¹ thiourea in 0.4 mol L⁻¹ HCl and desorption time: 3 min)

Tested ions	Tolerance limit (Ratio of interference concentration to Co ⁺²)
[Cl ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , Na ⁺ , K ⁺ , PO ₄ ³⁻ , F ⁻ , Mg ²⁺ , CH ₃ CO ₂ ⁻ , C ₂ O ₄ ²⁻ , C ₁₀ H ₁₄ O ₈ ²⁻ , SO ₄ ²⁻ , SCN ⁻ , Ir ³⁺ , Pt ⁴⁺ , Au ³⁺ , Rh ³⁺]	< 1000
Ag ⁺ , Cr ³⁺ ,	< 150
Ni ²⁺	< 250
Hg ²⁺ , Al ³⁺ , Cd ²⁺ , Cu ²⁺	< 200
Fe ³⁺ , Fe ²⁺	< 25

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to the low capacity or rates of adsorption for interfering ions under optimum condition. Thus, these results confirm that the procedure using Py-Fe₃O₄ NPs is independent of matrix interferences.

CONCLUSION

In this work Fe₃O₄ nanoparticle was functionalized by pyridine and it was utilized as an adsorbent for the separation of ultra-trace amounts of cobalt ion. This method is simple, rapid and reliable and found as a selective and sensitive method for the determination of trace levels of cobalt ion. The most important characteristic of the Py-Fe₃O₄ NPs were shown excellent selectivity toward cobalt ion over other ions. The convenient data was founds for detection limit and preconcentration factor in the determination of cobalt ion and confirmed that this method using modified Fe₃O₄ nanoparticles has high potential for extraction of metals.

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