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ORIGINAL ARTICLE

Preparation of Modified Magnetic Nanocomposites Dithiooxamide/Fe_3O_4 for Preconcentration and Determination of Trace Amounts of Cobalt Ions in Food and Natural Water Samples

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KEYWORDS

Magnetic nanocomposites;
Fe_3O_4;
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ABSTRACT: The first study on the high efficiency of nanometer-sized magnetic nanoparticles (Fe_3O_4) coated with sodium dodecyl sulfate (SDS) and dithiooxamide as a new sorbent solid phase extraction has been reported. Modified magnetic nanicomposites was used to preconcentrate and separate Co (II) ions in food and environmental water samples. Magnetic nanoparticles were prepared by chemical precipitation of Fe (II) and Fe (III) salts from aqueous solution by ammonia solution. These magnetic nanoparticles and nanocomposites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermo gravimetric analysis (TGA) and elemental analysis CHNS. A micro sample introduction system was employed for the nebulization micro-volume of diluted solution into flame atomic absorption spectrometry (FAAS). The extraction conditions were optimized by selecting the appropriate extraction parameters including the amount of nanosorbent, pH value, volume of dithiooxamide and condition of eluting solution. The detection limit of this method for Co (II) ions was 1.21 ng ml^{-1} and the R.S.D. was 0.9% (n=6). The advantages of this new method include rapidity, easy preparation of nanosorbents and a high preconcentration factor. The proposed method has been applied to the determination of Co (II) ions at trace levels in real samples such as, kiwi, orange, cucumber, apple, green pepper, honey, potato, tap water, river water and sea water with satisfactory results.

INTRODUCTION

Recently, mush attention has been focused on pollution of the environment by heavy metals. Among heavy

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metals, the pollution caused by cobalt is of considerable concern. Cobalt, in the form of cobalamin, is an essential component of Vit. B_{12} required for the production of red blood cells and prevention of pernicious anemia [1-2]. Cobalt ions concentration levels are very low in food and water samples and therefore sensitive and selective analytical techniques are required to carry out its detection [3-4].

Nanoparticles exhibit good adsorption efficiency especially due to high surface area and great active sites for interaction with metallic species and can easily be synthesized. Consequently, several researches have used nanoparticles as adsorbent [5–9] to measure trace level contaminants in environmental water samples. Preconcentration is usually necessary before instrumental analysis. Some extraction methods, such as liquid–liquid extraction [10], cloud point extraction [11], and solid-phase extraction (SPE) [12], have been employed to extract organic pollutants. In this regard, SPE is one of the most effective trace element preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor [13-15].

For determination of cobalt, some important instrument such as X-ray fluorescence spectrometry, spectrofluorimetry, neutron activation analysis [16-19], atomic absorption spectrometry (AAS), thin film sequential injection, inductively coupled plasma mass spectrometry (ICP-MS), polarography, chromatography, chemiluminescence and electrochemiluminescence [20-27] have been widely used. However, Flame atomic absorption spectrometry (FAAS) is an important technique due to its simplicity and lower cost.

Robinson et al. reported magnetic carrier technology in 1973 [28]. The synthesis of nano (or micro) magnetic carriers has been attracting intense interest due to their wide promising applications such as protein and enzyme immobilization, immunoassay, RNA and DNA purification, cell isolation, and target drug [29–32]. Among various sorbents, nanometer-sized materials have gained more attention because of their special properties [33].

In continuing of our research programs toward application of new sorbents for preconcentration and extraction of heavy metals, now we wish to disclose using of nano-sized magnetic nanoparticles coated with SDS-dithiooxamide, as a new and efficient nanosorbent for determination of Co (II) ions by flame atomic absorption spectrometry in real samples.

MATERIALS AND METHODS

Reagents

All reagents were provided by Merck (Germany), except dithiooxamid purchased from Sigma-Aldrich (Germany), used without further purification. All solutions were prepared in distilled water. A stock standard ammonia/ammonium chloride buffer solution (0.1 mol L^{-1}, pH 8.0) was prepared by dissolving an appropriate amount of ammonia in ultra-pure water and neutralizing to pH 8.0 with hydrochloric acid.

Instrumentation

The pH measurements were carried out using a Metrohm pH meter (model 744) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. A thermo M series (Model: M5) flame atomic absorption spectrometer was utilized, equipped with a 50 mm burner head, deuterium background correction and air-acetylene flame. Cobalt hollow cathode lamp (thermo scientific S51214) was used as radiation source, operated at 15 mA with a monochromator spectral bandpass of 0.1 nm for the cobalt detection, the wavelength was set at 240.7 nm resonance line. The acetylene and the air-flow rates were 0.8 and 10.0 L min^{-1}, respectively.

Preparation of nano size Fe_3O_4

To date, iron oxide nanoparticles synthesized by some known procedures [34–37], such as chemical coprecipitation procedure [38]. Toward this aim, ferrous chloride (2.0 g), ferric chloride (5.2 g), and hydrochloric acid (12 mol L^{-1}, 0.85 mL) were dissolved in 25 mL of pure deionized water for 20 min. The mixture was added dropwise into 250 mL of NaOH solution (1.5 mol L^{-1}) under vigorous stirring with nitrogen gas passing continuously through the solution during the reaction. After the reaction was completed, the obtained MNPs precipitate was separated from the reaction mixture under the magnetic field, and rinsed four times with 250 mL pure deionized water. Then, the product was dried at temperature of 80 °C in an oven, overnight.

Preparation of functionalized Fe_3O_4

For preparation of modified Fe_3O_4, 0.5 g of Fe_3O_4 was added to 10 mL nitric acid 4M and shaken for 10 min. Then 0.1 g sodium dodecyl sulfate and 0.2 mL dithiooxamide add to solution. The pH of solution was adjusted to 2 and the solutions was shaken for 10 min. Faintly, the powder obtained was dried at a temperature of about 40 °C in an oven for 24 h and stored in a desiccator for subsequent use.

General procedure

Magnetic nanoparticles (Fe_3O_4) added to the 100 mL of sample solution containing Co (II) ions in the range of 0.5-200 ng mL^{-1}. The pH value was adjusted to 8.0 using buffer solutions then shaked for 10 min. continually, the magnetic nanosorbent was separated easily and quickly with the help of an external magnet and the aqueous solution was poured away. Then the Co (II) ions retained on the sorbent were eluted by using 1 mL of 0.1 mol L^{-1} HNO_3. The metal ions in the eluate solution were determined by FAAS.

Preparation of real samples

Two g of each samples (kiwi, orange, cucumber, apple, green pepper and honey) were digested with 6 mL of concentrated HNO_3 (65%) and 2 mL of H_2O_2 (30%). After 30 min, samples were filtered and then the pH adjusted to 8.0 and made up to 100 mL with distilled water. Next, the method of standard addition was applied; thus, the equal volumes of samples were added to different volumes of cobalt (50.0 ng mL^{-1}) in 100 ml volumetric flasks. The pH of the solutions was adjusted to 8.0 using buffer solution and was diluted with distilled water.

The water samples, seawater (collected from Caspian, Iran), river water (collected from Tegen, Sari, Iran), and tap water (collected from Babol, Iran) were filtered with filter paper, pH of the samples were adjusted to 8.0, and the general procedure was carried out. On the other hand, 25.0 mL of Co (II) ion solution (200.0 ng mL^{-1}) was diluted with sea water, river water and tap water in 100 mL volumetric flasks respectively, and the general procedure was carried out.

RESUTS AND DISCUSSION

Characterization of Fe_3O_4 nanoparticles

As can be seen in Figures 1 and 2, the morphology of Fe_3O_4 nanoparticles before coating with sodium dodecyl sulfate and dithiooxamid is spherical and size of them is almost 10 nm.

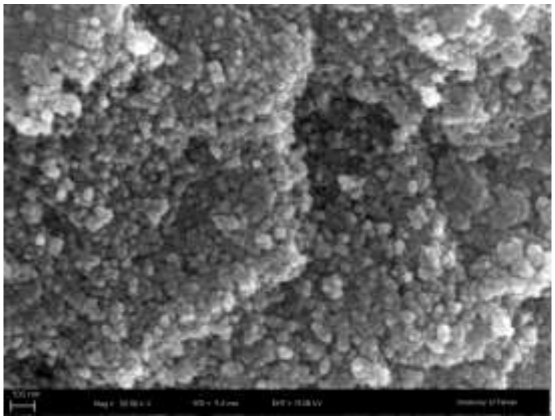

Figure 1. SEM images of Fe_3O_4 nanoparticles before coating with dithiooxamid.

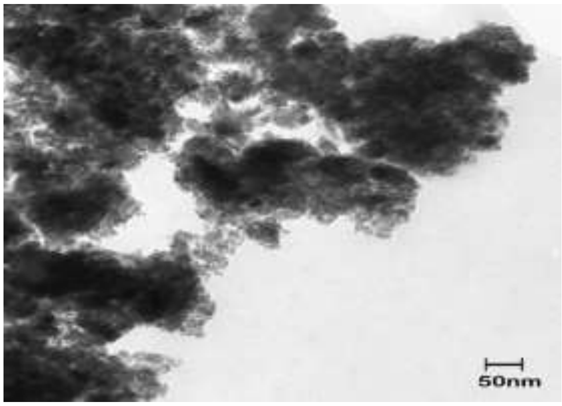

Figure 2. TEM images of Fe_3O_4 nanoparticles before coating with dithiooxamid.

The thermogravimetric analysis of the nanocomposites was employed to exhibit the stability of nanocomposites and the presence of organic group in the material (Figure 3). The weight loss 3.8% about 100 ˚C in the first step and the mass loss (25.8%) between 200.0 and 350.0 ˚C are due to adsorbed water on the nanocomposites and sodium dodecyl sulfate and ditiooxamide, respectively. At T>700 ˚C, a continuous and small weight loss is observed, attributed to the combustion of residual organic material.

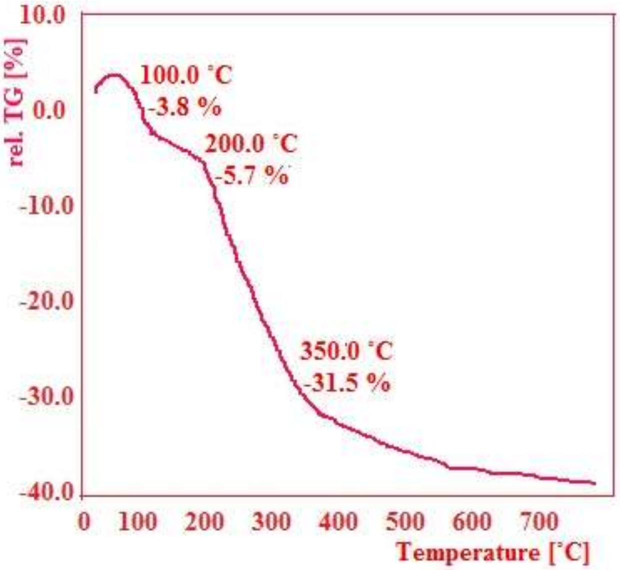

Figure 3. Thermogravimetric analysis (TGA) curves of nanocomposite

Elemental analysis CHNS is used as a qualitative and quantitative method, as it can be employed to identify the types of elements in nanocomposite and it can be used to determine the ratio of elements in the sample material. Practical values of elements of nanocomposite show in Table 1. The presence of nitrogen, sulphur and carbon in CHNS analysis of nanocomposite, confirms the functionalization of Fe_3O_4 with SDS and ditiooxamide.

Table 1. Elemental analysis of modified nanocomposite

Reten Time (min)	Response	Weight(mg)	Element Name
1.287	169.432	0.064	Nitrogen
2.194	5873.375	0.955	Carbon
7.896	4628.941	0.153	Hydrogen
18.103	164.739	0.073	Sulphur

Effect of pH

pH value plays a vital role in the solid-phase extraction procedure. Increasing the adsorption efficiency and depressing the interference of the matrix is obtainable by choosing an appropriate pH value. Interestingly, the sorption of SDS (commercially available in a high purified homogeneous form, with low toxicological properties and cost) on magnetic nanoparticles is also highly dependent on the pH of solution. Positively charged magnetic nanoparticles surfaces effectively sorbed negatively charged SDS at acidic pH values. Therefore, facile desorbtion of nonpolar organic compounds (dithiooxamid) on SDS-coated magnetic nanoparticles occurs. The anionic surfactant SDS is effectively retained on positively charged magnetic nanoparticles surfaces via formation of self-aggregates [35-36] over a wide pH range, whereas very little amount of SDS could be retained on inert surface of magnetic nanoparticles. Maximum sorption of SDS on magnetic nanoparticles was achieved at pH 1-2.9 by shaking the solution containing SDS and magnetic nanoparticles for 10 min. When solution was acidified, SDS would form hemi-micelles on magnetic nanoparticles by strong sorption (Figure 4).

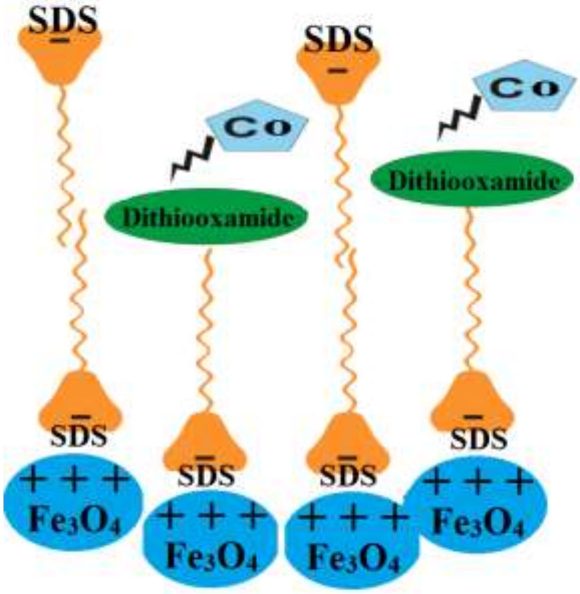

Figure 4. A suggested binding mode of SDS- ditiooxamide to Fe_3O_4 nanoparticles surface

The sorption behavior of Co (II) ions on the modified magnetic nanoparticles in water samples was studied in the pH range of 2.0-9.0. The pH of the solution was adjusted at the required value by addition of 1.0 mol L^{-1} NaOH or 1.0 mol L^{-1} HNO_3. A quantitative recovery (>95 %) was obtained for Co (II) ions at the pH 8.0. Therefore, the pH of 8.0 was chosen for further extraction (Figure 5).

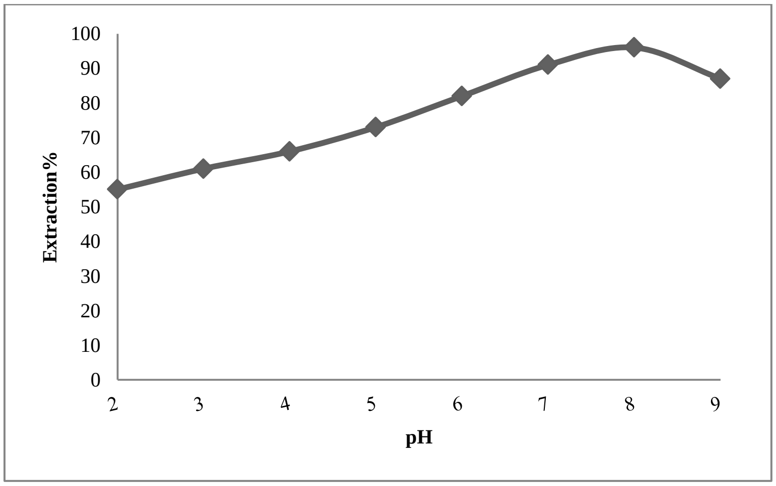

Figure 5. Effect of pH on sorption of Co (II) ions

Effect of the amount of nanosorbent

Solid phase extraction of 50.0 ng mL^{-1} of cobalt ions using dithiooaxamid from 100.0 mL of the sample solutions was conducted by various amounts of nanosorbent (modified magnetic nanoparticles) in the range of 100-500 mg. The results show that cobalt ions were completely adsorbed on the sorbent in the 100 mg of the modified magnetic nanoparticles (Figure 6). Therefore, 100 mg of nanosorbent was selected as optimum amount in order to achieve better and more the extraction recovery

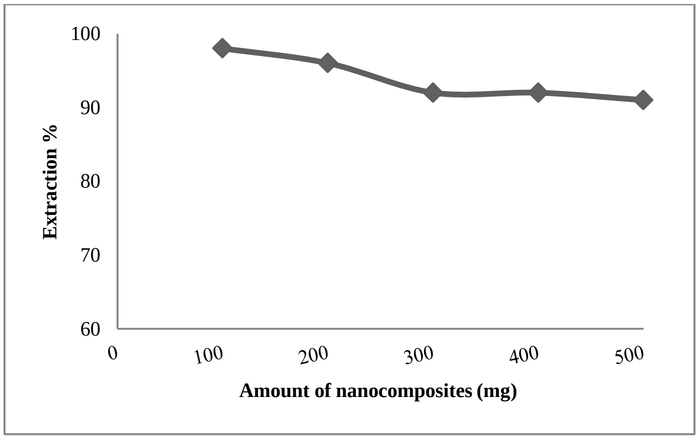

Figure 6. Effect of amount of modified nanocomposites on the sorption of Co (II) ions

Effect of eluting solution condition

Some experiences were carried out in order to obtain a reasonable eluent to elute completely Co (II) ions after their enrichment by chelation with dithiooxamid on the modified magnetic nanoparticles. Various acids with various concentrations (0.1-1 mol L^{-1}) were to obtain the optimal eluent for further experiments. HNO_3 0.1 mol L^{-1} accomplish the quantitative dissolve of Co (II) ions chelated with dithiooxamide in solid phase extraction (Table 2).

Table 2. Effect of type and concentration of eluent on the adsorption of Co (II) ions.

Eluent	Concentration(mol L^{-1})	Recovery(%)
H_2SO_4	0.1	49.6
	0.5	53.6
	1.0	67.3
H_3PO_4	0.1	40.1
	0.5	47.2
	1.0	54.0
CH_3COOH	0.1	25.5
	0.5	31.0
	1.0	38.6
HNO_3	0.1	98.3

Table 2. Continued.

	0.5	96.4
	1.0	96.3
HCl	0.1	71.6
	0.5	80.3
	1.0	92.1

Effect of volume of ligand

The extraction recovery for Co (II) ion as a function of the volume of chelating agent was evaluated in the range of 0.5-4.0 mL. Extraction recovery increases up to 1.5 mL of ligand and then remains constant (Figure 7). Thus, 1.5 mL of ligand was chosen to account for other extractable species that might potentially interfere with the assaying of Co. (II) ions.

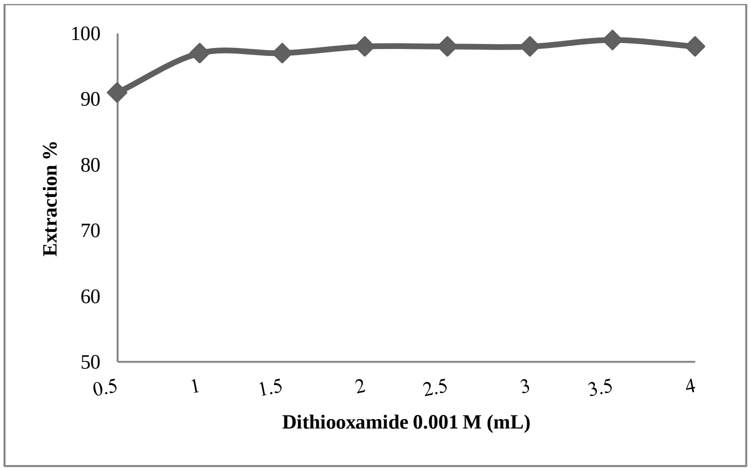

Figure 7. Effect of volume of ligand on the sorption of Co (II) ions.

Effect of other ions

The effects of common other ions in water samples on the recovery of Co (II) ions were studied. The fluencies of the some ions, known as interferic ions in the flame atomic absorption spectrometric determination were investigated. In these experiments, 100.0 mL of solutions containing 50.0 ng mL^{-1} of Co (II) ions and various amounts of interfering ions were treated according to the recommended procedure. The tolerance limit was defined as the ion concentration causing a relative error smaller than ± 5% related to the coprecipitation and determination of the examined elements. The Co (II) ions recoveries are almost quantitative in the presence of interfering ions at the concentration of 50 times higher than Co (II) ions concentration (Table 3).

Table 3. Influences of some foreign ions on the recoveries of analytes

Ion	Added as	Interferent/Co(II) (weight ratio)	Recovery (%)
Na^+	Na No_3	1000	103.7
Mn^{2+}	$MnCl_2$	100	97.5
NO_3^-	$AgNO_3$	200	102.4
Fe^{3+}	$Fe(NO_3)_3$	30	96.2
SO_4^{2-}	Na_2SO_4	1000	104.9
PO_4^{3-}	Na_3PO_4	1000	101.1
Cl^-	NaCl	1000	102.2
Ca^{2+}	$CaCl_2$	300	97.5
Ag^+	$AgNo_3$	200	96.8
Cu^{2+}	$CuSO_4$	50	97.5
Zn^{2+}	$ZnCl_2$	100	98.7
Ni^{2+}	$Ni(NO_3)_2$	50	96.6
Fe^{2+}	$FeSO_4$	20	95.2

Method validation

Figures of merit

Table 4 summarizes the analytical characteristics of the optimized method, including limit of detection, reproducibility, linear range, and preconcentration and enrichment factor. The limit of detection (LOD = 1.21 ng mL^{-1}) was calculated as $3S_b/m$ (S_b: standard deviation of the blank signals, m: slope of calibration curve after preconcentration). A good correlation coefficient (r^2 = 0.996) was obtained and the relative standard deviation (RSD) for six replicate measurements of 50.0 ng mL^{-1} Co (II) ion was 0.9%. The calibration curve was investigated up to 500 ng mL^{-1} which was linear. The enrichment factor and Preconcentration factor were 10.

Table 4. Analytical characteristics of proposed method

Parameter	Analytical feature
Linear range (ng mL^{-1})	5- 500
Limit of detection (ng mL^{-1}) (n =6)	1.21
Repeatability (RSD %) (n =6)	0.9
Preconcentration factor	100
Enrichment factor	100
Correlation coefficient (r^2)	0.996

Analysis of real samples

This method was applied to determine of Co (II) ions in water, food and herbal samples. In order to test the river water, sea water, tap water, kiwi, orange, cucumber, apple, green pepper, potato and honey. In all cases the spike recoveries confirmed the reliability of the proposed method (Tables 5 and 6).

Table 5. Determination of cobalt (II) ions in natural water samples

Sample	Co (II) spiked(ng mL^{-1})	Co (II) detected(ng mL^{-1})	Recovery(%)
Tap water	-	n.d.[a]	-
	50	49.2 (1.1)[b]	98.4
River water	-	12.8 (1.8)	-
	50	62.3 (1.3)	99.2
Sea water	-	21.5 (2.1)	-
	50	72.9 (2.7)	101.9

[a] Not detected

[b] RSD of three replicate experiments

Table 6. Determination of cobalt ions in herbal and food samples

Sample	Concentration ofCo (µg/g)
Kiwi	0.778 (1.9)
Orange	0.123 (1.5)
Cucumber	0.850 (2.1)
Apple	0.019 (2.3)
green pepper	0.036 (0.7)
Honey	0.004 (1.1)
Potato	0.188 (1.6)

Comparison other solid-phase extraction studies

A comparison of the presented method with other reported preconcentration methods for Co (II) ions determination is given in Table 7. The present work has relatively low LOD and RSD when compared to other sorbent, activated carbon, silica gel, cali resorcinarene and coated alumina

Table 7. Comparison of the proposed method with other methods reported

Sorbents	Technique	LOD (µg L)	RSD (%)	Ref
Modified Activated carbon	FAAS	0.08	0.85	39
Silica gel	FAAS	-	1.58	40
Cali resorcinarene	FAAS	2.3	1.1	41
Surfactant-coated alumina	FAAS	-	1.4-4.0	42
Styrene–EGDMA	FAAS	2.0	2.52	43
Modified Magnetic nanoparticles	FAAS	1.21	0.9	This Work

CONCLUSIONS

In this work, a new sorbent of dithiooxamide on SDS-MNPs Fe_3O_4 was prepared with the precipitation method and combined with FAAS. These results show that the ligand loaded on the modified magnetic nanoparticles is sensitive and accurate method for determination of trace amounts of Co (II) ions in low concentrations.

MNPs have a relatively high adsorption as compared to the similar materials due to their large surface area. In addition, MNPs Fe_3O_4 are highly mono dispersed and magnetically separable from the sample solution.

The results presented in this paper have confirmed the applicability of the separation and preconcentration of metals. Compared with reported methods, the proposed solid phase extraction method is superior for having lower RSD and lower detection limits (Table 7) and is simple, rapid and has a low analysis cost. The method has adequate accuracy and selectivity and can be used for the determination of cobalt in water, herbal and food samples with satisfactory results.

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