

Alternative Method of Exteraction of ultra-trace Co (II) with disks of octadecyl silica membrane modified nano-Fe₃O₄-encapsulated-dioctyl phthalate and linked-diethylenetriamine

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Abstract

In the present research, amounting of the trace little amount of Cobalt (II) ions in aqueous Samples by using modified disks of octadecyl silica membrane by nano-Fe₃O₄-encapsulated-dioctyl phthalate and linked-diethylenetriamine (magnetic nano- Fe₃O₄ -DOP- DTA)which in order to improve the performance of extraction and preconcentration was used. Amounting of the ions density in solution was performed by the method of flame atomic absorption spectrometry. The effective parameters on extraction such as: effect of pH, the amount and eluent solvent, time of extraction and effect of other cation were optimized. The preconcentration factor is 500 in the optimum analysis situations of whole parameters. Analysis parameters contain the limit of detection and the most capacity of Cobalt (II) ions sorption was achieved 7.0 µg/L and 468 ± 4 µg, respectively. Finally, the Co²⁺ ions were extracted in various aqueous solutions by this technique.

Keywords: Co²⁺; Separation; octadecyl silica membrane; Fe₃O₄-encapsulated; magnetic nano- Fe₃O₄ -DOP- DTA.

Introduction

Cobalt metal at little concentrations as a toxic substance causes environmental damage to pelagic and marine ecosystems [1-3]. Cobalt metal in high and low levels has different effects on herbs' life. At higher than allowed levels, Cobalt ions stop the transfer process from the cell wall. Normal metabolism of many organisms requires 38 µg/L of Co²⁺ ions [4]. Moreover, in many industries today, Cobalt is recognized as a key element. Therefore, research on new methods for effective extraction, and determination of the concentration of this metal at very low levels in a diversity of manufacturing, pharmaceutical, and environmental samples is important. Assessment of Co²⁺ ions is usually done by atomic absorption spectroscopy, and other spectrometric methods [5]. The preconcentration step of Cobalt ions from different biological and aqueous samples causes separation from other metals and more accurate measurement of Cobalt ions. Significant procedures for the extraction of Co²⁺ ions like liquid-liquid microextraction have been developed in the attendance of various classical co-extraction ligands, and macrocyclics[3] [6].

However, classical techniques for extracting various metals have disadvantages such as long-term use of major amounts of excellent purity solvents. Commonly used device methods for removal of Co²⁺ metal ions include liquid technique chromatography [7], flotation [8], liquid membrane [9], aggregate film formation [10], ion-pairing[11], supercritical fluid extraction [12], adsorption of the column from the composite of pyrocatechol violet-Cobalt on activating carbon (In this method, the extraction of heavy metal ions through a liquid membrane supported by hollow fibers containing a mobile carrier soluble in kerosene solvent) [13], and SPE extraction using disks cartridges and C₁₈ membrane[14].

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium [15-19] and lead[22].Meanwhile, other investigators have

successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead[21,23], copper[24-26], silver[27-28], mercury[29], cadmium[31], Cobalt[32], Ce[33] and UO_2^{30} . Ionic liquids (ILs) seem well positioned to address this challenge. Due to their wide solubility, and by introducing a surface charge, modification with ILs should enable the preparation of long-term stable and chemically converted graphene sheets (CCG) that can be dispersed in various matrices. To date, investigations into the covalent attachment of an ionic material to graphene surface have been not carried out. In this communication, we report a convenient method to obtain polydisperse chemically-converted graphene (CCG) sheets that are functionalized with 1-(3-aminopropyl) - 3-methylimidazolium bromide (IL- NH_2) [20]. The main goal of the present work is development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Cobalt(II) from aqueous media by means of a surfactant coated C_{18} modified with , chemically converted graphene sheets (CCG) (shown in Scheme 1) [20].

In this research, we have tried to develop a fast, selective, sensitive procedure for pre-concentration of an extremely low amount of Cobalt (II) in aqueous media with disks of octadecyl silica modified nano- Fe_3O_4 -encapsulated-dioctyl phthalate and linked-diethylenetriamine, and finally, by atomic absorption spectrometer, the Cobalt (II) ions desorbed has been determined.

Experimental

Chemicals

Acidic solutions (formic acid, hydrochloric acid, nitric acid), organic solvents (high purity), Methanol, and chloroform (HPLC grade) are prepared from Merck. The nitrate of lithium, magnesium, barium, potassium, lead, zinc, sodium, nickel, cadmium, calcium, zinc, strontium, cobalt (II, III) was prepared in analytical grade. The double-distilled water with ultra purity was used in the experiment.

The solution of Cobalt (II) as a stock solution was prepared following dissolved the powder of Co metal (0.1000g) in nitric acid solution (10 mL) and then diluted in a calibrated flask (1000 mL) with distilled water. The other solutions (working solutions) were prepared from stock Cobalt (II) solution. All the dilutions have been prepared with the highest pure deionized water. Dioctyl phthalate, sodium hydroxide (NaOH), DOP (purity > 99.55%) and diethylenetriamine (DTA) is purchased from BDH, UK.

Preparation of magnetic nano- Fe_3O_4 adsorbent

Magnetic nano- Fe_3O_4 is first prepared from the method that has been done before. A sample of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ powder (6.1 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ powder (4.2 g) was added in double-distilled water (100 mL). A solution of 6.5 M from NaOH (25.0 mL) was poured drop by drop into the before solution. This mixture shaking for 240 min. After adding the NaOH solution completely, the nano- Fe_3O_4 is formed (black precipitate) and this precipitate was washed with deionized water, and then separated with magnetic field, and collected precipitate dried at a temperature of 70 °C [20].

Preparation of nano- Fe_3O_4 -DOP adsorbent

The nano sorbent of Fe_3O_4 -encapsulated-DOP was synthesized by adding the DOP (20.0 mL) to the nano- Fe_3O_4 sorbent (10.0 g). This mixture was stirred for 180 min at 90 °C and then the product was separated, and washing with a solution of methanol, and then again separated with the magnetic field and lastly dried at a temperature of 70 °C [20].

Preparation of magnetic nano- Fe_3O_4 -DOP-DTA adsorbent

The nano- Fe_3O_4 -DOP (10.0 g) addition to DTA (5 mL) and this mixture was blended with heavy grinding, then was mixed for 300 min with mortar. The nano- Fe_3O_4 -DOP-TETA adsorbent is dried at 60 °C.

Apparatus

Determination of Cobalt (II) ions of samples performed by atomic absorption spectrometer with a model of Varian spectra A 200 and equipped with HI-HCl hollow cathode lamp. The other information includes 0.7 nm of slit width, 324.8 nm of resonance fine, 15 mA of current, background correction with Deuterium lamp, Air/acetylene (flame), and 1.7 mL/min for Acetylene flow. Measurement of pH was performed by a pH meter with GP 353 model.

Sample extraction

SPE has been carried out by disk of the glassy membrane, ENVI-18DISK™, phase of octadecyl silica bonded with 30 µm of particle and with a pore size of 70 Å (47 × 0.6 mm) prepared from Supelco in linkage with filtration apparatus in 47 mm of standard Millipore and equipped with a vacuum pump [21].

Sample Treatment

The nylon filters (45µm) was used for the filtration of aqueous samples. Polyethylene bottles were used for sampling. The containers were soaked in HNO₃ solution (1 M) overnight, then washed with distilled water. This experiment was performed in two days of sampling. Before analysis, a methanol solution (5mL) was poured into a 90 mL part of the sample. The surface of the disks that are not modified with magnetic nano-Fe₃O₄-DOP-DTA and therefore can not retain Cobalt (II) ions properly. In lieu, magnetic nano-Fe₃O₄-DOP-DTA (10 mg) was dissolved in 5 mL suitable of the water-miscible organic solvent. The most suitable solvent was acetone in process of analysis. The solution of magnetic nano-Fe₃O₄-DOP-DTA was poured Cobalt (II) aqueous solution and then stirred until extraction of Cobalt (II) metal ions.

The cleaning and conditioning of Disk

Contamination from the environment and construction process of the disks are eliminated by placing in the device with a solution of methanol (10 ml). Then, as the air passes, the discs dry in a few minutes. The disk was washed again for effective extraction of the analytes with methanol (10 ml) and water without disk surface drying. In the pre-extraction step, the surface of the disc must be wetted. Due to improper performance at this stage, it slows down the flow rate and low analyte recovering. Before adding the sample, a noteworthy point for the surface of the disk is to avoid contact with air.

Sample addition

After the homogenization step, the sample solution with the exact volume (100mL) transferring from the disk device to the top reservoir. Meanwhile, the sample solution was drained via disk using a moderate vacuum. Use the vacuum until the disks are dried (5 minutes).

Analyte elution

The analyte was selectively was eluted when only 5 ml of 0.1 M of acidic HCl solvent in methanol passed via a disk, and then solution collecting with a volumetric flask (5.0 ml) from the extraction funnel. The results showed that the excellent eluting agents are alcoholic organic solvents with the highest purity. By drawing the calibration curve by FAAS, the Co²⁺ ions concentration was determined.

Results and Discussion**Study of ligand role**

The efficacy of magnetic nano-Fe₃O₄-DOP-DTA adsorbent presence on the amount extraction of Co²⁺ ions has been performed by some experiments. The results showed which the membrane disk alone does not keep the Co²⁺ ions, but the usage of an aqueous sample of Co²⁺ ions (100mL) with Co²⁺ ions (10µg) and magnetic nano-Fe₃O₄-DOP-DTA (10mg) leads to proper retention (Table 1). Another cause could be a strong interaction between Co²⁺ ions and magnetic nano-Fe₃O₄-DOP-DTA. It must be mentioned that stable complexes formation between Co²⁺ and magnetic nano-Fe₃O₄-DOP-DTA at acidic pH is maybe due to the procedures of ion-pair. Meanwhile, at higher pH (>2), the retention of Co²⁺ ions recovery is insignificant.

Table 1. The effect of the presence of magnetic nano-Fe₃O₄-DOP-DTA on extraction percent of Co²⁺ ions^a.

magnetic nano-Fe ₃ O ₄ -DOP-DTA	pH	Co ²⁺ ions extraction (%)
Presence	2 to 5.5	95.9(2.6) to 63(2.9)
Absence	2 to 5.5	0.02(5.6) ^b

^a sample: Co²⁺ ions (10µg) in water (100mL).

^b RSD_s (five individual analyzes)

Eluent selection

In this section, the proper eluent was chosen to recover Co^{2+} ions from the disk. The 5 mL of various solvents of organic and different nonorganic (10% of methanol, V/V) were investigated. The result is deposited in Table 2. Methanol or ethanol solvents (5 mL) show the best results for quantitative washing of Co^{2+} ions of the disk. In this process, The hydrophobic surface of the disc will be further contacted with the eluent solvent by methanol.

Table 2. Effect of various solvents on elution of Co^{2+} ions from the disk ^a

Elution solvent	Recovery (%)		
	2 (ml)	5 (ml)	10 (ml)
Acetonitril	32.7(5.2) ^b	42.7(4.2)	53.3(4.5)
Acidified methanol ^c	55(2.2)	82.5(2.7)	83.7(2.5)
Ammoniacal methanol ^d	55 (2.0)	82.3(2.1)	83.7(2.3)
Methanol	81(2.2)	97.3(2.4)	93.8(2.4)
10% methanol (V/V), Formic acid (1M)	54.2(2.0)	65.6(1.8)	71.2(2.3)
10% methanol (V/V), Hydrochloric acid (1M)	58.3(1.7)	91.8(2.2)	91.4(2.6)
10% methanol (V/V), Hydrochloric acid(1M)	52.5(2.3)	85.6 (2.4)	92.8(1.7)
10% methanol (V/V), Nitric acid(2M)	52.7 (1.9)	82.7(2.0)	87.7 (1.8)
10% methanol (V/V), Nitric acid(1M)	33.9(2.3)	84.9(2.3)	89.4(1.9)
Ethanol	82.0(2.5)	95.3(2.0)	97.5(2.0)

^a sample: 10 μg of Co^{2+} ions in 100mL of water.
^b RSD_s (five individual analyzes)
^c solvents with HCl (0.1M)
^d solvents with NH_3 (0.1M)

The pH effect

All solutions pH was set to various pH value 2 to 9 by suitable buffer (sodium acetate, monosodium phosphate, hydrochloric acid, disodium phosphate, and acetic acid), and then these samples used for disks [22,23].

Finally, pure ethanol or methanol used for stripping the Co^{2+} ions, and then the eluted ions were determined by FAAS. Figure 1 displays the result of recovery from Co^{2+} ions in different pH. As the results show, the recovery of Co^{2+} ions at pH values between 4 and 4.5 is the maximum. It is also seen that with increasing pH, the recovery is decreased. This is since in an acidic solution with protonation of magnetic nano- Fe_3O_4 -DOP- DTA happens, as a result, little interaction will occur between Cobalt (II) and magnetic nano- Fe_3O_4 -DOP-DTA, whereas, at higher pH of 5, the $\text{Co}(\text{OH})_2$ is produced. Hence, the buffer with a pH of 4.5 (sodium acetate-acetic) was applied for Cobalt (II) preconcentration. Besides, Due to hydrolysis of the octadecyl silica within the disk and Because a pH above 7 causes the Co (II) ion to precipitate, other solvents with pH higher than 7 were not examined. Furthermore, at lower pH of 4, the atoms of nitrogen of the magnetic nano- Fe_3O_4 -DOP-DTA can be protonation and reduced the complex stability.

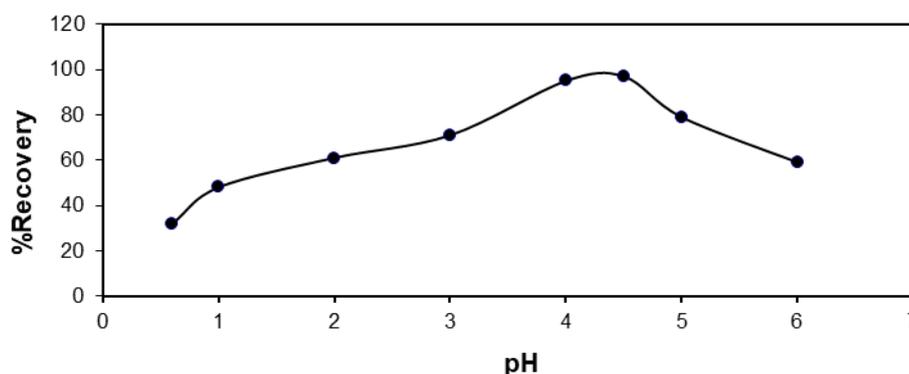


Figure 1. Effect of sample pH and solvent of magnetic nano- Fe_3O_4 -DOP- DTA on recovery of Cobalt (II).

Counter anions effect

The various counter anions have been investigated to evaluate their effect on the Cobalt (II) ions recovery. As can be seen, the counter anion nature directly affects the Co^{2+} ions retention with the modified disk.

The retention result ascertained that the magnetic nano- Fe_3O_4 -DOP-DTA acts like a neutral ionophore within a pH of 4.0 to 4.5, in consequence, the Co^{2+} ion has been retained like a complex with membrane disk. Based on the results, acetate ions have the greatest effect as a counter ion for the extraction of Cobalt(II) metal ions. Table 3 shows the results of the concentration effect of CH_3COONa ions on Co^{2+} ions recovery. As shown, by increasing the acetate concentration to 0.1 M, the recovery percentage of Co^{2+} also increases. Also, acetate ions act as an appropriate buffer in ion-pair formation. Therefore, no need to add a buffer solution in SPE extraction experiments.

Evaluation of the effect of various counter anions with a concentration of 0.01 M to recover Cobalt (II) metal ions from the modified disk

Table 3. Evaluation of the effect of various counter anions with a concentration of 0.01 M to recover Co^{2+} ions from the modified membrane disk ^a.

Anions	Recovery (%)
SCN^-	35.2
ClO_4^-	28.9
Br^-	27.0
Cl^-	20.4
Acetate	91.0
Picrate	75.2
^a sample: 10 μg of Co^{2+} ions in 100mL of water.	

Flow rate effect

Process rate is one of the significant factors affecting SPE extraction. Hereupon, the result of flow-rate on performances of extraction was studied. The results of Figure 2 display that the retention of Co^{2+} with a range of about 10-100 ml/min is not extremely affected flow rate and result in an acceptable and good result. So, the total flow-rate of the experiment was 89 mL/min.

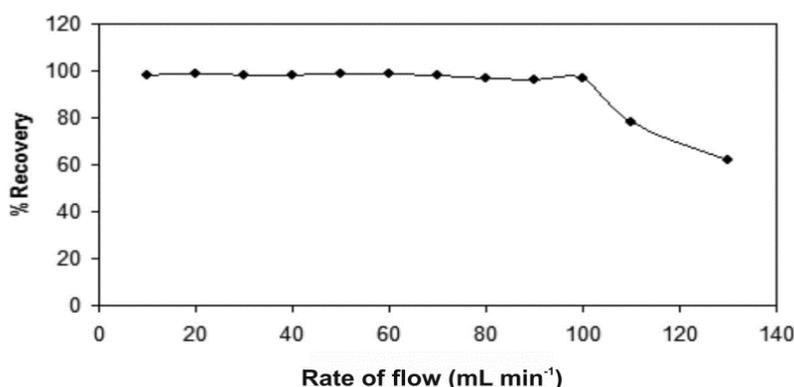


Figure 2. Extraction of Cobalt (II) against in rate of flow

Amount of the magnetic nano- Fe_3O_4 -DOP-DTA

The optimized amount of magnetic nano- Fe_3O_4 -DOP-DTA for extraction of Cobalt (II) ions evaluated by adding different amounts of magnetic nano- Fe_3O_4 -DOP-DTA (2-20 mg). Results of the test demonstrate that the Cobalt (II) ions extraction was maximized with 10 mg of magnetic nano- Fe_3O_4 -DOP-DTA in the solution (Table 4). Therefore, subsequent extractions were carried out with 15 mg value of magnetic nano- Fe_3O_4 -DOP-DTA.

Table 4. Influence of the magnetic nano- Fe₃O₄ -DOP- DTA value on the recovery of Co²⁺ ions ^a.

magnetic nano- Fe ₃ O ₄ -DOP- DTA amount (mg)	Recovery(%) of Co ²⁺
2	25.0(2.9) ^b
5	41.1(2.3)
8	82.0(2.4)
10	95.7(2.4)
15	95.8(2.9)
20	93.7(2.0)
^a sample: 10µg of Co ²⁺ ions in 100mL of water.	
^b RSD _s (five individual analyzes)	

Analytical Performance

When solutions of 10µg Co²⁺ in the range 10-3000 mL in optimum situations have been passed via the disk, Cobalt (II) ions were retained in samples. Afterward, To have a concentration factor greater than 500 in this method, the breakthrough volume must be greater than 2500 mL. The detection limit (LOD) for this procedure of determination of Cobalt (II) ions is 7.0 ng per 1000mL.

The modified disk's capacity (5mg magnetic nano-Fe₃O₄-DOP-DTA) was characterized with a solution of 50 mL volume, 8 mg of Co²⁺ and buffer of CH₃COONa/CH₃COOH (0.1M) with a pH value of 4.0-4.5, following with Co²⁺ ions determination with AAS. Maximum disk capacity achieved from measurements (three replicate) is 468 ± 4 µg of Co²⁺ on the disk.

In binary mixtures of heavy metals, to survey in selective separation and extraction of Co²⁺ ions, this method was used. The 50 mL of an aqueous solution comprising 10µg Cobalt (II) ions and mg value of different cations were derived. Results of Table 5 display that the Co²⁺ in the mixture is retained nearly entirely with the disks. However, disks retain very few other ion metals and can be effectively extracted from Cobalt (II) ions. In other tests, we found that concentrations greater than 0.5 M of NH₂OH.HCl was proper as a reducing agent.

Table 5. Extraction of Co²⁺ ions in a mixture contains a cation ^a

Cation	Amount (mg)	Found (%)	Co ²⁺ ions recovery(%)
Zn ²⁺	2.50	1.87(2.2)	95.4(2.2)
Mg ²⁺	14.0	0.90(1.9)	95.2(1.4)
Hg ²⁺	0.47	2.10(2.2)	95.4(2.5)
Sr ²⁺	2.40	2.70(2.3)	97.0 (2.4)
UO ²⁺	2.40	2.27 (1.4)	95.1(2.3)
Mn ²⁺	2.59	1.70(2.7)	94.2(2.9)
K ⁺	92.8	1.20(2.4) ^b	96.2(2.8)
Ni ²⁺	1.38	2.40(2.4)	96.7(2.7)
Na ⁺	92.7	1.19(2.6)	95.3(2.5)
Cd ²⁺	2.55	1.90(2.4)	95.2(2.5)
Pb ²⁺	0.45	2.70(1.3)	96.7(2.4)
Ca ²⁺	23.0	2.40(3.3)	95.7(2.3)
Ag ⁺	2.35	3.25(2.5)	93.2(2.7)
Cr ³⁺	1.77	2.26(2.1)	95.6(2.8)
Ba ²⁺	2.45	3.10(2.6)	94.0(2.9)

^a sample: 10µg of Co²⁺ ions in 100mL of water and acetate ions (0.1 M)

^b RSD_s (five individual analyzes)

Water sample analysis

Various aqueous samples were used in a real sample to assess the usability of the technique for the extraction and specification of Co²⁺ ions. Seawater from the Caspian sea, The rainwater (Tehran, 2

January 2021), Tap water (Tehran), and snow water (Tehran, 20 December 2020) samples have been analyzed (Table 6).

The Co^{2+} ions added to real samples can be successfully recovered (Table 6). According to the obtained results, the results of Co^{2+} ion recovering are entirely dependable and are satisfied with the result obtained by the ICP-AES method.

Table 6. Extraction of Co^{2+} ions added in 1000 mL from various aqueous samples (CH_3COONa (0.1M) at pH= 4.0-4.5).

Aqueous samples	Co^{2+} ions ($\mu\text{g/L}$)	Co^{2+} ions recovery ($\mu\text{g/L}$)	Analysis of ICP-AES
Rain water	0.0	2.29(2.0) ^a	ND ^b
	10.0	12.40(2.0)	12.25
Tap water	0.0	1.53(2.6)	ND
	10.0	11.73(2.6)	11.48
Sea Water	0.0	12.21(2.7)	12.4
	10.0	22.20(2.3)	22.5
Snow water	0.0	4.13(2.5)	ND
	10.0	14.04(2.4)	14.1

^a RSDs (five individual analyzes)

^b Not detected.

Conclusion

This study shows that small amounts of Cobalt (II) ions have been successfully extracted by Octadecyl Silica membrane disks modified with magnetic nano- Fe_3O_4 -DOP-DTA in aqueous samples. The proposed solid-phase extraction method is easy, reliable, and accurate and has a high ability to determine Cobalt (II) ions in water samples. Besides, this procedure was without interference comparing to other methods to assess Co^{2+} ions. This technique can be applied as an alternative procedure for the determination and extraction of Co^{2+} ions in binary mixtures.

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