Middle-East Journal of Scientific Research 12 (10): 1331-1338, 2012
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2012.12.10.1610

Solid Phase Extraction of Trace Amount Co(II) Using Organic-Solution-Processable Functionalized-Graphene

[1]Ali Moghimi and [2]Shahriare Ghammamy

[1]Department of Chemistry,
Varamin (Pishva) Branch Islamic Azad University, Varamin, Iran
[2]Department of Chemistry, Faculty of Science,
Imam Khomeini International University,Ghazvin, Iran

Abstract: A novel and selective method for the fast determination of trace amounts of Co(II)ions in aqueous solution has been developed. The first organic-solution-processable functionalized-graphene (SPFGraphene) hybrid material with porphyrins. porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin and its photophysical properties including optical (TPP) and grapheme oxide molecules covalently bonded together via an amide bond (TPP-NHCO-SPFGraphene) were used as absorbent for extraction of Co(II) ions by solid phase extraction method. The complexes were eluted with HNO_3 (2M)10% $V.V^{-1}$ mthanol in acetone and determined the analyte by flame atomic absorption spectrometry. The procedure is based on the selective formation of Co(II) at optimum pH by elution with organic eluents and determination by flame atomic absorption spectrometry.The method is based on complex formation on the surface of the ENVI-18 DISK™ disks modified porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together via an amide bond (TPP-NHCO-SPFGraphene) followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, TPP-NHCO-SPFGraphene, amount, stripping solvent and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to about 1000mL providing a preconcentration factor of 600. The maximum capacity of the disks was found to be 568± 3 µg for Co^{2+}.The detection limit of the proposed method is 5 ng per 1000 mL.The method was applied to the extraction and recovery of Co in different water samples.

Key words: Co(II) · SPE · Octadecyl slica disks · FAAS · Porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together via an amide bond (TPP-NHCO-SPFGraphene).

INTRODUCTION

The direct determination of trace amount of metals especially toxic metal ions such as Co, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step [1]. This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest [2]. This can be performed simply in many ways including liquid and solid phase extraction techniques [3,4]. The application of solid phase extraction technique for pre- concentration of traces of metal rations from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form [5].

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams [6], filter paper [7], cellulose [8] and ion exchange resins [9]. Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers

Corresponding Author: Ali Moghimi, Department of Chemistry, Varamin (Pishva) Branch, Islamic Azad University, Varamin, Iran.

on their surfaces [10] of which silica gel is the most widely used solid support material due to its well documented thermal, chemical and mechanical stability compared to other organic and inorganic solid supports [11]. The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes [12]. For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters [13]. Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place [10].

Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds [14-18]. The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Co(II) [19,20] and pre-concentration of various cations [21,28-50] and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations [22]. Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) has been reported by….. [5]. Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater [23]. Sorption of Co(II) by some sulfur containing complexing agents loaded on various solid supports [24] was also reported. 2-Amino-1-cyclopentene-1-dithiocaboxylic acid (ACDA) for the extraction of silver(I), Co(II) and palladium(II) [25], 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions [26] as well as thiosemicarbazide for sorption of different metal ions [27] and thioanilide loaded on silica gel for pre-concentration of palladium (II) from water [28-34] are also sulfur contaning silica gel phases.

In the present report, we wish to describe a proper concentrative method for assessment of trace levels of Co in different water samples. To the best of our knowledge, octadecyl silica membrane disks modified by (TPP-NHCO-SPFGraphene,) have not been used for Co isolation and preconcentration, previously of this work was the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Co^{2+} ions from aqueous media using octadecyl silica membrane disks modified by porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together via an amide bond (TPP-NHCO-SPFGraphene) and FAAS determination.

MATERIALS AND METHODS

Reagents: All acids were of the highest purity available from Merck Company and were used as received. Methanol and Chlorofom were of HPLC grade supplied by Merck Company. Analytical grade nitrate salts of litium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II) and Ni(II) were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstat, Germany and High Purity double distilled deionized water was used throughout the experiments.

The stock standard solution of Co^{2+} was prepared by dissolving 0.1000 g of the Co powder in 10 mL concentrated nitric acid and diluted to 1000mL with water in a calibrated flask. Working solutions were prepared by an appropriate dilution of the stock solution.

The synthesis of the TPP-NHCO-SPFGraphene, is illustrated in Fig. 1.a,b

Synthesis of TPP-NHCO-SPFG Raphene: The first organic-solution-processable functionalized-graphene (SPFGraphene) hybrid material with porphyrins. The synthesis of the porphyrin-Graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together vi a an amide bond (TPP-NHCO-SPF Graphene, Scheme 1 and 2) was carried out using an amine-functionalized prophyrin ($TPP-NH_2$) and Graphene oxide in N,N-dimethylformamide (DMF), following standard chemistry. Large-scale and water-soluble Graphene oxide was prepared by the modified Hummers method.[53-55] Results of atomic force microscopy characterization have confirmed that this grapheme material can be easily dispersed at the state of complete exfoliation, which consists of almost

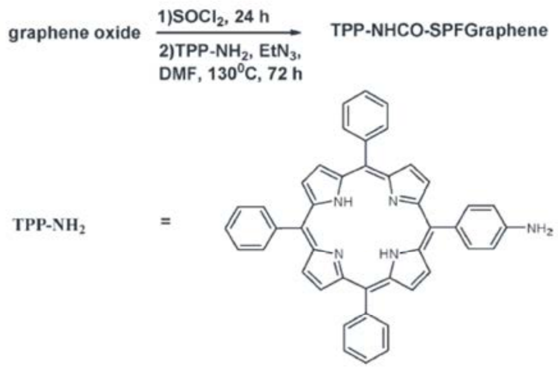

Fig. 1a: Synthesis scheme of TPP-NHCO-SPFGraphene.

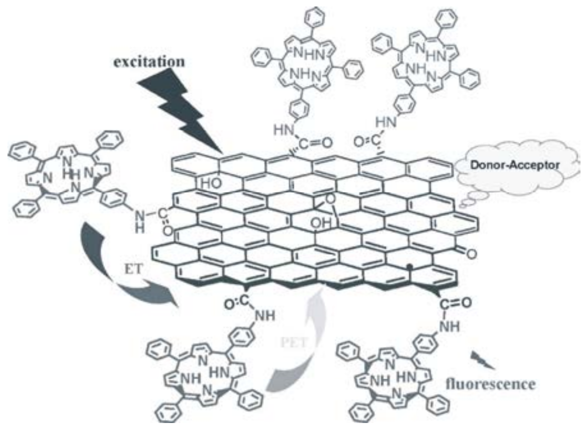

Fig. 1b: Schematic representation of part of the structure of the covalent TPP-NHCO-SPFGraphene

entire single-layered Graphene sheets in H_2O.[53,54] $TPP-NH_2$ and Graphene oxide molecules are covalently bonded together by an amide bond. Much care has been taken to make sure all the unreacted $TPP-NH_2$ has been removed using extensive solvent washing, sonication and membrane filtration. Details are given in the Experimental part. The attachment of organic molecules to Graphene oxide has made TPP-NHCO- SPFGraphene soluble in DMF and other polar solvents. [53,54]

Apparatus: Determination of Co^{2+} contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp(HI-HCl) according to the recommendations of the manufacturers. TPP-NHCO-SPFGraphene, (40 mg) were packed into an SPE ENVI-18 DISK™ disks. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 A° pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Sample Extraction: Extraction were performed with glassy membrane disks, ENVI-18 DISK™ 47mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 A° pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47mm filtration apparatus connected to water aspirator.[46]

Sample Treatment: The water samples were filtered through 45µm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 $molL^{-1}$ HNO_3 overnight and rinsed twice with deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of Co(II).Then, 5 mL of methanol was added to a 90 mL portion of each before analysis. The surface of the ENVI-18 DISK™ disks is modified with TPP-NHCO-SPFGraphene and therefore could retain Co^{2+} ions properly. Instead, 10 mg of TPP-NHCO-SPFGraphene, an appropriate volume of an organic solvent (5mL) miscible with water. The most suitable solvent under the experimental conditions was acetone.

Disk Cleaning and Conditioning: A disk was placed in the apparatus and was washed with 10 mL of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. To ensure optimal extraction of the analytes of interest, the disk was again washed with 10mL of methanol, immediately followed by 10mL of water, without leaving the surface of the disk dry. This step pre-wets the disk surface prior to extraction. Improper performance of this step causes slow flow - rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.

Sample Addition: After complete homogenization, accurate volumes of the sample solutions (100mL portions) were transferred to the top reservoir of the disk apparatus. At the same time, the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk was completely dry (about 5 minute).

Analyte Elution: In order to elute the analyte selectively, exactly 5 mL of acidified solvents 0.1M HCl in methanol was passed through the disk and collected into a 5.0 mL volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of Co(II) in the eluates were then determined by FAAS using an external calibration graph.

RESULTS AND DISCUSSION

Evaluation of the role of the TPP-NHCO-SPFGraphene: Some preliminary experiments were performed for investigation the role of absence or presence of TPP-NHCO-SPFGraphene, on the quantitative extraction of Co(II).It was concluded that the membrane disk itself does not show any tendency for the retention of Co(II), but introduction of 100 mL portions of aqueous Co(II) samples containing 10 µg of Co(II) and 10 mg of TPP-NHCO-SPFGraphene, led to its satisfactory its retention (Table 1). The latter case is most probably attributed to the existence of a considerable interaction between Co(II) and the TPP-NHCO-SPFGraphene. It should be mentioned that formation of stable complexes between Co(II) and TPP-NHCO-SPFGraphene, at pH=2 is probably due to an ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of Co(II) are negligible.

Choice of Eluent: In order to select the most appropriate eluent for the quantitative stripping of the retained Co(II) on the disks, 5mL of various non organic (each containing 10% $V.V^{-1}$ methanol) and different organic solvents were tested. The results tabulated in Table 1. As can be seen, the best eluting solvents were found to be 5mL of HNO_3 (2M)10% $V.V^{-1}$ mthanol, resulting in quantitative elution of Co(II) from the disk. It should be emphasized that presence of HNO_3 (2M)10% $V.V^{-1}$ mthanol in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disk.

The Effect of the pH: The pH of the sample solutions were adjusted to different values between 2-9 by addition of hydrochloric acid or a suitable buffer such as sodium acceate-acetic acid or sodium dihydrogen phosphate-disodium hydrogen phosphate and then solutions passed through the disks.

Table 1: The effect of presence of TPP-NHCO-SPFGraphene, on extraction percent of Co(II)a.

TPP-NHCO-SPFGraphene,	pH	Extraction percent of Co(II)
Absence	2-6	0.07(9.5)b
Presence	2-6	98.9(2.8) to 65(2.9)

[a] Initial samples contained 10µg of Co(II) in 100mL of water.

[b] Values in parentheses are RSDS based on five individual replicate analyses.

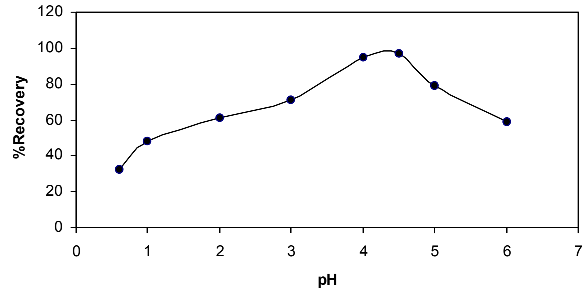

Fig. 2: Influence of sample pH on the percentage recovery of Co(II).

Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by flame atomic absorption determination of the eluted Co(II).Then, the percentage recovery at various pH values was determined (Fig.2). According to the results shown in Fig.2 up to pH 4.0-4.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of TPP-NHCO-SPFGraphene, occurs and there is a weak tendency for retention between Co(II) and TPP-NHCO-SPFGraphene,, whereas at higher values (pH>5), Co(II) reacts with hydroxide ions to produce $Co(OH)_2$. Therefore, sodium acceate-acetic acid buffer with pH=4.5 was used for the preconcentration step. Other solvents used for dissolving TPP-NHCO-SPFGraphene, were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Fig. 2. Mean while, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.[47,48] Co (II) ions can be retained quantitatively by the modified membrane disk through the pH range from 4.0 to 4.5 However, at lower pH (< 4.0), nitrogen atoms of the TPP-NHCO-SPFGraphene, could be protonated and the stability of complex is reduced.

Effect Amount of Counter Anion: In order to investigate the effect of counter ion on the recovery Co^{2+} ions by the modified disks, different counter anions were tested (Table 3), it is immediately obvious that the nature of the counter anion strongly influences the retention of Co ions by the disk. The results revealed that the TPP-NHCO-SPF Graphene, behaves in pH range 4.0-4.5 [28,27] so that the Co ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the SPE of Co(II).ions.

Table 2: Effect of different eluting solvents on Percentage recovery of Co(II) adsorbed on the disk[a]

	% Recovery		
Stripping solution	2ml	5ml	10ml
Nitric acid(2M)10% V.V-1 mthanol	82.9(2.6)b	92.8(2.6)	98.7(2.0)
Acidified methanol c	54.5(2.3)	83.2(2.2)	83.5(2.5)
Ammoniacal methanold	54.4 (2.5)	87.5(2.6)	86.0(2.6)
Nitric acid(1M)10% V.V-1 mthanol	82.7(1.6)	99.61.5)	99.5(2.3)
Acetonitril	36.6(4.8)	46.5(5.5)	69.0(2.2)
Formic acid(1M)10% V.V-1 mthanol	55.6(1.8)	68.3(2.0)	78.5(2.8)
Hydrochloric acid (1M)10% V.V-1 mthanol	52.7(1.9)	92.0(2.6)	90.2(2.0)
Hydrochloric acid (1M)10% V.V-1 mthanol	51.6(2.5)	65.3 (2.5)	97.5(1.6)
Methanol	52.8(1.9)	85.2(2.3)	80.4(2.0)
Ethanol	64.0(2.5)	85.6(2.1)	86.9(1.9)

[a] Initial samples contained 10 µg of each Co in 100 mL water.

[b]Values in parentheses are RSDs based on five individual replicate analysis.

[c] Acidified solvents obtained by addition of 0.1M Hcl.

[d]Ammoniacal solvents obtained by addition of 0.1M NH3

Table 3: Percent recovery of Co from the modified membrane disk in the presence of 0.01 M of different counter anions[a].

Counter anion	%Recovery
Cl^-	15.7
Br^-	20.6
ClO^{4-}	35.5
SCN^-	47.7
Picrate	74.8
Acetate	98.5

[a] Initial samples contained 10µg of Co(II) in 100mL of water.

Table 4: Influence of the TPP-NHCO-SPFGraphene, amount on the recovery of Co(II) ions a.

TPP-NHCO-SPFGraphene, amount (mg)	Recovery(%) of Co(II)
2	36.24(2.3)[b]
5	45.43(2.0)
8	83.21(2.2)
10	95.1(2.3)
15	98.5(2.4)
20	98.6(2.2)

[a] Initial samples contained 10 µg of each Co in 100 mL water.

[b]Values in parentheses are RSDs based on five individual replicate analysis.

The influence of the concentration of sodium acetate ion on Co recovery was investigated and the results are shown in Table 3. As seen, the percent recovery of Co^{2+} increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.

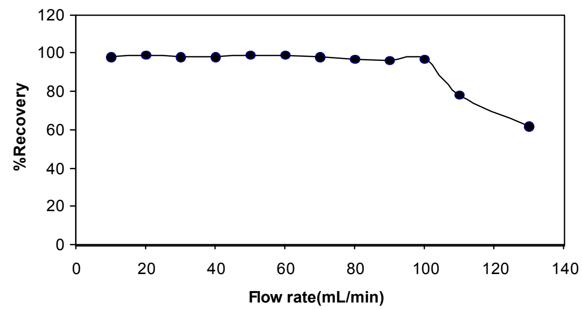

Fig. 3: The effect of the flow-rate on extraction percent of Co(II).

Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions- pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.

The Influence of Flow-Rate: One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-100 $mL.min^{-1}$, the retention of Co(II).was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Fig. 3). Thus, the flow-rate was maintained at $89mL.min^{-1}$ throughout the experiment.

Quantity of the TPP-NHCO-SPFGraphene: The optimum amount of TPP-NHCO-SPFGraphene, for the quantitative extraction of Co(II).was also investigated by adding various amounts of it to solution (between 2-20 mg). The results are listed in Table 4. The experimental results revealed that the extraction of Co(II).was quantitative using a sample solution containing more than 10 mg TPP-NHCO-SPFGraphene,. Hence, subsequent extractions were performed with 15mg of TPP-NHCO-SPFGraphene,.

Disk Efficiency: Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV-18 DISK™ disk could perform at least 14 replicate analyses if organic eluting solvents are used. On the other hand, acidic, eluents practically decrease the number of time a disk could be used to 10replicates. These observations are represented in Fig. 4.

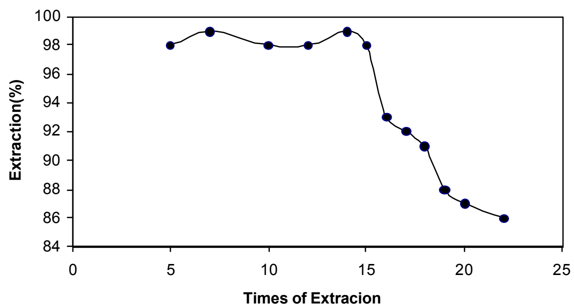

Fig. 4: Influence of eluent(5mL of methanol)type on disk efficiency.

Analytical Performance: When solutions of 10µg Co in 10, 50, 100, 600, 1000, 2000, 2500 and 3000mL solutions under optimal experimental conditions were passed through the disks, the Co(II).was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500mL, providing a concentration factor of >600. The limit of detection(LOD) of the method for the determination of Co(II) was studied under the optimal experimental conditions. The LOD based on 3ó of the blank(5mL of methanol) is 5 ng per 1000mL.

The capacity of modified disks(5mg TPP-NHCO-SPFGraphene,) was determined by passing 50mL portions of sample solutions containing 8mg of Co and 0.1M sodium acceate-acetic acid buffer with pH 4.0-4.5, followed by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disk obtained from three replicate measurements was 568±3µg of Co^{2+} on the disk.

In order to investigate the selective separation and determination of Co^{2+} ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions(50mL) containing 10µg Co^{2+} and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 5. The results show that the Co(II) ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100mg of various ions. Meanwhile, retention of other cations by the disk is very low and they can separated effectively from the Co^{2+} ion. Its is interesting to note that, in other experiments, we found that in the presence of high enough concentrations $NH_2OH.HCl$ as a suitable reducing agent (> 0.5M)[48].

Analysis of Water Samples: To assess the applicability of the method to real samples, it was applied to the extraction and determination of Co from different water samples. Tap water(Tehran, taken after 10 min operation of the tap), rain water(Tehran, 20January, 2012), Snow water (Tehran, 16 February,2012)and Sea water(taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table 6). As can be seen from Table 3 the added Co ions can be quantitatively recovered from the water samples used. As is seen, the recovered Co ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES.

Table 5: Separation of Co from binary mixtures[a]

Diverse ion	Amounts taken (mg)	% Found	%Recovery of Co^{2+} ion
Na^{+}	92.7	1.15(2.4)b	98.5(2.6)
K^{+}	95.8	1.32(2.3)	98.7(2.2)
Mg^{2+}	24.7	0.70(2.2)	98.2(2.7)
Ca^{2+}	26.6	2.20(3.0)	98.5(1.8)
Sr^{2+}	2.40	2.85(2.1)	97.9(2.3)
Ba^{2+}	3.65	3.16(2.5)	98.7(2.3)
Mn^{2+}	2.60	1.75(2.6)	96.3(2.3)
Ni^{2+}	2.18	6.40(1.7)	98.0(1.9)
Co^{2+}	1.64	2.23(2.1)	99.0(2.4)
Zn^{2+}	2.70	4.99(2.0)	97.9(2.6)
Cd^{2+}	2.57	2.90(2.0)	98.8(2.5)
Pb^{2+}	1.50	2.70(1.9)	97.8(2.4)
Hg^{2+}	1.69	2.81(2.1)	97.9(2.7)
Ag^{+}	2.6i	3.45(2.9)	98.6(2.6)
UO^{2+}	2.80	2.80(2.1)	98.3(2.5)

[a] Initial samples contained 10µg Co^{2+} and different amounts of various ions in 100 mL water(0.1 M acetate ion).

[b] Values in parentheses are RSDs based on five individual replicate analysis.

Table 6: Recovery of Co added to 1000mL of different water samples (contaning 0.1Macetate at pH= 4.0-4.5).

Sample	Co^{2+} added (µg)	Co^{2+}determined (ng.mL^{-1})	ICP-AES
Tap water	0.010.0	1.72(2.8)a11.94(2.5)	ND11.4
Snow water	0.010.0	4.85(2.4)14.93(2.3)	ND14.3
Rain water	0.010.0	2.82(2.1)12.83(2.2)	ND12.2
Sea Water	0.010.0	12.94(2.4)22.78(2.5)	12.422.90

[a] Values in parentheses are %RSDs based on five individual replicate analysisb Not detected.

CONCLUSION

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Co(II) in water samples using Octadecyl Silica membrane disks modified by (TPP-NHCO-SPFGraphene,) and its determination by

FAAS. The method developed was simple, reliable and precise for determining Co in water. Also, the proposed method was free of interference compared to conventional procedures to determine Co.[49-52]The methode can be successfully applied to the separation and determination of Co in binary mixtures.

ACKNOWLEDGEMENTS

The authour wish to thank the Chemistery Department of Varamin(pishva) branch Islamic Azad University and East Tehran branch Islamic Azad University for financial support.

REFERENCES

1. Leyden, D.E., G.H. Luttrell, W.K. Nonidez and D.B. Werho, 1978. Anal. Chem. 48: 67.
2. Jones, J.S., D.E. Harrington, B.A. Leone and W.R. Bramdstedt, 1983. Atom. Spectrosc. 4: 49.
3. Nambiar, D.C., N.N. Patil and V.M. Shinde, 1998. Fresenius J. Anal. Chem. 360: 205.
4. Caroli, C., A. Alimanti, F. Petrucci and Z.S. Horvath, 1991. Anal. Chim. Acta. 248: 241.
5. Alexandrova, A. and S. Arpadjan, 1993. Analyst 118: 1309.
6. Arpadjan, S., L. Vuchkova and E. Kostadinova, 1997. Analyst. 122: 243.
7. Leyden, D.E. and G.H. Luttrell, 1975. Anal. Chim. 47: 1612.
8. Gennaro, M.C., C. Baiocchi, E. Campi, E. Mentasti and R. Aruga, 1983. Anal. Chim. Acta. 151: 339.
9. Grote, M. and A. Kettrup, 1985. Anal. Chim. Acta. 175: 239.
10. Unger, K., Porous Silica, Elsevier, Amsterdam, 1979.
11. Boudreau, S.P. and W.T. Cooper, 1989. Anal. Chem. 61: 41.
12. Kvitek, R.J., J.F. Evans and P.W. Carr, 19821. Anal. Chim. Acta. 144: 93.
13. Bruening, M.L., D.M. Mitchell, J.S. Bradshaw, R.M. Izatt and R.L. Bruening, 1991. Anal. Chem., 63: 21.
14. Mahmoud, M.E., 1997. Talanta. 45: 309.
15. Mahmoud, M.E. and E.M. Soliman, 1997. Talata. 44: 15.
16. Mahmoud, M.E. and E.M. Soliman, 1997. Talanta. 44: 1063.
17. Tong, A., Y. Akama and S. Tanaka, 1990. Anal. Chim. Acta. 230: 179.
18. Dadler, V., L.F. Lindoy, D. Sallin and C.W. Schlaepfer, 1987. Aust. J. Chem. 40: 1557.
19. Mahmoud, M.E., 1998. in: Proceeding of the 25th FACSS Conference, Austin, TX, USA, pp: 11-15.
20. Mahmoud, M.E., 1999. Anal. Chim. Acta, 398: 297.
21. Leyden, D.E., G.H. Luttrell, A.E. Sloan and N.J. DeAngelis, 1976. Anal. Chim. Acta. 84: 97.
22. Qiaosheng, P., S. Qiaoyu, H. Zhide and S. Zhixing, 1998. Analyst. 123: 239.
23. Moghimi A., N. Tajodini, 2010. Asian Journal of Chemistry, 22(5): 3325-3334.
24. Tajodini, N. 2010. Moghimi Asian Journal of Chemistry, 22(7): 4994-5000.
25. Moghimi, A., M.S. Tehrani and S. Waqif Husain, 2006. Material Science Research India. 3(1a): 27.
26. Tehrani, M.S., A. Moghimi and S. Waqif Husain, 2005. Material Science Research India. 3(2): 135.
27. Campderros, M.E., A. Acosta and J. Marchese, 1998. Talanta. 47: 19.
28. Narin, I., M. Soylak, L. Elic and M. Dogan, 2000. Talanta. 52: 1041.
29. Zhou, T.Z., D.Y. Qi and C.P. Zhang, 1983. Acta Chim. Sin. 41: 237.
30. Zargaran, M., A.M. Shoushtari and M. Abdouss, 2008. J. Appl. Polym. Sci., 110: 3843.
31. Tabarzadi, M., M. Abdouss, S.A. Hasani and A.M. Shoushtary, 2010. Mat.-wiss. u.Werkstofftech. 41(4): 221
32. Shin, D.H., Y.G. Ko, U.S. Choi and W.N. Kim, 2004. Ind. Eng. Res., 43: 2060.
33. Nayebi, P. and A. Moghimi, 2006. Oriental Journal of Chemistry, 22(3): 507.
34. Mahmoud, M.E., 1998. in: Proceeding of the 25th FACSS Conference, *Austin, TX, USA*, pp: 11-15.
35. Pawliszyn, J., 1997. Solid-Phase Microextraction, Theory and Practice, Wiley-VCH, New York,
36. Izatt, R.M., J.S. Bradshaw and R.L. Bruening, 1996. Pure Appl. Chem. 68:1237.
37. Hagen, D.F., C.G. Markell and G.A. Schmitt, 1990. Anal. Chim. Acta. 236: 157.
38. Krueger, C.J. and J.A. Fild, 1995. Anal. Chem. 67: 3363.
39. Taylor, K.Z., D.S. Waddell, E.J. Reiner, 1995. Anal. Chem. 67: 1186.
40. Yamini, Y., M. Ashraf-Khorassani and J. High Resolut. Chromatogr. 17: 634.
41. Shamsipur, M., A.R. Ghiasvand and Y. Yamini, 1999. Anal. Chem. 71: 4892.
42. Shamsipur, M., A.R. Ghiasvand and H. Sharghi, 2001. Int. J. Environ. Anal. Chem. 82: 23.
43. Brunner, J., A. Mokhir and R.J. Kramer, 2003. Am. Chem. Soc. 125: 12410.

44. Zelder, F.H., J. Brunner and R. Kramer, 2004. Chem. Commun. pp: 902.
45. Boll, I., R. Kramer, J. Brunner and A. Mokhir, 2005. J. Am. Chem. Soc. 27: 7849.
46. Moghimi1, A., 2006. Oriental Journal of Chemistry 22(3): 527.
47. Nayebi, P. and A. Moghimi, 2006. Oriental Journal of Chemistry, 22(3): 507.
48. Moghimi, A., 2007. "Chinese Journal of Chemistry " 25: 640.
49. Moghimi, A., 2007. "Chinese Journal of Chemistry " 25,10, 1536.
50. Moghimi, A. and S. Ghammamy, 2007. "Environmental chemistry an Indian Journal, 2: 3.
51. Choi, Y.S. and H.S. Choi, 2003. Bull. Korean Chem. Soc. 24: 222.
52. Saber Tehrani, M., F. Rastegar, A. Parchehbaf and Z. Rezvani, Chinese Journal of Chemistry. 23: 1437.
53. Becerril, H.A., J. Mao, Z.F. Liu, R.M. Stoltenberg, Z.N. Bao and Y.S. Chen, 2008. ACS Nano, 2: 463.
54. Liu, Z.F., Q. Liu, X.Y. Zhang, Y. Huang, Y.F. Ma, S.G. Yin and Y.S. Chen, 2008. Adv.Mater., 20: 3924.
55. Hummers, Jr. W.S. and R.E. Offeman, 1958. J. Am. Chem. Soc. 80: 1339.