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Extraction of Co(II) by Isocyanate Treated Graphite Oxides (*i*GOs) Adsorbed on Surfactant Coated C_{18} Before Determination by FAAS

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ABSTRACT

A simple, highly sensitive, accurate and selective method for determination of trace amounts of Co(II) in water samples is presented. Isocyanate treated graphite oxides (*i*GOs) solid phase extraction adsorbent was synthesized by covalently isocyanate onto the surfaces of graphite oxides. The stability of a chemically (*i*GOs) especially in concentrated hydrochloric acid which was then used as a recycling and pre concentration reagent for further uses of (*i*GOs). The method is based on (*i*GOs) of Co(II) on surfactant coated C_{18}, modified with a isocyanate treated graphite oxides (*i*GOs). The retained ions were then eluted with 4 mL of 4 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) at 283.3 nm for Co. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5 g of surfactant coated C_{18} adsorbs 40 mg of the *i*GOs which in turn can retain 15.2±0.8 mg of ions. The limit of detection (3σ) for Co(II) was found to be 3.20 ng L^{-1}. The enrichment factor for both ions is 100. The mentioned method was successfully applied on determination of Cobalt in different water samples. The ions were also speciated by means of three columns system.

Keyword: Extraction of cobalt; Preconcentration; Isocyanate treated graphite oxides (*i*GOs); Flame atomic absorption spectrometry.

1. INTRODUCTION

The direct determination of trace metals especially toxic metal ions such as Co, Sn, As, Pb, Sb and Se from various samples require mostly an initial and efficient preconcentration step [1]. This preconcentration 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

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phase extraction techniques [3, 4]. The application of solid phase extraction technique for preconcentration of trace metals 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 on their surfaces [10] of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties 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 analysts [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 preconcentrators 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 preconcentration of various cations [21, 28]and 2-mercaptobenzothiazol modified silica gel for online preconcentration 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) was reported [5]. Mercapto modified silica gel phase was used in preconcentration 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 preconcentration of palladium(II) from water [28-33] are also sulfur contaning silica gel phases. The main goal of the present work is the development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Co(II) from aqueous media by means of a surfactant coated C_{18} modified with isocyanate-treated graphite oxides (*i*GOs). Such a determination has not been reported in the literature. The structure of isocyanate treated graphite oxides (*i*GOs) is shown in Figure 1. The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, *i*GOs or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C_{18} SPE mini-column.

2. EXPERIMENTAL

2.1. Reagents and apparatus

Graphite oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30 mL) by the Hummers [2]. Graphite oxide dried for a week over phosphorus pentoxide in a vacuum desiccators before use. 4-Isocyanato-benzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure [17]. All solutions were prepared with doubly distilled deionized water. C_{18} powder for chromatography with diameter of about 50 µm obtained from Katayama Chemicals. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water. Sodium dodecyl solfate (SDS) obtained from Merck and used without any further purification.

2.2. Synthetic procedures

2.2.1. Preparation of isocyanate-treated graphite oxides (iGOs)

In a typical procedure, graphite oxide (50 mg) was loaded into a 10 mL round bottom flask equipped with a magnetic stir bar and anhydrous DMF (5 mL) was then added under nitrogen to create an inhomogeneous suspension. The organic isocyanate (2 mmol) was next added and the mixture was allowed to stir under nitrogen for 24 h [17]. (In the case of solid isocyanates, both the isocyanate and graphite oxide were loaded into the flask prior to adding DMF.) After 24 h the slurry reaction mixture was poured into methylene chloride (50 mL) to coagulate the product. The product was filtered, washed with additional methylene chloride (50 mL), and dried under vacuum.

2.2.2. Column preparation

*I*GOs (40 mg) were packed into an SPE mini-column (6.0 cm × 9 mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L^{-1} HNO_3 and (double) distilled water were passed through the column to clean it.

2.3. Apparatus

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of *i*GOs were carried out from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Zn(II) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Zn(II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analysis was performed with a Perkin-Elmer.

2.3.1. Preparation of admicell column

To 40 mL of water containing 1.5 g of C_{18}, 150 mg of the above *i*GOs was loaded after washing acetone, 1 mol L^{-1} HNO_3 solution and water, respectively, solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO_3 and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained C_{18} was washed three times with water, then with 5 mL of 4 M HNO3 and again three times with water. The prepared sorbent was transferred to a polypropylene tube (i.d 5 mm, length 10 mm). 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. These characteristics are tabulated in (Table 1). A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

Table 1: *The operational conditions of flame for determination of Cobalt.*

Slit width	0.7 nm
Operation current of HI-HCL	10 mA
Resonance fine	283.3
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL.min^{-1}
Acetylene flow	1.7 mL.min^{-1}

2.3.2. Procedure

The pH of a solution containing 100 ng of Co(II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5 mL min^{-1}. The column was washed with 10 mL of water and the retained ions were desorbed with 1 mL of 4 M HNO_3 with a flow rate of 2 mL min^{-1}. Desorption procedure was repeated 3 more times. All the acid solutions (4 mL all together) were collected in a 10 mL volumetric flask and diluted to the mark with water. The concentrations of Cobalt in the solution were determined by FAAS at 283.3.

2.3.3. Determination of cobalt in water samples

Polyethylene bottles, soaked in 1 M HNO_3 overnight, and washed two times with water were used for sampling. The water sample was filtered through a 0.45 µm pores filter. The pH of a 1000 mL portion of each sample was adjusted to 2.0 (4 M HNO_3) and passed through the column under a flow rate of 5 mL min^{-1}. The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

2.3.4. Speciation of cobalt in water samples

This procedure is reported in several articles. The method has been evaluated and optimized for speciation and its application on complex mixtures [26-29]. The chelating cation exchanger (Chelex-100) and anion exchanger, Dowex 1X-8 resins were washed with 1 M HCl, water, 1 M NaOH and water respectively. 1.2 g of each resin was transfered to separate polyethylene columns. Each column was washed with 10 mL of 2 M HNO_3 and then 30 mL of water. The C_{18} bounded silica adsorber in a separate column was conditioned with 5 ml of methanol, then 5 mL of 2 M HNO_3 and at the end with 20 mL of water. 5 mL of methanol was added on top of the adsorber, and passed through it until the level of methanol reached just the surface of the adsorber. Then water was added on it and connected to the other two columns. A certain volume of water sample was filtered through a 0.45 µm filter and then passed through the three columns system, Dowex 1X-8, RP-C_{18} silica adsorber and Chelex-100 respectively. The columns were then separated. The anion and cation exchanger columns were washed with 10 mL of 2 M HNO_3 and the C_{18} column with 10 mL of 1 M HCl. The flow rate of eluents was 1 mL min^{-1}. The Cobalt content of each eluted solution was determined by FAAS.

3. RESULTS AND DISCUSSION

The treatment of GO with organic isocyanates can Cobalt to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides [20] or carbamate esters [21], respectively (Figure 1a). The chemical changes occurring upon treatment of GO with isocyanates can be observed by FT-IR spectroscopy as both GO and its isocyanate-treated derivatives display characteristic IR spectra. Figure 1b illustrates the changes occurring in the FT-IR spectrum of GO upon treatment with phenyl isocyanate (for FT-IR spectra of all *i*GO derivatives see Electronic Supporting Information (ESI)). The most characteristic features in the FT-IR spectrum of GO are the adsorption bands corresponding to the C=O carbonyl stretching at 1733 cm^{-1}, the O-H deformation vibration at 1412 cm^{-1}, the C-OH stretching at 1226 cm^{-1}, and the C-O stretching at 1053 cm^{-1} [5,8,12]. Besides the ubiquitous O-H stretches which appear at 3400 cm^{-1} as a broad and intense signal (not shown), the resonance at 1621 cm^{-1} can be assigned to the vibrations of the adsorbed water molecules, but may also contain components from the skeletal vibrations of un-oxidized graphitic domains [5, 22, 23].

Upon treatment with phenyl isocyanate, the C=O stretching vibration at 1733 cm^{-1} in GO becomes obscured by the appearance of a stronger absorption at 1703 cm^{-1} that can be attributed to the carbonyl stretching vibration of the carbamate esters of the surface hydroxyls in *i*GO. The new stretch at 1646 cm^{-1} can be assigned to an amide carbonyl-stretching mode (the so-called Amide I vibrational stretch). The new band at 1543 cm^{-1} can originate from either amides or carbamate esters and corresponds to the coupling of the C-N stretching vibration with the CHN deformation vibration (the so-called Amide II vibration) [24]. Significantly, the FT-IR spectra of *i*GOs do not contain signals associated with the isocyanate

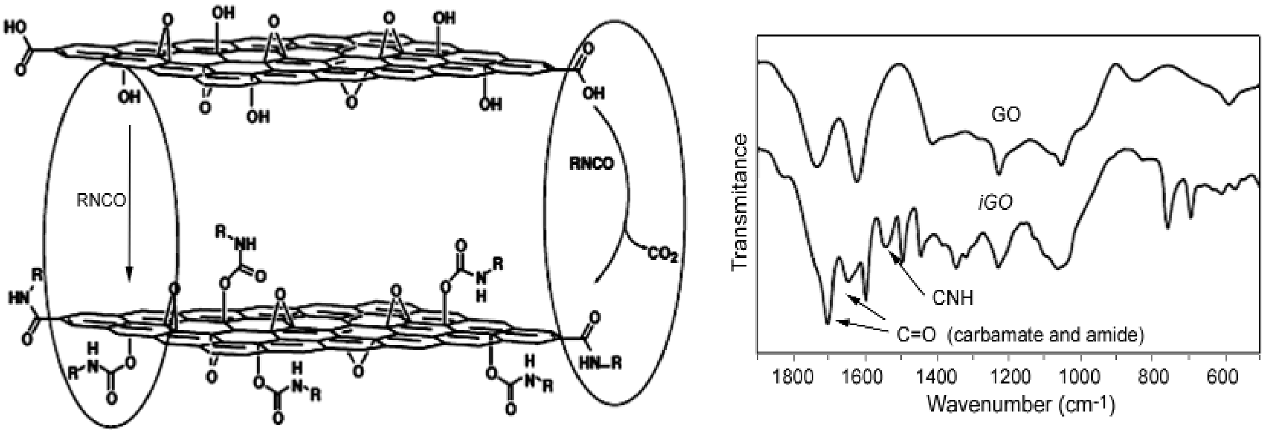

Figure 1: *(a) Proposed reactions during the isocyanate treatment of GO where organic isocyanates react with the hydroxyl (left oval) and carboxyl groups (right oval) of graphene oxide sheets to form carbamate and amide functionalities, respectively. (b) FT-IR spectra of GO and phenyl isocyanate treated GO.*

group (1275-1263 cm^{-1}), indicating that the treatment of GO with phenyl isocyanate results in chemical reactions and not mere absorption/intercalation of the organic isocyanate [30].

3.1. Stability studies

The stability of the newly synthesized *i*GO phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Co(II)s, this ion was used to evaluate the stability measurements for the *i*GO phase [14].

The results of this study proved that the *i*GO is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively. Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a nano poly-meric matrix [9]. Finally, the *i*GO phases were also found to be stable over a range of 1 year during the course of this work the *i*GO is insoluble in water. Primary investigations revealed that surfactant coated C_{18} could not retain Co(II) cations, but when modified with the *i*GO retains these cations selectively. It was then decided to investigate the capability of the *i*GO as a ligand for simultaneous preconcentration and determination of Cobalt on admicell. The C_{18} surface in acidic media (1<pH<6) attracts protons and becomes positively charged. The hydrophyl part of SDS (-SO3-) is attached strongly to these protons. On the other hand, the *i*GO are attached to hydrophobe part of SDS and retain small quantities of metallic cations [22].

3.2. Effect of pH in extraction

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Co(II) was studied in the pH rang of 1-10. The pH of the solution was adjusted by means of either 0.01 M HNO_3 or 0.01 M NaOH. The results indicate that complete chelation and recovery of Co(II) occurs in pH range of 2-4 and that of in 2-8 and are shown in Figure 2. It is probable that at higher pH values, the cations might be hydrolysed and complete desorbeption does not occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the C_{18}, pH=2.0 was chosen for further studies.

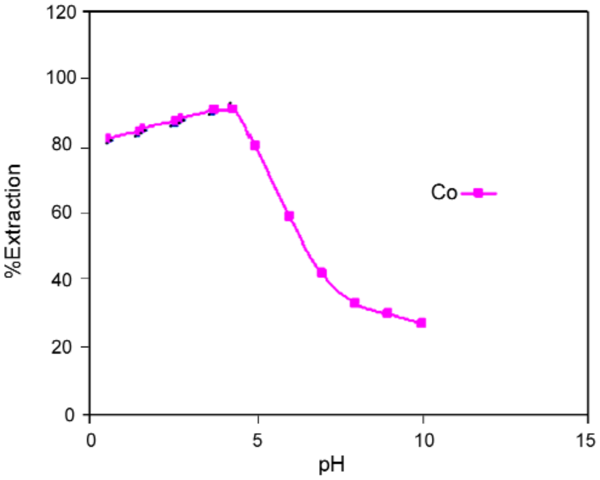

Figure 2: *Extraction percentage of Co(II) against pH.*

3.3. Effect of flow rates of solutions in extraction

Effect of flow rate of the solutions of the cations on chelation of them on the substrate was also studied. It was indicated that flow rates of 1-5 mL min^{-1} would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified C_{18} with SDS and an *i*GO has been reported in literature [21, 22]. Flow rate of 1-2 mL min^{-1} for desorption of the cations with 4 mL of 4 M HNO_3 has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5 mL min^{-1} and 2 mL min^{-1} were used for sample solution and eluting solvent throughout respectively.

3.4. Effect of the iGO quantity in extraction

To study optimum quantity of the *i*GO on quanti-tative extraction of Cobalt, 50 mL portions of solutions containing 100 ng of each cation were passed through different columns the sorbent of which were modified with various amounts, between 10-50 mg of the *i*GO. The best result was obtained on the sorbent which was modified with 40 mg of the *i*GO.

3.5. Figures of merit

The breakthrough volume is of prime importance for solid phase extractions. Hence, the effect of sample volume on the recovery of the Co (II) was studied. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 mL of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 mL. Because the sample volume was 1000 mL and the cations were eluted into 10 mL solution, the enrichment factor for both cations is 100, which is easily achievable. In other experiment for maximum capacity of 1.5 g of the substrate was determined as follow; 500 mL of a solution containing 50 mg of each cation was passed through the column. The chelated ions were eluted and determined by FAAS. The maximum capacity of the sorbent for three individual replecates was found to be 15.2±0.8 μg of each cation. The limit of detection (3σ) for the catoins [30] was found to be 3.20 ng.L^{-1} for Cobalt ions. Reproducibility of the method for extraction and determination of 100 ng of each cation in a 50 mL solution was examined. Results of seven individual replicate measurements indicated 2.85%.

3.6. Effect of foreign ions

Effect of foreign ions was also investigated on the measurements of Cobalt. Here a certain amount of foreign ion was added to 50 ml of sample solution containing 100 ng of each Co(II) with a pH of 2.5. The amounts of the foreign ions and the percentages of the recovery of Cobalt are listed in Table 2. As it is seen, it is possible to determine Cobalt without being affected by the mentioned ions. According to the Table 2 and comparison between the amount of cobalt (ng) and foreign ions (mg), recover trace of cobalt ions.

3.7. Analysis of the water samples

The prepared sorbent was used for analysis of real samples. To do this, the amounts of Cobalt were determined in different water samples namely: distilled water, tap water of Tehran (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 25 January, 2013), Snow water (Tehran, 7 February, 2013), and two synthetic samples containing different cations. The results are

Table 2: *Effect of foreign ions on the recovery of 100 ng of Co.*

Diverse ion	Amounts taken (mg) added to 50 mL	Found % Determination of Co^{2+}	Recovery % of Co^{2+} ion
Na^+	92.4	1.19(2.9)a	98.3(1.9)
K^+	92.5	1.38(2.1)	98.9(2.2)
Mg^{2+}	14.5	0.8(1.8)	98.6(2.7)
Ca^{2+}	28.3	1.29(2.0)	95.4(1.9)
Sr^{2+}	3.42	2.81(2.2)	98.2(2.1)
Ba^{2+}	2.66	3.16(2.4)	98.3(2.0)
Mn^{2+}	2.64	1.75(2.3)	98.5(1.8)
Ni^{2+}	2.65	2.0(2.14)	98.4(2.4)
Zn^{2+}	2.74	1.97(2.1)	98.7(2.2)
Cd^{2+}	2.53	1.9(2.0)	98.8(2.8)
Bi^{3+}	2.55	2.7(1.4)	98.4(2.7)
Cu^{2+}	2.46	2.81(2.3)	97.7(2.5)
Fe^{3+}	2.60	3.45(2.4)	96.6(2.8)
Cr^{3+}	1.70	2.92(2.2)	97.3(2.4)
UO^{2+}	2.89	1.3(2.2)	98.3(2.2)
NO^{3-}	5.8	2.3 (2.3)	98.4(2.6)
CH_3COO^-	5.0	2.2(2.6)	94.5(2.2)
SO_4^{2-}	5.0	2.9(3.0)	98.7(2.1)
CO_3^{2-}	5.6	1.8(2.5)	96.3(2.5)
PO_4^{3-}	2.5	2.1(2.0)	98.9(2.0)

a: Values in parenthesis are CVs based on three individual replicate measurements.

tabulated in Table 3. As it is seen, the amounts of Cobalt added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method.

Separation and speciation of cations by three columns system is possible to preconcentrate and at the same time separate the neutral metal complexes of *i*GO, anionic complexes and free ions from each other by this method [27]. Water samples were passed through the three connected columns: anoin exchanger, C_{18} silica adsorber and chelating cation exchanger. Each species of Cobalt is retained in one of the columns; anionic complexes in the first column, neutral complexes of *i*GO in the second, and the free ions in the third. The results of passing certain volumes of different water samples through the columns are listed in Table 4. According to the results, it is indicated that Cobalt present only as cations. On the other hand the t-test comparing the obtained mean values of the present work with those published indicate no significant difference between them. We have proposed a method for determination and preconcentration of Co in water samples using surfactant coated C_{18} impregnated with a Sciff's base. The proposed method offers simple, highly sensitive, accurate and selective method for determination of trace amounts of Co(II) in water samples.

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Table 3: *Recovery of Co (II) contents in different water samples.*

	Amounts added (µg)	Found (µg)	%Recovery
Sample distilled water (100 mL)	-	-	-
	0.005	0.043(2.40)[a]	96
Tap water (100 mL)	0.100	0.094(2.90)	97
	-	0.015(3.54)	-
Snow water (50 mL)	0.050	0.066(2.42)	96
	-	0.048(2.25)	-
Rain water (100 mL)	0.100	0.157(2.65)	98.0
	-	0.042(2.25)	-
Synthetic sample 1 Na^+, Ca^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Hg^{2+}, 1 mg L^{-1}	0.100	0.106(2.45)	98
	-	-	-
Synthetic sample 2 K^+ Ba^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}	0.100	0.104(2.46)	0.100
1 mg L^{-1} of each cation	-	-	-
	0.100	0.103(2.73)	99

a: Values in parenthesis are CVs based on three individual replicate measurements.

Table 4: *Results of speciation of Co^{2+} in different samples by three columns system.*

	Tap water (1000 mL)	water sample (1000 mL)[a]	River Water (50 mL)
Column	Co(II) (µg)	Co(II) (µg)	Co(II) (µg)
Dowex 1X8	-	-	-
Silica C-18	-	-	-
Chelex-100	0.012 (4.4)[b]	0.104 (2.3)	0.103 (2.2)

a: This was a solution containing 0.1 µg of Co(II) in 1000 mL of distilled water.
b: Values in parenthesis are CVs based on three replicate analysis. The samples are the same as those mentioned in Table 4.

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