

Separation and Extraction of Co(II) using Mesoporous Organo-Silicas and determination By FAAS

Ali Moghimi^{1,*} and Alireza Shahab Lavasani²

¹Department of Chemistry, Varamin(Pishva) branch, Islamic Azad University, Varamin, Iran.

²Department of Food Science and Technology, Varamin- Pishva Branch, Islamic Azad University, Iran.

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ABSTRACT

A novel and selective method for the fast determination of trace amounts of Co(II) ions in water samples has been developed. The procedure is based on the selective formation of Co(II) ions using mesoporous organo-silicas mesoporous silica at different pH followed by elution with organic eluents and determination by atomic absorption spectrometry. The preconcentration factor was 100 (1 ml elution volume) for a 100 ml sample volume. The limit of detection of the proposed method is 1.0 ng ml^{-1} . The maximum sorption capacity of sorbent under optimum conditions has been found to be 5mg of Co per gram of sorbent. The relative standard deviation under optimum conditions was 3.0% ($n = 10$). Accuracy and application of the method was estimated by using test samples of natural and synthetic water spiked with different amounts of Co(II) ion.

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Introduction

The direct determination of trace 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 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 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) was reported [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-dithiocarboxylic 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 containing silica gelpases. In this study, we report the synthesis of this new sorbent and its application as a selective sorbent for separation, preconcentration and determination of Co^{2+} ions by AAS determination.

Tele:

E-mail address: kamran9537@yahoo.com

Experimental

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 hollow cathode lamp (HI-HCl) according to the recommendations of the manufacturers. Separation of sorbent was assisted using a centrifuge (centurion scientific model: K 240R, West Sussex, U.K.). The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Reagents and solutions

All reagents were of the highest purity available from Merck and were used as received. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and copper(II) were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstadt, Germany, and High Purity double distilled deionized water was used throughout the experiments.

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

The chemicals used for the preparation of mesoporous silica-based materials were used as received: tetraethoxysilane TEOS (>98% Merck), γ -aminopropyltriethoxysilane APTES (99% Sigma–Aldrich), cetyltrimethylammonium bromide (CTAB) (98% Fluka), ethanol (95–96% Merck) and aqueous ammonia (28% Prolabo).

Preparation and characterisation of the mesoporous organo-silicas

The mesostructured amine-functionalised silica material was prepared according to a previously published procedure^{42,43}. First 2.4 g of CTAB was dissolved in a solution containing 50 mL distilled water + 50 mL ethanol + 13 mL ammonia 28%. Then, the precursors APTES and TEOS were introduced according to an APTES/(APTES + TEOS) molar ratio of 10%. The mixture was left under stirring at ambient condition for 2 h, then filtered on a Büchner funnel, rinsed alternatively with distilled water and ethanol, and dried under vacuum ($<10^{-2}$ bar) for 24 h. Surfactant extraction was achieved by refluxing 1 g of the as-synthesised solid into 100 mL of 1 M HCl in ethanol for 18 h. The final product was recovered by filtration after washing three times with ethanol. It will be denoted “APS” (aminopropylsilica) afterwards. The particles have been characterized by powder X-ray diffraction (XRD), the resulting XRD patterns being collected with an X'PERT PRO from Philips equipped with a Co anode ($\text{K}\alpha 1$ radiation, $k = 1.54056 \text{ \AA}$). Their porosity was analysed by the BET method on the basis of nitrogen adsorption–desorption measurements carried out at 77 K using a Coulter SA3100 apparatus after outgassing overnight at 323 K. Particle size distribution was measured using a light scattering analyser (model LA920, Horiba), based on the Mie scattering theory.

For some experiments, an amorphous silica material functionalised with the dipeptide carnosine was used as a solid-phase extractant for Co(II) species. It was obtained by allowing TEOS to co-condensate with a precursor synthesised by amide coupling between the amino group of APTES and the carboxyl group of carnosine, using ethanol as co-solvent and ammonia in a catalytic amount^{41,44}. The copolymer precipitates several hours

after mixing 1.21 g of the (triethoxysilyl)alkylamido-carnosine precursor with 1.95 g TEOS, in a solution containing 1.22 g water and 6.42 g ethanol, with 0.06 g NH_3 as the catalyst. The solvents are slowly evaporated to recover a dry white solid after about five days of reaction, the solid particles being washed thoroughly with dichloromethane and methanol before use. They are noted “Scar” (silica-carnosine) hereafter.

Procedure

A batch-wise process was employed for the extraction and preconcentration of Co. Extraction was performed in test tubes containing Co^{2+} in 10 ml acetate buffered solution (pH 3.0). Sixty milligrams mesoporous organo-silicas was added into the solution. After that, the mixture was shaken manually for an appropriate time to extract Co completely from the solution. Finally, test tubes were placed in centrifuge and separation of sorbent was achieved by centrifugation for 2.5 min at 3500 rpm. The bulk aqueous phase was removed with a pipette and any residual aqueous phase was easily decanted. The back extraction was performed using 1.0 ml of 1.0 mol l^{-1} methanol solution. The Co concentration was determined by Flame Atomic Absorption Spectrometry (FAAS).

Results and discussion

Some preliminary experiments were carried out in order to investigate the extraction of Co by the mesoporous organo-silicas from solution. The results showed that mesoporous organo-silicas can extract it quantitatively.

Characterisation of silica-based materials

The physico-chemical characteristics of both APS and Scar materials are as expected from previous studies^{41,43}.

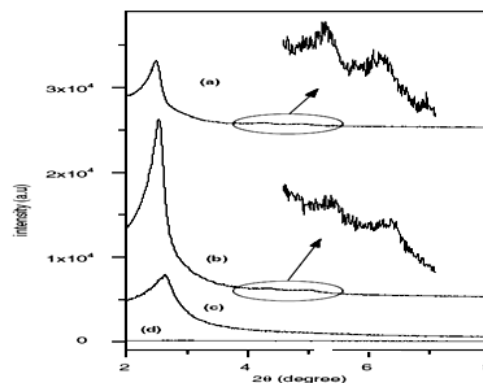


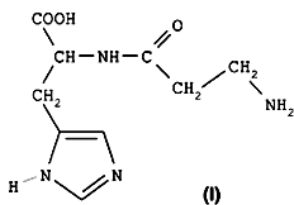
Fig. 1. Powder XRD patterns for: (a) as-synthesised APS, (b) surfactant-extracted APS, (c) surfactant-extracted APS after deprotonation in alkaline ethanol, and (d) surfactant-extracted APS after deprotonation in alkaline aqueous medium (0.01M NaOH)

X-ray diffractogram of APS (Fig. 1, curve ‘a’) reveals the existence of an ordered structure at the mesoporous scale, typical of a hexagonal MCM-41 structure, featuring one main correlation reflection at a 2θ angle of 2.49° and two weaker reflections at higher 2θ angles (diffraction planes indexed as 1 0 0, 1 1 0 and 2 0 0). The regular mesostructure was maintained after template removal (Fig. 1, curve ‘b’), this step resulting however in slight lattice contractions (2θ angle of main line at 2.54°) as previously observed for mesoporous organo-silicas prepared by the co-condensation route⁵². Nitrogen adsorption–desorption isotherms were of type IV (not shown here but similar as in⁴²), in agreement with what was usually observed with mesoporous materials⁵³. A specific surface area of $950 \text{ m}^2 \text{ g}^{-1}$ and pore size of 22 \AA were determined by BET and BJH

analyses, respectively. The synthetic method applied to prepare the mesoporous APS material led to the production of spherical particles of an average diameter of 600 nm, but most of them were in the form of bigger aggregates displaying a particle size distribution centred at 6.5 ± 1.4 μm . The content of aminopropyl groups in APS was 1.1 mmol g^{-1} , as determined from elemental analysis. These groups, however, were in the form of propylammonium chloride as a consequence of template extraction performed in HCl/ethanol medium.

The silica-carnosine hybrid material, Scar, was described in reference⁴¹ as an amorphous solid (flat XRD pattern) characterised by a specific surface area of $62 \text{ m}^2 \text{ g}^{-1}$, a total pore volume of $0.279 \text{ cm}^3 \text{ g}^{-1}$, and an average pore diameter of about 160 \AA . Due to a treatment of Scar with gaseous HCl during the synthesis protocol^{41,44}, the carnosine groups (b-alanyl-L-histidine I) attached to the silica framework were also protonated.

These materials are potentially good candidates for the extraction of Co(II) species from dilute aqueous medium because of the well-known tendency of amine derivatives to form stable complexes with Co(II). Indeed, both aminopropyl-grafted silica gels⁴⁰ and carnosine functionalised silica⁴¹ have been incorporated in carbon paste electrodes and successfully applied to electrochemical sensing of Co(II) after preconcentration. In the present case, however, APS and Scar contain a great majority of their N centres in a protonated form. This is expected to limit their binding properties (decreasing stability of amine-Co (II) complexes at pH below 7⁴⁰), thus requiring deprotonation of the material prior to use.

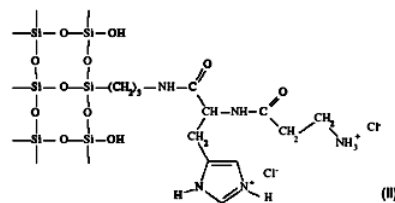


Deprotonation of APS without damage to the structural and chemical integrity of the material is not an easy task. As shown in curve 'd' on Fig. 1, a treatment of APS in aqueous NaOH (0.01 M) resulted in the complete crashing of the mesostructure, which was accompanied by dramatic leaching of aminopropyl groups and silicon moieties in solution. A similar treatment in 95% ethanol was less destructive as some order was maintained (Fig. 1, curve 'c') but the mesostructure was by far less ordered as the diffraction line corresponding to the 1 0 0 plane dropped significantly in comparison to the non treated solid while the weaker reflections at higher 2 θ angles disappeared. This XRD pattern also revealed a shift of the diffraction line at higher 2 θ values, indicating a significant contraction of the lattice with possible partial structure collapsing, as otherwise confirmed by BET measurements (specific surface area dropping by a factor of about 2.5 and pore volume by a factor 3).

Effect of pH

Basically, the approach described above for Co(II) detection at APS-MCPE should be applicable to any modified electrode system involving N-bearing ligands that would require a modulation of their properties by a pH change. To point out this generalisation aspect, we have revisited an earlier work dealing with the use of an amorphous silica sample functionalised with carnosine groups (Scar), which was applied as modifier of a carbon paste electrode (Scar-MCPE) to Co(II) preconcentration and detection⁴¹. The synthetic protocol to get the Scar material

involved protection/deprotection processes resulting in N-bearing ligands under their protonated form, counter-balanced by chloride anions (compound II).



The effect of pH on the extraction of Co^{2+} from water samples was studied in the pH range of 1.0–8.0. The higher pH values were not studied because functionalized mesoporous silicates were not stable in alkali solutions due to the breaking of the Si–O–Si bonds by hydroxide ions attack⁵⁴. pH of the solution was adjusted at the required value by adding 1.0 mol l^{-1} sodium hydroxide and/or 1.0 mol l^{-1} nitric acid. As can be seen in Fig. 2, extraction was nearly constant and quantitative in the pH range of 2–8.0. At lower pH (<2.5), the nitrogen atoms in mesoporous organo-silicas are protonated, so the stability of complex formation between the sorbent and Co^{2+} is reduced. Therefore, the extraction of Co decreased. Hence, pH of 3.0 was chosen as the optimum pH for extraction.

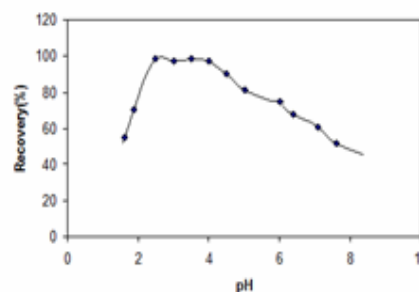


Fig. 2. Effect of pH on the extraction of Co. Experimental conditions: source, 10 ml of $0.1 \mu\text{gml}^{-1}$ Co^{2+} solution; amount of sorbent, 50.0 mg

Choice of eluent

In order to choose the most effective eluent for desorbing Co ion from the sorbent surface aliquots of 10 ml of $0.1 \mu\text{gml}^{-1}$ Co ion solution was contacted with 50.0 mg of mesoporous organo-silicas. A series of selected eluent solution such as nitric acid, formic acid, acetic acid, sodium thiosulfate, ethanol and methanol was used. A total of 10.0 ml of 0.1 mol l^{-1} of the above mentioned eluents were used for desorbing the adsorbed Co ion. The amount of Co ion back-extracted into the liquid phase by each eluent was measured using Flame Atomic Absorption Spectrometry (FAAS). Percent recoveries of Co ion were calculated for each sample. The results (Fig. 3) showed that recovery was the best when methanol was used as eluent. Also, higher concentrations of hydrochloric and nitric acid (0.5 and 1.0 mol l^{-1}) solutions were tested and the results showed the recovery of Co was not quantitative. Therefore, methanol was selected as eluent.

Effect of eluent concentration

The influence of the concentration of methanol on desorption of Co ion was studied. For desorbing $1.0 \mu\text{g}$ Co ion, already adsorbed on 50.0 mg of sorbent, 1.0 ml of different concentration of eluent (methanol) have been used. At a

concentration of more than 0.7 mol l^{-1} , methanol desorbs (recovery of almost 100%) Co ion completely from the sorbent surface. A concentration of 1.0 mol l^{-1} of methanol was selected for further studies.

Effect of the sample volume

In order to explore the possibility of concentrating low concentrations of Co from large volumes, the maximum applicable volume must be determined. For this purpose, the effect of the sample solution volume on the recovery was studied by keeping the total amount of Co^{2+} uptake constant ($1.0 \mu\text{g}$). The quantitative recoveries were obtained for sample volume of $\leq 100 \text{ ml}$. Therefore, the concentration factor was 100 for Co^{2+} since the final elution volume was 1.0 ml .

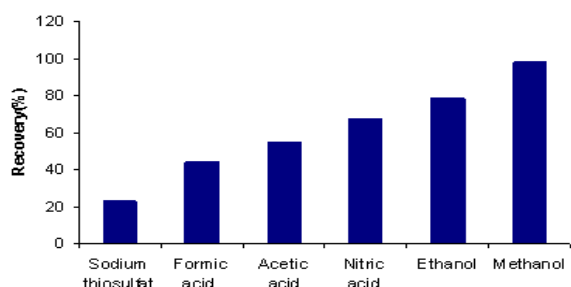


Fig. 3. Effect of nature of eluent on the recovery of Co.
Experimental conditions: source, 10 ml of $0.1 \mu\text{g ml}^{-1} \text{ Co}^{2+}$ solution at $\text{pH } 3.0$; sorbent 50.0 mg .

Effect of the amount of mesoporous organo-silica

To test the effect of the amount of mesoporous organo-silicas on quantitative retention of analyte different amounts of sorbent (range from 2.0 to 200.0 mg) were added into the solution following the experimental method. The results showed that the extraction of Co^{2+} was quantitative by using only 10.0 mg of mesoporous organo-silicas. Subsequent extraction experiments were carried out with 50.0 mg of mesoporous organo-silicas in order to achieve higher capacity and to account for other extractable species.

Adsorption capacity

The capacity of the sorbent is an important factor that determines how much sorbent is required to remove a specific amount of metal ions from the solution quantitatively. For investigation of adsorption isotherm of Co ion, the same volumes of Co ion solution with different concentrations of Co ion were contacted with 0.1 g of sorbent in the batch mode. Then, the concentration of the remaining Co in the solution was determined by Flame Atomic Absorption Spectrometry (FAAS). The adsorption isotherm that is the number of microgram absorbed per gram of adsorbent (N_f) versus the equilibrium concentration of cation (C_e) is shown in Fig. 4. According to these results, the maximum amount of Co that can be sorbed by mesoporous organo-silicas was found to be 5 mg g^{-1} at $\text{pH } 3.0$.

Effect of equilibrium time

In order to investigate the effect of shaking time on the extraction efficiency, extraction for a series of solutions containing $1.0 \mu\text{g Co}^{2+}$ were carried out. The results showed that the shaking time (from 20 to 350 s) has no effect on the extraction efficiency of Co and the extraction was quantitative. Although the extraction process can be continued during the centrifugation, however, the results showed that extraction was quantitative and very fast in all cases. Thus, the mixtures have

been shaken for 20 s to reach equilibrium in the subsequent experiments.

Effect of ionic strength

The influence of ionic strength on the extraction of Co was studied in the potassium nitrate solution with various concentrations from 0.01 to 1.0 mol l^{-1} . Results have shown that ionic strength has no considerable effect upon extraction efficiency up to 1.0 mol l^{-1} of KNO_3 . These observations showed the specific tendency of mesoporous organo-silicas for Co^{2+} and the possibility of using this method for separation of Co from highly saline solutions.

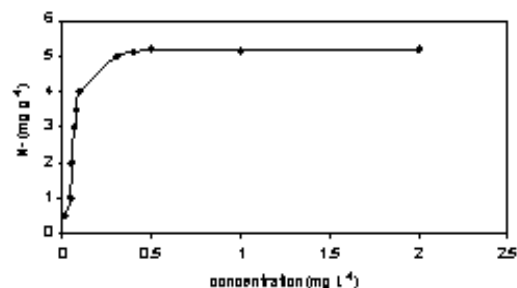


Fig. 4. Adsorption isotherm of Co(II) ion on sorbent
Effect of coexisting ions

The effects of common coexisting ions in natural water samples on the recovery of Co were studied. In these experiments, 10 ml of solutions containing $0.1 \mu\text{g l}^{-1}$ of Co and various amounts of interfering ions were treated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation in the extraction recovery of sample more than $\pm 5\%$. The results showed that, in excess of $10,000$ -fold Li^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} and 1000 -fold Cl^- , Br^- , SO_4^{2-} , Ag^+ , Cu^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Pb^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+} and Hg^{2+} ions had no significant interferences in the extraction and determination of Co. As can be seen, mesoporous organo-silicas has shown a high tolerance limit for alkali and alkaline earth metals. This is particularly useful for the analysis of Co in natural water samples, for example, seawater, which contain large amounts of alkali and alkaline earth metal ions.

Reusability and stability of mesoporous organo-silicas

Reusability is one of the key parameters to assess the effectiveness of a sorbent. A series of sorption/desorption experiments were performed to understand the reusability of the synthesized mesoporous organo-silicas. After sorption, the sorbent was treated with 1.0 mol l^{-1} methanol to desorb Co^{2+} and this sorption/desorption procedure was repeated five times. After each desorption step, the sorbent was washed with doubly distilled water to remove methanol and condition sorbent. On storing for a year under dark and dry conditions, the stability of sorbent was excellent and adsorption capacity did not change significantly.

Analytical Performance

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the amount of analyte necessary to yield a signal equal to three times (3σ) and ten times (10σ) the standard deviation of the blank signals, respectively. Using sample volume of 100 ml a LOD of $1.0 \mu\text{g l}^{-1}$ and a LOQ of $1.2 \mu\text{g l}^{-1}$ were obtained for the determination of Co. Ten replicate extraction and measurement of $1.0 \mu\text{g}$ of Co^{2+} ion in 100 ml water solution gave a R.S.D. of 3.0% .

Table 1			
Recovery of Co(II) added to 100mL of different water samples (containing 0.1M buffer acetic acid / acetate at pH= 3.0).			
Recovery (%)	Co ²⁺ detected (ng ml ⁻¹)	Co ²⁺ spiked (ng ml ⁻¹)	Sample
97.9	4.8 (2.0) ^b	5.0	Sample 1 ^a
98.6	9.7 (2.5)	10.0	
98.4	4.4 (3.0)	5.0	Sample 2 ^c
98.3	9.3 (3.0)	10.0	
98.5	2.5 (2.4)	0.0	Tap water ^d
97.5	7.5 (2.9)	5.0	
98.3	12.3 (2.4)	10.0	
—	N.D.	0.0	Rain water ^f
98.4	4.9 (2.3)	5.0	
98.6	10.1 (2.6)	10.0	
99.3	14.0(2.0)	0.0	Sea water ^g
96.9	18.9 (2.3)	5.0	
98.1	24.0 (3.0)	10.0	
^a Hg ²⁺ , Cu ²⁺ , Co ²⁺ , Fe ³⁺ , Ni ²⁺ , Cr ³⁺ , 5000 ng ml ⁻¹ of each cation; K ⁺ and Li ⁺ , 10,000 ng ml ⁻¹ of each.			
^b R.S.D of three replicate experiments.			
^c Hg ²⁺ , Cu ²⁺ , Co ²⁺ , Fe ³⁺ , Ni ²⁺ , Cr ³⁺ , 2500 ng ml ⁻¹ of each cation; K ⁺ and Li ⁺ , 5000 ng ml ⁻¹ of each.			
^d From drinking water system of Tehran.			
^e Not detected.			
^f Tehran, 26January, 2013, Iran.			
^g Caspian sea water.			

Calibration graph was obtained using preconcentration of 100 ml of standard solutions buffered at pH 3.0 with 50 mg of sorbent. For this purpose, standard solutions containing Co ion in the range of 1–1000 µg l⁻¹ were examined by the proposed procedure and it was observed that calibration curve were linear in this range. The regression equation was $I = 0.0085C (\mu\text{g l}^{-1}) + 0.0047$ and the correlation coefficient was 0.9996.

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 100 ml of different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2013), and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table 1). As can be seen from Table 1 the added Co ions can be quantitatively recovered from the water samples used.

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 of mesoporous organo-silicas and its determination by FAAS. The method developed was simple, reliable, high capacity, good stability and fast adsorption and desorption kinetics for determining Co in water. Also, the proposed method was free of interference compared to conventional procedures to determine Co.⁴⁸⁻⁵² The method can be successfully applied to the separation and determination of Co in binary mixtures.

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