



Research

# On-line determination of the trace amount of cobalt(II) in real samples by flame atomic absorption spectrometry method after pre-concentration by modified polyvinyl chloride

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## Abstract

This work reports a simple and sensitive on-line solid-phase extraction system for the pre-concentration and determination of a trace amount of Co(II) ions by flame atomic absorption spectrometry (FAAS). This method is based on the on-line retention of cobalt ions with polyvinyl chloride modified by 3-(2-thiazolylazo)-2,6-diaminopyridine in a mini-column system. The retained Co(II) ions were eluted with 1.0 mol L<sup>-1</sup> HCl, and direct aspiration to flame atomic absorption spectrometry (FAAS) for an accurate determination of it. The important experimental parameters such as the solution pH, length of column (adsorbent mass), sample flow rate, solvent eluent, type and concentration of the eluent, and co-existing ion effects were investigated in detail and optimized. Under the optimum conditions, the calibration graph was linear over the concentration range of 2–150 µg L<sup>-1</sup> for pre-concentration of 10.0 mL of the sample solution. The interassay precession (n=6) was in the range of 1.8–5.2% at the concentration levels of 10.0, 50.0, 100.0, and 140.0 µg L<sup>-1</sup>. The limit of detection and enhancement factor were 1.3 µg L<sup>-1</sup> and 40, respectively. The method was applied for determination of trace levels of Co(II) ions in different real samples such as tap water, waste water, vegetable, fruit, and drug with satisfactory results.

## Article Highlights

- PVC-TADAP advantages are stability and high adsorption capacity.
- Developed SPE method is on-line and environmentally friendly.
- This method has been successfully applied for determination of trace levels of Co(II) in different real samples.

**Keywords** Flame atomic absorption spectrometry · On-line solid-phase extraction · Cobalt(II) · PVC-TADAP

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## 1 Introduction

Heavy metals are potentially toxic elements. Thus, they can lead to serious ecological and health problems even at trace levels [1, 2]. Cobalt is one of these elements, which surplus in the concentration of it, can cause asthma, gastrointestinal tract irritation, rhinitis, prohibition of enzyme activities, allergic dermatitis vasodilation, and cardiomyopathy [3–5]. According to the World Health Organization (WHO), the maximum acceptable cobalt concentration in drinking water is  $40 \mu\text{g L}^{-1}$  [3]. Consequently, determination of trace amounts of this element with a highly sensitive and accurate method is essential.

Up to now, different analytical methods have been reported for the quantitative determination of a metal in various matrices. Among the cited methods, flame atomic absorption spectrometry (FAAS) is a popular technique because its accuracy and precision is high and its cost is low [4, 6]. However, the sensitivity of this method limits its application [1, 6, 7]. To resolve this problem, different separation and pre-concentration techniques such as solidified floating organic drop microextraction (SFODME) [8], hollow fiber-liquid phase microextraction (HF-LPME) [9], dispersive liquid-liquid microextraction [10], and solid-phase extraction [4, 5, 11] have been developed to enrich the analyte concentration to an appropriate concentration. Due to the high pre-concentration factor, low cost, low solvent usage, and off-line and on-line operation chance, solid-phase extraction (SPE) is an excellent pre-concentration method [4, 11, 12] <https://pubs.rsc.org/en/content/articlelanding/2020/ay/c9ay02762a>. The protocol applied in SPE is to use an adsorbent for adsorption of the analyte [13]. Thus, one of the main aspects of a SPE method is the nature of the adsorbent [11, 14]. Polymeric adsorbents have outstanding features such as cheapness, high porosity, and stability in acidic or basic media [12, 15], which make them suitable for the pre-concentration and determination of metals.

The Schiff base ligands form stable and selective complexes with transition metal ions [16, 17]. Therefore, by modification of the polymeric bed with the Schiff bases, one can create a new highly selective adsorbent for determination of a metal with a very low concentration.

In the present work, polyvinyl chloride (PVC) was modified with the 3-(2'-thiazolylazo)-2, 6-diamino pyridine (TADAP) Schiff base. TADAP reacts with heavy metal ions such as cobalt [18]. Considering this subject, the PVC-TADAP resin was used as an adsorbent in an on-line system (Fig. 2) for the pre-concentration and determination of cobalt in different samples. This is the first report for application of this polymeric adsorbent for the on-line pre-concentration of cobalt.

## 2 Experimental

### 2.1 Instrumentation

A Shimadzu flame atomic absorption spectrophotometer (AA-670) was used for detecting and quantifying cobalt. The FASS instrument was equipped with a cobalt hollow cathode lamp (wavelength of 240.7 nm). The flow rates of acetylene and air were fixed at 2.2 and  $8.0 \text{ L min}^{-1}$ , respectively. In the on-line column pre-concentration procedure, for pumping the sample solution, an electro-multichannel peristaltic pump (PP201V) was used. For selection of the sample or eluent flow through the column, a six-way rotary injection valve (model 5011) was applied. The used mini-column was fabricated from a polypropylene tube (2 mm i.d., 8 cm length). A Metrohm (model 744) pH-meter equipped with a combined glass electrode-calomel was used for the pH adjustments.

### 2.2 Reagents and solutions

All the reagents used including cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), nitric acid, hydrochloric acid, sodium nitrite, ethanol, sulfuric acid, citric acid, acetic acid, potassium hydrogen phthalate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, sodium hydroxide, PVC, sodium citrate, 2,6-diaminopyridine, and 2-aminothiazole were provided from the Merck company (Darmstadt, Germany). Deionized water was used for preparation of the aqueous solutions. The glassware and plastics were washed by 10% (v/v)  $\text{HNO}_3$  and deionized water, respectively, prior to use. A buffer solution (with pH 6.5) was obtained by mixing proper volumes of potassium dihydrogen phosphate (0.27 M) and potassium hydrogen phosphate (0.27 M). Hydrochloric acid (as the eluent solution) was prepared by dilution of its concentrated solution and standardized with sodium carbonate. The stock standard solution of cobalt(II) ( $1000 \mu\text{g mL}^{-1}$ ) was prepared from  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.2464 g in a 50 mL volumetric flask). The working solutions were obtained daily by stepwise dilutions from this solution.

### 2.3 Preparation of polyvinyl chloride functionalized with TADAP (PVC-TADAP)

In previous our work, the ligand TADAP was synthesized according to the procedure reported by Chotima [18] and the synthesis of TADAP was confirmed by the FT-IR spectra and melting point [11]. Polyvinyl chloride functionalized with TADAP (PVC-TADAP) was prepared according to our previously reported procedure and the formation of covalent bond between PVC and TADAP was confirmed

by FT-IR spectrum and the CHN analysis [11]. In this work, the scanning electron microscopy (SEM) images were also recorded for pure PVC (Fig. 1a) and PVC-TADAP (Fig. 1b). The SEM images for pure PVC (Fig. 2a) and PVC-TADAP (Fig. 2b) demonstrate that after immobilization of the ligand on the PVC bead, the surface of sorbent is rougher. This phenomenon that was reported by other researchers [19] confirms the loading of the ligand on the polymeric bead.

## 2.4 Preparation of mini-column

The mini-column prepared as follows: about 265.0 mg of the synthesized PVC-TADAP sorbent was packed inside a laboratory-made column with 8.0 cm length. Then to

prevent the loss of sorbent during the pre-concentration process, the two ends of the mini-column were blocked with a glass wool. The prepared mini-column was washed with HCl (concentration of 1.0 M) and then distilled water. It should be noted that re-packing of the column was not necessary because the packing material had an unlimited lifetime.

## 2.5 General procedure for quantitative determination of cobalt(II) ions

The designed flow system that was reported for the determination of cadmium was used [11]. In the designed flow system (Fig. 2) [11], the quantitative determination of cobalt(II) ions was made in a three-step process. (i):

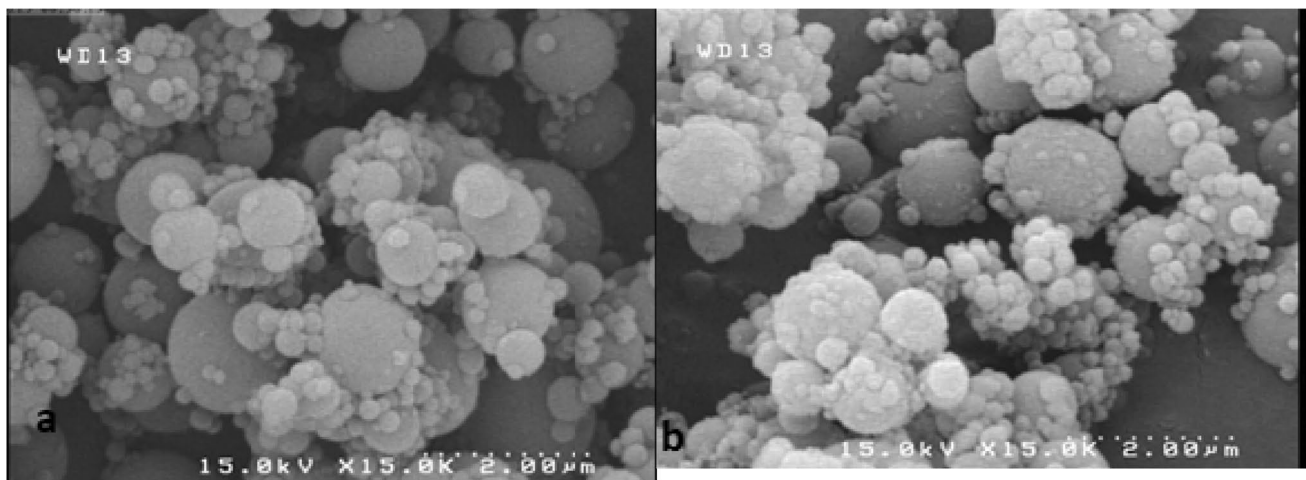
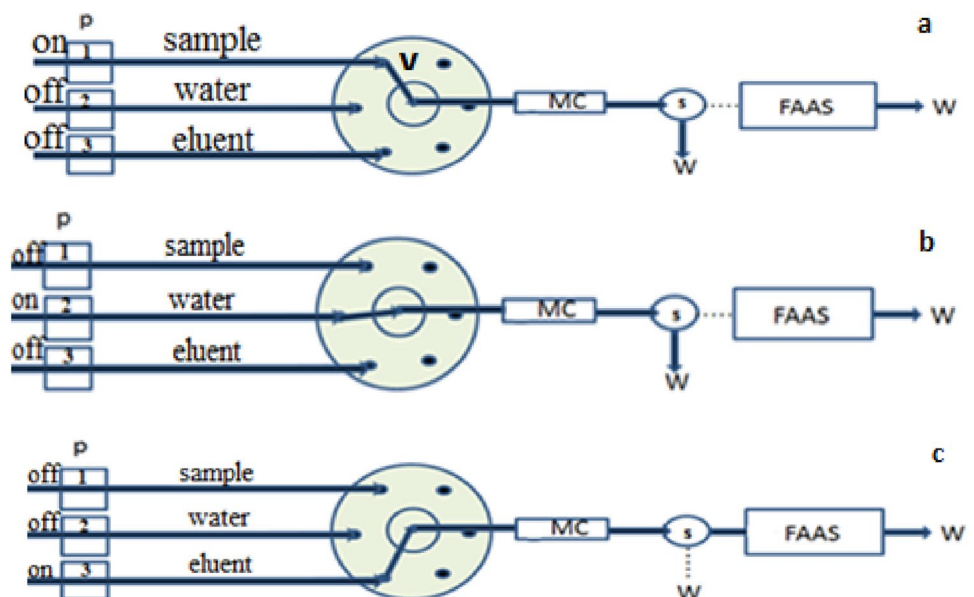


Fig. 1 SEM images for (a) PVC and (b) PVC-TADAP

Fig. 2 Schematic diagram of designed flow system (a) pre-concentration, (b) washing, and (c) elution. (P peristaltic pump, MC mini-column; FAAS flame atomic absorption spectroscopy; W waste.) [11]



Pre-concentration step: by rotation of valve V and turning on pump 1, an aliquot of 10.0 mL of sample with a definite pH and flow rate was passed through the prepared mini-column, and the cobalt ions were quantitatively retained on the adsorbent (PVC-TADAP). (ii): Washing step: by switching valve V and turning on pump 2, distilled water was directed into the packed mini-column for 60 s to remove the impurities weakly adsorbed on the adsorbent. (iii): Elution step: by turning on pump 3, a stream of HCl (1.0 M) was conducted to the packed column at a flow rate of 3.3 mL min<sup>-1</sup> to elute cobalt held by the PVC-TADAP bed, and then directed to the flame atomic absorption spectrometer to display the analyte absorption signal.

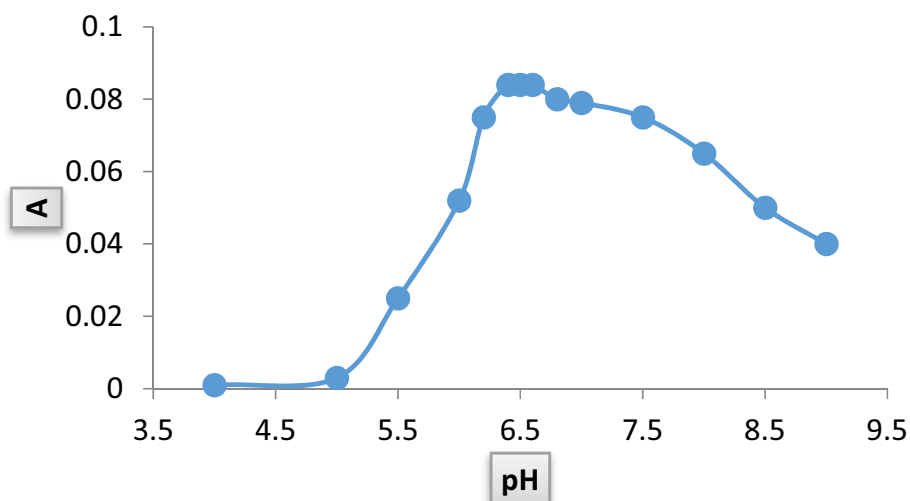
## 3 Results

### 3.1 Optimization of variables

#### 3.1.1 Effect of pH

Among the chemical variables affecting the pre-concentration process, the solution pH has a critical role in the effective interaction of the analyte of interest and the adsorbent [4, 19, 20]. For this purpose, 10 mL of cobalt(II) solutions (50.0 µg L<sup>-1</sup>) buffered in the pH range of 4.0–8.5 were passed through the packed mini-column at a flow rate of 3.3 mL min<sup>-1</sup>. The up-taken cobalt(II) ions were eluted by loading HCl (1.0 mol L<sup>-1</sup>) to the mini-column and directly determined by FAAS. As it can be seen in Fig. 3, the maximum signal was obtained at pH = 6.5. At a lower pH, due to the protonation of electron-donor groups (nitrogen and sulfur) that exist in the TADAP ligand, and at a higher pH due to the formation of various species such as Co(OH)<sub>2</sub>, Co(OH)<sub>3</sub><sup>-</sup>, etc. [21], the absorption signal

**Fig. 3** Effect of solution pH on analytical signal. (Conditions: 10.0 mL of 50.0 µg L<sup>-1</sup> of cobalt(II) with a flow rate of 3.3 mL min<sup>-1</sup>, 2 mL buffer, 1 mol L<sup>-1</sup> of HCl (as eluent) at a flow rate of 3.3 mL min<sup>-1</sup> in a mini-column (5.5 cm) and an elution time of 60 s)

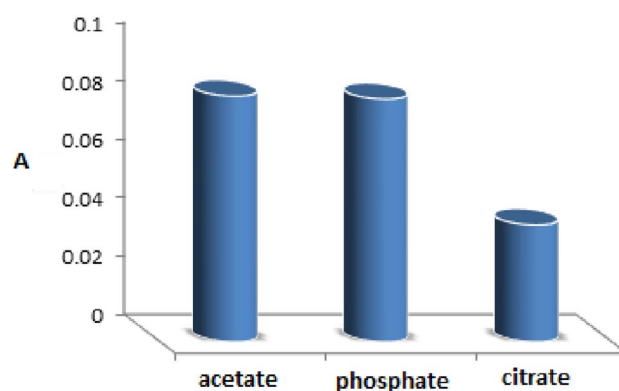


decreases. Thus, based on the obtained results for all the subsequent experiments, the pH value was adjusted to 6.5.

The effect of buffer type on the analytical signal was also investigated using different buffer solutions (e.g. acetate, phosphate, and citrate) at pH 6.5, and the resultant data was shown in Fig. 4. The formation of cobalt(II)-citrate complexes is responsible for reduction of the signal at the citrate buffer solution [22]. As it can be seen in this figure, the analytical signal is identical in the phosphate and acetate solutions. However, due to the higher buffer capacity of the phosphate buffer solutions (with respect to acetate), the phosphate buffer solution was chosen.

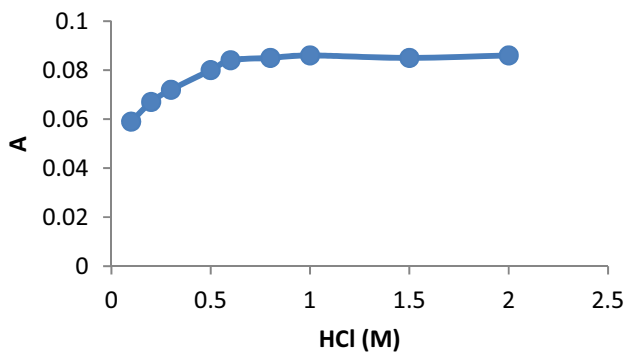
#### 3.1.2 Effects of type and concentration of eluent

The nature of the eluent solvent has a significant role in the desorption of the analyte. The protons of mineral

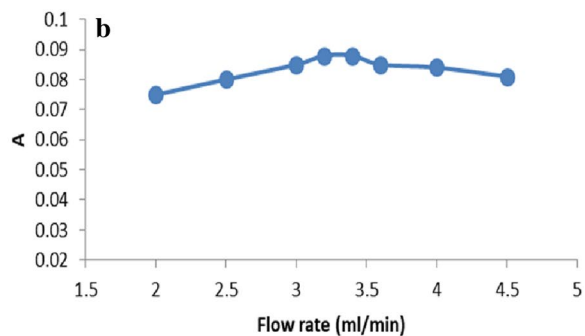
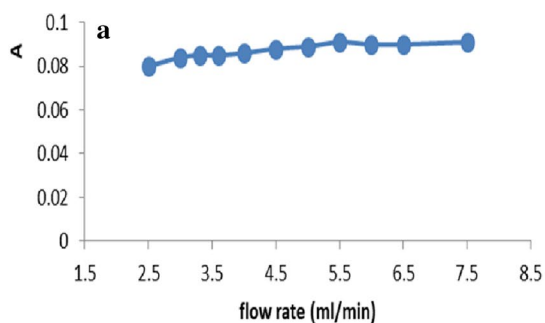


**Fig. 4** Effect of buffer type on the analytical signal. (Conditions: 10.0 mL of 50.0 µg L<sup>-1</sup> of cobalt(II) with a flow rate of 3.3 mL min<sup>-1</sup>, 2 mL of buffer with pH=6.5, 1 mol L<sup>-1</sup> of HCl (as eluent) at a flow rate of 3.3 mL min<sup>-1</sup> in a mini-column with a length of 5.5 cm and an elution time of 60 s)

acids can interact with the electron pairs in the ligand and break the metal-chelate bonds [11]. Therefore, different mineral acids such as hydrochloric acid, nitric acid, and sulfuric acid were investigated for the complete desorption of analyte from the polymeric bead. According to the experimental data, there is no difference between the selected acidic solvents. Nevertheless, since chloride ions have less interaction with the analyte, and due to a less corrosive effect of hydrochloric acid, this mineral acid was chosen as the desorption eluent. The effect of the eluent concentration was also investigated in the range of 0.1–2.0 mol L<sup>-1</sup>. The results obtained (Fig. 5) imply that by increasing the concentration of hydrochloric acid up to 0.8 M, the analytical signal increases, and then it is nearly constant. To ensure the complete elution of cobalt(II) ions, the concentration of 1.00 M HCl as the eluent was chosen.



**Fig. 5** Effect of eluent concentration on the analytical signal. (Conditions: 10.0 mL of 50.0  $\mu\text{g L}^{-1}$  of cobalt(II) with a flow rate of 3.3 mL min<sup>-1</sup>, 2 mL of buffer with pH=6.5, HCl with a flow rate of 3.3 mL min<sup>-1</sup> in a mini-column with a length of 5.5 cm and an elution time of 60 s)



**Fig. 6** Effects of (a) sample flow rate and (b) flow rate of eluent solvent on the analytical signal (Conditions: 10.0 mL of 50.0  $\mu\text{g L}^{-1}$  of cobalt(II), 2 mL of buffer with pH=6.5, mL min<sup>-1</sup> in a mini-column with a length of 5.5 cm and an elution time of 60 s)

### 3.1.3 Effects of sample flow rates

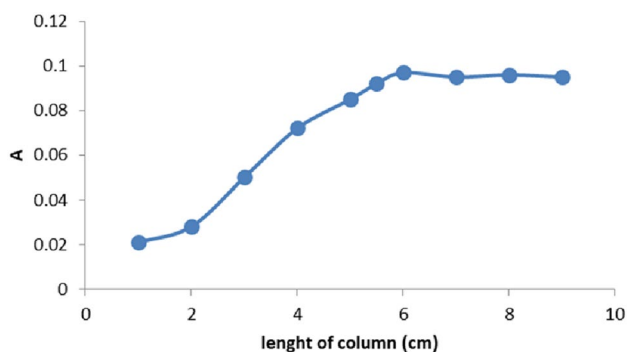
The amount of analyte adsorbed into the mini-column is dependent to the flow rate of the sample delivered through the column. This factor must be adjusted to get the highest amount of retained analyte on the sorbent in a considerably short time. For this purpose, 10 mL of the sample solution (50.0  $\mu\text{g L}^{-1}$ , pH 6.5) was passed through the mini-column with the flow rate in the range of 2.5–7.5 mL min<sup>-1</sup>. According to the results (Fig. 6a), it is clear that the analytical signal is independent from sample flow rate over the whole range examined, and that only a slight decrease in the analytical signal is observed at flow rates higher than 6.0 mL min<sup>-1</sup>. This means that the kinetic of the complex formation is fast, and that the contact time for complete sorption is sufficient. Due to the low repeatability of the analytical signal at a flow rate higher than 5 mL min<sup>-1</sup>, the flow rate of 5.0 mL min<sup>-1</sup> was adopted as the best one.

### 3.1.4 Effects of eluent flow rates

For optimization of the eluent flow rate, 10 mL of cobalt(II) solution (50  $\mu\text{g L}^{-1}$ ) at pH 6.5 and a flow rate of 5.0 mL min<sup>-1</sup> was passed through a packed mini-column. The flow rate of the eluent solvent was investigated in the range of 2.0–4.5 mL min<sup>-1</sup>. As it can be seen in Fig. 6b, the analytical signal was increased by increasing the flow rate of the eluent solution from 2.0 to 3.5 mL min<sup>-1</sup>. Upper it, due to the insufficient time for the complete elution of the retained cobalt, the signal was reduced. Thus the flow rate of 3.3 mL min<sup>-1</sup> was chosen as the optimum one for the eluent.

### 3.1.5 Effect of column length (amount of adsorbent)

To study the effect of column length (amount of polymeric sorbent) on the retained analyte, mini-columns



**Fig. 7** Effect of column length on the analytical signal. (Conditions: 10.0 mL of 50.0  $\mu\text{g L}^{-1}$  of cobalt(II) with a flow rate of 5  $\text{mL min}^{-1}$ , 2 mL of buffer with pH=6.5, 1  $\text{mol L}^{-1}$  of HCl (as eluent) at a flow rate of 3.3  $\text{mL min}^{-1}$ , and an elution time of 60 s)

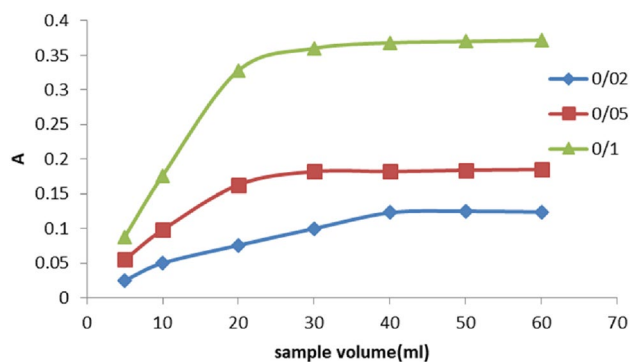
with different lengths (1.0–9.0 cm) were prepared, and their performance was investigated. The results obtained (Fig. 7) showed that the analytical signal improved with increase in the column length up to 6.0 cm. Behind it, the analytical signal was nearly constant. Therefore, a column of 8.0 cm length (265.0 mg of PVC-TADAP) was selected as optimum value for the complete adsorption of various concentrations of the cobalt(II) ions from 10 mL solutions.

### 3.1.6 Effect of sample volume

The sample volume is one of the important factors that affects the pre-concentration factor [4, 5]. To study the effect of loading time (sample volume) on the analytical signal, different volumes (from 5.0 to 50.0 mL) of cobalt solution with concentrations of 20, 50, and 100  $\mu\text{g L}^{-1}$  were passed through the column, and quantitative determinations were made. The experimental data (Fig. 8) implied that at a higher sample volume (up to 30 mL), the absorption signal increased linearly, and then it was constant. However, for compatibility between sensitivity and reduction of loading time, 10 mL was selected as the best one. It should be noted that for a low concentration, a higher volume could be used.

### 3.1.7 Salt effect

To survey the influence of the ionic strength (salt effect), different salts such as potassium nitrate, potassium chloride, and sodium chloride with the concentration range of 0.00–0.20  $\text{mol L}^{-1}$  were added to 10 mL of 50.0  $\mu\text{g L}^{-1}$  cobalt(II) solutions. Then they were subjected to the pre-concentration process, and the associated signals were recorded. The results obtained (Fig. 9) demonstrated that the analytical signal reduces with increase in the salt concentration. This manner can be explained based on the



**Fig. 8** Effect of sample volume on the analytical signal. (Conditions: 50.0  $\mu\text{g L}^{-1}$  of cobalt(II) with a flow rate of 5  $\text{mL min}^{-1}$ , 2 mL of buffer with pH=6.5, 1  $\text{mol L}^{-1}$  of HCl (as eluent) at a flow rate of 3.3  $\text{mL min}^{-1}$  in a mini-column with a length of 8 cm and an elution time of 60 s)

competition between the cationic ions and cobalt(II) ions for adsorption on the adsorbent. To solve this problem, one can use the standard addition technique.

## 3.2 Analytical performance of SPE- on-line system

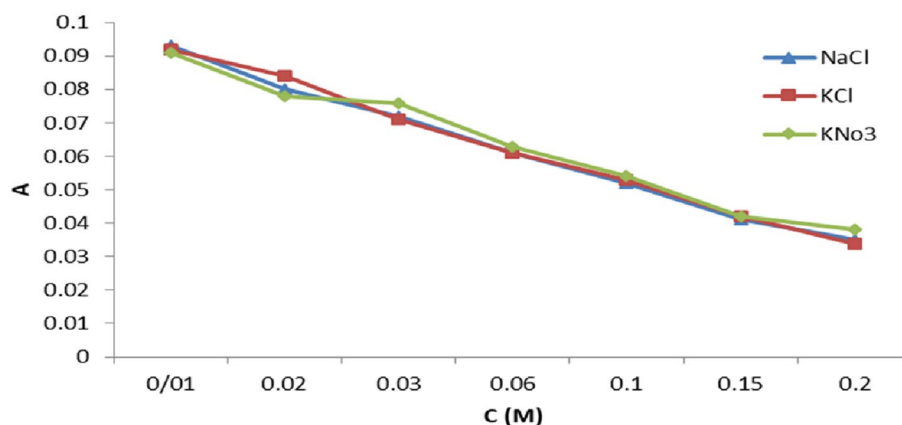
Under the optimum experimental conditions (pH value of 6.5, 10 mL of the sample with a flow rate of 5.0  $\text{mL min}^{-1}$ , and elution with HCl solution (1.0 M) at a flow rate of 3.3  $\text{mL min}^{-1}$ , and 265 mg of the adsorbent), various analytical parameters were computed. For a 10 mL sample volume of cobalt(II) ions, the calibration graph showed a linear manner over the concentration range of 2.0–150  $\mu\text{g L}^{-1}$ . The corresponding linear equation is  $A = 1.74C_{\text{Co(II)}} + 0.005$  ( $r = 0.9998$ ,  $n = 10$ ), where A is the absorbance and  $C_{\text{Co(II)}}$  is the cobalt(II) concentration in  $\text{mg L}^{-1}$ .

The limit of detection (LOD) was calculated by  $\text{LOD} = 3S_b/m$ , where  $S_b$  is the standard deviation for the signal of the blank solution (a mixture of buffer and distilled water), and m is the slope of the calibration graph [10, 11]. By taking ten replicate measurements on the blank solution, a detection limit of 1.3  $\mu\text{g L}^{-1}$  was obtained.

Evaluation of the precision of the proposed flow-FAAS technique was measured in terms of the relative standard deviations (RSDs) of six replicate measurements of cobalt(II) concentration containing 10.0, 50.0, 100.0, and 140.0  $\mu\text{g L}^{-1}$ . These values were 5.2%, 3.0%, 1.8%, and 1.8%, respectively, showing a good repeatability of the method.

The enhancement factor ( $\text{EF} = \frac{m_1}{m_2}$ , where  $m_1$  slope of the calibration curve with pre-concentration and  $m_2$  slope of calibration curve without pre-concentration (direct aspiration), was 40. The consumptive index (the consumed

**Fig. 9** Effect of ionic strength on analytical signal. (Conditions: 10.0 mL of  $50.0 \mu\text{g L}^{-1}$  of cobalt(II) with a flow rate of  $5 \text{ mL min}^{-1}$ , 2 mL of buffer with  $\text{pH}=6.5$ ,  $1 \text{ mol L}^{-1}$  of HCl (as eluent) at a flow rate of  $3.3 \text{ mL min}^{-1}$  in a mini-column with a length of 8 cm and an elution time of 60 s)



sample volume (mL) per unit of the enhancement factor (EF) was also 0.25 mL [11]. The low value for this factor states the suitable efficiency of the proposed on-line-FASS method.

The recovery percentage (R%) was defined by the following equation:

$$R\% = EF \left( \frac{VE}{VS} \right) \times 100\%$$

where EF, VE, and VS are the enhancement factor, volume of the eluent, and volume of the sample solution, respectively. Since the time required for the complete elution of the adsorbed cobalt(II) ions with a flow rate of  $3.3 \text{ mL min}^{-1}$  was 4 s, the computed VE value was  $220 \mu\text{L}$ , and consequently, the recovery percentage for 10 mL sample by the proposed on-line process was found to be 88.

The maximum capacity of the proposed sorbent was obtained in the batch technique. In this method, 100 mg of this adsorbent was added to 500 mL of  $10 \text{ mg L}^{-1}$  of the cobalt solution (buffered at  $\text{pH} 6.5$ ) and stirred mechanically for 1 h. Then the amount of cobalt remained in the solution was measured by direct aspiration to FAAS. The difference between the initial and remaining amounts of cobalt was applied to obtain the maximum capacity. The proposed adsorbent had a maximum capacity of  $22.5 \text{ mg g}^{-1}$ .

### 3.3 Effect of interference ions

In order to identify the possible interferences of different ions may be exist in the matrix of real samples in the measurement of cobalt, various amounts of diverse ions were added to the solutions containing  $50.0 \mu\text{g L}^{-1}$  of cobalt and analyzed using the proposed on-line-FAAS method. A variation more than  $\pm 5\%$  in the absorbance was considered as a criterion to identify a foreign ion as an interference [10]. As it could be seen in Table 1, among a large number of ions surveyed, only  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Mn}^{2+}$  had

**Table 1** Tolerance limits for matrix ions in determination of cobalt(II) ions

Matrix ions	Tolerated ratio ( $W_{\text{species}}/W_{\text{cobalt}}$ )
$\text{SCN}^-$ , $\text{HCOO}^-$ , $\text{SO}_4^{2-}$ , $\text{ClO}_3^-$	10,000
$\text{F}^-$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{NO}_3^-$ , $\text{Na}^+$	2000
$\text{CO}_3^{2-}$ , $\text{Li}^+$ , $\text{PO}_4^{3-}$ , $\text{I}^-$ , $\text{NO}_2^-$ , $\text{Pb}^{2+}$ , $\text{IO}_4^-$	1000
$\text{Mg}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Cr}_2\text{O}_7^{2-}$	400
$\text{Hg}^{2+}$ , $\text{Cu}^{2+}$	100
$\text{Mn}^{2+}$ , $\text{Al}^{3+}$ , $\text{Cd}^{2+}$ , $\text{Cr}^{3+}$	50
$\text{Ni}^{2+}$ , $\text{Ag}^+$ , $\text{Zn}^{2+}$	20

severe interferences. More investigation proved that the interference effect could be decreased to 200-fold using the masking agents such as dithizon (for  $\text{Ag}^+$ ), dimethylglyoxime (for  $\text{Ni}^{2+}$ ),  $\text{Cl}^-$  (for  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ), and  $\text{F}^-$  (for  $\text{Al}^{3+}$ ).

### 3.4 Application of developed method to real samples

#### 3.4.1 Analysis of tap water

The developed on-line-FAAS method was applied for the determination of cobalt(II) ions in tap water (Shahrood, Iran) by the standard addition technique. Since the concentration of cobalt in the sample was lower than the detection limit of the proposed method, the standard addition method was performed on the spiked solutions. The recovery values and calculated t values (Table 2) imply the accuracy of the proposed method.

#### 3.4.2 Analysis of wastewater of a pharmaceutical company

After filtering, an aliquot of 40 mL of wastewater sample was transferred to a 50 mL volumetric flask containing 2.5 mL buffer and marked to volume with distilled water.

**Table 2** Results of Co(II) measurements in tap water

No.	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Calculated t
1	–	<DL	–	–
2	20.0	19.6 ( $\pm 0.5$ )a	98.0	1.6
3	50.0	48.5 ( $\pm 1.8$ )	97.0	1.67
4	100.0	98.2 ( $\pm 2.5$ )	98.0	1.44
–	–	–	–	3.18b

<sup>a</sup>(Mean  $\pm$  standard deviation,  $n=4$ ), <sup>b</sup>( $t_{\text{critical, df}=3}=3.18$ )

**Table 3** Results of cobalt(II) measurements in pharmaceutical wastewater

No.	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Calculated t
1	–	4.0 ( $\pm 0.2$ )	–	–
2	20.0	25.0 ( $\pm 0.7$ )a	105.0	2.86
3	50.0	56.0 ( $\pm 1.5$ )	104.0	2.67
4	100.0	105.2 ( $\pm 2.0$ )	101.2	1.2
–	–	–	–	3.18b

<sup>a</sup>(Mean  $\pm$  standard deviation,  $n=4$ ), <sup>b</sup>( $t_{\text{critical, df}=3}=3.18$ )

Then a 10 mL aliquot of the prepared sample was subjected to pre-concentration and determination by the developed method by the standard addition method. The results obtained (Table 3) show that there were no statistical differences between the real and the experimental data.

### 3.4.3 Analysis of cobalt in vegetables and fruits

For the analysis of cobalt in vegetable and fruit by the developed method, to 1.5 g of the dried and powdered sample of white cabbage or cucumber, 10 mL  $\text{HNO}_3$  was added, and heated on a hot plate at 100 °C. After 1 h, 10 mL  $\text{HNO}_3$  and 4 mL  $\text{H}_2\text{O}_2$  were again added and stirred slowly for 1 h to decrease the volume by half [23]. Then the resultant filtered solution was neutralized with NaOH (3 M), transferred to a 250 mL flask, and diluted to 250 mL

with distilled water. 40 mL of the prepared solution was added to a 50 mL flask containing 2 mL phosphate buffer (pH 6.5), and diluted with distilled water. Then a 10.0 mL aliquot of the prepared solution was analyzed by the proposed FIA-FAAS technique for the quantitative determination of cobalt(II) ions. The results obtained (Table 4) approve the validity of the proposed method.

### 3.4.4 Analysis of vitamin B12 ampoule samples

An aliquot of 1.0 mL of vitamin B12 (a tetrapyrrole complex containing cobalt ion [24]) ampoule was placed in a 100 mL beaker, and 10 mL mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (with ratio of 10:1 v/v) was added. The solution was heated, and then the semi-residue mass was neutralized with a diluted solution NaOH and diluted to 100 mL with distilled water [25]. Then 40 mL of the prepared solution was transferred to a 50 mL flask, buffered at pH 6.5, and diluted to volume with distilled water. A 10.0 mL aliquot of the prepared solution was subjected to FIA-FAAS for measurement of Co(II). The results in Table 5 imply the capability of the developed method in determination of cobalt ions in different matrices.

### 3.5 Comparison of proposed SPE-FAAS method with some other on-line reports

A comparison between the proposed on-line-FAAS method and some recent on-line SPE methods is demonstrated in Table 6. As it can be seen, the figures of merit of the developed protocol are similar or comparable with most of the reported methods. The proposed method exhibits a higher detection limit compared to the method of reference [30]. However, the method of reference [30] requires a new microcolumn to be prepared and replaced for each measurement, which is time-consuming and reduces reproducibility. In contrast, our proposed method employs a mini-column for all measurements, which is advantageous in terms of experimental convenience, reproducibility, and reduction of consuming materials.

**Table 4** Results of cobalt(II) ion measurements in vegetables and fruits samples

Sample	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Calculated t	Content of Co(II) in dry vegetable and fruit samples ( $\mu\text{g g}^{-1}$ )
White cabbage	–	4.0 ( $\pm 0.2$ )a	–	2.85	0.85 ( $\pm 0.04$ )
	10.0	15.0 ( $\pm 0.7$ )	108.0		
Cucumber	–	5.0 ( $\pm 0.5$ )a	–	2.85	1.06 ( $\pm 0.1$ )
	10.0	16.0 ( $\pm 0.7$ )	108.0		
–	–	–	–	3.18b	–

<sup>a</sup>(Mean  $\pm$  standard deviation,  $n=4$ ), <sup>b</sup>( $t_{\text{critical, df}=3}=3.18$ )



**Table 5** Results of Co(II) determination in vitamin ampoule samples

Sample	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Calculated t	Content of Co(II) in B12 ampoule ( $\mu\text{g}$ )
B12c	–	33.9 ( $\pm 0.8$ ) <sup>a</sup>	–		4.24 ( $\pm 0.1$ )
	20.0	53.5 ( $\pm 0.9$ )	98.0	0.89	
–	–	–	–	3.18 <sup>b</sup>	–

<sup>a</sup>(Mean  $\pm$  standard deviation,  $n=4$ ), <sup>b</sup>( $t_{\text{critical, df}=3}=3.18$ ), <sup>c</sup>Caspian Tamin Pharm. Co. Iran: Each ampoule (1 mL) contains: vitamin B12 (100  $\mu\text{g}$ ) equivalent to 4.35  $\mu\text{g}$  Co

**Table 6** Comparison between analytical features of proposed method with literature

Adsorbent	SPE method	Sample volume (mL)	PF	LOD ( $\mu\text{g L}^{-1}$ )	Sample type	Ref.
BTAHQ-C18	Disks	1000	100	3.1	Human hair, Vitamin B12	[26]
PS-NAPdien	Mini-column	10	110	0.75	Water samples	[27]
Tween 80 coated alumina	Column	50	8.3	1.2	Tobacco, brewed tea and water samples	[28]
Silica-PEG	Mini-column	250	83.3	0.37	Black tea, sesame seeds, water samples	[6]
Multi-walled carbon nanotube	Column	10	40	5.31	Water samples	[29]
Sol-Gel functionalized silica	Micro-column	10	105	0.75	Urine, water samples	[21]
2-nitroso-1-naphthol immobilized on surfactant coated alumina	Micro-column	25	125	0.02	water samples, vitamin ampoules	[30]
PVC-TADAP	Mini-column	10	40	1.3	Water samples, cabbage, cucumber, ampule, wastewater	This work

## 4 Conclusion

A newly designed flow-FAAS method was used for the quantitative determination of trace amounts of cobalt(II) ions using the PVC-TADAP adsorbent. The prepared resin was an inexpensive and eco-friendly adsorbent because it could simply be recycled and used for different times. The major advantages of the proposed protocol are rapid kinetic in the adsorption and desorption process, simplicity, time-saving, and automation. This method showed reasonable results in the measurement of trace levels of cobalt in different samples (such as sample waters, waste water, vegetable, fruit, and drug) with complicated matrices. Comparing the figures of merit of the designed method with some reported research works indicate that although a number methods report better results they use a large volume of sample, and so require a more amount of sample. In the other word, the consumptive index of the proposed method is better or comparative with the reported methods.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability** All data generated or analysed during this study are included in this published article.

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