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## ORIGINAL ARTICLE

# A novel separation/preconcentration procedure using in situ sorbent formation microextraction for the determination of cobalt (II) in water and food samples by flame atomic absorption spectrometry

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## KEYWORDS

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Cobalt;  
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Flame atomic absorption spectrometer

**Abstract** A new, simple, low cost, and rapid solid phase extraction method, that was named in situ sorbent formation microextraction (ISSFME), was developed for the selective separation and determination of cobalt (II) in various water and food samples. In the present work, cetyltrimethylammonium bromide was used as a cationic surfactant, perchlorate ion as an ion-pairing agent, and 2-nitroso-1-naphthol as a complexing agent. After extraction, the concentration of cobalt was determined by flame atomic absorption spectrometer. Several variables that affect the extraction efficiencies were investigated and optimized. Under the optimized conditions, the limit of detection was  $0.8 \mu\text{g L}^{-1}$  with a preconcentration factor of 50. The RSD for 10 replicate measurements of  $50 \mu\text{g L}^{-1}$  of cobalt was 2.3%. The accuracy and applicability of the method were tested by evaluating the amount of cobalt in water certified reference materials and various water and food samples.

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## 1. Introduction

The determination of heavy metals at trace levels in the environment is one of the targets of analytical chemists, due

to their significance in our life. Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals. It is an essential micronutrient required for the growth of both plants and animals (Lemos et al., 2007). Cobalt deficiency leads to several diseases such as pernicious anemia (Agency for Toxic Substances and Disease Registry, 2001). On the other hand, large amounts of cobalt can produce toxicological effects including vasodilation, flushing, and cardiomyopathy in humans and animals (Chen and Teo, 2001). Therefore, the development of accurate and rapid determination methods for monitoring the level of cobalt concentration in real samples is necessary and indispensable.

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Due to the allowable low levels of cobalt in food and natural water samples and the interferences from matrix components, several methods have been proposed for the separation and preconcentration of trace cobalt, including liquid–liquid extraction (LLE) (Boukraa et al., 2006), coprecipitation (Divrikli and Elci, 2002), solid phase extraction (SPE) (Yamini et al., 2004), and cloud point extraction (CPE) (Nascentes and Arruda, 2003). Each technique has its advantages and disadvantages and should be chosen according to the analytical problem.

Among the preconcentration techniques, solid phase extraction (SPE) has received the most attention due to its simplicity, high concentration factor, and more environment friendly reagents (Ghaedi et al., 2009; Jamali et al., 2006, 2007; Kazi et al., 2010; Khan et al., 2011; Lemos et al., 2010; Wadhwa et al., 2013).

Recently, Yousefi and Shemirani (2011) developed a novel solid phase extraction technique that is based on in situ formation of very fine solid particles as sorbent. In this in situ sorbent formation microextraction (ISSFME) method, a cationic surfactant with a proper alkyl group is dissolved in the aqueous sample and then hexafluorophosphate as ion-pairing agent is added. Due to the interaction between the surfactant and the ion-pairing agent, very fine solid particles are formed. The alkyl group of the surfactant (on the sorbent particles) can act to extract hydrophobic analyte(s) from aqueous samples. Extraction occurs via hydrophobic bonding of the alkyl group of the sorbent with the hydrophobic parts of the extracted analyte molecules. After centrifugation, the solid particles are sedimented at the bottom of the centrifuge tube and the aqueous phase is removed by a simple decantation of the centrifuge tube. The sedimentary sorbent can be either dissolved in ethanol (or other organic solvent) or leached with acid in order to recover the analyte(s) (Yousefi and Shemirani, 2011). The advantages of this method are simplicity, rapidity, low cost, and high extraction recovery and enrichment factors.

The purpose of the present work is the improvement of ISSFME and its application for the preconcentration and determination of cobalt (II) in natural water and food samples. In this work, we used perchlorate ion as an ion-pairing agent that is safer, inexpensive, and more readily available than hexafluorophosphate.

## 2. Experimental

### 2.1. Instrumentation

A PG-990 (PG instrument Ltd., United Kingdom) atomic absorption spectrometer equipped with deuterium background correction and cobalt hollow cathode lamp was used for the determination of cobalt at a wavelength of 240.7 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations and the absorbance signal was measured according to the peak height in continuous aspiration mode. A Hettich Centrifuge (Model Universal 320R, Germany) was used for centrifugation. pH values were measured with a Metrohm pH-meter (model: 827) supplied with a glass-combination electrode.

### 2.2. Reagents and solutions

All reagents used were of analytical reagent grade. Ultrapure distilled water was used throughout the experiment. A

1000.0 mg L<sup>-1</sup> stock standard solution of cobalt (II) was prepared from pure Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck, Darmstadt, Germany). Before the investigations, working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. A 0.010 mol L<sup>-1</sup> solution of 2-nitroso-1-naphthol (Sigma–Aldrich, St. Louis, MO, USA) was prepared in pure ethanol. *n*-Cetyltrimethylammonium bromide (CTAB), tetra-*n*-butylammonium bromide (TBAB), *n*-dodecyltrimethylammonium bromide (DTAB), tetradecyldimethylbenzylammonium chloride (TBAC), sodium perchlorate, ethanol and sodium chloride were purchased from Merck. A buffer solution (pH 6.0, 1.0 mol L<sup>-1</sup>) was prepared by mixing an appropriate amount of acetic acid with sodium acetate solution. Pipettes and glass vessels used for trace analysis were stored in 10% nitric acid for at least 24 h and washed four times with ultrapure distilled water before use.

### 2.3. Preparation of the real samples

Spinach and black tea samples were purchased at a local supermarket. Spinach sample was washed with ultrapure distilled water, cut and oven-dried at 100 °C for 24 h. Next, it was ground in a household grinder. 500 mg of the sample was placed in a 100 mL beaker, and 10 mL of concentrated HNO<sub>3</sub> (65% w/w) was added to the beaker. The mixture was evaporated to near dryness on a hot plate at about 130 °C for 4 h. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide (30%, w/w) was added. The mixture was again evaporated to near dryness. The resulting solution was diluted to 25 mL with ultrapure distilled water. The result was filtered and the pH of the solution was adjusted at 6.0 by adding NaOH and buffer solution. Finally, the solution was diluted to 100 mL by ultrapure distilled water. The same preparation procedure was used for black tea sample. One blank test was performed for each sample. The samples were analyzed immediately after preparation.

All of the collected water samples (tap, mineral, river, and sea water) were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm and after acidification to 1% with concentrated nitric acid, were stored in polyethylene bottles.

### 2.4. ISSFME procedure

50 mL sample or standard solution containing cobalt (II) in the concentration range of 2–100 μg L<sup>-1</sup> and 1.0 × 10<sup>-4</sup> mol L<sup>-1</sup> 2-nitroso-1-naphthol was adjusted to pH 6.0 (acetate/acetic acid buffer solution) and was poured in a screw cap conical-bottom glass centrifuge tube. 1.0 mL of CTAB solution (0.05 mol L<sup>-1</sup>) was added into the sample solution and the tube was manually shaken to ensure complete homogenization of the CTAB in the aqueous sample. Then, 1.0 mL of NaClO<sub>4</sub> solution (1.0 mol L<sup>-1</sup>) was quickly added by using a syringe. A cloudy solution (dispersed very fine particles of the *n*-cetyltrimethylammonium perchlorate salt) was formed. In order to accelerate phase separation, the cloudy solution was centrifuged for 4 min at 4000 rpm. As a result, fine particles of the sorbent were sedimented at the bottom of the centrifuge tube. The aqueous phase was then separated completely by a syringe. Afterward, the sorbent was dissolved in 1.0 mL ethanol. The resultant solution was introduced into

the flame by conventional aspiration. The extraction steps are illustrated in Fig. 1.

### 3. Results and discussion

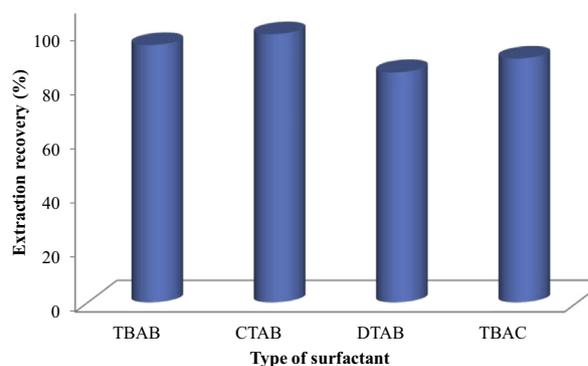
To attain high recovery, selectivity, and precision for the determination of cobalt (II) with the ISSME method, the influence of different parameters, which affect the complex formation and the extraction conditions such as the type and amount of the surfactant, concentration of the ion-pairing agent, pH, chelating reagent concentration, extraction time, ionic strength and centrifugation rate and time and potentially interfering ions were investigated and optimized.

#### 3.1. Selection of the surfactant

In ISSFME, formation of the fine solid particles (sorbent) depends on the interaction between the cationic surfactant and the ion-pairing agent. The alkyl group in the sorbent interacts with the hydrophobic parts in the extracted analyte and acts as an extraction medium. Several cationic surfactants such as *n*-cetyltrimethylammonium bromide (CTAB), tetra-*n*-butylammonium bromide (TBAB), *n*-dodecyltrimethylammonium bromide (DTAB), and tetradecyldimethylbenzylammonium chloride (TBAC) were examined. Experiments were performed using  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of surfactants and  $0.02 \text{ mol L}^{-1}$  of  $\text{NaClO}_4$ . In all cases, the sorbent formation occurred and cloudy solutions were observed. Fig. 2 shows the effect of surfactant type on the extraction recovery of cobalt (II). As can be seen, the best extraction recovery was obtained by the use of CTAB. Therefore, CTAB was chosen as the proper surfactant for subsequent experiments.

#### 3.2. The effect of pH

Separation of metal ions by ISSFME involves prior complex formation with sufficient hydrophobicity to be extracted by the fine particles of the sorbent. The pH of the aqueous phase is one of the most important factors in the extraction of metal ions from various media for the formation of metal complex. The influences of the pH on the quantitative recovery values of cobalt (II) at the presented microextraction system were

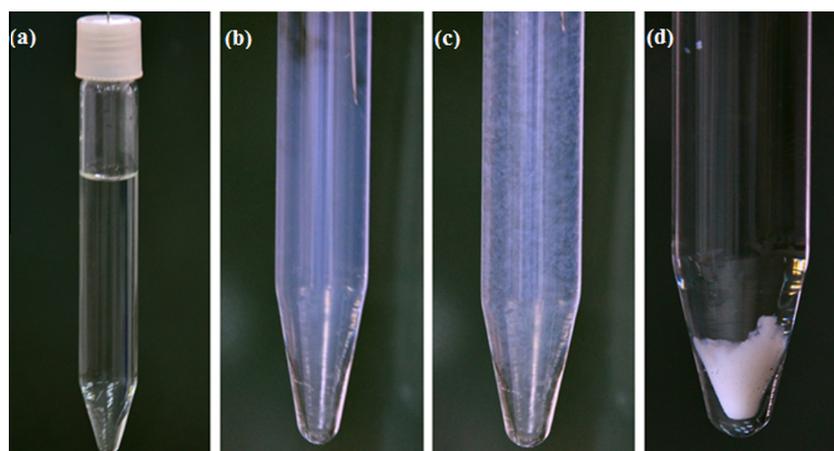


**Figure 2** Effect of type of surfactant on the extraction recovery of cobalt (II). Conditions: sample volume: 50 mL,  $\text{NaClO}_4$  concentration:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ , 2-nitroso-1-naphthol concentration:  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ , pH: 6.0, surfactants concentration:  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , cobalt (II) concentration:  $50 \mu\text{g L}^{-1}$ .

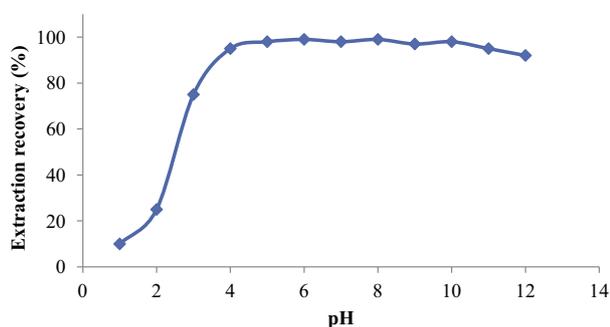
investigated at the pH range of 1.0–12.0 using HCl and NaOH while other parameters were kept constant. The results are depicted in Fig. 3. Recovery of cobalt (II) increases with the increase of solution pH and is effectively recovered within the pH range of 5.0–10.0. Competition between protons and metal species could thus explain the weak extraction recovery in acid medium. On further increase of the pH, extraction recovery decreases probably due to the formation of hydroxide of cobalt. Therefore, later works were performed at pH 6.0 and in order to control the pH during the analytical procedure, it was adjusted to 6.0 with acetate/acetic acid buffer solution.

#### 3.3. The effect of chelating reagent concentration

In this work, 2-nitroso-1-naphthol was used as the chelating agent due to the highly hydrophobic nature of its metal chelates. Concentration of the chelating agent is a critical variable to be optimized in preconcentration methods. Thus, it is highly important to establish the minimal reagent concentration that leads to total complex formation while achieving the highest extraction. In the light of these points, the effects of the amounts of 2-nitroso-1-naphthol on the quantitative recovery



**Figure 1** Photography of different steps in ISSFME: (a) sample solution (water + CTAB), (b) injection of  $\text{NaClO}_4$  solution, (c) end of injection, (d) enlarged view of sedimented phase after centrifuging.

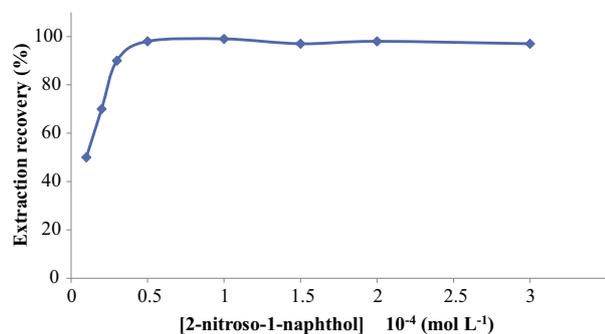


**Figure 3** Effect of pH on the extraction recovery of cobalt (II). Conditions: sample volume: 50 mL,  $\text{NaClO}_4$  concentration:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ , 2-nitroso-1-naphthol concentration:  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ , CTAB concentration:  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , cobalt (II) concentration:  $50 \mu\text{g L}^{-1}$ .

of cobalt (II) in ISSFME system were examined within the range of  $1.0 \times 10^{-5}$ – $3.0 \times 10^{-4} \text{ mol L}^{-1}$ . As is shown in Fig. 4, by the addition of an increased amount of 2-nitroso-1-naphthol, the extraction recovery was increased before  $5.0 \times 10^{-5} \text{ mol L}^{-1}$ , and then remained constant. At a low concentration of 2-nitroso-1-naphthol, the complexation was not complete and the extraction efficiency was low; hence, the recovery was decreased. Thus,  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  of 2-nitroso-1-naphthol was chosen as the optimum for the elimination of probable interference effects of some coexisting ions in real sample analysis.

### 3.4. The effect of CTAB concentration

The amount of sorbent has influence on the extraction efficiency of SPE methods. In ISSFME, the amount of sorbent that forms into the sample solution depends on the surfactant concentration. In order to investigate the effect of CTAB concentration, several experiments were carried out using different CTAB concentrations. In all experiments, the concentration of  $\text{NaClO}_4$  was  $0.02 \text{ mol L}^{-1}$ . The results showed that the extraction was quantitative when the CTAB concentration was higher than  $3.0 \times 10^{-4} \text{ mol L}^{-1}$ . At lower concentrations, the extraction recovery was low probably because of the inade-



**Figure 4** Effect of chelating reagent concentration on the extraction recovery of cobalt (II). Conditions: sample volume: 50 mL,  $\text{NaClO}_4$  concentration:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ , pH: 6.0, CTAB concentration:  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , cobalt (II) concentration:  $50 \mu\text{g L}^{-1}$ .

quacy of the sorbent to adsorb the hydrophobic complex quantitatively. Therefore, a concentration of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  CTAB was chosen for the subsequent experiments.

### 3.5. The effect of $\text{NaClO}_4$ concentration

The effect of  $\text{NaClO}_4$  as an ion-pairing agent was investigated within the range of  $1.0 \times 10^{-3}$ – $5.0 \times 10^{-2} \text{ mol L}^{-1}$  in the presence of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of CTAB. The results indicated that the extraction recovery increased by increasing the  $\text{NaClO}_4$  concentration up to  $1.5 \times 10^{-2} \text{ mol L}^{-1}$  and then remained constant. These results could be explained by increasing the amount of  $\text{NaClO}_4$ , which led to the formation of more solid sorbent and, therefore, an increase in extraction recovery. So,  $2.0 \times 10^{-2} \text{ mol L}^{-1}$  of  $\text{NaClO}_4$  was chosen for the subsequent experiments.

### 3.6. The effect of ionic strength

For investigating the influence of ionic strength on the performance of ISSFME, various experiments were performed by adding different amounts of  $\text{NaNO}_3$  ( $0.0$ – $2.0 \text{ mol L}^{-1}$ ). Other experimental conditions were kept constant. The results confirmed that the salt addition had no significant effect on the extraction process and the recovery of cobalt (II) was quantitative. The negligible influence of the salt can be ascribed to the rapidity of the cobalt (II) chelate distribution between the involved phases as the likely result of the dispersion process. Thus, no ionic strength buffer was used for subsequent experiments. These observations suggest the possibility of the application of the method for the separation of cobalt (II) from saline solutions such as seawater.

### 3.7. The effect of extraction time

In our study, extraction time is defined as the time interval between the injection of the ion-pairing agent ( $\text{NaClO}_4$ ) and the start of centrifugation. Similar results were observed with extraction times between 1 and 30 min. No significant effect was observed on the extraction recovery when the extraction time was increased. This may be due to the fact that the large contact surface area between the fine particles of the sorbent and the aqueous phase results in a very rapid adsorption of the analyte on the surface of the dispersed solid sorbent. Thus, 1 min (a short extraction time) was selected in subsequent experiments.

### 3.8. The effect of coexisting ions

The effects of common coexisting ions in natural water samples on the recovery of cobalt (II) were also studied. In these experiments, 50 mL of solutions containing  $50.0 \mu\text{g L}^{-1}$  of cobalt (II) and various amounts of interfering ions were treated according to the recommended procedure. Given species were considered to interfere if it resulted in a  $\pm 5\%$  variation of the AAS signal. The results showed that, in excess of 100,000-fold of  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ , 10,000-fold of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{PO}_4^{3-}$ , 1000-fold of  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , 500-fold of  $\text{Cr}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$ , 100-fold of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and 50-fold of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  ions had

**Table 1** Determination of cobalt (II) in water samples.

Sample	Co (II) amount ( $\mu\text{g L}^{-1}$ )		Recovery (%)
	Added	Found <sup>a</sup>	
Tap water (drinking water system of Behshahr, Iran)	0.0	n.d. <sup>b</sup>	–
	20.0	19.7 $\pm$ 0.6	98
	50.0	49.5 $\pm$ 1.4	99
Mineral water (damavand mineral water, Iran)	0.0	n.d.	–
	20.0	20.5 $\pm$ 0.7	102
	50.0	51.0 $\pm$ 1.3	102
River water (Tajan river, Sari, Iran)	0.0	6.5 $\pm$ 0.3	–
	20.0	26.2 $\pm$ 0.6	98
	50.0	57.4 $\pm$ 1.4	102
Sea water (Caspian sea water, Sari, Iran)	0.0	9.2 $\pm$ 0.4	–
	20.0	28.6 $\pm$ 0.8	97
	50.0	58.4 $\pm$ 1.6	98

<sup>a</sup> Mean value  $\pm$  standard deviation based on three replicate measurements.

<sup>b</sup> Not detected.

**Table 2** Determination of cobalt (II) in spinach and black tea.

Sample	Added ( $\mu\text{g g}^{-1}$ )	Found <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	Recovery (%)
Spinach	–	9.52 $\pm$ 0.33	–
	2.00	11.48 $\pm$ 0.37	98.0
	5.00	14.62 $\pm$ 0.55	102.0
Black tea	–	5.41 $\pm$ 0.23	–
	2.00	7.36 $\pm$ 0.28	97.5
	5.00	10.32 $\pm$ 0.42	98.2

<sup>a</sup> Mean value  $\pm$  standard deviation based on three replicate measurements.

**Table 3** Determination of cobalt (II) in standard reference materials using the ISSFME.

Certified reference material	Certified ( $\mu\text{g L}^{-1}$ )	Found <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	Recovery (%)
SRM 1643e	27.06 $\pm$ 0.32	26.22 $\pm$ 0.51	96.9
SRM 1640a	20.24 $\pm$ 0.24	19.73 $\pm$ 0.62	97.5

<sup>a</sup> Mean value  $\pm$  standard deviation based on three replicate measurements.

no significant interferences in the extraction and determination of cobalt (II). According to the results, the major ions in the real samples have no obvious influence on cobalt (II) ISSFME under the selected conditions.

### 3.9. Analytical figures of merit

Under the optimum conditions, the ISSFME procedure was applied for the extraction and preconcentration of various standard solutions of cobalt (II) and the calibration graph was linear within the range of 2–100  $\mu\text{g L}^{-1}$ . The LOD, defined as  $3S_b/m$  (where  $S_b$  and  $m$  are the standard deviation of the blank and the slope of the calibration graph, respectively), was found to be 0.8  $\mu\text{g L}^{-1}$ . The preconcentration factor that was calculated by dividing the aqueous phase volume to the final volume of the diluted phase was 50. Repeatability was carried out by spiking blank samples at the concentration of 50  $\mu\text{g L}^{-1}$ , and the relative standard deviation (RSD) for ten replicate experiments was 2.3%.

### 3.10. Analysis of real samples

Food samples (spinach and black tea) and real water samples (tap water, mineral water, river water, and sea water) were subjected to the proposed method to evaluate the concentration of cobalt (II). The obtained results are given in Tables 1 and 2. Recovery studies were also carried out after it was spiked to samples of known concentrations of cobalt (II) at levels of 20 and 50  $\mu\text{g L}^{-1}$ . The recovery values calculated for the added standards ranged from 97% to 102%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed preconcentration method.

Furthermore, the accuracy of the developed method was evaluated by applying the recovery experiments for the determination of cobalt (II) in water SRMs. The following standard reference materials were used to verify the accuracy of the proposed method: NIST SRM 1643e (National Institute of Standard and Technology, Trace elements in water) and SRM 1640a (Trace elements in natural water). The results listed in Table 3 reveal that there is a good agreement between the obtained results and certified values and indicate that the proposed procedure was helpful for the determination of cobalt (II) in real samples with complicated matrices.

**Table 4** Comparison of ISSFME with other methods for determination of cobalt (II) in water samples.

Method	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	RSD <sup>b</sup> (%)	Sample volume (mL)	PF <sup>c</sup>	Reference
US-DLLME	0.8	3.3	5	10	Wang et al. (2012)
CPE-FAAS	2.1	1.5	15	30	Ghaedi et al. (2008)
CPE-UV-vis	7.5	2.7	10	10	Safavi et al. (2004)
CPE-FAAS	1.0	3.6	50	25	Citak and Tuzen (2010)
SPE-FAAS	12.3	1.3	1000	200	Afzali and Mohammadi (2011)
SPE-FAAS	3.9	2.0	250	25	Baytak and Turker (2005)
DLLME-FAAS	0.9	5.8	5	16	Baliza et al. (2009)
ISSFME-FAAS	0.8	2.3	50	50	Present work

<sup>a</sup> Limit of detection.

<sup>b</sup> Relative standard deviation.

<sup>c</sup> Preconcentration factor.

### 3.11. Comparing ISSFME with other methods

A comparison of the presented method with other reported preconcentration methods for cobalt (II) determination in water samples is given in Table 4. The presented method has low LOD, high-enrichment factor, good RSD and these characteristics are comparable or even better than most of the other methods in Table 4. All these results indicate that ISSFME is a reproducible, simple, and low cost technique that can be used for the preconcentration of metal ions like cobalt from water samples.

## 4. Conclusion

The in situ sorbent formation microextraction (ISSFME) methodology was successfully used for the preconcentration of trace amounts of cobalt (II) in natural water and food samples. In this work, we used perchlorate ion as an ion-pairing agent that is safer, inexpensive, and more readily available than hexafluorophosphate that was used in the previous report (Yousefi and Shemirani, 2011). This method is simple, rapid, safe, environment friendly, and robust against very high contents of salt. The relative standard deviation, detection limit, and the duration time of this procedure are also satisfactory. The method significantly improved the performance of the FAAS detection of cobalt. The proposed preconcentration method allows cobalt (II) determination in natural water and food samples at  $\mu\text{g L}^{-1}$  levels.

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