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Development of an in situ solvent formation microextraction and preconcentration method based on ionic liquids for the determination of trace cobalt (II) in water samples by flame atomic absorption spectrometry

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Abstract A simple in situ solvent formation microextraction (ISFME) methodology based on the application of ionic liquid (IL) as an extractant solvent and sodium hexafluorophosphate (NaPF₆) as an ion-pairing agent was proposed for the preconcentration of the trace levels of cobalt ions. In this method cobalt was complexed with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and extracted into an ionic liquid phase. After phase separation, the enriched analyte in the final solution is determined by flame atomic absorption spectrometry (FAAS). Some effective factors that influence the microextraction efficiency were investigated and optimized. Under the optimum experimental conditions, the limit of detection and the enrichment factor were 0.97 µg L⁻¹ and 50, respectively. The relative standard deviation (R.S.D.) was obtained as 2.4%. The proposed method was assessed through the analysis of certified reference water and recovery experiments.

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1. Introduction

Cobalt is an important element, not only for industry but also for biological systems. The toxicity of cobalt is low and it is considered as an essential element, which is required in the

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normal human diet in the form of vitamin B₁₂ (cyanocobalamin). For this reason, cobalt has been used in the treatment of anemia (Underwood, 1971). However, the ingestion or inhalation of large doses of this analyte may lead to toxic effects (Bratter and Schramel, 1980; Tsalev and Zaprianov, 1983). Since one of the routes of incorporation of cobalt into the human body is by ingestion (Seiler et al., 1994), its determination in drinking water becomes important. Cobalt concentration levels are very low in water samples, and therefore sensitive analytical techniques are required to carry out its detection.

In spite of great improvements in the sensitivity and selectivity of modern instrumental analyses such as ICP-MS, ICP-OES and electrothermal atomic absorption spectrometry

(ETAAS), difficulties still lie in the analysis of trace heavy metals because of both their low abundance levels in the samples and the high complexity of the sample matrices (Abulhassani et al., 2010).

Separation and preconcentration procedures are of great importance in the elemental analysis as they eliminate or minimize matrix effects and concomitants, lowering the detection limit and enhancing the sensitivity of detection techniques toward metals and their species. Solvent extraction of metal cations is a very important technique for their mutual separation and preconcentration (Alegret, 1998; Rydberg et al., 2004). In solvent extraction, generally, various hydrophobic solvents are used as extraction phase solvents. However, most of the solvents are toxic, flammable and volatile, and it has been recommended that their use should be avoided. The demand to reduce solvent volumes and to avoid using toxic organic solvents in liquid-liquid extraction (LLE) has led to substantial efforts in adapting existing sample-preparation methods to the development of new approaches. Within these approaches, an important effort has been shifted to the development of microextraction procedures, mainly characterized for eliminating or minimizing the consumption of organic solvents commonly employed in conventional extraction methods. For this purpose, several microextraction methods, such as liquid-phase microextraction (LPME) (Pena-Pereira et al., 2010), dispersive liquid-liquid microextraction (DLLME) (Zgola-Grzeskowiak and Grzeskowiak, 2011), etc., have been developed to miniaturize the LLE procedure and to reduce the amount of organic solvent. In these procedures, however, the use of toxic solvents, such as benzene, toluene or chloroform, as the extraction phase is a common practice.

Recently, considerable interest has been raised by the use of ionic liquids (ILs) as attractive green solvents in microextraction methods, because of their unique chemical and physical properties. Ionic liquids (ILs) are salts with melting points below 100 °C, typically consisting of nitrogen-containing organic cations such as 1-alkyl-3-methylimidazolium or *N*-alkylpyridinium together with an inorganic or organic anion commonly containing fluorine, for example, BF_4^- , PF_6^- , CF_3COO^- , SbF_6^- , or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (Wasserscheid and Welton, 2003). ILs are being recently considered as replacement solvents in sample preparations, because of their unique chemical and physical properties such as negligible vapor pressure, non-flammability, good extractability for various organic compounds and metal ions as neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents which make their use very attractive in separation processes (Dadfarnia et al., 2010; Greaves and Drummond 2008; Liu et al., 2009; Marsh et al., 2004; Pandey, 2006; Soyak and Yilmaz, 2011; Sun et al., 2010). Furthermore, the high interest is also due to the capability of ILs to form a wider range of intermolecular interactions than typical volatile organic solvents. This includes interactions of the following type: strong and weak ionic, hydrogen bonding, van der Waals, dispersive, $n-\pi$ and $\pi-\pi$ interactions (Luczak et al., 2008).

In 2009, Baghdadi and Shemirani developed a novel microextraction technique as a high performance and powerful preconcentration method termed in situ solvent formation microextraction (ISFME) (Baghdadi and Shemirani, 2009). The approach is based on the dissolution of a hydrophilic IL in an aqueous solution containing the analytes of interest, followed by the addition of an ion-exchange reagent which under-

goes an in situ metathesis reaction forming an insoluble IL. Thus, analytes are extracted and preconcentrated once the IL is insolubilized. There is no interface between the aqueous media and the extraction phase. Thus, mass transfer from aqueous media into IL has no significant effect on the performance of the extraction method. ISFME is a simple and efficient method for the separation and preconcentration of metal ions from aqueous solutions with high ionic strength. The approach has been applied to the determination of metals (Baghdadi and Shemirani, 2009; Mahpishanian and Shemirani, 2010; Vaezzadeh et al., 2010; Zeeb et al., 2011).

In the present work, we have developed a simple, rapid, sensitive and highly selective in situ solvent formation microextraction method for the trace determination of cobalt in various water samples using 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol (5-Br-PADAP) as the complexing agent by FAAS.

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 centrifuging. The 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. Doubly distilled water was used throughout the experiment. A 1000.0 mg L^{-1} stock standard solution of Co (II) was prepared from pure Co (NO_3) $_2 \cdot 6 \text{H}_2\text{O}$ (Merck, Darmstadt, Germany). Before the investigations, working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. The all standard solution for calibration FAAS instrument was prepared in ethanol.

A 0.010 mol L^{-1} solution of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) (Sigma-Aldrich, USA) was prepared in pure ethanol. 1-Hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4]), ethanol and sodium chloride were purchased from Merck (Darmstadt, Germany). Sodium hexafluorophosphate (NaPF_6) was purchased from ACROS (Geel, Belgium).

Pipettes and vessels used for trace analysis were stored in 10% nitric acid for at least 24 h and washed four times with doubly distilled water before use.

2.3. ISFME procedure

50 mL sample or standard solution containing Co^{2+} in the concentration range of 5–100 $\mu\text{g L}^{-1}$ and 2.0×10^{-4} mol L^{-1} 5-Br-PADAP was adjusted to pH 3.0 (± 0.2) and was poured in a screw cap conical-bottom glass centrifuge tube. 150.0 μL

of [Hmim][BF₄] was added into the sample solution and the tube was manually stirred to ensure complete homogenization of the IL in the aqueous sample. Then, 4.0 mL of NaPF₆ solution (1.0 mol L⁻¹) was quickly added, followed by the formation of a turbid solution. In order to accelerate phase separation, the cloudy solution was centrifuged for 5 min at 5000 rpm. As a result, the IL-phase settled at the bottom of the centrifuge tube. The aqueous phase was then separated completely by a syringe. In order to reduce the viscosity of the IL-phase and facilitate sample handling prior to FAAS analysis, the extract in the tube was made up to 1.0 mL by adding ethanol. The resultant solution was introduced into the flame by conventional aspiration.

3. Results and discussion

To attain a high recovery, selectivity and precision for the determination of cobalt with the ISFME method, the influence of different parameters, which affect the complex formation and the extraction conditions such as the amount of IL, concentration of ion-pairing agent, pH, chelating reagent concentration, extraction time, ionic strength and centrifugation rate and time, were investigated and optimized.

3.1. The effect of pH

Separation of metal ions by ISFME involves prior complex formation with sufficient hydrophobicity to be extracted into the small volume of the IL-phase. 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 the metal complex. The influences of the pH on the quantitative recovery values of cobalt ions at the presented microextraction system were 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. 1. Recovery of Co (II) increases with the increase of solution pH and is effectively recovered in the pH range of 2.0–10.0. Thus, a pH value of 3.0 was chosen for further experiments.

3.2. The effect of chelating reagent concentration

The extraction efficiency depends on the hydrophobicity of the ligand, the kinetics of the chelate formation, the apparent equi-

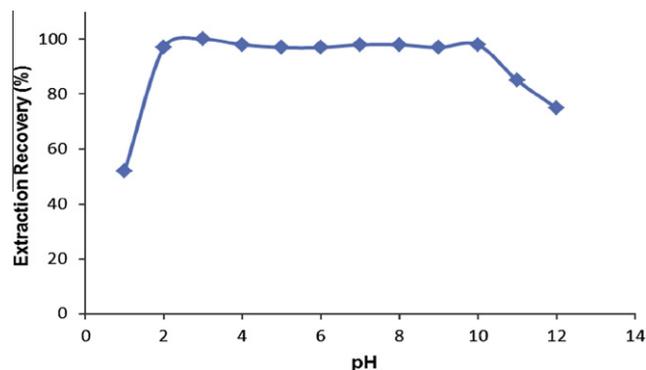


Figure 1 Effect of pH on the extraction recovery of cobalt. Conditions: Sample volume 50 mL, Cobalt 50.0 µg L⁻¹, 5-Br-PADAP 2.0×10^{-4} mol L⁻¹, [Hmim][BF₄] 150 µL, NaPF₆ 0.080 mol L⁻¹.

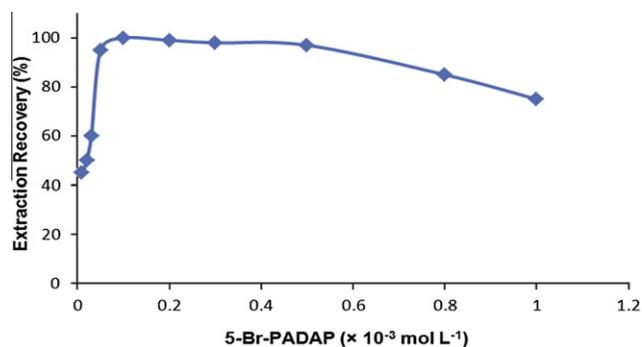


Figure 2 Effect of 5-Br-PADAP concentration on the extraction recovery of cobalt. Conditions: Sample volume 50 mL, Cobalt 50.0 µg L⁻¹, pH = 3.0, [Hmim][BF₄] 150 µL, NaPF₆ 0.080 mol L⁻¹.

librium constants in the ionic liquid medium and the partition coefficients. In this work, 5-Br-PADAP 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 the total complex formation while achieving the highest extraction (Martiniš et al., 2008). In light of these points, the effects of the amounts of 5-Br-PADAP on the quantitative recovery of cobalt ions in ISFME system were examined in the range of 1.0×10^{-5} – 1.0×10^{-3} mol L⁻¹. As is shown in Fig. 2, by the addition of an increased amount of 5-Br-PADAP, the extraction recovery was increased before 1.0×10^{-4} mol L⁻¹, then remained constant up to 5.0×10^{-4} mol L⁻¹ and remarkably decreased at a higher concentration. At a low concentration of 5-Br-PADAP, the complexation was not complete and the extraction efficiency was low, hence the recovery was decreased. Also the excessive chelating agent could be coextracted into the ionic liquid phase, thus decreased the extraction efficiency of target analyte. Thus, 2.0×10^{-4} mol L⁻¹ of 5-Br-PADAP was chosen as the optimum for the elimination of probability interference effects of some coexisting ions in real water samples' analysis.

3.3. The effect of ionic liquid volume

The small volume of IL resulted in a lower extraction efficiency, but a large volume of IL may lead to a longer period of time for the IL dissolved completely and mixed entirely. To examine the effect of extraction solvent volume, solutions containing different volumes of [Hmim][BF₄] were tested in the same ISFME procedure. IL volume was examined within the range of 70–250 µL while other experimental conditions were fixed, and the results are shown in Fig. 3. From Fig. 3, it was found that the recovery increased from 65% to 99% by increasing the volume of extraction solvent from 70 µL to 150 µL and then remained almost constant. Fine IL droplets increased along with the increase of the [Hmim][BF₄] volume and then more target analytes were transferred into the IL droplets, but larger volumes led to the increase of sedimented phase volume and have had no effect on extraction recovery. Thus, 150 µL of [Hmim][BF₄] was used as the extraction solvent in subsequent experiments.

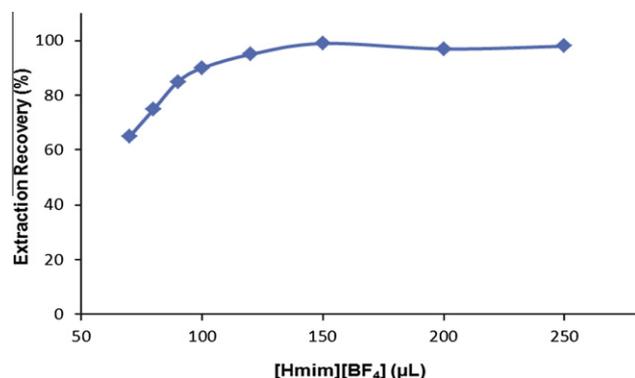


Figure 3 Effect of [Hmim][BF₄] volume on the extraction recovery of cobalt. Conditions: Sample volume 50 mL, Cobalt 50.0 μg L⁻¹, 5-Br-PADAP 2.0 × 10⁻⁴ mol L⁻¹, pH = 3.0, NaPF₆ 0.080 mol L⁻¹.

3.4. The effect of NaPF₆ concentration

In ISFME, during the addition of NaPF₆ as ion-pairing agent, hydrophobic [Hmim][PF₆] is formed. Due to the common ion influence, an increase in the amount of NaPF₆ causes a considerable decrease in the solubility of [Hmim][PF₆]. The effect of the amount of ion-pairing agent on the recoveries of cobalt was studied when the amount of [Hmim][BF₄] was 150 μL. As shown in Fig. 4, the recovery of cobalt increases with the increase of amount in the NaPF₆ from 0.010 to 0.070 mol L⁻¹, and when the amount of NaPF₆ is higher than 0.070 mol L⁻¹, recoveries do not change significantly. Therefore, a concentration of 0.080 mol L⁻¹ of NaPF₆ was selected as an optimum for subsequent experiments.

3.5. The effect of extraction time

In our study, extraction time is defined as the time interval between the injection of the ion-pairing agent (NaPF₆) 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

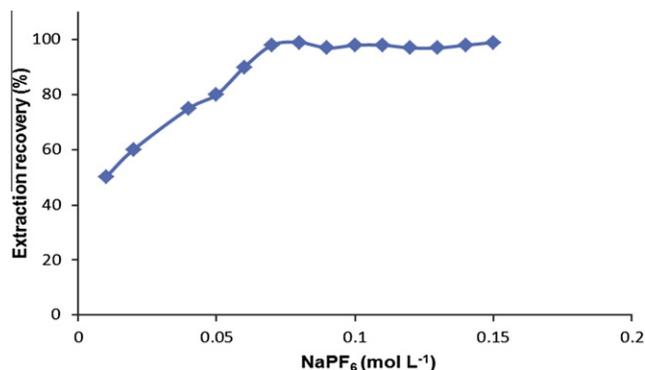


Figure 4 Effect of NaPF₆ concentration on the extraction recovery of cobalt. Conditions: Sample volume 50 mL, Cobalt 50.0 μg L⁻¹, 5-Br-PADAP 2.0 × 10⁻⁴ mol L⁻¹, pH = 3.0, [Hmim][BF₄] 150 μL.

contact surface area between the IL-phase and the aqueous phase results in a very rapid transport of analyte from the aqueous phase to IL-phase. Thus, 1 min (a short extraction time) was selected for subsequent experiments.

3.6. Centrifugation rate and time

The effect of centrifugation rate on the extraction recovery was studied in the range of 1000–6000 rpm. It was found that over 4000 rpm the IL-phase completely settled. Therefore, the rate of 5000 rpm was selected as the optimum point. At the optimum rate, recovery was investigated as a function of centrifugation time. Over 4 min, extraction recovery was constant indicating a complete transfer of IL-phase to the bottom of the centrifuge tube and 5 min was selected as the centrifugation time which ensured a reproducible drop to handle.

3.7. The effect of ionic strength

For investigating the influence of ionic strength on the performance of ISFME, various experiments were performed by adding different amounts of NaNO₃ (0.0–3.0 mol L⁻¹). Other experimental conditions were kept constant. The results showed that ionic strength has no significant effect on the extraction recovery. Thus no ionic strength buffer was used for subsequent experiments. Therefore, this method is a powerful sample preparation technique for saline solutions.

3.8. The effect of coexisting ions

The effects of common coexisting ions in natural water samples on the recovery of cobalt were also studied. In these experiments, 50 mL of solutions containing 50.0 μg L⁻¹ of cobalt

Table 1 Effect of foreign ions on the recovery of cobalt (50.0 μg L⁻¹).

Ion	Ion/Co (II) ratio (w/w)	Recovery (%)
Li ⁺	100000	99.7
K ⁺	100000	99.4
Ba ²⁺	10000	99.8
Mg ²⁺	10000	99.8
Ca ²⁺	10000	99.4
F ⁻	100000	100.2
Cl ⁻	100000	101.2
Br ⁻	10000	101.1
I ⁻	10000	99.1
ClO ₄ ⁻	100000	101.3
SO ₄ ²⁻	100000	99.7
PO ₄ ³⁻	10000	99.4
Mn ²⁺	1000	99.8
Cr ³⁺	1000	99.8
Cd ²⁺	500	99.7
Pb ²⁺	500	99.6
Al ³⁺	500	99.7
Zn ²⁺	500	99.4
Ag ⁺	500	99.8
Ni ²⁺	100	97.8
Cu ²⁺	100	97.7
Fe ²⁺	100	98.6
Fe ³⁺	100	97.5

Table 2 Analytical characteristics of the proposed method.

Parameter	Analytical feature
Linear range, $\mu\text{g L}^{-1}$	5–100
Limit of detection, $\mu\text{g L}^{-1}$ ($n = 10$)	0.97
RSD, % ($C = 50.0 \mu\text{g L}^{-1}$, $n = 10$)	2.4
Preconcentration factor	50

and various amounts of interfering ions were treated according to the recommended procedure. A substance should be considered as interferent if it resulted in more than 5% variation in the absorbance signal. The maximum tolerances of the investigated cations and anions (Ion/Co (II) ratio (w/w)) are given in Table 1. According to the results, the major ions in the water samples have no obvious influence on Co^{2+} ISFME under the selected conditions.

3.9. Analytical figures of merit

Table 2 summarizes the analytical characteristics of the optimized method, such as limit of detection, reproducibility and preconcentration factor. Under the optimum conditions, the ISFME procedure was applied for the extraction and preconcentration of various standard solutions of cobalt (II) and the calibration graph was linear in the range of 5–100 $\mu\text{g L}^{-1}$. 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 0.97 $\mu\text{g L}^{-1}$. The preconcentration factor that was calculated by dividing the aqueous phase volume to the final volume of 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 were 2.4%.

3.10. The analysis of real samples

Different real water samples such as tap water, mineral water, river water and sea water were subjected to the proposed method to evaluate the concentration of cobalt. The obtained results are given in Table 3. Recovery studies were also carried

Table 4 Determination of cobalt in standard reference materials using the ISFME.

Certified reference material	Certified ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)
CRM 1643d	25.0 ± 0.6	24.6 ± 0.7	98
GSBZ 50030–94	14.4 ± 1.0	14.0 ± 0.5	97

^a Mean value \pm standard deviation based on three replicate measurements.

out after it was spiked to samples of known concentrations of cobalt at levels of 20 and 50 $\mu\text{g L}^{-1}$. The recovery values calculated for the added standards ranged from 97 to 104%, 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 in water CRMs. The following standard reference materials were used to verify the accuracy of the proposed method: NIST CRM 1643d (National Institute of Standard and Technology, Trace elements in water) and GSBZ50030–94 (National Standard Reference Material for Environmental Water). The results listed in Table 4 reveal that there is a good agreement between obtained results with certified values and indicate that the proposed procedure was helpful for the determination of cobalt in real samples with complicated matrices.

3.11. Comparison of ISFME with other methods

A comparison of the represented method with other reported preconcentration methods for cobalt determination in water samples is given in Table 5. 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 5. All these results indicate that ISFME is a reproducible, simple and low cost technique that can be used for the preconcentration of metal ions like cobalt from water samples.

Table 3 Determination of Co (II) in tap, mineral, river and sea water samples and relative recoveries of spiked samples.

Sample	Co (II) amount ($\mu\text{g L}^{-1}$)		Recovery (%)
	Added	Found ^a	
Tap water (Drinking water system of Behshahr, Iran)	0.0	n.d. ^b	–
	20.0	19.6 ± 0.5	98
	50.0	49.4 ± 1.3	99
Mineral water (Damavand mineral water, Iran)	0.0	n.d.	–
	20.0	20.9 ± 0.6	104
	50.0	51.1 ± 1.2	102
River water (Tajan river, Sari, Iran)	0.0	7.8 ± 0.3	–
	20.0	28.4 ± 0.8	103
	50.0	57.3 ± 1.4	99
Sea water (Caspian sea water, Sari, Iran)	0.0	8.9 ± 0.4	–
	20.0	28.3 ± 0.8	97
	50.0	57.5 ± 1.5	97

^a Mean \pm standard deviation ($n = 3$).

^b Not detected.

Table 5 Comparison of ISFME with other methods for determination of cobalt in water samples.

Method	LOD ^a ($\mu\text{g L}^{-1}$)	RSD ^b (%)	Sample volume (mL)	PF ^c	Reference
CPE-Spectrophotometry	7.5	2.7	10	10	Safavi et al., 2004
CPE-FAAS	1.0	3.6	50	25	Citak and Tuzen, 2010
SPE-FAAS	3.4	1.3	1300	260	Ghaedi et al., 2007
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
ISFME-FAAS	0.97	2.4	50	50	This work

^a Limit of detection.

^b Relative standard deviation.

^c Preconcentration factor.

4. Conclusion

The in situ solvent formation microextraction (ISFME) methodology was successfully used for the preconcentration of trace amount of cobalt in water samples. This method is simple, rapid, safe and robust against the very high content of salt. ISFME has low toxicity since only very small amounts of an IL as a, "green extraction solvent", is used. 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 for cobalt. The proposed preconcentration method allows cobalt determination in natural water samples at $\mu\text{g L}^{-1}$ levels.

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