

2-Nitroso-1-naphthol as a selective reagent for preconcentration of cobalt by vortex assisted combined with solidification of organic droplet and its determination by flame atomic absorption spectrometry

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Abstract Highly rapid and selective vortex-assisted liquid–liquid microextraction based on solidification of organic drop has been used for determination of cobalt ion. 2-Nitroso-1-naphthol (2N1N) was used as a selective complexing agent to form stable cobalt–2N1N complex which can be extracted with 1-undecanol at a short time by the assistance of vortex agitator system followed by its determination using flame atomic absorption spectrometry. In vortex assisted, vigorous vortex stream as well as the vibrant effect of vortex system cause very fine droplets of extraction solvent to be produced and extraction occurred at a short time. Some parameters influencing the extraction process such as pH of samples, concentration of 2-nitroso-1-naphthol, extraction solvent volume, extraction time, ionic strength and surfactant addition, as well as interferences were evaluated in detail and optimum conditions were selected. At the optimum conditions, the calibration curve was linear in the range of 15 to 400 $\mu\text{g L}^{-1}$ of cobalt ions. The relative standard deviation based on ten replicate analysis of sample solution containing 50 $\mu\text{g L}^{-1}$ of cobalt was 3.4 %. The detection limit (calculated as the

concentration equivalent to three times of the standard deviation of the blank divided by the slope of the calibration curve after preconcentration) was 5.4 $\mu\text{g L}^{-1}$. The accuracy of the proposed method was successfully evaluated by the analysis of certified reference materials. This selective and highly rapid method was used for determination of cobalt ions in different water samples.

Key words Cobalt ion · Solidification of organic drop · Vortex-assisted liquid–liquid microextraction · Flame atomic absorption spectrometry

Introduction

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. Cobalt can be beneficial for human because it is a part of vitamin B₁₂. However, the metal can also be harmful because its exposure at high levels could result in lung and heart defects and dermatitis (Nordberg et al. 2007). Flame atomic absorption spectrometry (FAAS) is a widely used analytical technique for determination of cobalt because of its low cost and simplicity. However, conventional FAAS has a low detection limit, to determine cobalt at trace levels. Thus, in order to achieve accurate, sensitive, and

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reliable results, preconcentration and separation steps are needed prior to analyte determination by FAAS. The most common preconcentration methods for determination of cobalt are solid-phase extraction (Ghaedi et al. 2007), cloud point extraction (Lemos et al. 2007; Ghaedi et al. 2008), and liquid–liquid microextraction (Baliza et al. 2009; Shirani Bidabadi et al. 2009; Dadfarnia and Haji Shabani 2010). Dispersive liquid–liquid microextraction (DLLME) is a recent development of liquid–liquid microextraction that offers several traits including simplicity, rapidity, low amount of extraction solvent, and high recovery (Rezaee et al. 2006). In DLLME, with rapid injecting of a mixture of extraction and disperser solvent into aqueous samples, a cloudy solution is formed which is composed of very fine droplets of extraction solvent. In this system, the equilibrium is reached quickly, due to the large surface area between the extraction solvent and the aqueous sample. However, the presence of disperser solvent can reduce the extraction efficiency due to the reduction of the partition coefficient of analyte in the extraction solvent. To eliminate the disperser solvent, several methods including ultrasound-assisted dispersive liquid–liquid microextraction (Li et al. 2009; Ma et al. 2009), temperature-controlled ionic liquid microextraction (Bai et al. 2010; Berton et al. 2009), and vortex-assisted ionic liquid microextraction (Chamsaz et al. 2012; Leng et al. 2012; Chamsaz et al. 2013) have been used for determination of different analytes at a short time.

Solidification of organic droplet microextraction introduced by Zanjani et al. (2007) uses organic solvents (extraction solvents) with lower density than water. In this method, the extraction solvents with melting points near room temperatures are used to extract analyte from aqueous solution. In 2008, Leong and Huang (2008) introduced a new technique named dispersive liquid–liquid microextraction based on solidification of floating organic drop which is a combination of dispersive liquid–liquid microextraction and solidification of organic droplet microextraction. This method made it possible to use extraction solvents with lower density than water in DLLME. The application of preconcentration procedure for determination of cobalt by chelation with complexing agents have been reported frequently.

Berton and Wuilloud (2010) successfully used 1-nitroso-2-naphthol (1N2N) as complexing agent for selective separation and determination of cobalt by ionic

liquid DLLME. 1N2N forms stable complexes with numerous metal ions and it can selectively react with cobalt under the specific conditions (Cheng et al. 1992). However, this compound has an isomeric structure, 2-nitroso-1-naphthol (2N1N), with different positions of NO⁻ and OH⁻ groups on the aromatic ring. Haji Shabani et al. (2003) was used 2-nitroso-1-naphthol immobilized on surfactant-coated alumina for solid-phase extraction of cobalt in microcolumn system. However, no report has been so far published regarding its use for development of LLME procedures. To study the ability of this reagent for selective separation and determination of cobalt, 2N1N was used as complexing agent for determination of cobalt by vortex-assisted liquid–liquid microextraction procedure combined with solidification of organic droplet (VALLME-SFO). Based on our knowledge, no report on the VALLME-SFO for the extraction of metal ions has been published. The methodology is based on the complexation of cobalt with 2N1N followed by extraction of the complex with 1-undecanol as extraction solvent by the assistance of vortex-assisted liquid–liquid microextraction. In vortex assisted, vigorous vortex stream as well as the vibrant effect of vortex system cause very fine droplets of extraction solvent to be produced and extraction occurs at a short time. The advantages of this VALLME-SFO method are low cost, high speed, simplicity, high selectivity, and recovery.

Experimental

Instrumentation

A Shimadzu AA-670 (Shimadzu, Japan) flame atomic absorption spectrometer equipped with a 100-mm burner head, deuterium background correction, and an air–acetylene flame was utilized. A cobalt hollow-cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) at a wavelength of 240.7 nm was used as a radiation source. The pH values were measured with a pH meter (Metrohm 827 pH lab, Switzerland) supplied with a glass-combined electrode. A vortex Gilson mixer (Villiers Le Bel, France) was used for thorough mixing of the solutions. Phase separation was assisted using Centurion Scientific Centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany). A thermostated bath (Lauda, Germany) was used to heat and keep the solution at a constant temperature.

Reagents

All reagents were of analytical reagent grade and deionized water was used throughout. A stock solution of $1,000 \text{ mg L}^{-1}$ cobalt(II) ion was prepared by dissolving appropriate amounts of cobalt nitrate hexahydrate (Merck, Darmstadt, Germany) in 1 % (v/v) HNO_3 . Working standard solutions were prepared freshly at various concentrations by diluting the stock standard solution with deionized water. Suprapur HNO_3 (65 %), H_2SO_4 (98 %), and HF (38–40 %) were used for sample digestion. A solution of $10^{-2} \text{ mol L}^{-1}$ 2N1N was prepared by dissolving appropriate amounts of this reagent in ethanol. 1-Undecanol (Merck) was employed as the extractant solvent and $10^{-2} \text{ mol L}^{-1}$ Triton X-114 solution was used as anti-sticking agent. The buffer solution was 1.0 mol L^{-1} sodium acetate/acetic acid by dissolving appropriate amounts of sodium acetate and acetic acid.

Sample preparation

Different water samples including tap water (Mashhad, Iran), spring water (Now Chah, Mashhad, Iran), and seawater (Caspian Sea) were collected from their sources and kept in clean bottles at 4°C temperature. Seawater was filtered through $0.45\text{-}\mu\text{m}$ pore size membrane filters to remove suspended particles. The samples were analyzed according to the recommended procedure.

Two certified reference materials (CRMs) analyzed by the presented method were NCS DC 73301 (Rocks constituents) and JSd-3 (stream sediments from the geological survey of Japan). To prepare the CRMs, 0.125 g of JSd-3 and 0.5 g of NCS DC73301 were separately digested with 8 mL of concentrated H_2SO_4 and 10 mL of concentrated HNO_3 , and heated at low temperature on a heating block. To complete the sample digestion, 15 mL of HF was added to the mixture and the solution was heated to near dryness. After cooling down to room temperature, the resulting solutions were diluted to 25 mL with distilled water. Four milliliters of each CRM samples was adjusted at pH 3.5, and after dilution analyzed according to the microextraction procedure.

Microextraction procedure

Eight milliliters of sample containing Co^{2+} , $500 \mu\text{L}$ of 1 mol L^{-1} acetate/acetic acid buffer (pH 3.5), $1.25 \times$

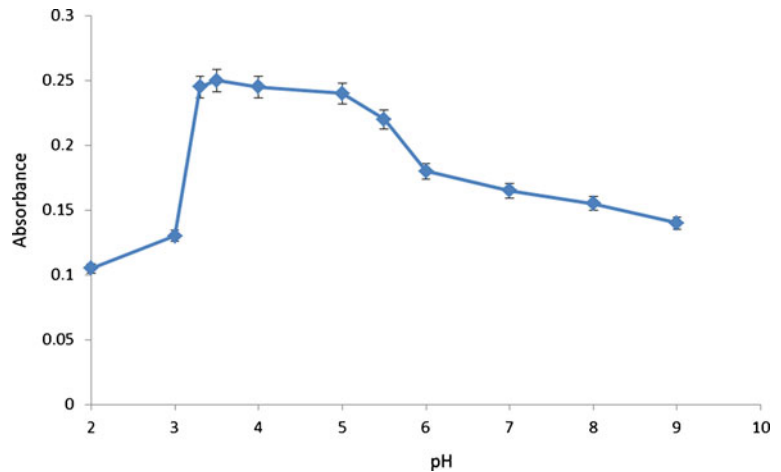
$10^{-4} \text{ mol L}^{-1}$ Triton X-114, and $2.5 \times 10^{-4} \text{ mol L}^{-1}$ 2N1N was transferred into a conical bottom glass centrifuge tube followed by addition of $30 \mu\text{L}$ of 1-undecanol as extractant solvent. The whole mixture was shaken by a vortex agitator for 60 s at $2,800 \text{ rpm}$. The extraction of Co-2N1N complex was performed at a short analysis time followed by the production of fine droplets of 1-undecanol. The resulting mixture was centrifuged for 3 min at $4,500 \text{ rpm}$, whereby the organic solvent droplet was floated on the surface of the aqueous solution. The test tube was transferred to a beaker containing ice and the organic solvent was solidified after 10 min ($27 \pm 2 \mu\text{L}$). The solidified organic solvent was transferred into a conical vial where it melted immediately. After dilution to $400 \mu\text{L}$ with ethanol, the resulting solution was sprayed into the flame atomic absorption spectrometer for quantification.

Results and discussions

Effect of pH and buffer concentration

The pH of sample plays an important role on the complex formation with sufficient hydrophobic nature and throughout the extraction process. Also, pH is a critical parameter for selective behavior of the complexing agent towards a special metal ion. To investigate the effect of pH on the absorbance of cobalt ion, different sample solutions with different pH values varying in the range of 2–9 were evaluated and the results are shown in Fig. 1. As data show, the optimum pH value was observed in the pH range of 3.3–5, showing formation of Co-2N1N complex in weak acidic conditions. Similar to its isomeric form (1N2N) because of the instabilities of other interfering metal-2N1N complexes such as Fe^{3+} and Cu^{2+} at pH 5, more acidic conditions are preferable (Cheng et al. 1992). Therefore, pH of 3.5 was selected for subsequent analysis. An acetic/acetate buffer was used to keep the pH at a constant value and to study the effect of buffer capacity on formation of Co-2N1N complex; different buffer concentrations in the range of $0\text{--}0.12 \text{ mol L}^{-1}$ were investigated. The results show that the extraction of complex increased with increasing buffer concentration up to $6 \times 10^{-2} \text{ mol L}^{-1}$ and it remains constant at higher buffer concentrations. This behavior is similar to 1N2N which shows that the extraction efficiency of cobalt ion improved in the presence of acetate/acetic acid buffer

Fig. 1 Effect of pH on the absorbance of cobalt ion, conditions: $200 \mu\text{g L}^{-1} \text{Co}^{2+}$, $6 \times 10^{-2} \text{ mol L}^{-1}$ acetate/acetic acid buffer, $1.25 \times 10^{-4} \text{ mol L}^{-1}$ Triton X-114, $2.5 \times 10^{-4} \text{ mol L}^{-1}$ 2N1N, $30 \mu\text{L}$ 1-undecanol, 60-s extraction time

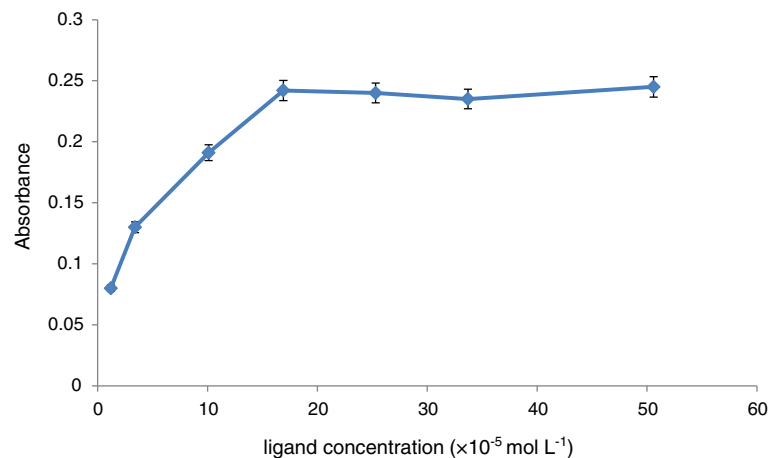


solution (Berton et al. 2009). Therefore, a buffer concentration of $6 \times 10^{-2} \text{ mol L}^{-1}$ was selected as the optimum value for subsequent analysis.

Effect of ligand concentration

Ligand concentration is important to establish the minimal reagent concentration leading to a complete complex formation while achieving the highest extraction. 2N1N is an isomeric structure of 1N2N, which previously used as a selective complexing agent for determination of cobalt ion (Berton and Wuilloud 2010). The effect of ligand concentration on the absorbance of cobalt ion was studied with different concentrations in the range of 1.2×10^{-5} – $5.1 \times 10^{-4} \text{ mol L}^{-1}$. The results in Fig. 2 show that the absorbance of sample solution increased with increasing 2N1N concentration up to $1.7 \times 10^{-4} \text{ mol L}^{-1}$ and it remained constant at higher ligand concentrations. Therefore, to ensure of the sufficient amounts of 2N1N

Fig. 2 Effect of 2N1N concentration on the absorbance of cobalt ion, pH 3.5, and other conditions are as Fig. 1



for interaction with cobalt ions, the concentration of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ 2N1N was selected as the optimum value.

Effect of temperature

The effect of temperature on the reaction kinetic of Co^{2+} with 2N1N was studied at different temperatures including room temperature (25 – $32 \text{ }^\circ\text{C}$), 40 and $60 \text{ }^\circ\text{C}$ in a thermostated bath at constant reaction time of 15 min. It was observed that (data not shown) no significant change in the absorbance value occurred at different temperatures. This is in contrast to its isomeric structure, 1N2N, which has higher extraction efficiency at higher temperatures (Berton and Wuilloud 2010); however, this might be related to the positions of OH - and NO - groups on the aromatic ring which can provide suitable structure for reaction with cobalt ion, at lower temperature and without the aid of heating. Therefore, all experiments were performed at room temperature.

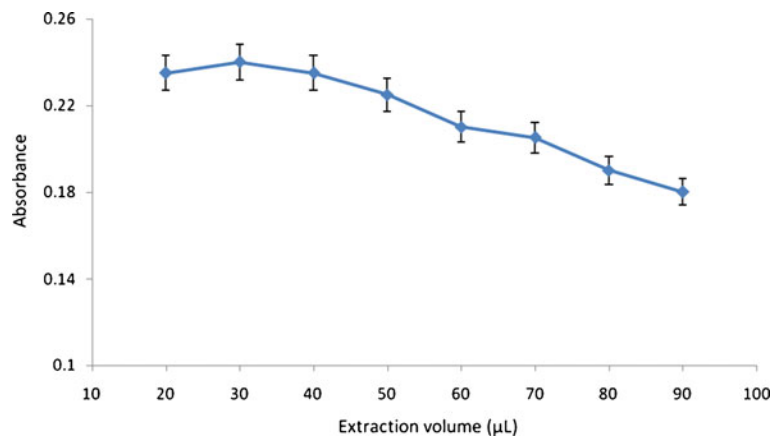
Extraction solvent volume

The extraction solvent has an important role to obtain high recovery and extraction efficiency. For this purpose, the extraction solvent must have low water solubility, low volatility, and high hydrophobic nature. 1-Undecanol is an organic solvent which having the advantages mentioned above and melting point near to room temperature can be used as extraction solvent for SFO (Asadollahi et al. 2010; Mirzaei et al. 2011; Shirani Bidabadi et al. 2009). The results in Fig. 3 show the effect of different volumes of 1-undecanol for extraction of Co-2N1N. According to the results, the absorbance remains constant up to 40 μL and it gradually decreases with further increasing of the acceptor phase (1-undecanol) volume. This behavior may be related to increasing the viscosity of the sprayed solution as the result of increasing of the acceptor phase ratio, so that the nebulization process is not effective and the absorbance decreases. Lower volumes of 1-undecanol were avoided because of poor reproducibility of the results. Therefore, 30 μL of 1-undecanol was used as the optimum volume.

Extraction time

Extraction time is one of the critical factors to achieve maximum sensitivity for the extraction process. The importance of this parameter originates from the equilibrium of Co-2N1N complex, between acceptor (1-undecanol) and donor phase (aqueous solution). In vortex-based extraction methods, the extractant solvent is dispersed in the sample solution by the assistance of vortex agitator system based on vigorous vortex stream and vibrating effect of vortex system

Fig. 3 Effect of extraction solvent volume on the absorbance of cobalt ion, conditions are as Fig. 1



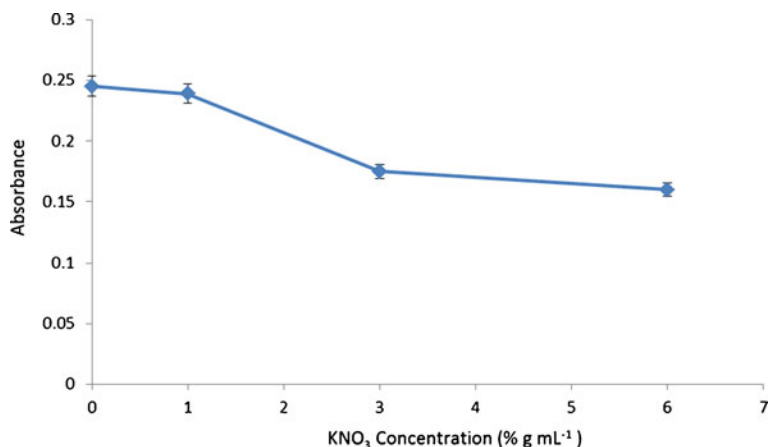
so that the extraction occurred in a short time. In the case of Co-2N1N, the effect of extraction time was studied from 30 to 300 s within a time interval 30 s. The results (data not shown) show that the absorbance reaches its maximum value at 60 s and it remains constant at longer extraction times. Therefore, 60-s vortex time was considered as the optimum extraction time for subsequent analysis.

Effect of ionic strength and anti-stacking addition

Addition of salt to the sample may have several effects on the extraction efficiency. The increase in the extraction efficiency as the result of salting out effect can be explained by the engagement of water molecules in the hydration spheres around the ionic salt and hence in the reduction of the water molecules available to dissolve analytes, so the availability of analyte increases and the extraction efficiency is improved. On the other hand, increasing salt concentration may decrease the extraction solvent solubility causing a decrease in extraction efficiency (Asadollahi et al. 2010; Ma et al. 2010; Ying-Ying et al. 2010). To study the effect of ionic strength on the extraction efficiency, different concentrations of KNO_3 in the range of 0–6 % (*m/v*) were evaluated. According to the results shown in Fig. 4, the absorbance is constant up to 1 % g mL^{-1} of KNO_3 and then decreases due to the decreasing extraction solvent solubility. Therefore, all stages of experiments were performed without salt addition.

The effect of surfactant concentration on the extraction efficiency was also studied with addition of different concentrations of nonionic surfactant, Triton X-114, in the concentration range of $0\text{--}2.5 \times 10^{-4} \text{ mol L}^{-1}$.

Fig. 4 Effect of ionic strength on the absorbance of cobalt ion, conditions are as Fig. 1



Triton X-114 can reduce the adherence of 1-undecanol to centrifuge tube and also prevent the precipitation of Co-2N1N complex in aqueous solution. The results show that (data not shown) the absorbance increases with increasing Triton concentration up to 1.25×10^{-4} mol L⁻¹ and it remains constant afterwards. Therefore, a concentration of 1.25×10^{-4} mol L⁻¹ Triton X-114 was selected as the optimum value.

Centrifuge time

The effects of centrifugation time on the absorbance were studied in the range of 1–5 min. The results show that 4-min centrifugation time at a constant 4,000 rpm is an optimum time for separation of two immiscible

phases. Therefore, 3-min centrifugation time at 4,000 rpm was selected as the optimum value.

Interference study

Because of high selectivity provided by FAAS, the only interferences studied were those related to the preconcentration step. Therefore, various amounts of metal ions were added to a solution containing fixed amounts of cobalt ions and the present procedure was followed. For this purpose, according to the recommended precedence, 8 mL of the solution of 200 µg L⁻¹ Co²⁺ and various amounts of interfering ions were preconcentrated and analyzed. An ion was considered to interfere when its presence produced a

Table 1 Study on the effect of coexisting ions on the absorbance of cobalt ion

Ion	Added as	Concentration (mg L ⁻¹)	Recovery, %
K ⁺	KNO ₃	3,000	98.1
Na ⁺	NaNO ₃	3,000	99.2
Mg ²⁺	Mg(NO ₃) ₂	3,000	100.0
Ca ²⁺	Ca(NO ₃) ₂	3,000	100.
Zn ²⁺	Zn(NO ₃) ₂	3,000	99.3
Cd ²⁺	Cd(NO ₃) ₂	3,000	100.0
Cu ²⁺	Cu(NO ₃) ₂	3,000	100.0
Fe ³⁺	Fe(NO ₃) ₃	3,000	99.1
Pb ²⁺	Pb(NO ₃) ₂	3,000	98.4
Mn ²⁺	MnSO ₄	2,000	96.4
Cl ⁻	KCl	2,000	100.0
Br ⁻	KBr	2,000	99.3
SO ₄ ²⁻	K ₂ SO ₄	2,000	97.0

Table 2 Results (mean±standard deviation based on three replicate analysis) of determination of cobalt in real samples

Sample	Spiked (µg L ⁻¹)	Found (µg L ⁻¹)	Recovery (%)
Tap water ^a	0	ND	–
	30	30.7±0.4	102.3
	100	104.4±0.9	104.4
Spring water ^b	0	ND	–
	30	29.9±0.5	99.6
	100	101.2±0.9	101.2
Seawater ^c	0	ND	–
	30	28.7±0.4	95.6
	100	100.0±1.0	100

ND not detected

^a Obtain from Mashhad, Iran

^b Obtain from Now Chah, Mashhad, Iran

^c Caspian Sea, Iran

Table 3 The results (mean±standard deviation based on three replicate analysis) of the analysis of the Certified Reference Materials (CRMs)

Sample	Certified ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	Recovery (%)
NCS DC 73301	3.4	3.3±0.3	97.1
JSd-3	12.7	12.2±0.5	96.1

variation in the absorbance of the sample of more than 5 %. The selectivity of 2N1N towards cobalt ion is depending on pH value. Here, with adjusting the pH value at 3.5 because of higher sensitivity (Fig. 1) and also instability of other metal ions complexes with 2N1N in more acidic solutions (Ssekaalo 1970) which make it as selective complexing agent for determination of cobalt ion, the effect of other ions on the extraction and determination of cobalt ion were investigated. The results are shown in Table 1. According to the results, 2N1N shows selective behavior toward cobalt ion which indicate that the developed method is applicable to analysis of cobalt in different water samples.

Analytical figure of merit

An extraction percentage higher than 99.9 % was achieved when the procedure was carried out under the optimal experimental conditions. Under the optimum conditions, the calibration curve was linear in the concentration range of 15–400 $\mu\text{g L}^{-1}$ of cobalt ions. The calibration equation was determined to be $A=0.0232+0.0011C$, where A is the analytical signal measured as absorbance and C is the concentration of cobalt ion (in microgram per liter). The relative standard deviation for ten replicate analysis of 50 $\mu\text{g L}^{-1}$ cobalt ion is 3.4 %.

Phase volume ratio, calculated as the ratio between the volume of the aqueous phase (8 mL) and the final volume of the extraction phase (400 μL), was 20. The detection limit (calculated as the concentration equivalent to three times of the standard deviation of the blank divided into the slope of the calibration curve after preconcentration) was 5.4 $\mu\text{g L}^{-1}$. The calibration curve for the direct determination of cobalt ion using flame atomic absorption spectrometry is represented by equation $A=1.00\times 10^{-3}+0.061C$ (for 0.5–6 mg L^{-1} cobalt ion). The enrichment factor was calculated as the ratio of the slope of a calibration curve prepared from aqueous solutions submitted to the recommended extraction procedure, and that obtained without the preconcentration and found to be 18.

Application of the method

The recommended procedure was examined to determine cobalt ion in real samples including tap water, spring water, and seawater. In order to validate the accuracy of the proposed procedure, recovery experiments were also carried out by spiking the samples with different amounts of cobalt ions before any pretreatment. The results are shown in Table 2. The accuracy of the presented procedure is performed by the analysis of two certified reference material: NCS 73301 and JSd3. The certified and observed values for the analysis of CRMs are shown in Table 3. The observed results were in good agreement with the certified values of the CRMs.

Comparison to other methods

A comparison of the proposed method with other reported preconcentration methods for determination of cobalt ion is given in Table 4. With the exception of

Table 4 Comparison of analytical characteristic of the proposed method with some published method for determination of cobalt

Method	Calibration range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Extraction time (min)	References
CPE-FAAS	250–5,000	1.0	3.6	20	Citak and Tuzen (2010)
CPE-FAAS	10–200	2.1	1.5	20	Ghaedi et al. (2008)
DLLME-FAAS	3–100	0.9	2.3–5.8	<1	Baliza et al. (2009)
SPE-FAAS	40–4,500	12.3	1.3	<15	Afzali and Zia Mohammadi (2011)
SPE-FAAS	12.7–5,000	3.8	–	<10	Yalcinkaya et al. (2011)
VALLME-SFO-FAAS	15–400	5.4	3.4	1	This work

DLLME, limit of detection and the precision (RSD %) of the method are comparable to other reported methods. Good linear range ($15\text{--}400\ \mu\text{g L}^{-1}$) in the short extraction time (1 min) was observed for the proposed method. This methodology is a reproducible, fast, simple, and low cost technique and does not require further instrumentation and it can be used with regular FAAS equipment.

Conclusions

Highly rapid and selective VALLME-SFO has been used for determination of cobalt ion in real samples. 2N1N was used as a selective ligand to form stable complex with cobalt ions which can be extracted into the extraction solvent by VALLME. In VALLME, vigorous vortex stream as well as vibrant effect causes very fine droplets of organic solvent (1-undecanol) to be dispersed in the whole solution so that the extraction of hydrophobic complex can be performed at a short time. This selective and highly rapid method was used for determination of cobalt ion in different water samples.

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