

Determination of cobalt in water samples by atomic absorption spectrometry after pre-concentration with a simple ionic liquid-based dispersive liquid–liquid micro-extraction methodology

Research Article

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Abstract: A rapid dispersive liquid–liquid micro-extraction (DLLME) methodology based on the application of 1-hexylpyridinium hexafluorophosphate $[C_6py][PF_6]$ ionic liquid (IL) as an extractant solvent was applied for the pre-concentration of trace levels of cobalt prior to determination by flame atomic absorption spectrometry (FAAS). 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was employed as a chelator forming a Co–PMBP complex to extract cobalt ions from aqueous solution into the fine droplets of $[C_6py][PF_6]$. Some effective factors that influence the micro-extraction efficiency include the pH, the PMBP concentration, the amount of ionic liquid, the ionic strength, the temperature and the centrifugation time which were investigated and optimized. In the optimum experimental conditions, the limit of detection (3s) and the enrichment factor were $0.70 \mu g L^{-1}$ and 60, respectively. The relative standard deviation (RSD) for six replicate determinations of $50 \mu g L^{-1}$ Co was 2.36%. The calibration graph using the pre-concentration system was linear at levels 2–166 $\mu g L^{-1}$ with a correlation coefficient of 0.9982. The applicability of the proposed method was evaluated by the determination of trace amounts of cobalt in several water samples.

Keywords: Cobalt • Ionic liquid • Dispersive liquid–liquid micro-extraction • Pre-concentration • Water samples

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1. Introduction

Cobalt is a natural earth element and is present in trace amounts in air, soil, water, plants and in our diets. It is used in many alloys (superalloys for parts in gas turbine aircraft engines, corrosion resistant alloys, high-speed steels, cemented carbides), in magnets and magnetic recording media, as catalysts for the petroleum and chemical industries, as drying agents for paints and inks. A small amount of cobalt is beneficial for humans because it is a part of vitamin B_{12} , which is essential for human health. Cobalt is used to treat anemia with pregnant women, because it stimulates the production of red blood cells [1]. However, too high concentrations of cobalt may damage human health. Toxicological effects caused by the intake of excess cobalt include interstitial lung disease, vasodilatation, flushing, and cardiomyopathy in humans and animals [2]. Since one of the routes of incorporation of cobalt into the human body is by ingestion, its determination in food and drinking water becomes important. Cobalt concentration levels

are very low in water samples, and therefore, simple and sensitive analytical techniques are required to carry out its detection [3].

Several analytical techniques such as UV–Vis spectrometry [4–6], spectrofluorimetry [7], flow injection chemiluminescence (FI-CL) [8,9], electroanalytical techniques [10–12], laser induced thermal lens spectrometry [13], X-ray fluorescence [14], neutron activation analysis (NAA) [15,16], flame atomic absorption spectrometry (FAAS) [17–19], electrothermal atomic absorption spectrometry (ET-AAS) [3,20,21], inductively coupled plasma optical emission spectroscopy (ICP-OES) [22–24] and inductively coupled plasma mass spectrometry (ICP-MS) [25,26] have been reported for the determination of cobalt in different samples.

For most applications, separation and pre-concentration of cobalt are still often recommended before detection due to its extremely low concentration or complicated matrices in the real samples [27]. In combination with the above-mentioned techniques,

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various pre-concentration and separation procedures such as liquid-liquid extraction (LLE), solid-phase extraction (SPE), flow injection extraction (FIE), cloud point extraction (CPE) and dispersive liquid-liquid micro-extraction (DLLME) have also been used [28]. Among these, LLE has been used for decades, but it has some disadvantages such as the requirement for relatively large amounts of organic solvents having toxic properties. Recently, efforts have been placed on miniaturizing the LLE procedure to greatly reduce the amount of organic solvent resulting in the development of micro-extraction methodologies such as liquid-phase micro-extraction (LPME), liquid-liquid micro-extraction (LLME), solid-phase micro-extraction (SPME), etc. [29,30]. DLLME is a mode of LPME, which is based on the same principles as the traditional LLE, but with the advantages of simplicity, rapidity, low sample volume, low cost, high recovery, and a high enrichment factor [31]. Although DLLME has been widely used for the extraction of organic compounds, it has also been utilized in trace metal ions analysis [32–36]. In these procedures, however, toxic solvents such as benzene, toluene or chloroform have been used as extraction phase.

Ionic liquids (ILs) are a class of low melting point ionic compounds, which have a variety of properties allowing many of them to be sustainable green solvents in the sample preparation. Besides their low melting points, ILs have many other unique physicochemical properties, such as broad liquid ranges, negligible vapor pressures, good thermal stabilities, non-flammability as well as tunable viscosity and miscibility with water and organic solvents. These properties make them good for extraction of various organic compounds and metal ions as neutral or charged complexes, which is very attractive in separation processes [37–40].

Several sample preparation methods such as LLME, single-drop micro-extraction (SDME), cold-induced aggregation micro-extraction (CIAME), *in situ* solvent formation micro-extraction (ISFME) and DLLME have been used in extractions with an ionic liquid for the separation and pre-concentration of metal ions, *i.e.*, Hg, Pb, Cd, Co, Mn, V *etc.* [41–51]. But, it should be noted that in all of the developed sample preparations of metal ions were performed using imidazolium ILs with some of these methods needing anti-sticking agents for improving micro-extraction efficiency [48] or a back-extraction step prior to detection. The attempt of our research group has currently focused on the application of pyridinium ILs in DLLME of metal ions and in the present work, 1-hexylpyridinium hexafluorophosphate [C_6py][PF_6] ionic liquid was employed as an extractant solvent considering its good performance, water-immiscibility, high hydrophobicity, and quite viscosity

[52] for the separation and pre-concentration of trace cobalt. The proposed procedure is very simple and does not need any anti-sticking agent, heating, long equilibration time, cooling before or after centrifugation and back-extraction step prior to detection. The effects of various experimental parameters on the extraction were investigated, and the method was applied to determine the amount of Co in real water samples using air-acetylene flame atomic absorption spectrometry detection.

2. Experimental procedure

2.1. Apparatus

A Varian model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was utilized, equipped with a 100 mm burner head, deuterium lamp background correction and an air-acetylene flame. A cobalt hollow cathode lamp (operated at 7 mA) was used as the radiation source at the wavelength of 240.7 nm with 0.2 nm spectral bandpass. The acetylene and air-flow rates were 1.5 and 3.5 L min⁻¹, respectively. A centrifuge (Beckman GS-6, USA) was used to accelerate the phase separation process. The pH values were measured with a Metrohm pH-meter (model 827, Switzerland), supplied with a glass-combined electrode. A thermostatted water bath (Julabo) model GMBH D-77960 was obtained from Germany. An electronic analytical balance (Mettler Toledo, PB303, Switzerland) was used for weighing the solid materials.

2.2. Standard solutions and reagents

All chemicals used were of analytical-reagent grade and all solutions were prepared with doubly distilled, deionized water (Ghazi Co, Tabriz, Iran). Stock solutions of cobalt (II) and those used for the interference study (1000 µg mL⁻¹) were prepared by dissolving appropriate amounts of their respective pure nitrate salts (Merck, Darmstadt, Germany) in deionized water. Working standard solutions were obtained daily by suitable stepwise dilution of the stock solutions with deionized water and shaking them just before use.

1-Hexylpyridinium hexafluorophosphate (97% Acros organics, Belgium) was employed as an extractant solvent without further purification. The chelating reagent PMBP was purchased from Fluka. Acetone, tetrahydrofuran (THF), ethanol, acetonitrile, methanol and all salts used were purchased from Merck.

A 50.0 mL of 2.5% (m/v) solution of PMBP was prepared by dissolving 1.25 g of the reagent in 4 mL of aqueous ammonia (25% Merck), diluting with deionized water, and adjusting the pH of the solution to 5.5–6.0 with dilute nitric acid. [C_6py][PF_6] ionic liquid is solid at room temperature (melting point: 45–48°C) and requires

dissolution with an organic solvent. Therefore, a solution of 0.15 g mL⁻¹ [C₆py][PF₆] was obtained by dissolving appropriate amount of this IL in acetone. A stock sodium acetate-acetic acid (NaAc-HAc) buffer solution (0.5 mol L⁻¹) was prepared by diluting appropriate volumes of acetic acid (Merck) with deionized water and adjusting to pH 5 by adding 1 mol L⁻¹ NaOH solution. A 2 mol L⁻¹ NaCl (Merck) solution was used for an ionic strength study. Thiourea, sodium fluoride (both from Merck) and sodium citrate (Acros organics) were used as masking agents. The pipettes and vessels used for the trace analysis were kept in 15% (v/v) nitric acid minimally over night and subsequently washed three times with deionized water prior to use.

2.3. Preparation of water samples

Water samples including mineral water, tap water and spring water were collected from local sources. After sampling, they were filtered through Rund filter paper (blue band, no. 300210) to remove suspended particulate matter. Aliquots of 25.0 mL from each sample solution were used for the analyses.

2.4. General procedure

A 25.0 mL aliquot of sample or standard solution containing Co²⁺ in the range of 2–166 µg L⁻¹, 1.2 mL of 0.5 mol L⁻¹ acetate/acetic acid buffer solution (pH 5) and 1.8 mL of 2.5% (m/v) PMBP solution (chelating agent) was placed in a screw-cap conical-bottom polypropylene centrifuge tube. Then, 2 mL of acetone (disperser solvent) containing 0.3 g of [C₆py][PF₆] ionic liquid (extraction solvent) was added. Finally, the total volume of the solution was made up to 30.0 mL. Afterward, the tube was simply shaken to obtain a dispersion of the IL into the aqueous media. After shaking, the resultant solution was immediately turbid at room temperature resulting in extracting the Co-PMBP complex into the fine droplets of IL. In order to accelerate phase separation, the cloudy solution was centrifuged at 4000 rpm for 5 min. As a result, the IL-phase settled to the bottom of the centrifuge tube. The upper aqueous phase was manually removed completely with a syringe centered in the tube without need of cooling in an ice bath. Finally, 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 500 µL by adding the acetone. The resultant solution was introduced into the flame by conventional aspiration. A reagent blank was prepared using a similar procedure but without cobalt. The optimized conditions are listed in Table 1. In the impact parameters optimization procedure, the limits marked on the figures were obtained from three experiments that repeated under the same conditions.

Table 1. Instrumental and experimental conditions for Co determination.

FAAS conditions	
Wavelength (nm)	240.7
Lamp current (mA)	7
Spectral bandpass (nm)	0.2
Acetylene flow rate (L min ⁻¹)	1.5
Air flow rate (L min ⁻¹)	3.5
Integration time (s)	0.1
Micro-extraction conditions	
Working pH	5
Co ²⁺ concentration (µg L ⁻¹)	50
PMBP concentration (% m/v)	0.15
Amount of [C ₆ py][PF ₆] (g)	0.3
Buffer concentration (mol L ⁻¹)	0.02
Centrifugation time (min)	5
Extraction time (min)	<10
Sample volume (mL)	25
Disperser solvent volume (mL)	2

3. Results and discussion

In order to obtain a high extraction efficiency, the effect of different parameters affecting the complex formation and extraction conditions such as pH, concentration of the chelating agent, amount of IL, extraction time, ionic strength, diluting agent, temperature and centrifugation time were investigated and optimized. One variable at a time was studied to obtain the optimum conditions for the IL-based DLLME.

The enrichment factor (EF) was defined as the ratio between the cobalt concentration of the IL-phase in the final solutions (C_{IL}) after extraction and the initial concentration of the cobalt (C_i) within the sample:

$$EF = \frac{C_{IL}}{C_i}$$

Meanwhile, the extraction efficiencies (Ec) were calculated by

$$Ec (\%) = \frac{C_{IL} \times V_{IL}}{C_i \times V_{aq}} \times 100 \text{ or } Ec (\%) = EF \left(\frac{V_{IL}}{V_{aq}} \right) \times 100$$

Where V_{IL} and V_{aq} are the final volume of IL-phase (500 µL) and the volume of the aqueous sample (30.0 mL), respectively. The C_{IL} was obtained from the calibration graph (250–10000 µg L⁻¹) of the standard Co–PMBP–acetone solutions.

3.1. Selection of disperser solvent and diluting agent

For IL-based DLLME method, the dispersive solvent should be miscible with both water (aqueous phase) and the extraction solvent ([C₆py][PF₆] IL). For this purpose, different solvents such as acetonitrile, acetone, THF, ethanol and methanol were tested. Several sample solutions were studied using 2.0 mL of each disperser

solvent, which contains 0.3 g $[C_6py][PF_6]$ IL. The minimum enrichment factor (50 ± 2) was obtained in the presence of the ethanol. Nevertheless, no significant differences in enrichment factor value (60 ± 1) about the other disperser solvents were found, and acetone was finally selected as disperser solvent in all of the subsequent experiments. At low volumes of acetone, dispersion was incomplete, while for volumes exceeding 3.0 mL the enrichment factor decreased. Therefore, an optimal volume of 2.0 mL of acetone was chosen to achieve a better and more stable cloudy solution.

Due to its very high viscosity, the IL-rich phase had to be conditioned before its introduction into the nebulizer of the spectrometer by addition of a diluting agent. The viscosity of the IL-rich phase is drastically decreased using diluting agents. Different solvents such as methanol, ethanol, acetone, THF and acetonitrile were tested in order to select the one that can dissolve the IL-rich phase completely and give the best sensitivity. Maximum analytical signal with very negligible background absorption was obtained in the presence of acetone and ethanol. Acetone was chosen as the IL-rich phase diluting agent.

3.2. Effect of pH

Separation of metal ions by the IL-based micro-extraction methods involve prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of IL-rich phase. It is well known that the pH of the media has a great effect on the existing form of the reagent and plays an important role on metal-chelate formation and subsequent extraction. Therefore, it is necessary to determine the pH of the system that

will give the maximum complex formation. The effect of pH upon the extraction of Co-PMBP complex from the solution was studied within the pH range 4–11 by adding appropriate volumes of HCl or NaOH solution to the samples. The results are shown in Fig. 1. As can be seen, the pH optimum value was observed in the range of 4–7. The reduced analytical signal at higher pH could be due to the formation of cobalt hydroxide resulting in decreased concentration of free Co^{2+} ions in sample solution. Thus, in subsequent experiments, a solution of pH 5.0 adjusted by a 0.02 mol L^{-1} acetate/acetic acid buffer solution, was used.

3.3. Effect of chelating agent concentration

In this work, PMBP was used as the chelating agent due to the highly hydrophobic nature of its metal chelates. Concentration of chelating agent is a critical variable to be optimized in a pre-concentration method. Fig. 2 shows the effect of PMBP concentration on the micro-extraction of cobalt ions. The concentration of PMBP tested ranged from 0.01 to 0.3% (m/v). The extraction efficiency for Co^{2+} ions increased as the concentration of PMBP increased from 0.01 to 0.12% (m/v), and then remained constant up to a PMBP concentration of 0.3% (m/v). Therefore, a 0.15% (m/v) PMBP concentration was employed for further experiments.

3.4. Effect of IL amount

The extraction system was carefully studied in order to obtain the lowest IL-phase mass necessary for achieving the highest pre-concentration factor possible. The variation in the recovery as a function of the amount of IL, which was added to 30.0 mL sample,

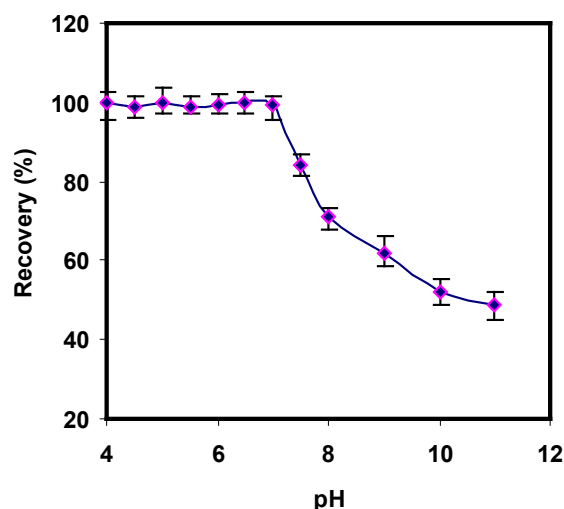


Figure 1. Effect of pH on the extraction efficiency of cobalt. Utilized conditions: Co^{2+} , 50 $\mu g L^{-1}$; PMBP, 0.2% (m/v); $[C_6py][PF_6]$, 0.30 g; centrifugation time, 10 min.

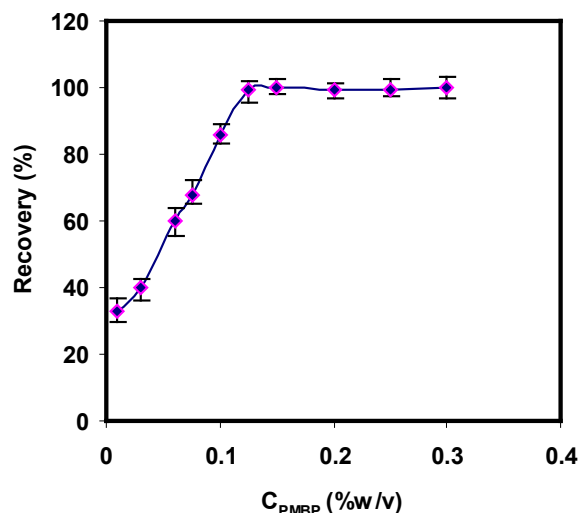


Figure 2. Effect of PMBP concentration on the extraction efficiency of cobalt.

was investigated within the range of 0.05–0.45 g. It was determined that the extraction efficiency of this pre-concentration procedure was markedly affected by the IL amount. The results indicated that the extraction efficiency is very poor when the IL amount is smaller than 0.15 g because of the difficulty of $[C_6py][PF_6]$ IL to form an immiscible extraction phase when its amount is less 0.15 g due to dilution with water. The extraction efficiency rapidly increased with the amount of IL, and then leveled off for an IL amount greater than 0.27 g using a single step extraction procedure. Therefore, in order to achieve a good enrichment factor, a 0.30 g amount of IL was chosen as the optimum value.

3.5. Effect of ionic strength

In some sample pretreatment techniques, the addition of salt often increases the extraction performance due to the salting out efficiencies. To investigate the influence of ionic strength on the developed micro-extraction system, various experiments were performed by adding different amounts of NaCl with the rest of the experimental conditions being held constant. It was determined that the addition of NaCl within the interval of 0.0–0.5 mol L⁻¹ had no considerable effect on the extraction efficiency of the present system.

3.6. Effect of temperature and equilibration time

Optimal equilibration temperature and time are necessary to complete reactions, and to achieve the most efficient phase separation and pre-concentration as possible. Therefore, the effect of the equilibration temperature was investigated from 4°C to 50°C before shaking the IL-containing solutions. It was found that the increase of temperature had no significant effect upon the extraction efficiency; consequently, room temperature was used in the extraction procedure.

In IL-based DLLME, extraction time is defined as an interval between the injection of the mixture of disperser solvent (acetone) and extraction solvent ($[C_6py][PF_6]$ IL) and starting to centrifuge. At room temperature, the extraction time was studied in the range of 20–3600 s under constant other experimental conditions. It is obvious from the data that the extraction time has no significant effect on the extraction efficiency for Co. This can be explained as follows: after adding the mixture of disperser solvent and extraction solvent, numerous small droplets of extract were instantaneously dispersed within the aqueous solution as cloudy phase indicating an infinitely large interface between the extraction solvent and the aqueous phase. Therefore, quick equilibrium was achieved due to the fast transition of analytes from aqueous phase to extraction solvent. The short

extraction time is one of the remarkable advantages of the IL-based DLLME technique. So, in order to keep analysis time as short as possible, the turbid solution was centrifuged immediately after the preparation at room temperature.

3.7. Effect of centrifugation time

Centrifugation accelerates the phase separation and the final performance benefits from a full phase separation. Therefore, the effect of centrifugation time upon extraction efficiency was studied for the range of 1–10 min. Based on the obtained results, extraction efficiency was constant after times of 4 min indicating complete transfer of IL-phase to the bottom of centrifuge tube. So, a centrifugation time of 5 min at 4000 rpm was selected for the entire procedure, since complete separation occurred for this time and longer times would not give much larger extraction efficiencies.

3.8. Sample volume and pre-concentration factor

In order to obtain the best pre-concentration factor, the extraction system was studied to allow the highest volume ratio between sample solution and IL-phase. Thus, the effect of sample volume was examined in a range of 10–45 mL for 50 µg L⁻¹ Co. After addition of constant amount of IL into different volumes of aqueous samples, extraction procedure was performed for each solution. The data is shown in Fig. 3, illustrating that extraction efficiency of cobalt was quantitative in the range of 10–35 mL and that, for higher sample

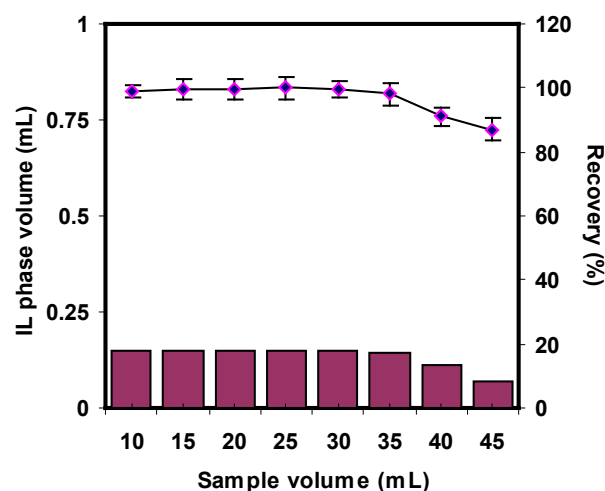


Figure 3. Evaluation of the extraction efficiency of Co²⁺ by using the different sample volumes and constant amount of $[C_6py][PF_6]$. Dots show the IL-phase volumes. Utilized conditions: Co²⁺, 50 µg L⁻¹; acetate/acetic acid buffer (pH 5.0); PMBP, 0.15% (m/v); $[C_6py][PF_6]$, 0.3 g; centrifugation time, 5 min.

Table 2. Tolerance limits of interfering ions in the determination of 50 $\mu\text{g L}^{-1}$ of Co.

Ions	Interferent-to-analyte weight ratio
Li^+ , Na^+ , K^+ , Cs^+ , Ba^{2+} , Sr^{2+} , F^- , Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , PO_4^{3-} , CH_3COO^- , $\text{Cr}_2\text{O}_7^{2-}$, VO_3^- , $\text{Al}^{3+(a)}$, $\text{Cu}^{2+(b)}$, thiourea, citrate	1000:1
Pb^{2+} , Ca^{2+} , $\text{Ni}^{2+(c)}$, $\text{Zn}^{2+(c)}$	800:1
Mg^{2+} , Ag^+ , Cr^{3+} , Cd^{2+} , Bi^{3+} , $\text{Fe}^{3+(a)}$	500:1
Al^{3+} , Sn^{2+}	200:1
Ni^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+}	50:1

(a) In the presence of 0.1 mol L^{-1} F^- .

(b) In the presence of 0.1% (m/v) thiourea.

(c) In the presence of 0.1% (m/v) citrate.

volumes, extraction efficiency decreased. This could be due to the IL-phase partial dissolution in the aqueous phase. Because, based on the obtained results, when the amounts of IL and sample volumes increased in parallel, the extraction efficiency was constant. Thus, the magnitude of pre-concentration factor is limited by the solubility of $[\text{C}_6\text{py}][\text{PF}_6]$ in aqueous media. Hence, a 30 mL sample volume was recommended for work with 0.3 g IL. The obtained pre-concentration factor for a sample volume of 30 mL and a final IL-phase volume of 500 μL was 60.

3.9. Study of interferences

In view of the selectivity provided by AAS, the possible interferences can primarily be attributed to the pre-concentration step. In order to demonstrate the selectivity of the developed micro-extraction system, the effects of coexisting ions in real water samples on the recovery of cobalt were also evaluated. In these experiments, different amounts of ions were added to the test solutions containing 50 $\mu\text{g L}^{-1}$ of cobalt and then followed according to general procedure. An ion was considered to interfere when its presence produced a variation of more than $\pm 5\%$ in the absorbance of the sample. The results are given in Table 2. Most of the cations and anions examined did not interfere with

the extraction and determination of Co^{2+} . However, some of species tried, such as Cu^{2+} , Zn^{2+} , Ni^{2+} and Fe^{3+} probably interfered with the determination of Co^{2+} . These interferences were eliminated in the presence of proper masking agents, such as (0.1 mol L^{-1}) F^- for Fe^{3+} , 0.1% (m/v) thiourea for Cu^{2+} and 0.1% (m/v) citrate for Zn^{2+} and Ni^{2+} . In the presence of the masking agents, no interference was observed for Al^{3+} and Cu^{2+} up to 1000, Zn^{2+} and Ni^{2+} up to 800 and Fe^{3+} up to 500 times relative to Co^{2+} concentration. On the other hand, analytical signal of the blank was not modified in the presence of the concomitant ions assayed. Thus, quantitative extraction of Co^{2+} was possible.

3.10. Analytical figures of merit

An extraction efficiency higher than 99.9% was achieved when the procedure was carried out under the optimum experimental conditions (Table 1). Table 3 summarizes the analytical characteristics of the optimized method. The calibration graph was linear between 2 to 166 $\mu\text{g L}^{-1}$, with a correlation coefficient of 0.9982. The regression equation was $A = 0.0045 C_{(\text{Co})} + 0.0128$, where A is the absorbance and $C_{(\text{Co})}$ is cobalt concentration in $\mu\text{g L}^{-1}$. The limit of detection (LOD) calculated as three times the standard deviation of the blank signal was 0.70 $\mu\text{g L}^{-1}$ for the pre-concentration of 30 mL of sample solution.

Table 3. Analytical characteristics of the proposed method.

Analytical parameters	With preconcentration	Without preconcentration
Linear range ($\mu\text{g L}^{-1}$)	2–166	250–10000
Intercept	0.0128	0.0025
Slope	0.0045	7.5×10^{-5}
Detection limit ($\mu\text{g L}^{-1}$) ^a	0.70	143.75
Correlation coefficient	0.9982	0.9963
Relative standard deviation (RSD %) (n=6) ^b	2.36 (50)	2.19 (4000)
Enrichment factor ^c	60	—

^a Calculated as the amount of Co required to yields a net peak equal to three times the standard deviation of the background signal (3s).

^b Values in parentheses are the Co concentration ($\mu\text{g L}^{-1}$) for which the RSD was obtained.

^c Calculated as the ratio of the final concentration of the Co in the IL-phase and its concentration in the original sample solution.

The relative standard deviation (RSD) resulting from the analysis of 6 replicates of 30 mL solution containing $50 \mu\text{g L}^{-1}$ Co^{2+} was 2.36%. Regarding the frequency of analysis, although pre-concentration of the analyte for a single sample could take more than 5 minutes, it is possible to simultaneously treat as many samples as can be placed in the centrifugation equipment. Practically, about 40 analyses could be performed within a 1 h time period.

3.11. Analysis of real samples

In order to test the reliability of the proposed methodology for the assaying of cobalt, it was employed to determine the trace amounts of Co^{2+} in three local water samples (*i.e.*, mineral water, tap water and spring water). In order to validate the accuracy of the established procedure, recovery experiments were also carried out by spiking the samples with different amounts of cobalt before any pretreatment. The solutions were analyzed using the standard additions calibration and the percentage recoveries were calculated. Table 4 shows the obtained

results. As can be seen, recoveries between 97.0 and 104.0% were obtained, which confirm the accuracy of the proposed method.

3.12. Comparison of the proposed procedure with other methods

We compared in Table 5 the linear range, limit of detection (LOD), enhancement or enrichment factor, relative standard deviation (RSD) and the sample volume in the proposed technique and by other related literature pre-concentration methods for the extraction and determination of cobalt in real samples. Relative to the other reported methods, ionic liquid was used instead of a volatile, possibly toxic organic solvent, as the extraction solvent. The proposed method has relatively low LOD (0.70 g L^{-1}), good enrichment factor (60) and short extraction procedure (less than 10 min) with a sample volume of 25 mL. Simple operation procedure make the sample preparation very easy and rapid, only a few minutes are needed before instrumental analysis. In addition, owing to high viscosity of ILs, removing

Table 4. Determination of cobalt in water samples (results of recoveries of spiked samples).

Samples	Added Co^{2+} ($\mu\text{g L}^{-1}$)	Found Co^{2+} ^a ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water ^b	–	not detected	–
	10.0	9.7 ± 0.3	97.0
	20.0	19.7 ± 0.5	98.5
Spring water ^c	–	11.4 ± 0.2	–
	10.0	21.3 ± 0.5	99.0
	20.0	32.2 ± 0.2	104.0
Mineral water ^d	–	not detected	–
	10.0	9.9 ± 0.4	99.0
	20.0	19.6 ± 0.5	98.0

^a Mean of three experiments $\pm$ standard deviation.

^b From drinking water system of Maragheh, Iran.

^c From spring water of Pirchupan village, Iran.

^d Obtained from Zam Zam Co., Iran.

Table 5. Characteristic performance data obtained by using the proposed method and other preconcentration techniques for determination of cobalt in real samples.

Preconcentration technique	Linear range ($\mu\text{g L}^{-1}$)	EF ^a	L.O.D. ^b ($\mu\text{g L}^{-1}$)	R.S.D. ^c %	Sample volume (mL)	References
SPE/Spectrophotometry	10–400	100	10	2.23 (10)	250	[5]
CPE/Spectrophotometry	20–200	10	7.5	2.7 (50)	10	[6]
Online sorbent preconcentration/ FAAS	0–250	17.2	3.2	1.6 (100)	n.r. ^d	[17]
CPE/FAAS	0.9–100	28	0.9	2.9 (50)	10	[18]
SPE/FAAS	18–900	330	0.8	<2 (50–100)	1650	[19]
DLLME/Spectrophotometry	2–60	125	0.5	2.5 (50)	50	[35]
IL-based DLLME/ FAAS	2–166	60	0.70	2.36 (50)	25	This work

^a Enhancement or enrichment factor.

^b Limit of detection.

^c Relative standard deviation. Values in parentheses are the Co concentration ($\mu\text{g L}^{-1}$) for which the RSD was obtained.

^d Not reported.

bulk aqueous phase is easier and this method is more suitable for extraction of heat-susceptible species in comparison with CPE. In conclusion, IL-based DLLME presents a sensitive, reproducible, simple, low cost and environment friendly technique that can be used for the pre-concentration of cobalt in routine analytical laboratories.

4. Conclusions

A simple dispersive liquid-liquid micro-extraction method based on 1-hexylpyridinium hexafluorophosphate [C_6py] [PF_6] ionic liquid has been developed and optimized for the pre-concentration of trace levels of cobalt before its determination by FAAS. In this procedure, phase separation can be achieved at room temperature and the extraction efficiency is high, resulting in low detection limits and high enrichment factors. The results of this work show the possibility of using the PMBP- $[C_6py]$

[PF_6] system for Co pre-concentration, since quantitative extraction (99.9%) and a pre-concentration factor of 60 were achieved. This method proved simple, sensitive and fast with good extraction efficiency as well as being environment-friendly. Environmental pollution is limited to a very small amount of IL. This fact is particularly attractive, because the 'green chemistry' concept can be employed here. The sensitivity of the method could be enhanced by using GF-AAS as the detection step. Moreover, if the IL-phase volume required for detection system is little, high pre-concentration factor can be obtained. The pre-concentration method was successfully applied to monitor low concentrations of cobalt in water samples with good accuracy and precision.

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