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Determination of cobalt in natural water samples after separation and preconcentration by dispersive liquid-liquid microextraction based on the solidification of floating organic drop

Mohammad Reza Jamali*, Salah Rahimpour and Reyhaneh Rahnama

Department of Chemistry, Payame Noor Universtiy, Tehran, I. R. of IRAN

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Abstract

A simple, rapid and environmentally friendly method has been developed for the determination of cobalt ions in water samples by dispersive liquid–liquid microextraction based on the solidification of floating organic droplet (DLLME-SFO) coupled with flame atomic absorption spectrometry (FAAS). In this method, cobalt was complexed with 2-nitroso-1-naphthol and extracted into a small volume of 1-dodecanol, which is of low density, low toxicity and proper melting point near room temperature. Several variables that affect the extraction efficiencies, including pH, concentration of chelating agent, type and volume of the extraction solvent and dispersive solvent, extraction time and salt addition, were investigated and optimized. Under the optimized conditions, the limit of detection was 1.6 μg L^{-1} with a preconcentration factor of 25 for 25 mL of sample. The proposed method has been successfully applied for the determination of cobalt in real water samples.

Keywords: Dispersive liquid–liquid microextraction, Solidification of floating organic droplet, Preconcentration, Cobalt, Water samples.

1. Introduction

Trace metals are widely spread in environment and may enter the food chain from the environment. Some trace metals are essential elements and play an important role in human metabolism. On the other hand, at higher concentrations all metals are recognized as potentially toxic [1]. Therefore, determination of trace heavy metals in different environmental samples is of great interest to analytical chemists. Cobalt is one of the common trace metals affecting the environment. The toxicity of cobalt is low and it is considered as an essential element, which is required in the normal human diet in the form of vitamin B_{12} (cyanocobalamin). For this reason, cobalt has been used in the treatment of anemia [2]. However, the ingestion or inhalation of large doses of this analyte may lead toxic effects [3, 4]. High levels of cobalt may affect several health troubles such as paralysis, diarrhea, low blood pressure, lung irritation and bone defects [5]. A study found average cobalt levels in drinking water of 2 μg L^{-1}, but values up to 107 μg L^{-1} have been reported [6]. Since one of the routes of incorporation of cobalt into the human body is by ingestion [7], its determination in drinking water becomes important.

In spite of great improvements in the sensitivity and selectivity of modern instrumental analysis 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 [8]. Thus separation and preconcentration procedures is required for elimination or minimization of matrix effects and concomitants, lowering the detection limit of many metals with different techniques and enhancing the detectability for many metals [9]. Up to now, several sample preparation methods have been developed for the determination of trace cobalt from various sample matrices, including liquid–liquid extraction [10], coprecipitation [11], clod point extraction [12], solid phase extraction [13, 14], etc. Nevertheless, these methods are time consuming, tedious and often require large amounts of samples and toxic organic solvents.

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*. **Corresponding Author**: *mr_jamali@ymail.com ; Tel:+98-152-6434062*

Recently, much attention is being paid to the development of miniaturized, more efficient and environmentally friendly extraction techniques which could greatly reduce the organic solvent consumptions [15]. Dispersive liquid-liquid microextraction (DLLME) is one of the effective microextraction techniques [16]. In DLLME method, the extraction is carried out between the sample and a cloud of fine extractant drops that formed when the mixture of extraction and disperser solvents is injected in the aqueous sample. The contact surface between phases is widely increased, reducing the extraction time and improving the enrichment factor. At this moment, DLLME has been discussed in various review papers [17–20]. The main advantages of DLLME are: simplicity of operation, rapidity, low sample volume, low cost, high recovery and high enrichment factors. Another attractive microextraction technique is liquid phase microextraction method based on solidification of a floating organic drop (LPME-SFO) [21]. In LPME-SFO method an extracting solvent must have a melting point which is near to room temperature. A droplet of the extracting solvent is floated on the surface of aqueous solution containing target analytes and solution is stirred for a required time. Afterwards, the sample vial is cooled by inserting it into an ice bath. After solidification the floating organic drop is transferred into a small conical vial where it melts quickly at room temperature and an aliquot of the solvent is taken for the analysis. Solidification of a floating organic drop facilitates the process of extract collection as the extract after solidification can easily be separated from the aqueous solution. The main advantages of LPME-SFO are: simplicity of operation, small amount of low toxic solvent used, good repeatability, low cost, high preconcentration factors and more suitability for the analysis of complex matrix samples [22, 23]. However, the extraction time was somewhat long, thus it cannot satisfy the demand of fast analysis.

In 2008, Leong and Huang combined DLLME with LPME-SFO, and developed a new microextraction technique termed dispersive liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) [24]. In this method, an appropriate extraction solvent with low density, low toxicity and melting point near room temperature was dissolved in a water-miscible dispersive solvent. The resultant mixture was rapidly injected into an aqueous sample by syringe. A cloudy solution containing the fine droplets of the extraction solvent dispersed entirely in the aqueous phase was formed. The analytes in the sample were extracted into the fine droplets, which were further separated by centrifugation. The floated extractant droplet on the top of the test tube was rapidly solidified in an ice bath and could be easily collected. The collected sample extractant melted immediately at room temperature and then was used for subsequent instrumental analysis. In DLLME-SFO, the analysis time can be as fast as DLLME and is much shorter than LPME-SFO [25, 26]. Its major advantages are low cost, rapidity, simple experimental procedures, high preconcentration factors and personal and environmental safety.In this research, DLLME-SFO combined with FAAS was developed for the preconcentration and determination of trace amounts of cobalt in water samples. 2-nitroso-1-naphthol, which is known to be one of the effective chelating reagents for Co^{2+} ions [27, 28], was selected as the chelating agent. Some experimental parameters that influenced the extraction efficiencies were optimized. The proposed method has been applied for the determination of cobalt in real water samples.

2. Experimental

2.1. Instrumentation

A PG-990 (PG instrument Ltd., United Kingdom) flame atomic absorption spectrometer equipped with deuterium background correction and cobalt hollow cathode lamp was used for determination of cobalt at wavelength of 240.7 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations.
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-combined 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 $(NO_3)_2$, 6 H_2O (Merck, Darmstadt, Germany). Before investigations, working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. A 0.01 mol L^{-1} solution of 2-nitroso-1-naphthol (Sigma-Aldrich, USA) was prepared in pure ethanol. 1-undecanol, 1-dodecanol, 2-dodecanol, 1-bromohexadecane, *n*-hexadecane, 1, 10-dichlorodecane, 1-chlorooctadecane, acetone, acetonitrile**,** ethanol, methanol and sodium chloride were purchased from Merck (Darmstadt, Germany).

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. DLLME-SFO Procedure

A 25.0 mL sample or standard solution containing 5-120 μg L^{-1} of cobalt was poured into a screw cap glass test tube; 1.0 mL acetate/acetic acid buffer (pH= 4.0, 1.0 mol L^{-1}) and 0.75 mL 2-nitroso-1-naphthol (0.01 mol L^{-1}) solution were added. Then, a mixture of 400 μL of ethanol (as disperser solvent) and 80 μL of 1-dodecanol (as extraction solvent) was injected rapidly into the sample solution by using 1.0 mL syringe. A cloudy solution that consists of very fine droplets of 1-

dodecanol dispersed into aqueous sample was formed, and the analytes were extracted into the fine droplets in a few seconds. Emulsions were then disrupted by centrifugation at 5000 rpm for 5 min, which resulted in the organic phase floating on the surface of the solution. After this process, the test tube was transferred into an ice bath and the organic solvent solidified after 2 min. The solidified solvent was then transferred into a conical vial where it melted immediately at room temperature. Finally, the extract was diluted to 1.0 mL with ethanol and it was aspirated to flame atomic absorption spectrometer for analysis.

3. Results and discussion

In order to obtain the optimum DLLME-SFO conditions, the influence of different experimental parameters including the type and volume of the extraction and dispersive solvent, extraction time, sample volume, the concentration of chelating agent and salt addition on the performance of DLLME-SFO were investigated.

3.1. Effect of type and volume of extraction solvent

The selection of an appropriate extraction solvent is of great importance for the optimization of the DLLME-SFO process. The extraction solvent has to fulfill some requirements: to have low volatility and low water solubility in order to be stable at the extraction period, to extract analytes well and to have melting point near the room temperature (in the range of 10–30 ˚C). Accordingly, several extracting solvents, including 1-undecanol (mp: 13–15 ˚C), 1-dodecanol (mp: 22–24 ˚C), 2-dodecanol (mp: 17–18 ˚C), 1-bromohexadecane (mp: 17–18 ˚C), *n*-hexadecane (mp: 18 ˚C), 1, 10-dichlorodecane (mp: 14–16 ˚C) and 1-chlorooctadecane (mp: 20–23 ˚C) were investigated. The experiments showed that the best extraction efficiency for the target analyte was obtained when 1-dodecanol was used as the extraction solvent.

The influence of the volume of the 1-dodecanol as the extraction solvent on the extraction efficiency was studied. For this purpose, different volumes of 1-dodecanol (50–200 µL) were subjected to the same DLLME-SFO (the volume of the ethanol was fixed). The results are presented in Figure 1.

As can be seen, when the volume of 1-dodecanol is increased, the extraction recovery of the ions increases until 80 µL, by further increasing the volume of 1-dodecanol, it remained constant. At lower volume of 1-dodecanol, the extraction recovery is low probably because of the inadequacy of the extraction solvent to entrap the hydrophobic complex quantitatively. Therefore, 100 µL of 1-dodecanol was chosen as the optimum extracting solvent volume.

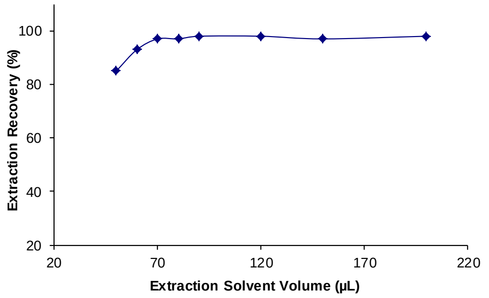

Figure 1. Effect of the extraction solvent volume on extraction recovery of cobalt.Extraction conditions: sample volume, 25.0 mL; extraction solvent, 1-dodecanol; dispersive solvent, 400 µL ethanol; pH = 4.0; chelating reagent, 3 × 10^{-4} mol L^{-1} 2-nitroso-1-naphthol.

Effect of sample solution pH

Separation of metal ions by DLLME-SFO involves prior complex formation with sufficient hydrophobicity to be extracted into the small volume of the extraction solvent. The pH of the aqueous phase is one of the most important factors in extraction of metal ions from various media for the formation of metal complex. The influence of the pH on the extraction recovery of cobalt was investigated in the pH range from 1 to 12 when the other experimental conditions were kept constant. The results are depicted in Figure 2. Extraction recovery of Co (II) increases with increasing solution pH and were effectively recovered in pH range 4.0–9.0. Competition between protons and cobalt ions could explain the weak recovery in acid medium. On further increase of pH recovery decreases probably due to the formation of hydroxide of cobalt. Therefore the further works for microextraction were performed at pH 4.0 by adding the acetate/acetic acid buffer solution.

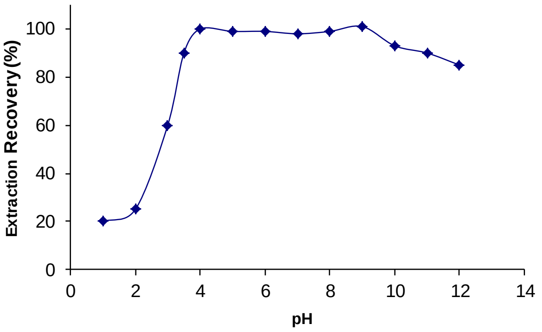

Figure 2. Effect of sample solution pH on extraction recovery of cobalt. Extraction conditions: sample volume, 25.0 mL; extraction solvent, 100 µL 1-dodecanol; disperser solvent, 400 µL ethanol; chelating reagent, 3 × 10^{-4} mol L^{-1} 2-nitroso-1-naphthol.

3.2. Effect of the concentration of 2-nitroso-1-naphthol

The influence of the concentration of 2-nitroso-1-naphthol as a chelating agent was studied in the range from 1.0 × 10^{-5} to 4.0 × 10^{-4} mol L^{-1}. As is shown in Figure 3, by the addition of increased amount of 2-nitroso-1-naphthol, the extraction recovery was increased before 1.0 × 10^{-4} mol L^{-1} and then remind constant. At a low concentration of 2-nitroso-1-naphthol, the complexation was not complete and the extraction efficiency is low, hence the recovery was decreased. Thus, 3 × 10^{-4} mol L^{-1} of 2-nitroso-1-naphthol was chosen as the optimum to account for other extractable species in real water samples analysis.

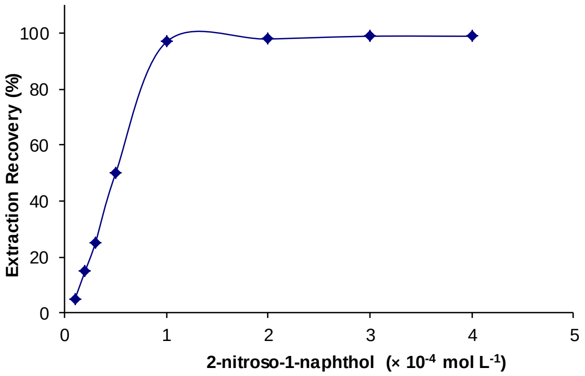

Figure 3. Effect of 2-nitroso-1-naphthol concentration on extraction recovery of cobalt.Extraction conditions: sample volume, 25.0 mL; extraction solvent, 100 µL 1-dodecanol; disperser solvent, 400 µL ethanol; pH = 4.0; chelating reagent, 2-nitroso-1-naphthol.

3.3. Effect of type and volume of disperser solvent

The main selection criterion of disperser solvent for DLLME-SFO is its miscibility with both extraction solvent and water. Moreover it should form a dispersive solution when injected together with the extraction solvent into aqueous samples. Thereby, acetone, methanol, acetonitrile and ethanol were investigated. The results showed that the recovery variations using different disperser solvents were not remarkable. Therefore, ethanol was selected as disperser solvent because of low toxicity. After selecting ethanol as the disperser solvent, its volume should be optimized. At low volume, ethanol cannot disperse extraction solvent properly and cloudy solution is not formed completely. However, at high volume, the solubility of analyte in water increases, which will result in the decrease of the extraction efficiency.

To obtain optimized volume, the effect of dispersant volume on the extraction efficiency was investigated in the range of 0.2–1.5 mL (the volume of 1-dodecanol was fixed as 100 µL). As shown in Figure 4, extraction efficiency increased with the increase of the volume of ethanol when it was less than 0.4 mL. Reduction in extraction efficiency was observed after the volume of ethanol exceeded 0.8 mL. So, 0.4 mL was chosen as the optimum volume of the disperser solvent.

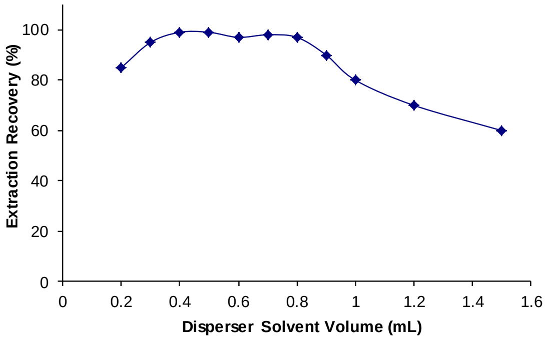

Figure 4. Effect of the disperser solvent volume on extraction recovery of cobalt. Extraction conditions: sample volume, 25.0 mL; extraction solvent, 100 µL 1-dodecanol; disperser solvent, ethanol; pH = 4.0; chelating reagent, 3 × 10^{-4} mol L^{-1} 2-nitroso-1-naphthol.

3.4. Effect of the extraction time

In DLLME–SFO, the extraction time is defined as the time interval between the injection of the mixture of disperser solvent and extraction solvent and the time at which the sample is centrifuged. 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 extraction solvent and aqueous phase results very rapid transport of analyte from the aqueous phase to extraction solvent. Thus, a short extraction time (less than a minute) was selected in subsequent experiments. In this method, time-consuming step is centrifuging of sample solution, which is about 5 min and solidification of 1-dodecanol, which is about 2 min.

3.5. Effect of ionic strength

In order to investigate the influence of the ionic strength on the DLLME-SFO performance, several experiments were performed with different NaCl concentrations (0.0–1.0 mol L^{-1}) while keeping other experimental parameters constant. Increasing the NaCl concentration showed no significant statistical differences throughout the studied range. Consequently, further extractions were performed in the absence of any salt.

3.6. 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, 25.0 mL of solutions containing 50 µg L^{-1} of cobalt and various amounts of interfering ions were treated according to the recommended procedure. A given species was considered to interfere if it resulted in a ± 5 % variation in the absorbance signal. The tolerable concentration ratio of interfering ions to 50 µg L^{-1} Co^{2+} was found to be as follows: 10000 for Na^{+} , K^{+}; Li^{+}, Ba^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Cd^{2+}, Zn^{2+}, Cr^{3+}, Ag^{+}, Cl^{-}, Br^{-}, SO_4^{2-}, PO_4^{3-}; 1000 for Al^{3+} and Cu^{2+} ; 500 for Fe^{2+}. The major ions in the water samples have no obvious influence on Co^{2+} DLLME-SFO under the selected conditions.

3.7. Analytical figures of merit

Table 1 summarizes the analytical characteristics of the optimized method, such as limit of detection, reproducibility and preconcentration factor. Under the optimum conditions, the calibration graph was linear in the range of 5–120 µg 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 1.6 µg L^{-1}. The preconcentration factor that was calculated by dividing the aqueous phase volume to the final volume of diluted phase was 25. Repeatability was carried out by spiking blank samples at the concentration of 50 µg L^{-1}, and the relative standard deviation (RSD) for ten replicate experiments was 2.5 %.

Table 1. Analytical characteristics of proposed method.

Parameter	Analytical feature
Linear range, µg L-1	5-120
Limit of detection, µg L-1 (n =10)	1.6
RSD, % (C = 50 µg L-1, n=10)	2.5
Preconcentration factor	25

3.8. Analysis of real samples

To demonstrate the performance of the present method, it was utilized to determine of cobalt concentration in different water samples. The obtained results are given in Table 2. Recovery studies were also carried out after it was spiked to samples known concentrations of cobalt at levels of 20 and 50 µg L^{-1}. The recovery values calculated for the added standards were ranged from 94 to 105 %, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed preconcentration method.

4. Conclusions

In this work, a new dispersive liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) method combined with FAAS was developed for the separation/enrichment and determination of cobalt in water samples. A low density and low toxicity organic solvent (1-dodecanol) was utilized as extraction solvent. The results indicate that this extraction procedure is noticeable due to its outstanding advantages, including minimum organic solvent consumption, simplicity, low cost, speediness, high efficiency and environment friendly.

5. Acknowledgements

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Table 2. Determination of Co (II) water samples and relative recoveries of spiked sample.

Sample	Co (II) amount (µg L^{-1})		Recovery (%)
	Added	Found [a]	
Tap water	0.0	n.d.[b]	–
(Drinking water system of Behshahr, Iran)	20.0	19.4 ± 0.5	97
	50.0	49.0 ± 1.2	98
Mineral water	0.0	n.d.	–
(Damavand mineral water, Iran)	20.0	21.0 ± 0.6	105
	50.0	51.4 ± 1.3	103
River water	0.0	7.3 ± 0.4	–
(Tajan river, Sari, Iran)	20.0	27.5 ± 0.8	101
	50.0	57.0 ± 1.5	99
Sea water	0.0	8.6 ± 0.3	–
(Caspian sea water, Sari, Iran)	20.0	27.4 ± 0.7	94
	50.0	56.7 ± 1.6	96

[a] Mean ± standard deviation (n = 3)

[b] Not detected

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اندازه گیری کبالت در نمونه آب های طبیعی پس از جداسازی و پیش تغلیظ آن با استفاده از روش میکرو استخراج مایع-مایع پخشی بر پایه جامد شدن قطره آلی شناور

محمد رضا جمالی[*]، صلاح رحیم پور و ریحانه راهنما

گروه شیمی، دانشگاه پیام نور، تهران، ایران

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چکیده:

در این تحقیق یک روش ساده، سریع و دوست دار محیط زیست برای اندازه گیری کبالت در نمونه های آبی توسعه یافته است. این روش بر اساس تکنیک استخراج مایع-مایع پخشی بر پایه جامد شدن قطره آلی شناور بنا شده است و اندازه گیری غلظت کبالت با استفاده از دستگاه جذب اتمی شعله صورت می پذیرد. در این روش ابتدا یون های کبالت با لیگاند ۲-نیتروزو-۱-نفتول تشکیل کمپلکس داده و سپس به حجم کوچکی از حلال ۱-دودکانول استخراج می شوند. اثر چندین پارامتر موثر بر کارایی استخراج از قبیل pH، غلظت عامل کمپلکس دهنده، نوع و حجم حلال های استخراج کننده و پخش کننده، زمان استخراج و اثر نمک مورد بررسی قرار گرفت و بهینه سازی شد. تحت شرایط بهینه، حد تشخیص روش ۱/۶ میکروگرم بر لیتر و فاکتور تغلیظ، با استفاده از حجم ۲۵ میلی لیتر از نمونه آبی، ۲۵ تعیین گردید. روش ارائه شده بطور موفقیت آمیزی برای اندازه گیری کبالت در آب های طبیعی مورد استفاده قرار گرفت.

کلمات کلیدی: میکرو استخراج مایع- مایع پخشی، جامد شدن قطره آلی شناور، پیش تغلیظ، کبالت، نمونه های آبی

***. نویسنده مسوول:** استادیار شیمی تجزیه دانشگاه پیام نور *Email: mr_jamali@ymail.com*