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Dispersive liquid–liquid microextraction based on solidification of floating organic drop combined with flame atomic absorption spectrometry for determination trace amount of cobalt in water samples

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Abstract

An efficient, rapid, simple, and highly selective dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFOD), combined with flame atomic absorption spectrometry was developed for preconcentration and determination of trace amounts of cobalt in water samples. In this method, an appropriate mixture of acetone and 1-undecanol was injected rapidly into the aqueous sample containing cobalt-2N1N complex, as a result cloudy mixture was formed. After centrifugation, the test tube was cooled for 5 min. The solidified 1-undecanol on top of the solution was transferred into a suitable vial. Then, it was dissolved in 100 μL of methanol and finally introduced into the flame atomic absorption by microsampler injector. Several factors influencing the microextraction efficiency, such as the nature and volume of organic solvent, pH of aqueous solution, amount of complexing agent, stirring rate and extraction time were investigated and optimized. Under the optimum conditions, the enhancement factor was 68. The limit of detection, 6 μgL^{-1} and relative standard deviation (RSD) 2.64% (n=8) were obtained. The proposed method was applied to the analysis of various water samples.

Keywords: DLLME; Cobalt; Water analysis; Flame atomic absorption spectrometry.

1. Introduction

Despite the great technological advances, over the last decades, still most analytical instruments cannot handle sample matrices directly and as a result, a sample preparation step is commonly introduced. In the last few years, efforts have been directed towards miniaturizing the LLE procedure by greatly reducing organic to aqueous phase ratio, such as single drop microextraction (SDME) [1-3], hollow fiber-liquid phase microextraction (HF-LPME) [4-5], cloud point extraction (CPE) [6-8], homogeneous liquid-liquid microextraction (HLLME) [9-11], and dispersive liquid-liquid microextraction (DLLME) [12-14], cold induced aggregation microextraction (CIAME) [15-17] which are fairly new methods of LPME, which are used in separation and preconcentration of samples and can solve some of the problems encountered with the conventional pretreatment techniques.

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Recently dispersive liquid liquid microextraction based on solidification of floating organic drop (DLLME-SFOD), was introduced by Leong and Huang [18-20]. At first, DLLME-SFO was developed for the determination of halogenated organic compounds (HOCs) and polycyclic aromatic hydrocarbons (PAHs) in water samples [18, 21], but in following it was used to preconcentration and determination of metal ions. DLLME-SFO use solvents with the densities lower than water and lower toxicity; furthermore, there is no need to use conical bottom glass tubes such as DLLME, which are easily damaged and hard to clean. Since, the melting point of extraction solvent is low (in the range of 10–30 °C); the organic drop could be solidified at low temperatures, so it was easily scoped out from the water sample.

2N1N is one of the foremost organic spectrophotometric reagents. It provides the basis of sensitive methods for the determination of cobalt. It has often been used in the extractive separation of traces of cobalt before its determination. In the present work a simple, selective, sensitive and cost effective LLME -SFOD method for preconcentration and FAAS determination of cobalt ions in various water samples using 2N1N as complexing agent and 1-undecanol as extraction solvent was established. Furthermore in this study, we used microsampler injector to overcome the most important problem in reproducibility that it encounters when the small volume of sample injected to flame atomic absorption spectrometry.

2. Experimental

2.1. Instrumentation

The experiments were performed using a Shimadzu atomic absorption spectrometer (AA-680) equipped with deuterium background correction. A Cobalt hollow cathode lamps (Hamamatsu, Photonic Co. Ltd, L233-series) operating at 345.4 nm, was used as the radiation sourced. The Behdad Universal Centrifuge (Tehran, Iran) equipped with a swing out rotor was used for centrifugation. All 15 ml screw cap, centrifuge tube (extraction vessel) were maintained into 0.1 mol L^{-1}, HNO_3 for cleaning of any inorganic compound and washed with distilled water. The pH measurement of aqueous phase was performed by using a combined glass electrode with Horiba M-12 pH meter.

A Hamilton plug valve (HVP model 2-5, Cat. No. 86786, Hamilton) coupled with the nebulizer needle 1/4 in.-28UNF Hub (Cat. No. 88986, Hamilton) and the female Luer fitting (1/4 in.-28 UNF, Cat. No. 35031, Hamilton) was used for microsample introduction.

2.2. Reagents

Reagent grade methanol, 1-octanol, 1-undecanol, 1-dodecanol, decanol, acetone, acetonitril, methanol, and ethanol were purchased from Merck (Darmstadt, Germany). All solutions were prepared using ultra pure water (18.2 MΩ). Chelating agent, 2-nitroso-1-naphthol 0.01 mol L^{-1} solution was prepared by dissolving an appropriate amount of reagent (analytical grade, from Merck) in acetone. Analytical grade cobalt sulfate, NaCl and nitrate salts of other cations and nitric acid (all from Merck) with high purity were available and used without further purification.

2.3. General procedure for DLLME-SFOD

In 15 mL of round bottom glass tube, 10 mL sample solution or standard solution containing 10-500 $\mu g L^{-1}$ of Co^{2+} and 100 µL of 10^{-2} mol L^{-1} , 2-nitroso-1-naphthol, the pH was adjusted to 6 using HCl 0.1 mol L^{-1} . Then the mixture was heated in thermostated bath at 50 °C for 15 min to cobalt complex formation. After cooling the solution, pH was adjusted in 2 with HCl 1 molL^{-1}. One mL of aceton (disperser solvent) containing 50 µL of 1-undecanol (extraction solvent) was then injected rapidly into the sample solution. Accordingly, a cloudy solution was formed, and cobalt complex was extracted into fine droplet of extraction solvent. After 10 min (extraction time), the solution was centrifuged for 5 min at 4000 rpm, the organic solvent droplet was floated on the surface of the aqueous solution due to its lower density than water. Thereafter, the test tube was dipped into an ice bath for 5 min; as a result, the extraction solvent was solidified. Afterward the solidified solvent was transferred into a 1.5 mL conical vial by simple spatula, in which it melted rapidly at room temperature. Finally, the extract was diluted to 100 µL with methanol and 90 µL of its injected into the flame atomic absorption spectrometer by microsampler injector.

3. Results and discussion

In order to determine cobalt ions by DLLME-SFOD, several parameters were optimized to achieve a high preconcentration factor and quantitative extraction. So the influence of different parameters, such as pH, the nature and amount of extraction solvent, the nature and amount of disperser solvent, concentration of chelating agent, extraction time, microsampler injection volume, ionic liquid strength, and stirring rate, were investigated by an aqueous solution containing 10 µg L^{-1} of Co^{2+}. The enhancement factor was calculated as the ratio between the slope ratio of calibration curves obtained after and before DLLME-SFOD.

3.1. Influence of pH

pH plays a critical role in the formation of sufficient hydrophobic compounds (metal complexes) and subsequent extraction by DLLME-SFOD procedure. The effect of pH on the complex formation and the extraction of cobalt from water samples were investigated in the range of 1-9. According to results in Fig. 1, Co^{2+} could be efficiently complexed in the pH range of 4.0-6.5.

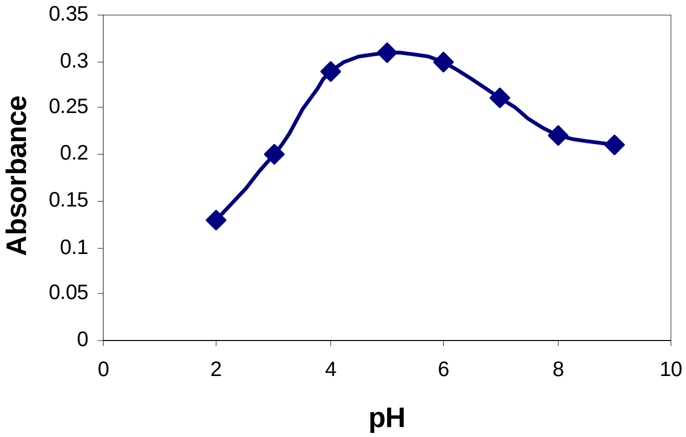


Fig. 1. Effect of pH of the sample on absorbance. Conditions: sample volume: 10 mL; extraction solvent volume: 50 µL; 2-nitroso-1-naphthol concentration: 1×10^{-2} M; concentration of Co: 100 µg L^{-1}; injection volume to FAAS: 90 µL.

After cobalt complex formation, the pH was adjusted in 2 by adding appropriate volumes of HCl, therefore Co(II) chelate was oxidized to Co(III) chelate. In this circumstance, most of the metal chelates other than Co(III) are easily decomposed. The influence of pH on recovery of cobalt complex in acidic media (in the pH range of 2.0-5.0) by DLLME-SFOD procedure was about 100%. Consequently, in order to increase the extraction selectivity of Co–2N1N complex, the IL-DLLME procedure was performed at pH 2.

3.2. Type and volume of organic solvent

In the DLLME-SFO procedure, selecting a suitable extraction solvent is crucial in this method. It should have low solubility in water, lower density than water, high affinity to analytes, and melting point near room temperature (in the range of 10 –30 ºC). Several extraction solvents, including decanol, 1-undecanol, 1-dodecanol, 2-dodecanol, and hexadecane were investigated. Hexadecane has a good melting point (18 °C) but its hydrophobicity was high, therefore it cannot be dissolved in the common dispersive solvent. According to obtained results the best extraction efficiency was obtained for 1-undecanol.

In order to evaluate the effect of extracting solvent volume, a series of injection solvents with difference volumes of 1-undectanol (i.e., 20-200 µL) were used in DLLME-SFOD procedures. According to obtained results,by increasing the volume of 1-undectanol, the interfacial area was increased, so the analytical signal increases slowly up to 50 µL and then further increasing causes to increase organic solvent volume, therefore the analytical signal was decreased slowly. Thus 50 µL of 1-undecanol was selected as the optimum volume of extracting solvent.

3.3. Effects of type and volume of the disperser solvent

The most important point for the selection of a suitable disperser solvent is its mutual miscibility in organic phase (extraction solvent) and aqueous phase (sample solution). Thereby, acetone, methanol, ethanol, and acetonitrile which possess these abilities were tested as potential disperse solvents. Thus, under the same experimental conditions, a series of sample solutions were prepared by using 1.0 mL of each disperser solvent containing 50 µL of 1-undecanol and the recommended procedure was followed. The results showed that, in all cases, the recovery is almost quantitative, and variations in percent recovery are not remarkable. Thus, among the three candidate solvents acetone was selected as disperser solvent for further studies due to its low toxicity and cost.

The influence of the volume of acetone in the range of 0.2-1.6 mL on the extraction efficiency of cobalt was examined (the volume of 1-undeconol was fixed at 50 µl) (Fig.2). At the low volume of acetone the 1-undeconol was not completely dispersed and the extraction efficiency was low.

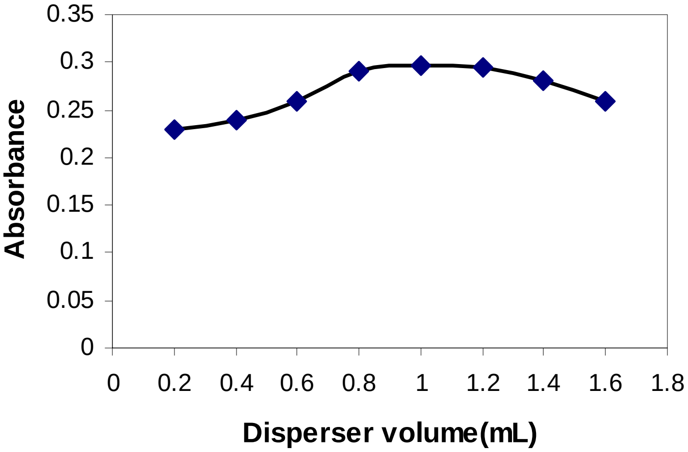


Fig. 2. Effect of disperser solvent volume on the absorbance. Conditions: sample volume: 10 mL; pH of sample: 5.0; extraction solvent volume: 50 µL; 2-nitroso-1-naphthol concentration 1×10^{-2} M; concentration of Co: 100 µg L^{-1}; injection volume to FAAS: 90 µL.

The absorbance of analyte was maximized from 0.8 to 1.2 mL of acetone and then slightly decreased with further increase of the acetone volume. The slight decrease in absorbance in high volume of acetone is due to the increase of solubility of the cobalt complex in the aqueous solution. Thus 1.0 mL of acetone was used as the optimal volume of the dispersive solvent.

3.4. Effect of 2-nitroso-1-naphthol (2N1N) concentration

The effect of the amount of 2N1N on the absorbance was studied in the range of 0.1 - 1×10^{-5} molL^{-1}. According to the obtained results (Fig.3), the absorbance was increased by increasing the amount of 2N1N up to 1×10^{-3} molL^{-1} and then remained nearly constant. Therefore, the amount of 1×10^{-2} molL^{-1} of 2N1N was chosen for further application.

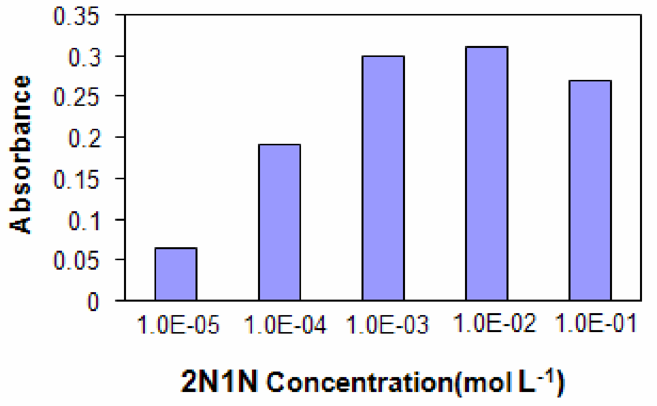


Fig. 3. Effect of 2-nitroso-1-naphthol concentration on the absorbance. Conditions: sample volume: 10 mL; pH of sample: 5; extraction solvent volume: 50 µL; concentration of Co: 100 µg L^{-1}; injection volume to FAAS: 90 µL.

3.5. Extraction time

In DLLME–SFO method, extraction time is defined as interval time between injecting the mixture of disperser solvent and extraction solvent, before starting to centrifuge. The effect of extraction time on the extraction efficiency was examined in the range of 0–20 min under constant experimental conditions. The obtained results showed that the extraction time did not have significant influence on the FAAS signals of the metal ions. In this method after the formation of cloudy solution, the surface area between extraction solvent and aqueous sample is infinitely large, therefore, transition of complex from aqueous sample to extraction solvent is fast. In this method, time-consuming step is centrifuging of sample solution, which is about 3min and solidification of 1-undecanol, which is about 5min. This is one of the considerable advantages of the DLLME-SFO method over the SFODME technique.

3.6. Effect of Salt

To investigate the salt effect on the performance of DLLME-SFOD, various experiments were performed by adding different amounts of sodium chloride (0-10%). The results showed that, the recovery was nearly constant for cobalt. This is one of the good properties of this method for analyses of real sample.

3.7. Analytical Performance

In order to evaluate the accuracy and applicability of the proposed method for the analysis of real samples, it was applied to the extraction and determination of cobalt ions in several water samples (i.e., tap, river, and mineral water). The results are summarized in Table 1. Tap, mineral and river water samples were filtrated with a 0.45 µm membrane filter and adjusted to pH 5.5, followed by extraction at pH 2, for further analyses. To evaluate the proposed method, the standard solutions of cobalt were spiked to assess matrix effects. The relative recoveries of cobalt from water samples at spiking level, 50 µg L^{-1} were in 99.4-95% range, which showed no significant matrix effect on the analysis of cobalt by DLLME-SFOD.

Table 1
Determination of cobalt in several samples.

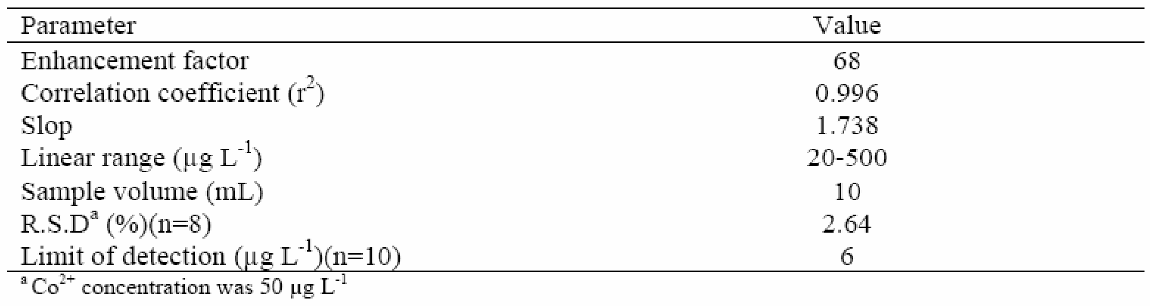
Sample	Cobalt spiked (µg L^{-1})	Cobalt founded (µg L^{-1})	Recovery (%)
Tap water [a]	0.0	n.d	-
	50.0	49.2 ± 0.3	98.4
Spring water [b]	0.0	n.d.	-
	50.0	49.7 ± 0.2	99.4
Well water [c]	0.0	n.d.	-
	50.0	48.8 ± 0.3	97.6
Sea water [d]	0.0	n.d.	-
	50.0	47.5 ± 0.4	95.0

[a] From drinking water system of Arak, Iran.
[b] From Sarband mountaine, Arak, Iran.
c From Islamic Azad University-Arak Branch, Arak, Iran.
d From caspian sea, Iran
[e] n.d. = Not detected

3.8. Figures of merit

Under the optimized extraction and determination conditions, the limit of detection defined as $3S_b/m$, where S_b and m are standard deviation of the blank and the slope of the calibration graph, respectively, was 6 µg L^{-1}. The linear dynamic range was from 20 to 500 µg L^{-1} with R^2 = 0.996. The relative standard deviation (RSD) for eight replicate measurements of the 50 µg L^{-1} Co^{2+} was 2.64%. The enhancement factor was 68, calculated from the slope ratio of the calibration curves obtained after and before preconcentration. The results are given in Table 2.

Table 2
Analytical features of proposed procedure.



Parameter	Value
Enhancement factor	68
Correlation coefficient (r^2)	0.996
Slop	1.738
Linear range (µg L^{-1})	20-500
Sample volume (mL)	10
R.S.D[a] (%)(n=8)	2.64
Limit of detection (µg L^{-1})(n=10)	6

[a] Co^{2+} concentration was 50 µg L^{-1}

3.9. Comparison of DLLME-SFOD –FAAS with other methods

Table 3 compares the main analytical characteristics (i.e., LOD, RSD, EF) of the proposed method with those of some of the best previously reported methods for the determination of cobalt. As could be seen, rapidity, low consumption of organic solvents, simplicity and selectivity of this method are advantageous of our proposed method in analysis of trace amount of cobalt ions.

Table 3
Comparison of the proposed method with the other cobalt preconcentration methods.

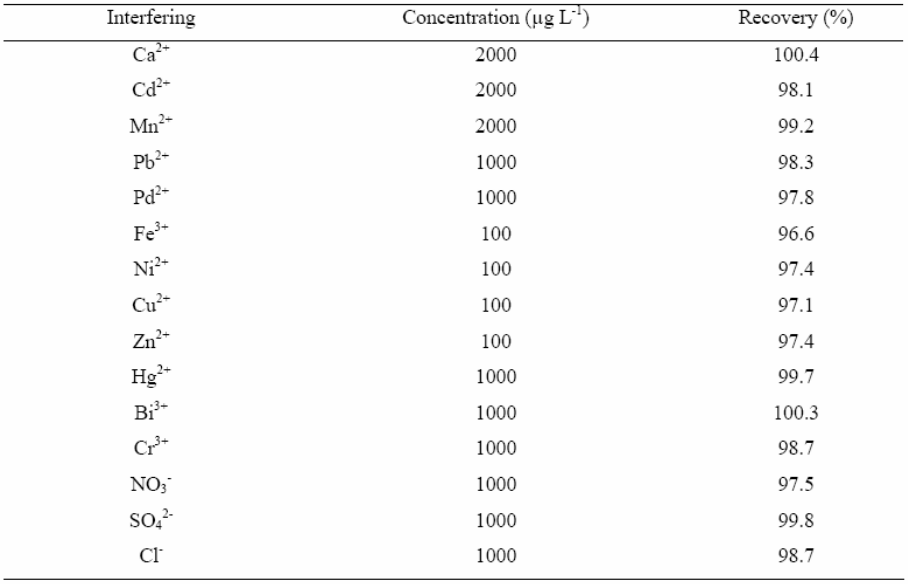
Method	RSD [a] (%)	LOD [b] (μg L^{-1})	EF [c]	Calibration range (μg L^{-1})	Ref.
DLLME-Spectrophotomtry	2.5	0.5	125	2-50	[29]
SPE/ Spectrophotometry	2.23	10	100	10-400	[30]
CIAME-FO-LADS	2.32	0.14	165	1.5-65	[31]
CPE/ Spectrophotometry	2.7	7.5	10	20-200	[32]
IL-DLLME	2.36	0.7	60	2-166	[33]
Online sorbent preconcentration/ FAAS	1.6	3.2	17.2	0-250	[34]
LLME-FAAS	2.3	0.9	16	3-100	[35]
DLLME-SFOD	2.64	6	68	20-500	This work

[a] Relative standard deviation
[b] Limit of detection
[c] Enrichment factor

3.10. Effect of diverse ions

The influence of the common co-existing ions in natural water samples on the cobalt recovery was investigated. For this purpose, according to the recommended procedure, 10.0 mL of solution that contains 50 μgL^{-1} of cobalt and various amounts from interfering ions, were preconcentrated and determined.

Table 4
Effect of foreign ions on the preconcentration and determination of 50 μg L^{-1} cobalt ion.



Interfering	Concentration (μg L^{-1})	Recovery (%)
Ca^{2+}	2000	100.4
Cd^{2+}	2000	98.1
Mn^{2+}	2000	99.2
Pb^{2+}	1000	98.3
Pd^{2+}	1000	97.8
Fe^{3+}	100	96.6
Ni^{2+}	100	97.4
Cu^{2+}	100	97.1
Zn^{2+}	100	97.4
Hg^{2+}	1000	99.7
Bi^{3+}	1000	100.3
Cr^{3+}	1000	98.7
NO_3^-	1000	97.5
SO_4^{2-}	1000	99.8
Cl^-	1000	98.7

An ion was considered to interfere when its presence produced a variation greater than ±5 % in the FAAS signal of the sample (Table 4). The results showed that, the ionic strength of the system has no significant influence on extraction efficiency, and only Ni^{2+}, Zn^{2+}, Fe^{3+} and Cu^{2+} have very little interferences .

4. Conclusions

Dispersive liquid–liquid microextraction based on solidification of floating organic drop combined with flame atomic absorption spectrometry allows the determination of cobalt in several water samples. In comparison with DLLME this method uses a different extraction solvent with lower toxicity. The main benefits of the method were: minimum use of toxic organic solvent, simplicity and selectivity, rejection of matrix constituent, enhancement of sensitivity, and rapid analysis time.

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