

## Application of Choline Chloride:4-Bromo Phenol Deep Eutectic Solvent-Based Dispersive Liquid-Liquid Microextraction for Cobalt Sensitive Determination and Preconcentration in Water Samples and Agricultural Products

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Received: 5 August 2020

Accepted: 17 September 2020

DOI: 10.30473/ijac.2021.59496.1197

### Abstract

This work presents a fast, feasible, and sensitive method for the preconcentration and separation of cobalt in various real samples through the use of deep eutectic solvent-based dispersive liquid-liquid microextraction (DES-DLLME) in which deep eutectic solvent, methanol, and 1-(2-pyridylazo)-2-naphthole (PAN) were employed as extraction solvent, dispersive solvent, and complexing agent, respectively. Co concentration was measured by flame atomic absorption spectrometer. Effective parameters which may influence the extraction efficiencies (like type and volume of the dispersive and extraction solvent, pH, PAN concentration, and salt concentration) were examined and the optimal values were determined. The use of optimal conditions resulted in a limit of detection equal to 1.5  $\mu\text{g/L}$  with a preconcentration factor of 40. RSD value, after measuring 20.0  $\mu\text{g/L}$  of cobalt for 10 times, resulted in a value of 3.0 %. The method's accuracy and applicability were assessed through the evaluation of Co content in water certified reference materials and different agricultural and water specimen.

### Keywords

Deep Eutectic Solvent Based Dispersive Liquid-Liquid Microextraction; 1-(2-pyridylazo)-2-Naphthole; Cobalt; Water samples; Agricultural Products.

### 1. INTRODUCTION

Trace metals can enter food due to their wide distribution throughout the environment. However, some of them are essential for the body and possess a key role in metabolic activities. As a natural earth element, trace amounts of cobalt (Co) can be found in air, soil, water, plants, and even our diets. It is among the prevalent trace metals influencing the environment. Cobalt has low toxicity and has been regarded as an essential element. In small levels, Co is beneficial as it is one of the components of vitamin B<sub>12</sub> [1]. However, excess concentrations of cobalt could result in several health-related problems including paralysis, diarrhea, hypotension, lung irritation, and bone defects [2]. As ingestion has been considered as one of Co incorporation routes to human body [3] and because it exists in water, food and agricultural samples at very low concentrations, the determination of Co level in drinking water through sensitive analytical methods has found crucial importance [4]. Co determination in complex matrices is limited and requires analyte preconcentration and/or separation owing to its low concentration in real samples as well as complexity of samples's matrix [5]. In this content, a vast range of approaches has been developed for Co preconcentration such as liquid-liquid extraction [6, 7], coprecipitation [8], microextraction [9, 10],

solid phase extraction [11, 12], etc. Among the mentioned techniques developed for Co (II) separation, liquid-liquid extraction (LLE) has been extensively investigated prior to analytical measurements. However, this approach possesses several limitations including being laborious and time-consuming, tendency to form emulsion, and requirement of organic solvent in large quantities which have made it less environmentally friendly. Green chemistry principles require the development of analytical methods possessing the least environmental effects. So far, several microextraction methods have been introduced for preconcentrating different analytes (to name some: single drop microextraction (SDME) [13], cloud point extraction (CPE) [14, 15], homogeneous liquid-liquid extraction (HLLE) [16, 17], dispersive liquid-liquid microextraction (DLLME) [18, 19], and solidified floating organic drop microextraction (SFODME) [20]. These methods require a small amount of organic solvent. Among these microextraction methods, DLLME has been considered as the fastest and most convenient technique, which is based on a ternary component solvent system. This method involves the quick introduction of extraction and disperser solvents into the aqueous sample which would give rise to a cloudy solution. Owing to extensive extraction solvent droplet-sample surface contact, extraction equilibrium will be

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rapidly achieved. Centrifugation normally results in the sedimentation of the extraction solvent at the tube bottom (if its density is higher than water); therefore, it can be easily collected by a micro syringe for later analyses [21]. Despite the lower consumption of organic solvents in this method, the substitution of organic solvents by less harmful ones (such as ionic liquids (ILs)) [22] will be beneficial. Due to their negligible vapor pressure, non-flammability, good extractability toward various organic compounds and metal ions as neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents, ILs have attracted considerable attention.

A new family of solvents, known as deep eutectic solvents (DESs) which are similar to ILs, has been recently employed for analytes separation and preconcentration from various matrices. The mentioned solvents can be obtained through mixing a hydrogen bonding acceptor (HBA) with a hydrogen bonding donor (HBD) followed by continuous heating and stirring. DESs properties are similar to ionic liquids. Ease of synthesis, biodegradability [23], high solubility strength [24], and low or even non-toxicity [25] are among the superiorities of DESs over ionic liquids. Therefore, DESs have replaced conventional volatile organic solvents and ionic liquids as a hot scientific topic.

This research applied deep eutectic solvent based dispersive liquid-liquid microextraction method for a sensitive and precise determination and preconcentration of cobalt in water samples and agricultural products. In this method, a water-immiscible DES (ChCl: 4-bromophenol) was used as the extraction solvent in the DLLME of cobalt from water samples and agricultural products for the first time. Effective parameters were studied and optimized to achieve high extraction efficiency.

## 2. EXPERIMENTAL

### 2.1. Reagents

The chemicals of this study were employed in their analytical grade. 1000 mg/L cobalt was dissolved in HNO<sub>3</sub> stock standard solution (0.5 mol/L) through the use of cobalt nitrate (Merck, Darmstadt, Germany). Lower concentrations of standard solutions were obtained by dilution. Other used materials included nitric acid, sodium hydroxide, ethanol, methanol, acetonitrile, acetone, sodium nitrate, 1-(2-pyridylazo)-2-naphthole (PAN), (2-hydroxyethyl)-trimethylammonium chloride (choline chloride) (ChCl), and 4-bromo phenol (BPh) (Merck Darmstadt, Germany). Water certified reference materials NIST SRM 1643e (National Institute for Standards and Technology, Gaithersburg, MD, USA) were applied. The employed glassware was washed with deionized water, maintained in 10 % (v/v) nitric acid (24 h), and

re-washed with deionized water for several times.

### 2.2. Instruments

Atomic absorption spectrometer, SensAA (GBC, Australia), was employed for Co determination at the wavelength of 232.0 nm. Background correction was carried out by deuterium lamp. Phase separation process was conducted by a centrifuge (Hettich, EBA 20). pH was measured by a Metrohm digital pH-meter model 827 (Herisau, Switzerland) with combined glass electrode.

### 2.3. Preparation of DES

ChCl (1.39 g) and BPh (3.46 g) were added to a 10 mL screw cap tube. It was then put inside a water bath at 75 °C for 10 min. Afterwards, it was vortexed for 5 min. The heating/vortexing cycle was repeated and a homogeneous liquid was achieved. At 20 °C, the prepared DES possessed the viscosity and density of 1.32 Pa s and 1.21 g/cm<sup>3</sup>, respectively.

### 2.4. Sample preparation

Spinach, and broccoli samples were purchased from the local supermarket at Sari in Iran. First, samples were cleaned with tap water and deionized water. Then, these samples were dried at 110°C. The dried samples were ground to reduce particle size and then thoroughly mixed to ensure the homogeneity of the samples. The samples (1.0 g) were digested by adding 5.0 mL HNO<sub>3</sub> and 5 mL H<sub>2</sub>O<sub>2</sub>. The mixtures were heated on a hot plate (130°C) until 2 mL acidic solution remained in the beaker. After cooling to room temperature, and filtering, the digested samples were diluted with deionized water to 50.0 mL, and their pH was set to 6.0.

### 2.5. Extraction procedure

For this procedure, 40.0 mL of the solution which contained the analyte,  $6.0 \times 10^{-5}$  mol/L PAN and 0.02 mol/L acetate buffer (pH=6) was transferred to a glass tube. Afterwards, using a glass syringe, 0.1 mL of methanol and 100 µL of DES were quickly injected into the aqueous solution as disperser and extraction solvents, respectively. Owing to the dispersion of small DES droplets, the solution turbidity increased. These droplets were precipitated by centrifugation at 4000 rpm for 5 min. The volume of DES precipitants was increased to 1.0 mL by addition of 1.0 mol/L ethanolic HNO<sub>3</sub>. The obtained solution was manually injected into FAAS. Fig. 1 provides a schematic diagram of Co preconcentration by DES-DLLME.

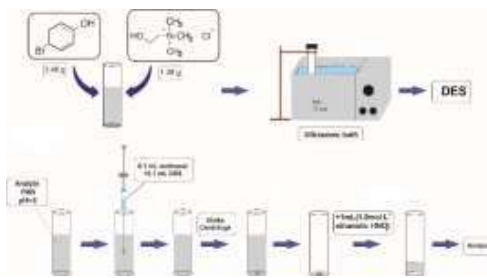


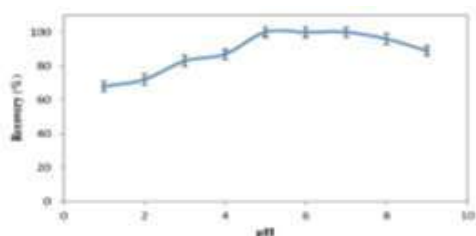
Fig. 1. Schematic diagram of preconcentration of cobalt by DES-DLLME.

### 3. RESULT AND DISCUSSION

#### 3.1. The effect of pH

Regarding the structure and cobalt chelate constancy, pH plays a key role in the extraction recovery of Co ions. Creation of cobalt ion-complexing agent complex is highly dependent on pH value; since pH is influential on analyte chemistry and the complexing agent ionization state which in turn are crucial factors in the availability of binding sites [26]. The impact of pH on the extraction efficiency was assessed through various experiments by altering the pH value in the range of 1-9 using HNO<sub>3</sub> or NaOH solutions.

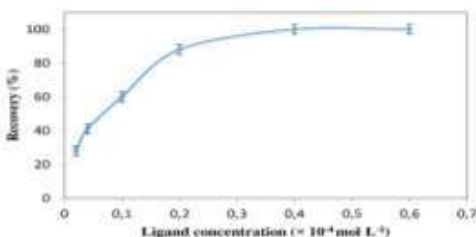
The results indicated almost unchanged recovery in the pH range of 5-7 (Fig. 2). However, lower recovery at pH<5 could be associated with the competition between H<sup>+</sup> and Co<sup>2+</sup> for complex formation. Eventually, pH=6 was selected as the optimum pH value which was adjusted by 0.02 mol/L of acetate buffer.



**Fig. 2.** The effect of pH on extraction recovery of cobalt. (Sample volume: 40 mL; cobalt concentration: 20.0 µg/L; ligand concentration:  $6.0 \times 10^{-5}$  mol/L; DES volume: 100 µL; disperser solvent: 0.1 mL methanol).

#### 3.2. The effect of chelating agent concentration

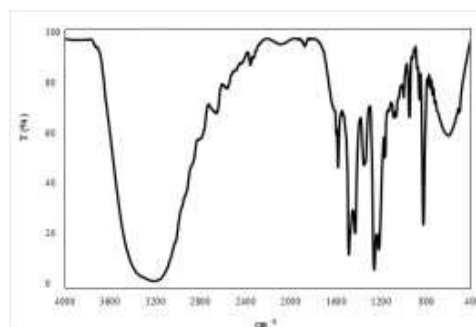
For optimizing chelating agent concentration, PAN concentration was varied from  $2 \times 10^{-6}$  to  $6.0 \times 10^{-5}$  mol/L (Fig. 3). As the results suggest, full Co extraction can be observed at concentrations over  $4.0 \times 10^{-5}$  mol/L which led to Co recovery of 100%. PAN, in smaller concentrations, was not adequate for complete complexation. Hence,  $6.0 \times 10^{-5}$  mol/L of PAN was selected as the optimal value for the elimination of any possible interference from other extractable species.



**Fig. 3.** The effect of ligand concentration on extraction recovery of cobalt. (Sample volume: 40 mL; cobalt concentration: 20.0 µg/L; pH=6; DES volume: 100 µL; disperser solvent: 0.1 mL methanol).

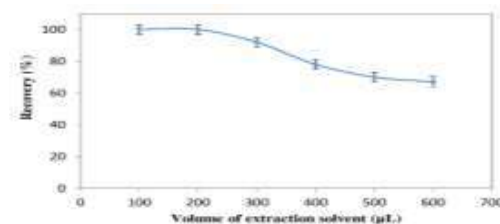
#### 3.3. Structural characterization and the effect of amounts of extraction solvent

DES was obtained from ChCl and BPh and its structure was studied by means of Fourier transform infrared spectroscopy (FT-IR) (Fig. 4). Based on the FT-IR spectrum, a broad band at 3206 1/cm represents the stretching vibration of BPh O-H group in DES. The change in the wave number of OH group in DES (in comparison with BPh) is due to the formation of hydrogen bonding between BPh and ChCl. Therefore, it can be concluded that DES was successfully and correctly synthesized.



**Fig. 4.** Infrared spectrum of DES.

To investigate the impact of the extraction solvent volume, preconcentration process was applied on solutions containing various volumes of DES. The experimental conditions were kept constant (100 µL methanol was used while the volume of DES was varied in the range of 100-600 µL at 100-µL intervals). The results are provided in Fig. 5. It is clear that the increase of DES volume from 100 to 200 µL resulted in constant and complete recoveries which declined at higher volumes. The reduction in recovery at volume > 200 µL could be attributed to the enhancement of the organic phase volume which led to viscosity elevation in resultant samples as they were diluted to 1.0 mL by ethanolic HNO<sub>3</sub>. The enhanced viscosity drastically declined the sampling efficiency of pneumatic nebulization of FAAS [27]. So, 100 µL of DES was selected as the optimal extraction solvent volume.

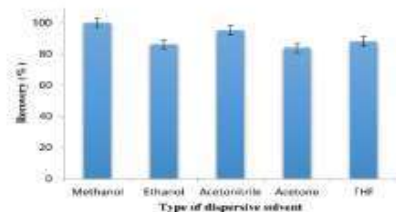


**Fig. 5.** The effect of extraction solvent volume on extraction recovery of cobalt. (Sample volume: 40 mL; cobalt concentration: 20.0 µg/L; pH=6; ligand concentration:  $6.0 \times 10^{-5}$  mol/L; disperser solvent: 0.1 mL methanol).

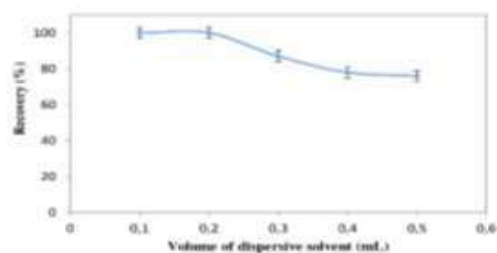
### 3.4. The effect of type and volume of disperser solvent

Acetone, acetonitrile, methanol, THF, and ethanol were examined as disperser solvents. Some characteristics including miscibility in the extraction solvent and the aqueous sample are crucial in selecting these disperser solvents. The mentioned properties influence the turbidity of the solution, its toxicity, and cost. Fig. 6 presents the obtained results. According to the results, methanol offered the highest recovery. So, it was selected as the optimal disperser solvent.

Then, numerous experiments were performed through the use of various methanol volumes (0.1- 0.5 mL) containing different amounts of DES to obtain the optimized methanol content. It was revealed that, increase in the methanol content from 0.1 to 0.2 mL, will result in the constant rate of recovery which declined by further increase of the methanol volume (Fig. 7). Such reduction could be related to the enhanced water-solubility of the complex. Based on the findings, 0.1 mL of methanol was used as the optimal volume of the disperser solvent.



**Fig. 6.** The effect of type of disperser solvent on the extraction recovery of cobalt. (Sample volume: 40 mL; cobalt concentration: 20.0  $\mu\text{g/L}$ ; pH=6; ligand concentration:  $6.0 \times 10^{-5}$  mol/L; DES volume: 100  $\mu\text{L}$ ; disperser solvent: 0.1 mL).



**Fig. 7.** The effect of disperser solvent volume on the extraction recovery of cobalt. (Sample volume: 40 mL; cobalt concentration: 20.0  $\mu\text{g/L}$ ; pH=6; ligand concentration:  $6.0 \times 10^{-5}$  mol/L; DES volume: 100  $\mu\text{L}$ ; disperser solvent: methanol).

### 3.5. The effects of centrifuge conditions

Phase separation (organic and aqueous) was achieved by centrifugation. Hence it is necessary to examine the centrifugation rate and time.

According to the results, a rate of 4000 rpm and centrifugation time of 5 min were optimal.

### 3.6. The effect of ionic strength

The incorporation of salt into the aqueous solution generally leads to a decline in the organic compounds' water-solubility. So, this approach has been widely applied to increase the analyte extraction. The effect of ionic strength on DES-DLLME performance was addressed by various experiments carried out in the presence of 0–25 % w/v  $\text{NaNO}_3$ . The results indicated no significant effect of ionic strength (up to 25.0%) on the extraction efficiency and sensitivity.

### 3.7. Matrix effects

The impact of different cations and anions on  $\text{Co}^{2+}$  recovery by the proposed method was examined. Recovery variation above  $\pm 5\%$  was regarded as interference in the Co preconcentration and determination. Various interfere-to-cobalt ratios of the interfering ions were incorporated into the solution containing 20.0  $\mu\text{g/L}$  of  $\text{Co}^{2+}$  followed by performing DES-DLLME method. The results showed that, in excess of 5000-fold of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and 1000-fold of  $\text{PO}_4^{3-}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr(VI)}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$  (\*In the presence of  $\text{Na}_2\text{C}_2\text{O}_4$  0.02 mol/L) ions had no significant interferences in the extraction and determination of cobalt. These results indicate that this technique leads to acceptable outcomes for Co determination in real samples.

### 3.8. Figures of merit

After the optimization of the parameters the figures of merit were determined for DES-DLLME of cobalt. The results are: Dynamic linear range for Co determination varies from 5.0 to 30.0  $\mu\text{g/L}$  ( $R^2=0.9998$ ). The relative standard deviation (RSD) was obtained as 3.0 % ( $n = 10$ ,  $C=20 \mu\text{g/L}$ ); while the limit of detection (LOD) was measured as 1.5  $\mu\text{g/L}$  ( $3S_b/m$ ). The preconcentration factor was obtained as 40 for 40 mL of sample solution.

### 3.9. Validation of the proposed methodology

The proposed method was validated by analyzing CRM NIST SRM 1643e after proper dilution. The results are listed in Table 1. No significant difference was observed between the result of this study and the certified values. Hence, the proposed preconcentration method can be successfully employed for Co determination in water samples.

**Table 1.** Determination of cobalt in certified reference material.

Sample	Certified ( $\mu\text{g/L}$ )	Found <sup>a</sup> ( $\mu\text{g/L}$ )	Recovery (%)
GSBZ 50,030-94	14.38 $\pm$ 1.00	14.35 $\pm$ 0.43	99.8

<sup>a</sup> Mean of replicate experiments (n = 3)  $\pm$  standard deviation

### 3.10. Comparison

In comparison with previous methods, the proposed method exhibited effectiveness in Co determination from water samples and agricultural products with proper and improved figures of merit (Table 2). Clearly, the performance of this method is comparable with those of other reported methods. Furthermore, being fast, inexpensive, easy to apply, and timesaving are some of the other superiorities of the proposed method.

**Table 2.** Comparison of the presented method with other preconcentration methods.

Method	LODa ( $\mu\text{g/L}$ )	R.S.D.b (%)	PFc	Sample volume (mL)	Ref.
CPE-FAAS	2.1	1.5	30	15	[28]
CPE-UV-Vis	7.5	2.7	10	10	[29]
SPE-FAAS	12.3	1.3	200	1000	[30]
SPE-FAAS	3.4	1.3	260	1300	[31]
DLLME-HPLC-UV	3.0	3.3	40	5	[32]
DES-DLLME-FAAS	1.5	3.0	40	40	This work

<sup>a</sup> Limit of detection; <sup>b</sup> Relative standard deviation;

<sup>c</sup> Preconcentration factor

### 3.11. Cobalt determination in real samples

Optimized DES-DLLME technique was employed for Co determination and preconcentration in different water samples (i.e., tap, river, mineral, and sea water) and agricultural products (Broccoli and Spinach) samples (Table 3, 4). In order to analyze the water samples, a 0.45  $\mu\text{m}$  Millipore membrane was utilized to filter the collected water samples (river and sea water) prior to the extraction procedure. To verify the accuracy of the method, different amounts of cobalt was dispersed in the samples before extraction. Results indicated the relative recoveries and RSDs in the range of 95.0-101.2% and 2.9-3.3%, respectively. Experimental results verified the method to be used for Co determination in real samples with good reproducibility and satisfactory precision and accuracy.

**Table 3.** Determination of cobalt in water samples.

Sample	Cobalt amount ( $\mu\text{g/L}$ )		Recovery (%)
	Added	Found	
Tap water (Drinking water system of Sari, Iran)	0.0	ND <sup>a</sup>	–
	15.0	(3.2) <sup>b</sup>	99.3
	20.0	14.9	99.5
		19.9 (3.1)	
Mineral water (Plour mineral water, Iran)	0.0	ND*	–
	15.0	(3.0)	98.7
	20.0	14.8	99.0
		19.8 (2.9)	
River water (Tajan river, Sari, Iran)	0.0	6.5 (2.9)	–
	15.0	(3.2)	98.7
	20.0	21.3	99.5
		26.4 (3.0)	
Sea water (Caspian Sea water, Sari, Iran)	0.0	10.7 (3.1)	–
	15.0	(3.3)	100.7
	20.0	25.8	100.5
		30.8 (3.2)	

<sup>a</sup> Not detected

<sup>b</sup> RSD of three replicate experiments

**Table 4.** Determination of cobalt in agricultural products.

Sample	Cobalt amount ( $\mu\text{g/g}$ )		Recovery (%)
	Added	Found	
Broccoli	0.00	0.28 (3.2)	–
	0.40	(3.0) <sup>a</sup>	97.5
	0.80	0.67	101.2
		1.09 (3.0)	
Spinach	0.00	0.31 (3.3)	–
	0.40	(2.9)	95.0
	0.80	0.69	98.8
		1.10 (3.0)	

<sup>a</sup> RSD of three replicate experiments

## 4. CONCLUSION

This study presents deep eutectic solvent-based dispersive liquid-liquid microextraction (DES-DLLME) method coupled with FAAS which was developed for sensitive Co determination in water samples and agricultural products. DLLME is a rapid, feasible, cost-effective and sensitive technique which can lead to a low LOD, a high preconcentration factor along with extraction recovery in Co extraction and preconcentration from water samples and agricultural products. Moreover, unique properties of deep eutectic solvent including its low vapor pressure, low toxicity, non-flammability, and non-volatility have made DES-DLLME, a facile, vigorous and environmentally friendly approach.

## Acknowledgements

The author thanks the research council at Payame Noor University for financial support.

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## کاربرد میکرواستخراج مایع-مایع پخشی بر اساس کاربرد حلال اتکتیک عمیق کولین کلراید: ۴-برومو فنل برای پیش تغلیظ و اندازه گیری دقیق کبالت در نمونه های آبی و محصولات کشاورزی

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تاریخ دریافت: ۱۵ مرداد ۱۳۹۹ تاریخ پذیرش: ۱۷ شهریور ۱۳۹۹

در این تحقیق یک روش سریع، کاربردی و حساس برای پیش تغلیظ و جداسازی کبالت از نمونه های حقیقی مختلف بر اساس استفاده از روش میکرواستخراج مایع-مایع پخشی بر پایه حلال های اتکتیک عمیق ارائه شده است که در آن از حلال اتکتیک عمیق، متانول و ۱-(۲-پیریدیل آزو)-۲-نفتول به ترتیب به عنوان حلال استخراج کننده، حلال پخش کننده و عامل کمپلکس دهنده استفاده شده است. غلظت کبالت به وسیله دستگاه جذب اتمی شعله ای اندازه گیری شده است. پارامترهای موثر بر کارایی استخراج (مانند نوع و حجم حلال استخراج کننده و پخش کننده، pH، غلظت عامل کمپلکس دهنده و غلظت نمک) مورد بررسی و بهینه سازی قرار گرفتند. تحت شرایط بهینه حد تشخیص برای کبالت ۱/۵ میکروگرم بر لیتر با فاکتور پیش تغلیظ ۴۰ بدست آمد. انحراف استاندارد نسبی برای ۱۰ بار اندازه گیری غلظت ۲۰ میکروگرم بر لیتر کبالت ۳/۰ درصد بدست آمد. صحت و کاربرد روش توسط اندازه گیری مقدار کبالت در نمونه های مرجع آبی و نمونه های آبی و محصولات کشاورزی مختلف مورد ارزیابی قرار گرفت.

### واژه های کلیدی

میکرواستخراج مایع-مایع پخشی بر اساس کاربرد حلال اتکتیک عمیق؛ ۱-(۲-پیریدیل آزو)-۲-نفتول؛ کبالت؛ نمونه های آبی؛ محصولات کشاورزی.