ORIGINAL PAPER



Deep eutectic solvent-based ligandless ultrasound-assisted liquid-phase microextraction for extraction of cobalt ions from food samples prior to spectrophotometric determination

Akram Torabi¹ · Mahboube Shirani² · Abolfazl Semnani¹ · Ali Akbari²

Received: 7 May 2020 / Accepted: 29 September 2020 © Iranian Chemical Society 2020

Abstract

An innovative environmentally friendly deep eutectic solvent-based ligandless ultrasound-assisted liquid-phase microextraction was introduced for spectrophotometric determination of trace amount of cobalt. *n*-phenyliminodiacetic acid: choline chloride (2:1 mol ratio) as a novel DES was prepared for extraction of cobalt ions which is both as chelating agent and extraction solvent. The pivotal factors affecting the proposed method including pH, time, temperature, extraction solvent volume, ionic strength, and sample volume were investigated. At optimum conditions, limit of detection and limit of quantification of 5.23 μ g L⁻¹ and 17.67 μ g L⁻¹ were achieved respectively. The linear range of 20–200 μ g L⁻¹ and precision (relative standard deviation %) of 3.4 for 100 μ g L⁻¹ Co⁺² solution were gained. The proposed method was successfully applied in water samples, tomato sauce, black and green tea, and dark chocolate with high recovery values (%) of 94–105.

Keywords Deep eutectic solvent · Liquid-phase microextraction · Ultrasound assisted · Ligandless · Cobalt

Abbreviations

DES-LL-USA-LPME	Deep eutectic solvent-based		
	ligandless ultrasound-assisted		
	liquid-phase microextraction		
LOD	Limit of detection		
LOQ	Limit of quantification		
SPE	Solid phase extraction		
HBD	Hydrogen bond donor		

Introduction

The existence of metal ions at trace/ultra trace levels can be either essential or harmful to body mechanism and metabolism [1]. Cobalt has crucial role in chemical processes of all living beings. Cobalt is the main part of vitamin B12

Mahboube Shirani m.shirani@ujiroft.ac.ir

Abolfazl Semnani a.semnani1341@gmail.com and has a remarkable function in synthesis of hemoglobin and iron metabolism. The daily intake of 50-200 µg is recommended for cobalt [2]. Excess amount of cobalt in body results in dermatitis, cardiovascular disease, asthma, rhinitis, poisoning, prevention of the DNA repair process, and respiratory problems [3, 4]. Therefore, application of a potent analytical method for separation and determination of trace amount of cobalt is essential. Conventional extraction methods including solid phase extraction (SPE) [3, 5], liquid-liquid extraction (LLE) [6], and cloud point extraction (CPE) [7], have been reported for determination of trace amount of cobalt in food and environmental samples. However, these methods suffer from long extraction time, usage of large amounts of toxic solvents, and inappropriate enrichment factor, Therefore, miniaturized extraction techniques were introduced and grabbed attention [8]. Solid-phase microextraction (SPME) was first introduced in 1990 which is based on the interaction and distribution of analyte between sample matrix and a fiber coating [9]. However, the applied fibers have week and fragile structure and limit SPME application [10]. Therefore, liquidphase microextraction (LPME) was developed to overcome SPME drawbacks [11, 12]. Dispersive liquid–liquid microextraction (DLLME) [13, 14], homogeneous liquid-liquid microextraction (HLLME) [15], hollow fiber-liquid-phase microextraction (HF-LPME) [16], air-assisted liquid-liquid

¹ Department of Chemistry, Faculty of Science, Shahrekord University, P.O. Box 115, Shahrekord, Iran

² Department of Chemistry, Faculty of Science, University of Jiroft, P. O. Box 7867161167, Jiroft, Iran

microextraction [17], and single drop microextraction (SDME) [18] are some LPME techniques. LPME is the most prevalent and facile preconcentration technique in which the analyte is extracted into the low volume (µL) of extraction solvent [19]. Simple operational setup, facile substitution of green solvent for toxic organic solvent, and short extraction time are noticeable advantages of LPME comparing to other microextraction techniques [20]. Application of toxic organic solvents is the main drawback of most analytical techniques. Introduction of green solvents including ionic liquids (ILs) and deep eutectic solvents (DESs) has been an appropriate solution to environmental challenges of analytical methods [21]. DESs are new descendant of ILs which conquer the impediments of ILs owing to their substantial advantages including the lower costs of raw materials, more facile and milder synthesis process, more biodegradability, and insignificant toxicity [22]. A DES is the mixture of two constituents including one hydrogen bond donor (HBD) and one hydrogen bond acceptor in which the melting point of the DES is lower than the melting point of each individual [20]. In recent years, DESs have been desirable alternatives of toxic organic solvents mostly in LPME techniques [19]. Reported DESs have shown superb extraction efficiencies which highlight the application of these solvents. Novel DES has been also reported for extraction of cobalt. For instance, Werner introduced trihexyl (tetradecyl)phosphonium chloride-thiosalicylic acid at a molar ratio of 1:2 for ligandless preconcentration and extraction of cobalt [23]. In this study, a novel ecofriendly deep eutectic solvent, i.e., *n*-phenyliminodiacetic acid: choline chloride (2:1 mol ratio) as a highly efficient extraction solvent was synthetized and used in deep eutectic solvent (DES)-based ligandless ultrasound-assisted liquid-phase microextraction (DES-LL-USA-LPME) for spectrophotometric determination of cobalt. The DES-LL-USA-LPME was applied in food samples as complex matrixes.

Materials and method

Chemicals

The used reagents were all in analytical grade with the highest purity. The stock solution (1000 mg L⁻¹) of cobalt was prepared by dissolving 0.3104 g cobalt (II) nitrate hexahydrate (99.999%, Sigma-Aldrich) in a 100 mL volumetric flask with deionized water. Standard solutions were prepared daily by dilution of the stock solution. Chloroacetic acid (\geq 99.0%, Sigma-Aldrich), aniline (\geq 99.5%, Sigma-Aldrich), and choline chloride (\geq 99%, Sigma-Aldrich) were prepared for synthesis of DES. Sodium hydroxide, nitric acid, hydrogen peroxide were all provided from Merck. Acetic acid (100%), sodium acetate, potassium chloride, hydrochloric acid (37%), potassium dihydrogen phosphate, potassium hydrogen phosphate, potassium hydrogen phthalate, and disodium tetraborate were all purchased from Merck and used for preparation of buffer solutions.

Instrumentation

The Jenway pH meter (DHS700, 3310 model, England) was used for pH measurements. Ultrasonic bath (Elema, Germany) was employed for sonication of extraction solvent and sample solution. UV–Visible spectrophotometer (Pharmecia, model 3100, USA) was used for the analysis. FT-IR spectrometer (Tensor, model 27, Bruker, USA) and NMR spectrometer (500 MHz, Inova, Germany) was applied for characterization of the synthetized DES. Centrifuge (Mahan Co., Shiraz, Iran) were applied for the extraction process.

Real samples preparation

Water sample including tap water (from chemistry lab, Shahrekord University, Shahrekord, Iran) and river water (from Zavanderoud River, Saman, Iran) was filtered with No. 42 Whatman[®] paper to eliminate any dispersed or suspended particles and then used for the analytical process. Tomato sauce, green and black tea, and dark chocolate were purchase from a local supermarket in Shahrekord, Iran. 2.5 g of each tea sample and 3 g tomato sauce was separately digested in 10 mL concentrated nitric acid and was heated at 70 °C for 20 min. Then, 8 mL hydrogen peroxide was added for entire digestion of the sample. After heating for 15 min, the solution was filtrated with No. 42 Whatman[®] paper and the obtained solution was diluted to 25 mL with deionized water and used for determination of cobalt through DES-LL-USA-LPME [24]. Dark chocolate sample was stored at 4 °C in the refrigerator. Then freeze-dried chocolate was homogenized in a blender. 0.5 g of the sample was transferred to a falcon tube and 6 mL solution containing of nitric acid (4 mol L^{-1}), hydrochloric acid (4 mol L^{-1}), and hydrogen peroxide (0.5 mol L^{-1}) with the volume ratio (v/v) of 3:2:1 was added to the chocolate sample. The solution was sonicated for 15 min at 50 °C to achieve a homogeneous solution. Then, the solution was centrifuged at 4000 rpm for 5 min. After filtration of the solution, the obtained clear solution was diluted to 25 mL with deionized water and used for further studies [13].

Preparation of *n*-phenyliminodiacetic acid

9.45 g chloroacetic acid (0.1 mol) was neutralized with 50 mL sodium hydroxide solution (2 mol L^{-1}), and then 4.56 mL of aniline (0.05 mol) was added to the solution. The mixture was refluxed for 15 min to completely dissolve aniline. The solution was cooled to room

temperature and *n*-phenyliminodiacetic acid was isolated in crystalline form. The synthetized white compound was collected on a Buchner funnel and washed with ice-cold water, and dried in an evacuated desiccator over potassium hydroxide [25].

Preparation of deep eutectic solvent

A 250 mL jacketed glass vessel with a magnetic stirrer was used to mix 0.01 mol choline chloride with 0.02 mol *n*-phenyliminodiacetic acid at 80 °C for 10 h until a homogeneous viscous brown liquid appeared. The obtained DES was used for extraction process.

DES-LL-USA-LPME analytical process

A solution containing 4 mL of 60 μ g L⁻¹ cobalt ions was transferred to a glass vial and 20 μ L synthetized DES was added and then in order to carry out the extraction process, the solution was ultrasonicated for 4 min. The solution was centrifuged for 3 min at 3000 rpm. Aqueous upper phase was removed by a syringe and 14 μ L of the DES containing cobalt ions was collected and then, diluted with 16 μ L ethanol. The solution was transferred into a quartz microcell spectrometer and analyzed with UV–Visible spectrophotometer. The Visible spectrum of Co-DES after DES-LL-USA-LPME-UV process on different concentrations of cobalt at optimum conditions is presented in Fig. 1.

Results and discussion

Characterization of synthetized DES

¹H-NMR spectra were recorded on Bruker 500 MHz spectrometers (Fig. 2a). Chemical shifts were reported relative to internal tetramethylsilane (TMS) ($\delta 0.00$ ppm). The position of each carbon and hydrogen in the chemical structure of the synthetized DES is indicated in Scheme 1. The ¹H-NMR spectrum of N- Phenyliminodiacetic acid: Choline Chloride DES, shows a triplet at 7.155 (2H) for the 6 aromatic protons, a triplet at 6.658 (1H) for the 7 aromatic protons, a doublet at 6.501 (2H) for the 5 aromatic protons, a singlet at 4.118 (4H) for the 4 alpha carbonyl protons, in n-phenyliminodiacetic acid and a triplet at 3.898 (2H) and 3.421 (2H) for the methylene group, a singlet at 2.695 (9H) for the methyl group in choline chloride. ¹³C-NMR spectra were recorded on Bruker 125 MHz spectrometers (Fig. 2b). The peak at 173.05 for the carbonyl carbons of the acyl groups and the peak at 148.10 cm⁻¹, 129.37, 117.24, 111.90 cm⁻¹ for the aromatic carbon and 44.26 for the alpha carbonyl carbon in *n*-phenyliminodiacetic acid and 67.56, 56.14 and 53.63 peak for the carbon in choline chloride. The FT-IR spectra are shown in Fig. 2c. The main characteristic band of DES was 2500-3413 cm⁻¹, which was assigned to O-H stretching vibration. The band at 1721 cm⁻¹ was assigned to C=O strong stretching vibration, and the bands medium at 1368 cm⁻¹ C–N refers to the stretching vibration in *n*-phenyliminodiacetic acid. In addition to the characteristic bands of DES, the strong band at 1178 cm⁻¹ C–O assigned to the stretching vibration of choline chloride.



Fig. 1 The UV–visible spectrum of Co-DES after DES-LL-USA-LPME-UV process on different concentrations of cobalt at optimum conditions



Fig. 2 a CNMR, b HNMR and c FT-IR spectra of phenyliminodiacetic acid: choline chloride DES



Scheme 1 The structure of phenyliminodiacetic acid: choline chloride DES indicated for NMR characterization

The ¹H-NMR spectrum of phenyliminodiacetic acid shows a triplet at 7.015 (2H) for the 6 aromatic protons, a multiplet at 6.557 (1H) for the 7 aromatic protons, a doublet at 6.370 (2H) for the 5 aromatic protons, and a singlet at 3.979 (4H) for the 4 alpha carbonyl protons. The peak at 172.08 for the carbonyl carbons of the acyl groups and the peak at 147.12, 128.37, 116.27, 110.96 for the aromatic carbon and ⁵43.64⁵ for the alpha carbonyl carbon in *n*-phenyliminodiacetic acid (Fig. 3a, b). The main characteristic bands of phenyliminodiacetic acid show a very strong and broadband covering a wide range between 2800 and 3500 cm^{-1} for the O–H stretch. very broad stretching vibration, 1723 cm⁻¹, which was assigned to C=O strong stretching vibration, and the bands medium at 1349 cm⁻¹ C–N stretching vibration in *n*-phenyliminodiacetic acid (Fig. 3c).

The 1H-NMR spectrum of Choline Chloride shows a triplet 1 3.930 (2H) and 3.487 (2H) for the methylene group, a singlet at 2.707 (9H) for the methyl group in choline chloride. The peak at 66.91, 55.94 and 53.11 peak for the carbon in choline chloride (Fig. 4a, b). Therefore, carboxylic acids show a very strong and broadband covering a wide range between 2800 and 3500 cm⁻¹ for the O–H stretch. In addition to the characteristic bands of choline chloride, O–H stretch will show up as a sharp weak peak at 3200–3500 cm⁻¹ and the bands strong at 1142 cm⁻¹ C–O stretching vibration of choline chloride (Fig. 4c). Table 1 indicates the H-NMR and C-NMR comparison



Fig. 3 The a HNMR, b CNMR, and c FT-IR spectra of *n*-phenyliminodiacetic acid

of the raw materials including choline chloride and Phenyliminodiacetic acid.

Extraction mechanism

The complexation occurs by interacting with two groups of *n*-phenyliminodiacetic acid in DES structure through non-bonded electron pair of nitrogen atoms and oxygen atoms of acetate groups. Cobalt (II) also has been extracted as ion-pair complexes together with Complex Cobalt (II) *n*-phenyliminodiacetic acid ([Co (*n*-phenyliminodiacetic acid)2]⁻²). The schematic structure of cobalt-DES interaction is shown in Scheme 2.

The effect of pH

Extraction and separation of metal ions in aqueous solutions mostly contribute to the acidity or basicity of the media. The pH of the solution in the range of 1–9 was investigated. As the results in Fig. 5(a) show the absorption of cobalt-DES increased from 1 to 4, then became constant in the range of 4–6 and had a decreasing trend from pH of 6 to 9. At acidic media, the nitrogen and oxygen atoms of DES would be protonated and cannot react with cobalt ions. The decrease in absorption at basic media refers to the formation of cobalt hydroxide. Cobalt can form a stable complex with DES at pH range of 4–6. For ease of operation pH of 6 was considered for further studies (Fig. 5).



Fig. 4 The a HNMR, b CNMR, and c FT-IR spectra of choline chloride

Phenyliminodiacetic acid: choline chloride	Phenyliminodiacetic acid	Choline chloride	
¹³ C-NMR			
44.26	43.64	53.11	
53.63	110.96	55.94	
56.14	116.27	66.91	
67.56	128.37		
111.90	147.12		
117.14	172.08		
129.48			
148.10			
173.05			
H-NMR			
2.69 (s, 9H)	3.98 (s, 4H)	2.71 (s, 9H)	
3.42 (t, 2H)	6.37 (d, 2H)	3.49 (t, 2H)	
3.90 (t, 2H)	6.56 (m, 1H)	3.93 (t, 2H)	
4.12 (s, 4H)	7.01 (t, 2H)		
6.50 (d, 2H)	10.44 (br, H)		
6.66 (m, 1H)			
7.15 (t, 2H)			

Table 1	Comparison	results	of the raw	materials	and DES
---------	------------	---------	------------	-----------	---------

Scheme 2 The structure of DES-Co interaction

С Н₂ Н₂О

H₂C

H₂O

 H_3

ĊH₃

Cl

H₃C

 H_2

The effect of temperature and time

Temperature has an important effect on the separation and extraction of analyte. Increasing temperatue can enhance the kinetic energy and mass transfer of analyte into the extraction phase. However, the temperature increase can accelerate

0

0

OH₂

OH₂

0

0

O



Fig. 5 The effect of influential parameters: the UV-vis spectra of \mathbf{a} pH solution of cobalt ion, \mathbf{b} temperature m, \mathbf{c} sonication time, \mathbf{d} extraction solvent volume, \mathbf{e} ionic strength, \mathbf{f} sample volume

the solvent solubility of organic solvent which leads to the reduction of the extraction efficiency of analyte. The effect of the temperature in the range of 20–60 °C was studied. As indicated in Fig. 3b, the absorption of Co-DES increased from 20 to 40 °C which refers to the mobility enhancement of cobalt ions which leads to the increasing of the kinetic of Co-DES formation. The absorption reduction for temperatures upper than 40 °C can be due to the solubility of organic solvent and degradation of Co-DES at higher temperatures. Therefore, the temperature of 40 °C was chosen as optimum.

One of the potent factors which affects the speed and sensitivity of the extraction process is the extraction time. In LPME techniques, the proper extraction time generates equilibrium between aqueous and organic phase to reach maximum extraction of analyte to organic phase. Moreover, ultrasonic technique enhances the efficacious interaction of analyte solution and extraction solvent in which the effective mass transfer of analyte into the extraction phase occurs in shorter time. Therefore, the sonication time in the range of 1-10 min was studied. According to the obtained results, the extraction time of 4 min was selected for further studies (Fig. 3c).

The effect of extraction solvent volume

The volume of extraction solvent is an indicative parameter which impacts the extraction of analyte and also determines the preconcentration factor. Therefore, the extraction solvent volume in the range of 10–125 μ L was studied and according to the obtained results in Fig. 3d, the absorption of

cobalt increases from 5 to 20 μL and then becomes constant. Therefore, the volume of 20 μL was selected as optimum for further studies.

The effect of ionic strength

Ionic strength is the consideration of salt concentration (mostly NaCl concentration) on the extraction of the analyte which confirms the potential of the method for application in saline matrixes. To this aim, the concentration of NaCl in the range of $0-2 \text{ mol } \text{L}^{-1}$ was investigated. As Fig. 3e show the NaCl concentration had no significant effect on absorption of cobalt and the proposed method can be acceptably applied in saline matrixes.

The effect of sample volume

Preconcentration factor is directly influenced by the sample solution volume and can ideally illustrate the extraction ability of the proposed method. The volume of sample solution in the range of 2–10 mL was investigated. As the results revealed in Fig. 3f, the absorption is almost constant from 2 to 4 mL and then decreased. Since, 14 μ L of DES was collected after the extraction process and 16 μ L ethanol was added for dilution, the total volume of extraction solvent would be 30 μ L. Therefore, with the sample volume of 4 mL and extraction solvent of 30 μ L the preconcentration factor of 133.3 was achieved.

The effect of foreign ions

The selectivity of the proposed method for determination of cobalt ions was considered in presence of different interfering ions. The interference relegates to the competition of other heavy metal ions for the interaction with the synthetized DES which acts both as chelating agent and extraction solvent. The tolerance limit of interfering ions is designated as the largest amount making variation of less than 5% in the recovery of analyte. According to the obtained results in Table 2, the considered ions represent no remarkable interference and the cobalt recovery was approximately quantitative in the presence of excessive amount of the possible interfering cations and anions.

Analytical performance of the method

The analytical performance of DES-LL-USA-LPME including limits of detection (LODs) and quantification (LOQs), linear range, correlation coefficient, and precision (RSD %) was investigated under the optimum conditions. The results are summarized in Table 3. The limits of detection and quantification were defined as $3S_b/m$ and $10S_b/m$, respectively (where S_b is the standard deviation of the blank signals and

Table 2 Effect of interfering ions on the recovery of cobalt: concentrated volume 4 mL, cobalt concentration 100 μ g L⁻¹

Foreign ions Concentration $(mg L^{-1})$		Salts	Recoveries	
Na ⁺	2000	NaCl	$100.1 \pm 1.2^*$	
K^+	2000	KI	99.5 ± 0.3	
NH_4^+	1000	$NH_4 NO_3$	98.9 ± 0.6	
Mg ²⁺	300	MgCl ₂	97.8 ± 1.6	
Ca ²⁺	250	CaCl ₂	96.5 ± 0.7	
Zn^{2+}	25	$Zn(NO_3)_2$	98.5 ± 0.5	
Pb ²⁺	25	$Pb(NO_3)_2$	98.3 ± 1.0	
Fe ³⁺	75	Fe(NO ₃) ₃ ·9H ₂ O	99.3 ± 0.4	
Cu ²⁺	5	Cu(NO ₃) ₂ ·3H ₂ O	97.6 ± 0.8	
Ni ²⁺	5	$Ni(NO_3)_2 \cdot 6H_2O$	98.1 ± 0.5	
Al ³⁺	500	$Al(NO_3)_3 \cdot 9H_2O$	95.9 ± 1.4	
NO_3^-	2000	NaNO ₃	98.3 ± 0.5	
Cl-	2000	NaCl	98.8 ± 0.6	
I-	2000	KI	99.0 ± 0.3	
SO_4^{2-}	1000	$Na(SO_4)_2$	97.5 ± 0.8	

^{*}Mean \pm standard deviation

Table 3 Analytical characteristics of DES-LL-USA-LPME

Linear range ($\mu g L^{-1}$)	20–200
Linear equation ($\mu g L^{-1}$)	Y = 0.0023X + 0.2979
Correlation coefficient (r^2)	0.9918
$LOD (\mu g L^{-1})$	5.23
$LOQ (\mu g L^{-1})$	18.83
Preconcentration factor	133.3
R.S.D. (%) $(n=7)$	3.4

m is the slope of calibration curve after extraction). The limit of detection of 5.23 µg L^{-1} , and limit of quantification of 18.83 µg L^{-1} were attained for cobalt. The linear dynamic ranges and the correlation coefficients (r^2) are shown in Table 3. The relative standard deviations (%) for 60 µg L^{-1} of cobalt solution were 3.4 which showed desirable precision of the process.

Analysis of the real samples

The potential of DES-LL-UA-LPME was exploited for separation/preconcentration and determination of cobalt ions in tap water, river water, tomato sauce, black tea, green tea, and dark chocolate as complex matrixes. The sample preparation procedures were explained in "Real samples preparation" section. The accuracy and reliability of the method were considered through two common ways of analyte spiking in the sample, and using CRM (certified reference material). Furthermore, in order to verify the accuracy of the method, the procedure was used for the determination of cobalt in certified Accu Trace Reference Standard (Cat. No. ICP-14N-10X) as CRM. The concentration of cobalt in the sample was found to be 29.2 ± 1.3 , which at 95% confidence limit, are in good agreement with the certified values of 30.

 Table 4
 Application of DES-LL-USA-LPME-UV for simultaneous separation/determination of cobalt in food samples

Sample	Added metal ions ($\mu g L^{-1}$)	Founded ($\mu g L^{-1}$)	Relative recov- eries (%)	
Tab water ^a	_	N.D. ^b	_	
	50	52.5	105.0 ± 0.5	
	100	101.7	101.7 ± 0.3	
Tomato sauce ^c	_	N.D	_	
	50	49.3	98.6 ± 0.4	
	100	97.4	97.4 ± 0.6	
Black tea	_	71.0	-	
	50	120.1	98.2 ± 0.5	
	100	168.6	97.6 ± 1.4	
Green tea	_	133.6	_	
	50	181.2	95.2 ± 2.5	
	100	227.5	93.9±1.8	
Dark chocolate	_	141.2	_	
	50	188.9	95.4 ± 2.3	
	100	239.6	98.4 ± 1.0	
CRM ^d	30 ± 1	29.2 ± 1.3	$97.3^{e} \pm 2.1$	

The results are the mean of three replicates (n=3)

^aTap water was obtained from chemistry lab, Shahrekord University ^bN.D. is defined as not detected

^cGreen tea, black tea, tomato sauce and dark chocolate were purchased from a local supermarket in Shahrekord, Iran

^dCertified Accu Trace Reference Standard (Cat. No. ICP-14N-10X) ^eThe absolute recovery is obtained for CRM

^o The absolute recovery is obtained for CRM

The blank samples were analyzed with DES-LL-USA-LPME under optimum conditions, and the concentration of cobalt was not detected. Then, the samples were spiked with two standard concentrations of 50 and 100 μ g L⁻¹ of cobalt and the relative recoveries of 94.0–105.0% were acquired which corroborates high capability of DES-LL-USA-LPME -UV for application in samples with high matrix effects (Table 4).

Comparison to other methods

The proposed DES-LL-USA-LPME was compared with other studies for determination of the cobalt, and the results are presented in Table 5. DES-LL-USA-LPME revealed good preconcentration factor and linear range, and acceptable precision which represent the proposed method as highly capable method for preconcentration and determination of cobalt. Furthermore, easier operation, facile accessibility, and lower cost are the main benefits of UV–Visible spectrophotometer compared with reported determination techniques. However, selection and preparation of a proper and selective DES with the lowest solubility in water are considered as a limitation to DES-LL-USA-LPME as choline chloride-based DES technique.

Conclusion

In the present research work, a ligandless ultrasound-assisted liquid-phase microextraction using a novel deep eutectic solvent (DES) was developed and proposed for preconcentration of cobalt ions in water and food samples followed by UV–Visible spectrophotometry as a facile detection technique. DESs with the significant features including great biodegradability, low vapor pressure, non-volatility, low

Table 5 Comparison of DES-USA-LPME-UV for preconcentration and determination of cobalt

Method	LOD ($\mu g L^{-1}$)	RSD (%)	Preconcentra- tion factor	Extraction time (min)	Linear range ($\mu g L^{-1}$)	References
VA-IL-DLLM ^a	0.2	2.7-4.1	62.5	<10	0.7–400	[13]
DES-LPME-MS-FAAS ^b	4.6	0.9-4.3	100	30	5-30	[19]
DLLME-SFO-ICP-OES ^c	0.2	3.4	76	3	1.25-250	[26]
SPE-FAAS	0.25	2	80		250-5000	[27]
CPE ^d -FAAS	0.24	2.1	57	>20	10-100	[28]
Co-MP-DSPME-SQT ^e -FAAS	7.78	4.2-4.5	64.3	<2	25-500	[8]
DES-USA-LPME-UV	5.23	3.4	133.3	4	20-200	This study

^aVortex assisted-ionic liquid-based dispersive liquid-liquid microextraction

^bDeep eutectic solvent liquid-phase microextraction microsampling flame atomic absorption spectrometry

^cDispersive liquid–liquid microextraction-solidified organic drop induce coupled plasma optical emission spectrometry

^dCloud point extraction

^eCobalt magnetic particles based dispersive solid-phase microextraction prior to slotted quartz tube-flame atomic absorption spectrometry

toxicity, and non-flammability have upgraded the sample treatment techniques to green and environmentally friendly techniques. The findings of this study led to the synthesis of a novel DES as an efficient extraction solvent by the mixture of choline chloride and *n*-phenyliminodiacetic acid. The results revealed noticeable merits such as sustainable analytical process, green extraction solvent, ligandless method, low detection limit, high preconcentration factor, good linearity, and acceptable precision which nominate DES-LL-USA-LPME-UV as a facile and efficient method. The privileged performance of DES-LL-USA-LPME in analysis of cobalt confirmed prosperous application of the method in complex matrixes.

Acknowledgments The authors gratefully appreciate Shahrekord University and University of Jiroft for the valuable supporting of this research study.

Authors' contribution AT carried out the experimental analysis and data collection as Master student. MS and AS designed the project, handled writing the manuscript and data analysis. AA synthetized and prepared the DES.

Funding This manuscript has no funding.

Data availability Research data have been provided in the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

- 1. S.M. Sorouraddin, M.A. Farajzadeh, H. Dastoori, Talanta 208, 120485 (2020)
- Z. Tekin, S. Erarpat, A. Şahin, D. Selali Chormey, S. Bakırdere, Food Chem. 286, 500 (2019)

- F. Shakerian, Y. Chelongar, A.M. Haji Shabani, S. Dadfarnia, Microchem. J. 146, 234 (2019)
- Ç. Büyükpınar, N. San, O.T. Komesli, S. Bakırdere, Environ. Monit. Assess. 191, 313 (2019)
- M. Shirani, F. Salari, S. Habibollahi, A. Akbari, Microchem. J. 152, 104340 (2020)
- A. Łukomska, A. Wiśniewska, Z. Domańska, U. Dąbrowski. J. Mol. Liq. 307, 112955 (2020)
- 7. L. Chen, Z. Lei, S. Yang, X. Wen, Microchem. J. 130, 452 (2017)
- E. Akkaya, F.A. Erulas, Ç. Büyükpinar, S. Bakirdere, Food Chem. 297, 124947 (2019)
- 9. C.L. Arthur, J. Pawliszyn, Anal. Chem. 62, 2145 (1990)
- M.R. Afshar Mogaddam, A. Mohebbi, A. Pazhohan, F. Khodaddeian, M.A. Farajzadeh, TrAC Trends Anal. Chem. 110, 8 (2019)
- 11. Z.M. Memon, E. Yilmaz, M. Soylak, J. Mol. Liq. 229, 459 (2017)
- 12. E. Öztürk Er, E.G. Bakırdere, T. Unutkan, S. Bakırdere, J. Trace Elem. Med Biol. **49**, 13 (2018)
- 13. N. Altunay, A. Elik, R. Gürkan, Microchem. J. 147, 277 (2019)
- A. Jouyban, M.A. Farajzadeh, M.R. Afshar Mogaddam, Talanta 206, 120169 (2020)
- M. Behpour, S. Nojavan, S. Asadi, A. Shokri, J. Chromatogr. A 1621, 461041 (2020)
- C. Worawit, W. Alahmad, M. Miró, P. Varanusupakul, Talanta 215, 120902 (2020)
- 17. M. Torbati, A. Mohebbi, M.A. Farajzadeh, M.R. Afshar Mogaddam, Anal. Chim. Acta **1032**, 48 (2018)
- M.M. Abolghasemi, M. Piryaei, R.M. Imani, Microchem. J. 158, 105041 (2020)
- 19. M. Soylak, M. Koksal, Microchem. J. 147, 832 (2019)
- R.A. Zounr, M. Tuzen, N. Deligonul, M.Y. Khuhawar, Food Chem. 253, 277 (2018)
- H. Vanda, Y. Dai, E.G. Wilson, R. Verpoorte, Y.H. Choi, C. R. Chim. 21, 628 (2018)
- 22. M. Shirani, S. Habibollahi, A. Akbari, Food Chem. 281, 304 (2019)
- 23. J. Werner, J. Sep. Sci. 43, 1297 (2020)
- E. Beikzadeh, A.H.M. Sarrafi, J. Food Meas. Charact. 11, 994 (2017)
- S. Dadfarnia, A.M. Haji Shabani, M. Shirani, A.A. Jafari, J. Hazard. Mater. 173, 534 (2010)
- Y. Yamini, M. Rezaee, A. Khanchi, M. Faraji, A. Saleh, J. Chromatogr. A **1217**, 2358 (2010)
- 27. M. Tuzen, M. Soylak, L. Elci, Anal. Chim. Acta 548, 101 (2005)
- 28. J. Chen, K.C. Teo, Anal. Chim. Acta 434, 325 (2001)