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Ion Pair Dispersive Liquid-Liquid Microextraction for the Determination of Trace Amounts of Copper(II) in Soil, Multivitamin Tablet, Tea and Water Samples Using Flame Atomic Absorption Spectrometry

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Ion pair dispersive liquid-liquid microextraction (IP-DLLME) method combined with flame atomic absorption spectrometry was proposed for the determination of trace amounts of copper(II). By using pyrocatechol violet as chelating agent and cetyltrimethyl ammonium bromide as an ion pairing agent, the trace amount of copper(II) was extracted in chloroform. The factors influencing the formation copper-ligand complex and the extraction efficiency such as, sample pH, extraction time, type and volume of extraction solvent and dispersive solvent, ion pair and ligand concentration were optimized. Under optimum experimental conditions, the enhancement factor of 10.0 was obtained from only 5.0 ml of aqueous phase. The linear dynamic range and the detection limit were 6.0-100 μg l^{-1} and 3.7 μg l^{-1}, respectively. The relative standard deviation for ten replicate determinations of 40.0 μg l^{-1} of Cu^{2+} was 1.9%. Developed method was successfully applied for determination of copper in soil, multivitamin tablet, tea and water samples with good spike recoveries.

Keywords: Ion pair dispersive liquid-liquid microextraction, Copper(II) determination, Pyrocatechol violet, Flame atomic absorption spectrometry

INTRODUCTION

Copper is a metal that exists as Cu(II) and Cu(I) states in all living organisms. It is needed for survival and used as an important catalytic cofactor in redox chemistry for proteins that carry out many fundamental roles in biological processes.

Excess of copper can be cytotoxic [1]. It is known to be one of the most toxic metals for living organisms and it is one of the contaminants that pollute the environment widely. In industry, the potential sources of copper are metal cleaning and plating baths, electrical industry, chemical catalysis, pulp, paper board mills, wood pulp production and the fertilizer industry [2]. The pollution of water and soil by heavy metals creates drastic ecological problems in the world so, at present the determination of trace amount of metals such as copper is important in environmental samples and requires analytical techniques with low detection limits. Maximum permissible concentration of copper in drinking water by the United State environmental protection agency (USEPA) is 1.3 mg l^{-1} [3,4].

Many methods such as UV-Vis spectrometry [5], atomic absorption spectrometry (AAS) [6] and electrochemical method [7] have been used for the determination of copper in different samples. Amongst these methods, atomic absorption spectrometry is a popular technique that has been frequently used for the determination of copper in different samples such as water, human hair, gasoline, vegetables, cereals, serum, bovine liver and peanut [8-14]. To improve the detection limit and reduce interference effects, this technique requires coupling with a preconcentration method that isolates analytes in a sample to transfer to a new sample matrix [15]. For this aim, several extraction methods such as solid-phase extraction [16,17], dispersive liquid-liquid microextraction (DLLME) [18], cloud point extraction

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(CPE) [19,20], solidified floating organic drop microextraction (SFODME) [21] and ion-pair dispersive liquid-liquid microextraction [22-24] (IP-DLLME) have been coupled with atomic absorption spectrometry as a preconcentration method.

In DLLME, an appropriate mixture of extraction and disperser solvents is rapidly injected into a sample solution with a syringe. After formation of a cloudy solution, the analyte is extracted into fine droplets of the extraction solvent. Then, the phases are separated by centrifugation, and the analyte is determined in the sedimented phase. The method is simple, fast and uses negligible volumes of the extraction solvent [25-27].

In this study, we report a simple and sensitive ion-pair dispersive liquid-liquid microextraction (IP-DLLME) method coupled with flame atomic absorption spectrometry (FAAS) for determination of copper ions in soil, multivitamin tablet, tea and water samples. In this work, various parameters affecting the extraction efficiency including type and volume of extraction solvent and dispersive solvent, sample pH, and extraction time were also investigated.

EXPERIMENTAL

Instrumentation

Determination of copper was performed on Shimadzu AA-670 atomic absorption spectrometer (Kyoto, Japan) under recommended conditions (wavelength of 324.8 nm, bandwidth of 0.7 nm and current of 3 mA). SAF-T-ANGLE No. 42 centrifuge was used to accelerate phase separation. All pH measurements were made using a Metrohm E-691 digital pH meter with a combined glass electrode.

Reagents

Pyrocatechol violet(PCV), cetyltrimethylammonium bromide (CTAB), ethanol, methanol, acetone, acetonitrile, carbon tetrachloride, dichloromethane, chloroform, dichlorobenzene, dimethylformamide (DMF), nitric acid, sodium hydroxide, and nitrate salts of cations were obtained from Merck (Darmstadt, Germany). The stock solution of Cu(II) (1000 mg l^{-1}) was prepared by dissolving appropriate amounts of $Cu(NO_3)_2.3H_2O$ in double distilled water. Working solutions were prepared daily by appropriate dilution of the stock solution. The phosphate buffer of pH 4.5 was prepared with NaH_2PO_4 and H_3PO_4 in one liter of deionized water and pH was adjusted by H_3PO_4 or NaOH with a pH meter to desired pH.

General Procedure

A 5.0 ml aqueous solution of 100 µg l^{-1} copper(II) or real sample with pH of 4.5 was transferred into a 15 ml conical bottom glass centrifuge tube and then 120 µl of PCV 0.01 M was added. Then, a mixture containing 1.0 ml of dimethylformamide as disperser solvent and 250 µl chloroform as an extraction solvent, and 500 µl CTAB 0.15 M in $CHCl_3$ were rapidly injected into the aqueous sample solution using a microsyringe. This mixture was centrifuged for 15 min at 800 rpm until Cu(II)-pyrocatechol complex settled at the bottom of the centrifuge tube. Extraction phase was separated and transferred to another tube, then the chloroform was evaporated and the remaining solid was dissolved in 0.5 ml dimethylformamide and then determined by FAAS.

Calculation of Preconcentration Factor

Preconcentration factor (PF) was defined as the ratio of Cu(II) in the organic phase after extraction of C_{org} to the initial analyte concentration in the aqueous phase C_{aq}:

$$PF = C_{org}/C_{aq}$$

In this work, C_{org} was obtained from the calibration graph of the Cu(II) standard solution in the DMF.

Preparation of Tea Sample

The tea sample (Menthe tea, Bio Migros Company, Switzerland) was digested by acid digestion procedure. First, the tea sample was dried in an oven at ~110 ºC, and then 10.0 mg of the dried sample was placed in a 50 ml beaker. Next, 7.0 ml nitric acid was added to the beaker and covered with a watch glass for 24 h. The content of the beaker was heated on a hot plate (~150 °C for 15 min). Then, the sample was cooled and 8.0 ml of perchloric acid was added, the mixture was heated again until the solution became transparent (about one hour). The watch glass was removed and the acid evaporated to dryness at ~150 °C. The residue was dissolved in 5.0 ml of 1.0 M nitric acid and the

solution was neutralized with a NaOH solution. Then, its pH was adjusted at 4.5 with 0.1 M phosphate buffer and diluted to the mark in a 100.0 ml calibrated flask. A 5.0 ml of this solution was used to determine Cu(II) in a tea sample [28].

Preparation of Dynamisan Multivitamin Tablet Certified by Novartis Company from Switzerland

Five tablets were weighed, powdered in a crucible and then dissolved in an aqueous solution containing HNO_3/H_2SO_4 with a ratio of 1:10. The solution was heated until a black color formed, then HNO_3 (65%) was added drop wise to the solution and boiled until a colorless solution was obtained. After that, a few milliliters of distillated water were added and heating was continued to produce white fumes. After addition of a few milliliters of 0.1 M $HClO_4$, the resulting solution was filtered by using Whatman No.40 filter paper. After pH adjustment, the solution diluted into a 100.0 ml volumetric flask with distilled water [29].

Preparation of Soil Sample

A 20.00 g of soil sample from Sanandaj was weighed and transferred into a 200 ml beaker. The soil sample was digested by addition of 10.0 ml nitric acid (65%) and 2.0 ml $HClO_4$ (70%), and then heated for one hour. The contents of the beaker was dissolved in distillated water and filtered by using Whatman No. 40 filter paper and its pH was adjusted at 4.5 with 0.1 M phosphate buffer and diluted to the mark into a 250.0 ml of volumetric flask [20]. Then, 5.0 ml of this solution was used to determine Cu(II) concentration by the developed method.

RESULTS AND DISCUSSION

Pyrocatechol violet (H_4L) has a different form in aqueous solution and the color of the solution changes with pH as a result of proton dissociation of the reagent. The solution is red at pH < 0, it is yellow in the pH range of 2.0-7.0 and is violet around pH 8.0 [30,31]. The PCV forms colored complexes with various metal ions, mostly in weak acidic and basic solutions. The main species of the color complexes may be ML_2^-, M_2L and MHL^- where M represents a divalent metal ion [31].

In order to determine the appropriate conditions for IP-DLLME, experimental parameters such as effect of cetyltrimethylammonium bromide and ligand concentrations, type and volume of extraction solvent, pH, type and volume of disperser solvent, salt, centrifugation time and extraction time were investigated.

Effect of Cetyltrimethylammonium Bromide (CTAB) Concentration

The effect of CTAB concentration as an ion-pair reagent on the extraction efficiency of Cu(II) was investigated in the concentration range of 0.00-0.25 M and the results are shown in Fig. 1. It can be seen that the absorbance was increased by increasing the CTAB concentration up to 0.15 M, and then it became nearly constant by further increase in the CTAB concentration. Therefore, an optimum amount of 0.15 M of CTAB was selected for further studies.

Effect of Ligand Concentration

The amount of ligand on the extraction efficiency is also a key variable to be optimized. A PCV solution with concentration of 0.01 M was prepared and then different volumes of this solution ranging from 0-160 µl were added to the sample solution. As shown in Fig. 2, the absorbance increases by increasing the ligand concentration. However, the signal was not altered by addition of ligand beyond 120 µl. This observation might be interpreted by considering a highest extraction of the analyte under such conditions. Thus, a volume of 120 µl of 0.01 M ligand was selected as a suitable amount of PCV for the extraction process.

Effect of Extraction Solvent Type

An essential parameter in DLLME is the selection of suitable extraction solvent. The extraction solvent should have higher density than water because it is easily separated by centrifugation from the sample solution. On the other hand, extraction solvent should have high extraction efficiency, extraction capability of interested compounds and low solubility in water [22,27,32]. Halogenated hydrocarbons were usually selected as extraction solvent in DLLME because of their high density. In this research, chloroform, carbon tetrachloride, dichloromethane and 1,2-dichlorobenzene were used as an extraction solvent. The effect of these solvents on extraction efficiency was

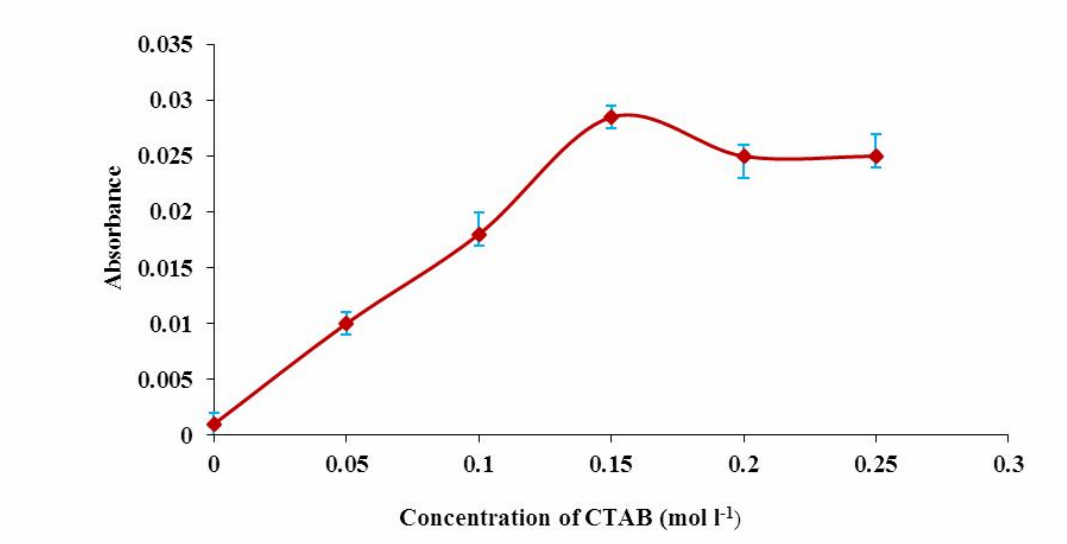

Fig. 1. Effect of cetyltrimethylammonium bromide concentration on the Cu(II) absorbance signal. Experimental conditions: 5.0 ml Cu(II) with concentration of 100 µg l^{-1}, extraction solvent volume 250 µl (chloroform), disperser solvent volume 0.5 ml ethanol, diluting solvent volume 0.5 ml ethanol, 0.01 M ligand, various concentrations of CTAB.

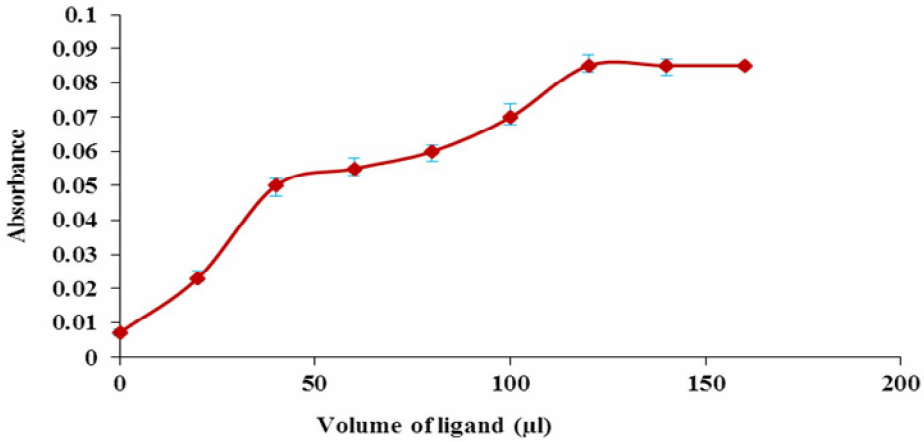

Fig. 2. Effect of ligand concentration on the Cu(II) absorbance signal. Experimental conditions: 5.0 ml Cu(II) with concentration of 100 µg l^{-1}, extraction solvent volume 250 µl chloroform, disperser solvent volume 0.5 ml ethanol, diluting solvent volume 0.5 ml ethanol, various concentrations of ligand, 0.15 M CTAB.

investigated. According to the obtained results, chloroform shows higher extraction efficiency when compared with the other solvents, therefore chloroform was selected for further studies.

Effect of Extraction Solvent Volume

In the liquid extraction, volume of extraction solvent has a significant effect on the extraction efficiency and enrichment factor [22]. In this study, effect of the extraction

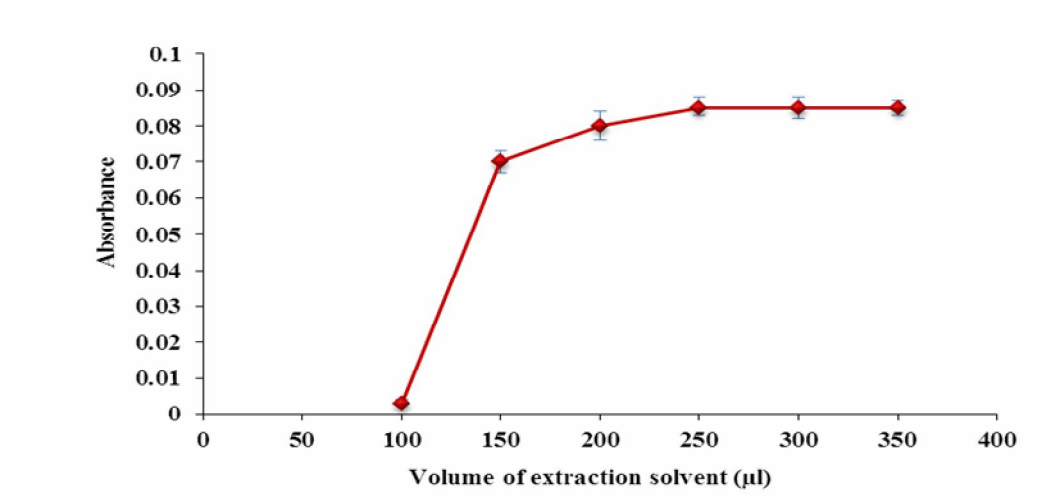

Fig. 3. Effect of extraction solvent volume on the Cu(II) absorbance. Experimental conditions: 5.0 ml of sample containing 100 µg l^{-1} of Cu(II), extraction solvent volume chloroform 100-350 µl, 0.5 ml disperser solvent volume (ethanol), 0.5 ml diluting solvent volume (ethanol), 120 µl 0.01 M ligand, 0.15 M CTAB.

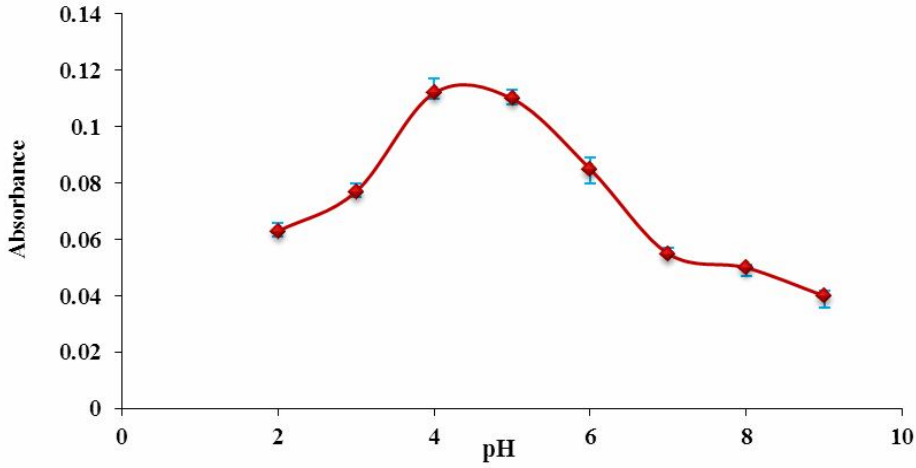

Fig. 4. Effect of pH on the Cu(II) absorbance signal. Conditions: 5.0 ml Cu(II) with concentration of 100 µg l^{-1}, extraction solvent volume 250 µl chloroform, disperser solvent volume 0.5 ml ethanol, diluting solvent volume 0.5 ml ethanol, 120 µl 0.01 M ligand, 0.15 M CTAB.

solvent volume on the extraction efficiency was investigated by adding different volumes of extraction solvent under the same conditions. As seen in Fig. 3, absorbance increased with the increase of chloroform volume in the range of 100-250 µl, and then remained constant when the volume was continuously increased. This effect can be explained by the fact that higher volumes of the extraction solvent lead to the efficient extraction of Cu(II) into the organic phase, thus increasing absorbance signal. Therefore, in the subsequent studies, 250 µl was selected as the optimum volume of the extraction solvent.

Effect of pH

Amongst the chemical parameters, acidity of sample introduced by pH has an essential role in efficiency of extraction. The pH influences on the stability of complexes formed in the aqueous phase. In this experiment, the pH of the sample solution was adjusted using 0.1 M phosphate buffer in the pH range of 2.0-9.0 (Fig. 4). According to the results shown in Fig. 4, the maximum extraction of Cu(II) was obtained at the pH range of 4.0-5.0. At higher pHs, the absorbance of Cu(II) decreases probably due to the reaction of hydroxide ions with Cu(II) that decreases extraction efficiency of Cu(II) ions. Thus, a pH of 4.5 was selected for further studies and the pH was adjusted by 0.1 M phosphate buffer.

Effect of Disperser Solvent Type and Volume on the Cu(II) Extraction

The disperser solvent must be miscible in the extraction solvent and also aqueous phase. The disperser solvent helps to make droplet of extraction solvent very tiny in the aqueous phase and forms a cloudy solution that increases the contact area between the aqueous phase and the extraction solvent which enhances the efficiency and velocity of the extraction process [18]. Considering the appropriate price and low toxicity of methanol, ethanol, acetone, acetonitrile and dimethylformamide, they are often used as disperser solvents. In this study, acetone, ethanol, acetonitrile and dimethylformamide were investigated as disperser solvents. The maximum absorbance was obtained when dimethylformamide was used. Therefore, dimethylformamide was chosen for the subsequent experiments as the disperser solvent.

The effect of the volume of dimethylformamide on the absorbance was also studied. Different volumes of dimethylformamide in the range of 0.3-2.5 ml were examined. Maximum absorbance was obtained when 1.0 ml of dimethylformamide was used. Therefore, 1.0 ml of dimethylformamide was chosen for the subsequent experiments as the disperser solvent.

Effect of Diluting Solvent on the Extraction Efficiency

In order to determine the most appropriate solvent as a diluting solvent, ethanol, methanol, acetonitrile and DMF were examined. The best result was obtained when a volume 0.5 ml of DMF was used. Thus, DMF was selected as a diluting solvent in further studies.

Effect of Salt on the Extraction Efficiency

The effect of ionic strength on the Cu(II) extraction efficiency was also investigated by adding sodium chloride solutions with concentrations between 0.0-6.0% w/v while other parameters were kept constant. The obtained results showed that the Cu(II) absorbance signal decreases by increasing the NaCl concentration in the sample solution. The reason for this observation may be attributed to the fact that addition of salt increases the solution viscosity which reduces dispersion phenomenon, and hence decreases the absorbance signal [33]. Therefore, no salt was added in subsequent experiments.

Effect of Extraction Time on the Extraction Efficiency

Extraction time in DLLME is the time interval of mixing sample solution (aqueous solution), disperser solvent and extraction solvent until a cloudy solution forms before the centrifugation process. This effect was investigated under optimum conditions by changing the extraction times between 1 to 25 min on 5.0 ml aqueous solution at a concentration of 0.1 mg l^{-1} Cu(II). The obtained results showed that the extraction time has no significant effect on the extraction efficiency because transfer of the complex to extracting phase is fast and the equilibrium state is established between the two phases very quickly. Thus, one minute was chosen for the extraction time.

Effect of Centrifugation Time on the Extraction Efficiency

The effect of centrifugation time on the extraction of Cu(II) under optimum condition was investigated in an interval time between 5-30 min. The results showed that the absorbance is increased by increasing the centrifugation time to 15 min. It was difficult to separate phases from each other at centrifugation time of less than 15 min, thus 15 min was selected as the optimum centrifugation time for further studies.

Table 1. Effect of Interfering Ions on the Extraction of 100 μg l^{-1} Cu(II)

Coexisting ions	Tolerable concentration (Interfering ion/iron ratio)
K^+, Na^+, Ca^{2+}, Pb^{2+}, Zn^{2+} , Ni^{2+}, Hg^{2+}, Mg^{2+}, I^-	1000
Cl^-	700
Cd^{2+}, NO_3^-	500
SCN^-	300
Fe^{3+}, Bi^{3+}, V^{3+}, Co^{2+}, $C_2O_4^{2-}$	10

Table 2. Application of the Proposed Method for Determination of Cu(II) in Waters and Soil Samples (N = 3)

Sample	Certified value	Added (μg l^{-1})	Found	Recovery (%)
Well water (μg l^{-1})	-	0.0	10.0 ± 1.5[a]	-
(Kurdistan, Iran)		10.0	19.6 ± 1.0	96.0
		50.0	58.0 ± 1.0	96.0
				-
Tap water(μg l^{-1})	-	0.0	20.0 ± 0.3	-
(Ravanser, Iran)		10.0	29.8 ± 1.2	98.0
		50.0	70.0 ± 0.5	100.0
Mineral water	-	0.0	10.0 ± 1.3	-
		10.0	19.9 ± 1.1	98.2
		50.0	60.0 ± 1.8	99.8
Sea water(Caspian sea)		0.0	<BDL	-
		10.0	10.3 ± 0.7	103.0
		50.0	50.0 ± 0.2	100.0
Soil (road of Kurdistan,		0.0	<BDL	-
Iran)		10.0	9.2 ± 0.3	92.0

[a]Mean ± SD, [b]Bellow detection limit.

Effect of Diverse Ions on the Cu(II) Extraction

The effects of common coexisting ions on the recovery of copper were also studied. This investigation was performed by analyzing 5.0 ml solution with 0.1 mg l^{-1} Cu(II) concentration at pH 4.5 which was adjusted with 0.1 M phosphate buffer. The tolerance limit was defined as the concentration of added ion that caused less than ±5% relative error in the determination of Cu(II). Table 1 shows tolerance limit of the studied ions. The results illustrate that Co^{2+}, Fe^{3+}, V^{3+}, Bi^{3+} and $C_2O_4^{2-}$ have the maximum tolerance limit, 10.0, in concentration ratio. The interference effect of the investigated cations is probably due to the formation of a stable complex between them and PCV. On the other hand, the Cu^{2+}-pyrocatechol violet complex interacts with $C_2O_4^{2-}$ by formation of a $Cu(C_2O_4)_2^{2-}$ stable complex that causes dissociation of complex between Cu^{2+}-PCV[34]. The reported thermodynamic data shows that bonding between $C_2O_4^{2-}$ and Cu^{2+} is more stable than that between PCV and Cu^{2+}. Therefore, it is not surprising that these ions interfere more than the other ions.

Extraction Mechanism of IP-DLLME Procedure in Extraction of Cu(II)

It has been demonstrated that just at pH of 1.0-7.0, the sulphonic group of pyrocatechol violet dissociates and can form a H_3L^- chelating reagent. The reagent could form a 1:1(ML) or 1:2(ML_2) complex with Cu(II). This complex might be extracted into the chloroform by the following mechanisms [35].

$$Cu^{2+}_{(aq)} + H_3L^-_{(aq)} + CTAB^+_{(aq)} \rightleftharpoons Cu(HL)^-CTAB^+_{(org)} + 2H^+_{(aq)}$$

or

$$Cu^{2+}_{(aq)} + 2H_3L^-_{(aq)} + CTAB^+_{(aq)} \rightleftharpoons Cu(HL)_2^{2-}(CTAB)_2^+_{(org)} + 2H^+_{(aq)}$$

Figures of merit

Under optimum experimental conditions, the analytical curve was obtained by analyzing 5.0 ml Cu(II) solutions with concentrations between 2.0-1500.0 µg l^{-1}. The linear dynamic range was 6.0-100.0 µg l^{-1}. The limit of detection (LOD), calculated as the concentration of the absolute amount of analyte yielding a signal equivalent to three times of the standard deviation of the blank (n = 10, LOD = $3\sigma_{blank}$ /slope) based on IUPAC recommendation was 3.75 µg l^{-1} while the relative standard deviation (RSD) was 1.9% (at 40 µg l^{-1} of Cu(II) and n = 10). The regression equation for Cu(II) with IL-DLLME was A = 0.0012C + 0.0362 (R^2 = 0.998), where A is absorbance and C is the concentration of Cu(II) in µg l^{-1}. The preconcentration factor calculated as the concentration ratio of the organic phase after extraction to that initial analyte concentration was found to be 10.

Applications

The proposed method was successfully used for the determination of Cu(II) in well water, tap water, mineral water, sea water, soil, tea and drug samples. The results along with the recovery for the spiked samples are given in Tables 2 and 3. As can be seen, added copper is quantitatively recovered from the samples. The accuracy of the proposed method for the drug sample was also evaluated by the analysis of a certified amount of copper in Dynamisan tablet. As can be seen in Table 3, there is no a significant difference between experimental result and certified value. These results indicate the validity of the proposed methodology for the analysis of copper in real samples.

Comparison of Developed Technique with other Cu(II) Determination Methods

Determination of copper by IP-DLLME method was compared with other reported methods, and results are shown in Table 4. As illustrated, the proposed method shows a good detection limit, high precision and wide linear dynamic range which are comparable with several reported methods. In this technique, the consumption organic solvent ($CHCl_3$) which is volatile and toxic was minimized. Moreover, this methodology is fast, simple and low cost and can be used with regular FAAS equipment. These characteristics can be of key interest for laboratories doing trace metal ion analysis [36-43].

CONCLUSIONS

In this work, an IP-DLLME was used for extraction and determination of trace amounts of Cu(II) in soil,

Table 3. Application of the Proposed Method for Determination of Cu(II) in Tea and Tablet Samples (N = 3)

Sample	Labeled amount ($\mu g\ l^{-1}$)	Added ($\mu g\ l^{-1}$)	Found ($\mu g\ l^{-1}$)	Recovery (%)
Menthe tea	-	0.0	BLD	-
		10.0	10.4 ± 0.5	104.0
		50.0	48.1 ± 1.0	96.2
Dynamisan tablet	100	-	96.0 ± 0.5	96.0

Table 4. Comparison of Analytical Features of the Proposed Method with other Published Methods

Method	Detection technique	LDR ($\mu g\ l^{-1}$)	RSD (%)	Preconcentration factor	LOD ($\mu g\ l^{-1}$)	Ref.
CPE	FAAS	5-200	2.1	21	1.07	[36]
USAE-SFODME	FAAS	20-600	2.65	13.8	0.76	[37]
UA-IL-DLLME	FAAS	8-400	3.8	50	1.9	[38]
DLLME	FAAS	50-2000	5.1	-	3	[15]
Membrane filtration	FAAS	-	≤9	150	33	[39]
HF-LPME	FAAS	10-5000	5.7	551	4	[40]
HLLE	FAAS	10-2000	7.6	25	1.74	[41]
LL-DLLME	FAAS	1.0-600	1.4	-	0.5	[18]
Coprecipitation	FAAS	-	2.5	20	1.32	[42]
DSDME	FAAS	25-1200	2.1	25	1.84	[43]
IP-DLLME	FAAS	6.0-100	1.9	10	3.7	This work

Abbreviations: CPE: Cloud point extraction, USAE-SFODME: Ultrasound-assisted emulsification Solidified floating organic drop microextraction, UA-IL-DLLME: Ultrasound-assisted ionic liquid dispersive liquid- liquid microextraction, DLLME: Dispersive liquid-liquid microextraction, HF-LPME: Hollow fiber supported liquid membrane microextraction, HLLE: Homogeneous liquid-liquid extraction, LL-DLLME: Ligandless dispersive liquid-liquid microextraction, DSDME: Directly suspended droplet Microextraction.

multivitamin tablet, tea and water samples using FAAS. Under optimal conditions, the linear dynamic range and the detection limit were 6.0-100 μg l^{-1} and 3.7 μg l^{-1}, respectively. The preconcentration factor of 10.0 was obtained in this technique. This method has advantages such as simplicity, low cost, good accuracy and high precision, minimum organic solvent consumption and good selectivity that can be used for determination of Cu(II) in different samples.

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