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Separation/preconcentration of trace copper by extraction into [C_4mim] [PF_6] RITL containing p-tert-butyl-calix[4]arene functionalized with o-phenanthroline prior to flame absorption atomic spectrometry

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ABSTRACT

A liquid–liquid extraction (LLE)-flame atomic absorption spectrometry (FAAS) for the separation/analysis of copper has been developed. The method was based on the fact that the inclusion complex of copper(II) with 25, 27-di (5-phenanthrolinylaminocarbonylmethoxy)-26,28-dihydroxy-p-tert-butylcalix[4]arene (TBCP) could be extracted into room temperature ionic liquids (RTILs, 1-butyl-3-methylimidazolium hexafluoro-phosphate [C_4mim] [PF_6] as the green extractant, TBCP as the complexlant), and the copper(II) was subsequently determined by FAAS. The LLE was optimized in detail. The selectivity and mechanism of LLE were approached. Under optimized experimental conditions, the linear range of calibration curve for the determination of copper(II) was 0.020–10.0 μg/mL. The detection limit estimated (S/N = 3) was 3.59 ng/mL with 3.0% RSD. It has been applied for the determination of copper(II) in water samples with satisfactory results.

1. Introduction

Copper is one of the essential micronutrients for human bodies, animals and plants. Lack of copper could cause coronary heart disease, vitiligo, blindness or anemia [1]. But excessive copper is toxic and the free cupric ion is highly toxic for marine organisms and its determination is an important analytical task. The upper control limit of the copper in drinking water was 1000 ng/mL in China [2]. Therefore, it is necessary to develop sensitive and economical methods for the determination of trace amount of copper [3].

Useful analytical methods for Cu(II) include spectrophotometry [4], atomic absorption spectrometry (AAS) [5,6], atomic emission spectrometry (AES) [7], chromatography [8], mass-spectrography [9], potentiometric stripping out analysis [10] and so on. FAAS is the most common determination method in this group due to its low cost, friendly operation and high sample throughput, but it suffers from poor sensitivity and/or matrix interferences in the analysis of heavy elements in environmental samples like natural water and other real samples. This drawback could be overcome by the combination of a suitable preconcentration technique with subsequent AAS [11,12].

Several methods have been reported for the separation and preconcentration of Cu(II), such as liquid–liquid extraction (LLE) [13], solid phase extraction (SPE) [14], cloud point extraction (CPE) [15] and so on. Liquid–liquid extraction (LLE) was among the oldest of the preconcentration and matrix isolation techniques in analytical chemistry. However, there were some disadvantages for LLE, such as the emulsion formation, the use of large sample volumes and toxic organic solvents and the generation of large amounts of pollutants [3]. For this reason, the green of the liquid–liquid extraction attempts to eliminate or minimize these drawbacks.

Room temperature ionic liquids (RTILs) were an important green solvent, which have attracted considerable attention in the fields of extraction separation due to its low melting point, tunable acidity and good solubility characteristics [16–18]. Rogers et al. firstly reported that ionic liquids ([C_4mim] [PF_6]) were used for the metal ion liquid–liquid extraction system and the extraction distribution coefficient was 0.05 [19]. The extraction distribution coefficient could be over 1 when PAN or TAN is used as chelating agent in the above LLE and it could be more than 100 or even higher when crown ethers will serve as chelating agents [16,20,21]. Therefore, the properties (hydrophobic property, selectivity) of the chelating agent were significant for the LLE system.

Calixarenes, appeared after crown ethers and cyclodextrins, as the third generation of inclusion compounds, are largely easily modifiable ring receptors. There are hydrophobic cavities or many regular phenolic hydroxyl groups at the top or bottom of cup-like structure of calixarenes, which could develop the inclusion complexes with neutral molecules or cations [22]. The special modified functional group (1,10-phenanthroline) at the bottom of the derivatives of calixarene is a highly selective host molecule which has a highly selective recognition function and has been applied in metal ions analysis [23–25]. So calixarenes which have a more complicated structure than crown ethers as chelating agents must be bound to get higher extraction

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distribution coefficient [26]. At present, the combination of [C_4mim] [PF_6] ionic liquid as the green extractant and calyx[4]arenes chelating agent for developing an extraction/preconcentration analytical methodology has not been established.

In this paper, copper(II) was chelated with TBCP, then the chelate was extracted into the RTILs ([C_4mim] [PF_6]), and analyzed by FAAS. The selectivity and mechanism of LLE were approached with the inclusion interaction of TBCP and transition metal ions. The method was applied for the separation/analysis of copper(II) in Slender West Lake water sample with satisfactory results.

2. Experimental

2.1. Apparatus and chemicals

The absorbance measurements were performed with AAS ZEEnit700 atomic absorption spectroscopy (Manufacturer Analytik Jena AG), the task selection of WinAAS was application/cookbook (Table 1).

F-4500 fluorescence spectrophotometer (Hitachi, Japan); JJ-1 precise intensifier electric mixer (Changzhou Guohua Electric Appliances Co., Ltd); pHS-25 type pH meter (Shanghai Precision kore magnetic Factory); TDL80-2B Feige high-speed centrifuge (Shanghai Anting Scientific Instruments Plant); Electronic balance (Beijing).

N-methylimidazole (Shanghai Dagro Fine Chemical Co., Ltd); potassium hexafluorophosphate (Shanghai Bangcheng Chemical Co., Ltd); N-butyl-bromide, diethyl ether, ammonium acetate, acetic acid, ammonium chloride, stronger ammonia water, N, N-dimethylformamide (Sinopharm Chemical Rwagent Co., Ltd).

25,27-di(5-phenanthrolinylaminocarbonylmethoxy)-26,28-dihydroxy-p-tert-butylcalix[4]arene (TBCP, Fig. 1, 99.9% purity) was prepared by the Organic Chemistry Lab in the Chemistry College of Yangzhou University. A stock solution of TBCP (6.0×10^{-4} mol/L) was prepared in N,N-dimethylformamide (DMF).

A working standard solution of Cu^{2+} (100.0 μg/mL) was prepared from stock solution of Cu^{2+} (1.000 mg/mL) by dilution with distilled water.

The different pH values of CH_3COOH–CH_3COONH_4 buffer solution (c: 1.2 mol/L) and NH_3–NH_4Cl (c: 1.8 mol/L) buffer solution were employed.

All chemicals were of analytical grade.

2.2. Procedure

2.2.1. Synthesis and spectroscopic characterization of ionic liquid [27,28]

Briefly, 1-butyl-3-methylimidazolium bromide[C_4mim][Br] was synthesized by adding equal amount (0.2 mol) of n-methylimidazole (16.4 g) and n-butyl-bromide (27.4 g) to a 250 mL round bottom flask fitted with reflux condenser. The flask and its content were stirred and heated at 75 °C for 2 h until a golden viscous liquid was formed. Then, 100 mL potassium hexafluorophosphate (36.8 g, 0.2 mol) solution was added slowly and the mixture solution was stirred at room temperature for 5 h. Subsequently, the product was washed three times with 10 mL water and 10 mL diethyl ether in a separation funnel, respectively. Finally, the collected ionic liquid was heated at 80 °C under vacuum for 24 h to remove the solvent.

The final RTILs were also identified and approved by IR (Table 2) and NMR (TMS as the reference for NMR) (Table 3), and the data and results were in good accordance with that of the literatures [29,30].

Table 1
Operational parameter of FAAS.

Instrument parameter		Atomizer	
Sensitive line	213.9 nm	C/O-stoichiometric (C_2H_2/air)	0.075
Slit width	0.5 nm	Fuel flow	50 NL/h
HCL current	4.0 mA	Usable burner height	6 mm

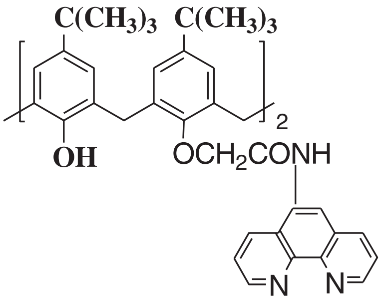

Fig. 1. The molecular formula of TBCP.

2.2.2. Ionic liquid extraction procedure

In a 5.0 mL scale centrifugal tube 0.4 mL Cu^{2+} (100.0 μg/mL), 0.5 mL CH_3COONH_4 (pH = 7.0) buffer solution, 1.0 mL TBCP (6.0×10^{-4} mol/L) and 1.5 mL [C_4mim] [PF_6] were added. The mixed solution was diluted to a final volume with distilled water, shaken thoroughly. Phase separation was achieved by centrifugation at 3500 rpm for 4 min, and then 1.5 mL of the organic phase was visibly observed at the bottom of the centrifuge tube. The aqueous phase (3.5 mL) on the upper of the centrifuge tube was easily removed with a pipette to a 5 mL centrifuge tube and diluted to 5 mL with distilled water, shaken thoroughly, and then determined by FAAS (A_W). Following the same method, a solution without [C_4mim] [PF_6] was prepared as reference solution (A_0). The extraction ratio could be calculated by Eq. (1), where A_0 was the absorbance before extraction, and A_W was the absorbance of the bulk aqueous phase after extraction [31].

$$E(\%) = 100(A_0 - A_w)/A_0 \qquad (1)$$

2.2.3. The Benesi–Hildebrand method

In this experiment, the Benesi–Hildebrand method [32,33] (double reciprocal plot) was used for calculating the inclusion constant (K) of M-TBCP assuming a 1:1 inclusion model. And the expression was given by Eq. (2), where $[TBCP]_0$ was the total concentration of TBCP, [M] was the concentration of metal ions, ΔF was the fluorescence quenching value and α was constant. Thus, the inclusion constant (K) of the 1:1 complex, which had been calculated by dividing the intercept with the slope of the double reciprocal plot.

$$\frac{1}{\Delta F} = \frac{1}{K\cdot\alpha\cdot[TBCP]_0} \times \frac{1}{[M]} + \frac{1}{\alpha\cdot[TBCP]_0} \qquad (2)$$

3. Results and discussion

3.1. Optimization of extraction

3.1.1. Effect of pH

The influence of pH on the extraction ratio (E%) was investigated. As could be seen in Fig. 2 that (1) E% was gradually enhanced with the

Table 2
IR data of RTIL.

υ_{max} (cm^{-1})	Spectral bands belongs
3171, 3125	ν_{C-H} of imidazole ring
2967, 2877	ν_{CH_3-}, ν_{-CH_2-} of imidazole side chain
1572, 1466	the skeleton vibration of imidazole ring
1169	δ_{C-H} of imidazole ring
881	ν_{P-F}

Table 3
^{1}H NMR data of RTIL.

$\delta \times 10^{-6}$	[Bmim] [PF_6]
1H,s,NCHN	9.06
1H,m,$CH_3NCHCHN$	7.73
1H,m,$CH_3NCHCHN$	7.66
2H,t,$NCH_2(CH_2)_2CH_3$	4.15
3H,s,NCH_3	3.84
2H,m,$NCH_2(CH_2)_2CH_3$	1.77
2H,m,$NCH_2(CH_2)_2CH_3$	1.26
3H,t,$NCH_2(CH_2)_2CH_3$	0.90

increase of pH and reached the maximum when pH = 6.0–8.0; and (2) E% was diminished when pH > 8.0. This was because that the appropriate value of pH was subject to the formation of hydrophobic inclusion complex of TBCP-Cu(II), which was easily extracted into RTIL phase. E% was drastically reduced caused by $Cu(OH)_2$ precipitation ($K_{sp} = 2.2 \times 10^{-20}$) when pH > 8.9. Thus, CH_3COONH_4 buffer solution of pH = 7.0 was chosen for the determination, and 0.5 mL of the buffer solution was selected as suitable for the optimized method.

3.1.2. Effect of TBCP amount

The effect of the amount of TBCP was tested. The results were shown in Fig. 3. E% was gradually increased with the amount of TBCP due to the formation of hydrophobic inclusion complex of TBCP-Cu(II) extracted into RTIL phase. When the amount of TBCP (6.0×10^{-4} mol/L) was 0.8 mL, E% reached the maximum and tended to be steady. Thus, 1.0 mL TBCP (6.0×10^{-4} mol/L) was chosen for the assay.

3.1.3. Effect of RTIL amount

The effect of the amount of RTIL was investigated. As was shown in Fig. 4, E% was remarkably raised with the increase of RTIL amount. Meanwhile, the quantitative extraction ratio (90%) was observed for a minimal RTIL amount of 1.0 mL. No significant change was observed on the extraction efficiency with the higher RTIL amounts. Thus, 1.5 mL RTILs were chosen for the following experiments.

3.1.4. Effect of equilibrium time and centrifugation time

In this experiment, the effect of equilibrium time and centrifugation time was studied. The system was quickly separated into two phases after the mixture solution was diluted to a final volume and shaken thoroughly, which illustrated that the equilibrium time was very short. E% was maintained a higher value(90%) and kept a steady trend when t ≥ 4 min. So the process of centrifugation was taken on the heels of shaking thoroughly and the centrifugation time of 4 min at 1000 rpm was sufficient for the separation process.

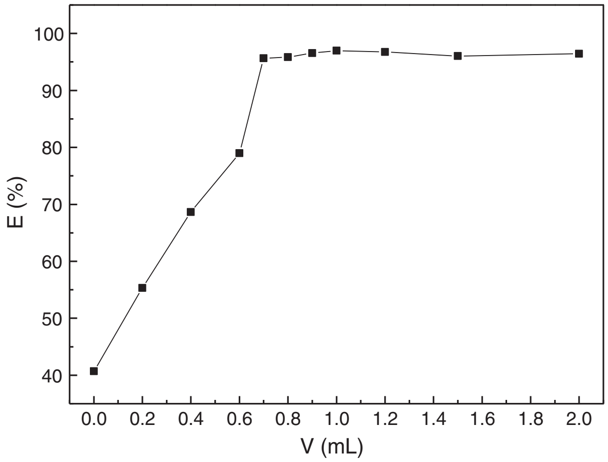

Fig. 3. Effect of the amount of TBCP on extraction ratio. The apparent concentration: (1) Cu = 8.0 μg/mL.

3.1.5. Effect of equilibrium temperature

The effect of equilibrium temperature on E% was tested. It was found that E% was steady ranging from 5 to 45 °C, in which extraction efficiency keep higher. Therefore, the suitable equilibrium temperature of 25 °C was recommended for the work.

3.2. Effect of foreign substances

The effects of the different foreign substrates were discussed in the determination of the 8.0 μg/mL of Cu^{2+}. The results are shown in Table 4. It was observed that most of the common metal ions did not influence the determination of Cu^{2+}.

3.3. Analytical performance

Under optimum conditions, the linear regression equation was determined to be: A = 0.00456 + 0.0489c (μg/mL), R = 0.9977. A linear relationship was observed over the range of 0.020 μg/mL–10.0 μg/mL.

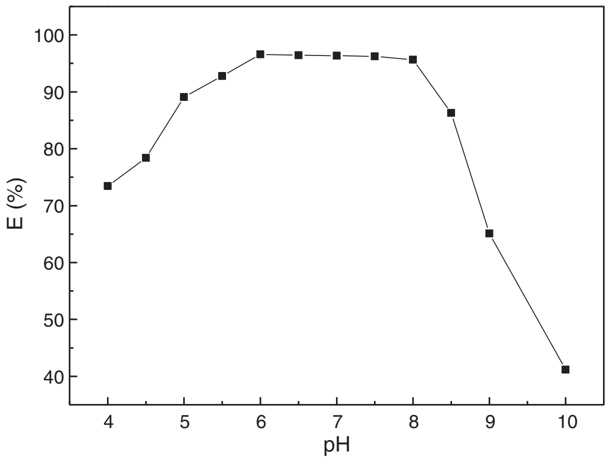

Fig. 2. Effect of pH on extraction ratio. The apparent concentration: (1) Cu = 8.0 μg/mL; (2) TBCP = 1.2×10^{-4} mol/L.

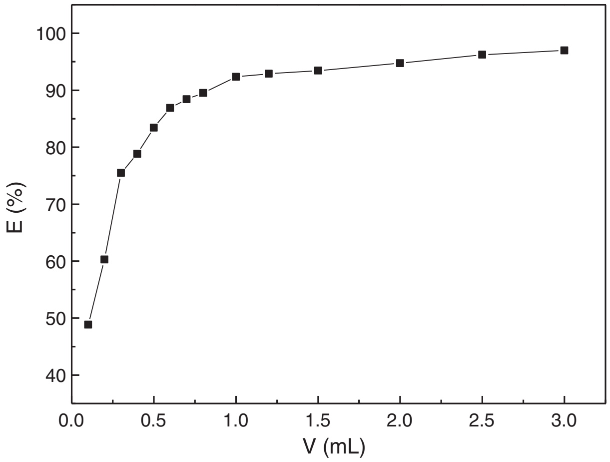

Fig. 4. Effect of the amount of RTIL on extraction ratio. The apparent concentration: (1) Cu = 8.0 μg/mL; (2) TBCP = 1.2×10^{-4} mol/L.

Table 4
Tolerance of interfering ions.

Foreign ions	Foreign/Cu(II) (w/w)	Foreign ions	Foreign/Cu(II) (w/w)
Na^+	750	Fe^{3+}	18
K^+	750	Al^{3+}	9
Ca^{2+}	285	Cd^{2+}	3
Mg^{2+}	143	NO_3^-	750
Mn^{2+}	38	Cl^-	750
Cr(VI)	38	Br^-	750
Mo(VI)	38	CO_3^{2-}	285
Zn^{2+}	12	SO_4^{2-}	38

Table 5
Determination results of standard sample (n = 3).

Standard sample	Certified (μg/mL)	Measured (μg/mL)
GBW(E) 080397[a]	10.0 ± 0.020	10.4 ± 0.040

[a] The standard sample was diluted by 10 times.

The detection limit estimated (S/N = 3) was 3.59 ng/mL, and RSD was 3.0%.

3.4. Sample analysis

The proposed method was satisfactorily applied to the determination of Cu^{2+} in standard sample (Table 5). The result agreed well with the certified values.

The standard addition method was used for the determination of trace amount of Cu^{2+} in Slender West Lake water sample (in Table 6). The recovery ratio ranged from 96.7% to 103.5%.

3.5. Discussion of extraction mechanism

3.5.1. The inclusion interaction of TBCP and transition metal ions

TBCP was an easy-to-selective modified calix[4]arene with 1,10-phenanthroline at the bottom of calix[4]arene. 1,10-Phenanthroline is rigid and contains two nearby nitrogen atoms, which acted as π-electron acceptors and have good coordination capacity with the transition metal ions.

The inclusion constant K is an important parameter for characterizing the inclusion interaction of host molecule with guest molecule or ions [33]. The value of the inclusion constant K reflects the intensity of the binding force of host molecule with metal ions. In this paper, the inclusion constants of host molecule (TBCP) with transition metal ions (Cu^{2+}, Zn^{2+}, Fe^{3+}, Cd^{2+}) were determined and shown in Fig. 5. According to the Benesi–Hildebrand method, it was found that the double reciprocal plot had good linear relationships ($R_{Cu(II)} = 0.9981$, $R_{Zn(II)} = 0.9956$, $R_{Fe(III)} = 0.9952$, $R_{Cd(II)} = 0.9976$), which could support the formation of a 1:1complex. And the values of inclusion constant were shown in Table 7 ($K_{Cu(II)} \gg K_{Zn(II)} > K_{Fe(III)} > K_{Cd(II)}$). The larger the value of K, the more steady the inclusion complex. As a result, the inclusion complex of TBCP-Cu(II) was the most steady complex in this experiment.

Table 6
Determination results of Slender West Lake water.

Sample	Concentration of Cu^{2+} (μg/mL)	Concentration of recovery Cu^{2+} (μg/mL)	Recovery ratio (%)
Slender West Lake water	0	ND	
	2.0	2.16	103.0%
	4.0	4.62	103.5%
	6.0	5.80	96.7%
	8.0	7.80	97.5%

ND: non detected.

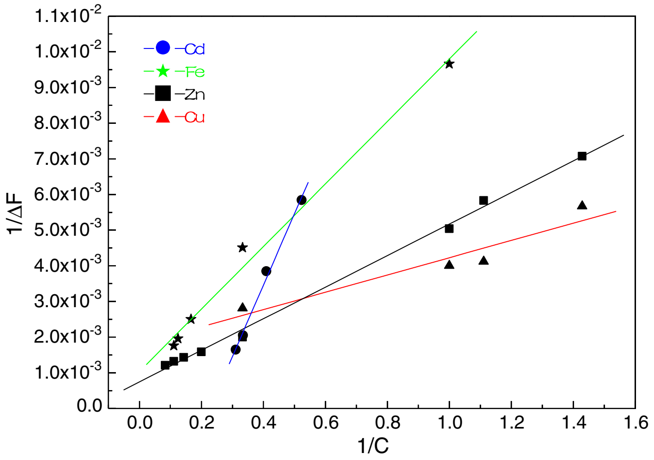

Fig. 5. Double reciprocal plot of transition metal ion in TBCP. M^{n+}: μg/mL.

3.5.2. The inclusion constant and the extraction efficiency

The hydrophobicity of the extracted object directly affects itself into the extraction phase. The hydrophilic transition metal ions were included into the hydrophobic cavities of TBCP to form a stable hydrophobic inclusion complex, which was beneficial for hydrophobic RTIL to extract the inclusion complex of TBCP-metal ions. Thus it was assumed that the inclusion constant K of TBCP-metal ion (M-TBCP) influences the extraction efficiency of RTIL. Under optimum experimental conditions, the extraction ratio of transition metal ions (Cu^{2+}, Zn^{2+}, Fe^{3+}, Cd^{2+}) was determined in Table 7. The trend of the extraction ratio E% ($E\%_{Cu(II)\text{-}TBCP} > E\%_{Zn(II)\text{-}TBCP} > E\%_{Fe(III)\text{-}TBCP} > E\%_{Cd(II)\text{-}TBCP}$) was consistent with the inclusion constant K ($K_{Cu(II)} > K_{Zn(II)} > K_{Fe(II)} > K_{Cd(II)}$). So TBCP had a stronger recognition ability to the special transition metal ion who had the larger value of inclusion constant K. In other words, the larger the K, the higher the E%. Hence, TBCP had very good selectivity extraction for Cu(II).

4. Conclusion

In this paper, hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (RTIL, [C_4mim] [PF_6]) as the green extractant was researched to extract inclusion complex of TBCP-Cu(II) at pH = 7.0. Based on this, a novel LLE-FAAS for the separation/analysis of Cu(II) has been developed. The method has been applied for the determination of Cu(II) in Slender West Lake water sample with satisfactory results.

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Table 7
Determination results of inclusion constant and extraction ratio.

Transition metal ion	Inclusion constant (K)	Extraction ratio (E)
Cu^{2+}	3.79×10^5 L/mol	91.4%
Zn^{2+}	1.42×10^4 L/mol	77.0%
Fe^{3+}	6.57×10^3 L/mol	74.0%
Cd^{2+}	1.72×10^3 L/mol	71.5%

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