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Determination of Trace Cu(II) in Environmental Water Samples by Ionic Liquid Solvent Flotation and GF-ASS

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Ionic liquid solvent flotation was established for detecting trace Cu(II) in environmental water by graphite furnace atomic absorption spectrometry (GF-AAS), with the mixture of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) and ethyl acetate (1:1, v/v) as floating agent, tetracycline (TC) as trapping agent. It is a new method. The effects of pH of solution, the composition of the complexes, gas flow rate, floating time and interference ions were studied. The optimum conditions were ensured. When gas flow rate was 50 mL min^{-1} and floating time was 50 min, enrichment factor (α) of Cu(II) was up to 98 (500 mL initial sample/5 mL determination liquid). Linear range was 0.08-0.56 mg/L, detection limit was 0.3 μg/L. The proposed method was applied to determine Cu(II) in environmental water. Recovery was 91.5-103.0 %, RSD ≤ 3.6 %. This method is non-poisonous, low pollution, high enrichment factor. It is fit for analysis trace/ultra-trace Cu(II) of environmental water samples.

Key Words: Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6), Ionic liquid gas-solvent sublation, Separate/enrich, Tetracycline, GF-ASS.

INTRODUCTION

Copper is an indispensable micronutrients for human health. It is important for maintaining normal activities. Human body absorbs copper mainly through drinking water and food, so an efficient and sensitive measurement is of a great significance. Atomic absorption spectrometry and spectrophotometry are measurements of trace copper. Spectrophotometry usually uses hydrazine compounds[1], 4,6-dichloro-2-(2-tetrahydrogen imidazole)-amino pyrimiidine[2], ferrozine[3], acetaldehyde-BCO[4] and tetra(*o*-chloro-*p*-sulfophenyl)porphin[5] as colour reagents. Tetracycline (TC) is a broad-spectrum antibiotic. Its structure is shown in Fig. 1. The existence of electron donor can form complexes with copper[6], magnesium and calcium[7] and other metal ions. Tetracycline as colour agent in the determination of trace copper has not been reported. Solvent extraction[8] and SPE[9] are common methods of sample separation, but a large number of organic solvents are necessary, for example 4-methyl-acetophenone, acetonitrile and so on. Ionic liquid solvent flotation is non-toxic, less organic reagents and high enrichment factor. It has been applied to tetracycline antibiotics[10] and Al(III)[11] separation.

The mixture of [Bmim]PF_6 with low toxicity, inexpensive ethyl acetate (volume ratio is 1:1) was selected as floating agent in this study. Tetracycline and Cu (II) formed a stable 1:1 hydrophobicity complex under acidic conditions. The complex is soluble in flotation agent and showed the maximum absorption at 373 nm. The procedure was applied to environmental water samples and the recovery was 91.5-103.0 %, RSD ≤ 3.6 %.

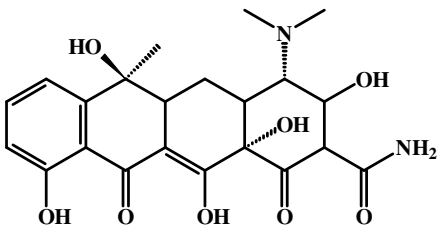

Fig. 1. Tetracycline

EXPERIMENTAL

UV-2550 UV-VIS spectrophotometer (Shimadzu Instruments Co. Ltd.) was used for optimizing the parameters of the solvent sublation. pHS-4 Intelligent pH Meter (Jiangsu Jiangfen Electroanalytical Instrument Co. Ltd.) was used for pH measurements. BN0828 Electronic Analytical Balance (Shanghai Precision Scientific Instrument Co. Ltd., China

Bridge) was used for measuring reagents. Self-made solvent flotation tank, Solvent flotation device (Fig. 2) was used for floating. Trace amounts of Cu(II) were determined by GF-AAS (operating conditions given in Table-1).

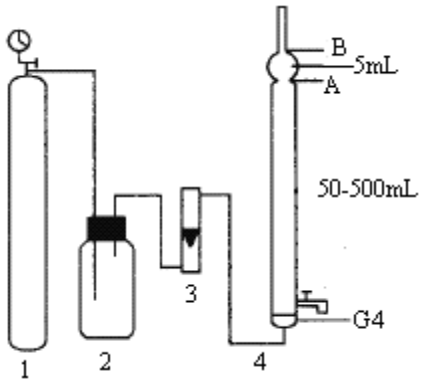

Fig. 2. Solvent sublation apparatus (1) nitrogen cylinder; (2) cushion bottle; (3) rotameter; (4) solvent sublation column

TABLE-1
OPERATIONAL CONDITIONS FOR Cu(II) BY GF-AAS

	Cu(II)
Wavelength (nm)	324.8
Current (mA)	7.5
Bandwidth (nm)	1.3
Drying (ºC)	80-120 (30 s)
Charring (ºC)	600 (30 s)
Atomization (ºC)	2700 (10 s)
Cleaning (ºC)	2800 (3 s)
Notice: Don't correct background.	

Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) was purchased from Shanghai Cheng Jie Chemical Company. Ethyl acetate was purchased from Shenyang Sinopharm. Tetracycline was purchased from National Institute for Control of Pharmaceutical and Biological Products. Reserve liquid (1.0×10^{-3} mol L^{-1}) were prepared by dissolving $CuSO_4$ and diluting to the mark in a 250 mL measuring flask with proper amount of deionized water working solution (1.0×10^{-4} mol L^{-1}) were freshly prepared by diluting the stock solutions with deionized water before use. Tetracycline solution (1.0×10^{-4} mol L^{-1}): a suitable amount of tetracycline was weighed with electronic analytical balance, placed in 50 mL beaker, dissolved to the mark in a 250 mL measuring flask with proper amount of water. Clark-Lubs buffer solution: 0.2 mol L^{-1} H_3BO_3, 0.2 mol L^{-1} KCl and 0.2 mol L^{-1} NaOH were mixed according to a certain percentage to form different pH buffer solutions and calibrated them with pH meter. Analytical reagents and second distilled water were used in the experiment.

Methods: A 250 mL water sample was transferred to a 500 mL beaker and a certain amount of 1.0×10^{-4} mol L^{-1} tetracycline solution was added. Then the pH of the solution was adjusted to 5.8 with a small amount of Clark-Lubs buffer solution. The solution was held still for 10 min and 70 mL NaCl solution (30 %) was added, then the mixed solution was transferred to 500 mL flotation cell (Fig. 2). 30 % NaCl solution was increased to the scale A (500 mL) and mixed intensively. 5 mL mixture of [Bmim]PF_6 and ethyl acetate (1:1, v/v) was added on the surface of sample solution. The system was passed into N_2, stopped ventilation after 50 min, kept still for a moment. When there was no micro-bubble in flotation cell. The complexes were pre-concentrated in the [Bmim]PF_6-EA layer and this was used to determine analytes by GF-AAS directly.

RESULTS AND DISCUSSION

Absorption spectrum: In this study, UV-VIS spectrometry was used to optimize the parameters of the flotation, because it was more economical, rapid, simple and convenient than GF-AAS. But Cu(II) in the real samples as tetracycline-Cu(II) complexes were simultaneously floated into ionic liquid phase, so it was more suitable to determine them by GF-AAS than by UV-VIS spectrometry.

Fig. 3 shows absorption spectrums that are measured tetracycline-Cu(II) complexes with blank reagent as reference. As can be seen, tetracycline appears two absorption peaks at 275 and 356 nm. After forming tetracycline-Cu(II), absorption peak of tetracycline shift from 275-277 nm, another absorption peak of tetracycline shift from 356-373 nm. Changes in absorption spectrum indicate that tetracycline could form a stable complex with Cu(II).

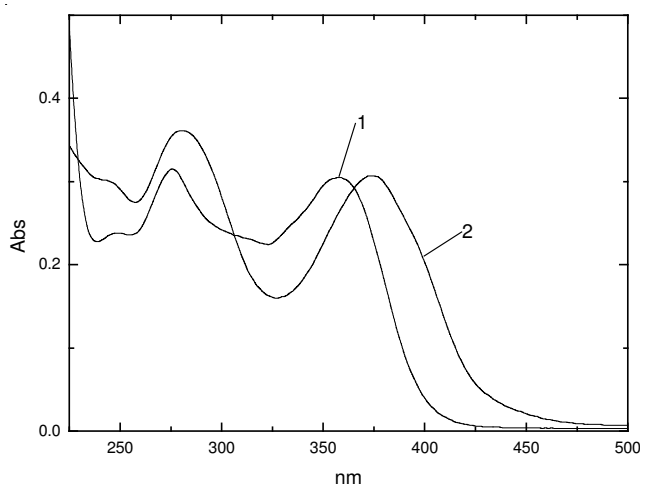

Fig. 3. Absorption spectrum of tetracycline-Cu(II) (1) tetracycline (2) tetracycline-Cu

Fig. 4 shows absorption spectra that tetracycline-Cu(II) complexes in aqueous solution before and after flotation, blank ionic liquid phase and ionic liquid phase after flotation. As can be seen, absorbance changes of complex in aqueous phase before and after flotation are large. After flotation, absorbance of complexes in aqueous phase reduced remarkably. Blank ionic liquid phase does not appear maximum absorption at 300-700 nm, while ionic liquid phase appear maximum absorption at 373 nm after flotation. This shows that tetracycline-Cu(II) complexes have floated to the ionic liquid phase. The maximum absorption wavelength of 373 nm was chosen as optimized flotation condition.

Influence of the pH: 1 mL 1.0×10^{-4} mol L^{-1} $CuSO_4$ was added by an excessive amount of tetracycline. The pH of liquid was adjusted with Clark-Lubs buffer solution and calibrated aqueous with pH meter. The absorbance of system was detected with UV. Different pH values impacted on the formation of tetracycline-Cu(II) complexes were shown in Fig. 5. The

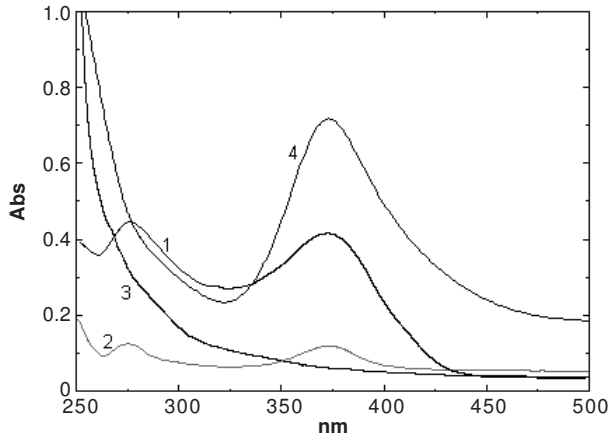

Fig. 4. Absorption spectrum of flotation (1) Absorption spectrum of aqueous phase before flotation; (2) Absorption spectrum of aqueous phase after flotation; (3) Absorption spectrum of [Bmim]PF_6-EA phase before flotation; (4) Absorption spectrum of [Bmim]PF_6-EA phase after flotation

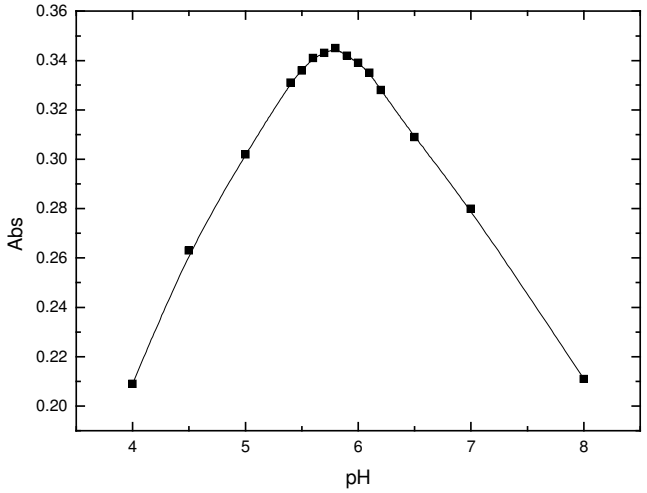

Fig. 5. Effect of pH

results showed that the absorbance increase gradually below pH 5.8 and absorbance reached the maximum value when pH was 5.8; absorbance decreased significantly when pH was over 5.8. The experimental results showed that tetracycline formed complex in the weak acidic conditions. The most optimum acidity for forming complexes was pH 5.8. So pH 5.8 was chosen in present experimental system.

Composition of the complexes: The ratio of tetracycline-Cu(II) complexes was determined by equimolar continuous varied method and mobile equilibrium method in this experiment. The results of two methods are same. When the concentration of Cu(II) below the concentration of tetracycline, complex that ratio (L:M) is 1:1 can be formed; When the concentration of Cu(II) is higher than the concentration of tetracycline, complexes that ratio (L:M) is 1:2 can be formed. Experiment is in line with literature values[12]. This study analyzed the content of Cu and tetracycline is excessive, so the type of generating complexes is 1:1.

Influence of gas flow rate: The system was floated according to experimental method. Gas flow rate were different for each flotation, they were 10, 20, 30, 40 and 50 mL min^{-1}. Then [Bmim]PF_6-ethyl acetate phase was removed and measured their absorbance after the flotation. The results showed that 50 mL min^{-1} was the best.

Influence of floating time: Floating time was changed from 20-70 min and the impacts of flotation efficiency with time were examined. The results showed that flotation efficiency increased with the flotation time within a certain range, flotation efficiency was the highest when the floating time was 50 min; when floating time was increase sequentially, there was no significant change in flotation efficiency. So 50 min was chosen in present study.

Impact of coexisting substances: Under the optimal experimental conditions, a variety of coexistence components of 5 mL 1.0×10^{-4} mol L^{-1} tetracycline were inspected in the 500 mL solution (relative error is not exceeding 5 %). For example, Na^+, Cl^-, K^+, Cd^{2+}, Pb^{2+}, SO_4^{2-}, Mn^{2+} (700); Fe^{3+}, Mg^{2+} (110); Ca^{2+}, Al^{3+}, Zn^{2+} (60); chloramphenicol, penicillin, gentamycin, erythromycin (1000) and so on. Experiment results showed that coexistence substances did not affect the formation of complexes, it also did not disturb flotation behaviour and determination.

Linear range and detection limit: In the optimal experimental conditions, the standard solution of serial concentration were floated and measured (Table-2). Tetracycline-Cu(II) complexes were shown a good linear relationship in 0.08-0.56 mg L^{-1}. Blank reagent were measured 11 times under the same conditions, detection limit of Cu(II) is calculated by $3\sigma/\kappa$. It is 0.3 μg L^{-1}. This satisfies the determination of real samples. Detection limit of Cu(II) is far below the national standard of the maximum limit of Cu(II) that is required in water by this method. It is also lower than detection limit by the national standard method.

TABLE-2
REGRESSION EQUATION, CORRELATION COEFFICIENT AND DETECTION LIMIT OF Cu(II)

System	Regression equation	Correlation coefficient (r)	Linear range (mg L^{-1})
Tetracycline-Cu(II)	0.082ρ (mg/L) + 0.0038	0.9996	0.08-0.56

Flotation effects: Experimental optimum floating conditions was that 5 mL 1.0×10^{-4} mol L^{-1} $CuSO_4$, added 5 mL 1.0×10^{-4} tetracycline, adjusted pH 5.8 with Clark-Lubs buffer solution. The concentration of NaCl solution was 30 %, solvent flotation was [Bmim]PF_6-ethyl acetate (v/v = 1:1), gas flow rate was 50 mL min^{-1}, floating time was 50 min. Under these conditions, the experiment was done with gas-solvent sublation. Flotation efficiency and enrichment factor were calculated using the following formula. Flotation rate (E) is 98 %, enrichment factor (α) is 98.

$$\text{Flotation rate: } E = \frac{C_t V_t}{C_0 V_b}$$

$$\text{Enrichment factor: } \alpha = \frac{C_t}{C_0}.$$

wherein C_0 is the total concentration of $CuSO_4$; C_t is the concentration of $CuSO_4$ in [Bmim]PF_6-ethyl acetate phase after flotation; C_b is the concentration of $CuSO_4$ in aqueous phase after flotation; V_t is volume of [Bmim]PF_6-ethyl acetate phase; V_b is volume of aqueous phase.

Recovery and sample determination: Drinking water samples in three different regions were determined by experimental methods. Cu(II) was detected in two samples and measured values were 0.8 and 0.2 mg L^{-1}. They were in the limited of national requirements. The drinking water sample that was not detected Cu(II) was measured parallel 5 times by standard addition method. Standard addition experiments of two concentration levels were done. Recoveries and RSD were calculated, the results were shown in Table-3. Recoveries were 91.5-103.0 %, RSD ≤ 3.6 %. The recovery and reproducibility were good.

TABLE-3
DETERMINATION RESULTS OF Cu(II) IN WATER SAMPLES BY SOLVENT SUBLATION GF-AAS

Sample	Spiked (mg L^{-1})	Recovered (mg L^{-1})	Recovery (%)	RSD (%, n = 5)
1	1.00	1.03	103.0	3.6
	2.00	1.85	92.5	2.4
2	1.00	0.94	94.0	2.1
	2.00	2.01	100.5	1.5
3	1.00	0.95	95	3.1
	2.00	1.83	91.5	1.5

Conclusion

The trace of the Cu(II) in environmental water samples was determined by ionic liquid solvent flotation and GF-AAS in this experiment. The method is non-toxic, low pollution and high enrichment factor. The results are satisfactory. A new approach for analysing trace/ultra-trace Cu(II) in environmental water samples was provided.

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