Study on Spectrophotometric Determination of Trace Copper after Flotation Separation using Sodium Chloride-Ammonium Thiocyanate-Dodecyl Dimethyl Benzyl Ammonium Chloride System

Changqing Tu[a] , Xinrong Wen[b]

College of Chemistry and Environment,Jiaying University,Meizhou,Guangdong 514015,China

atcq@jyu.edu.cn, bwxrong5093@hotmail.com

Keywords:copper; flotation separation; ammonium thiocyanate; dodecyl dimethyl benzyl ammonium chloride; environmental water samples

Abstract: The paper presents a novel method for the spectrophotometric determination of trace Cu^{2+} after flotation separation using sodium chloride-ammonium thiocyanate-dodecyl dimethyl benzyl ammonium chloride system.The effects of the dosages of NH_4SCN and dodecyl dimethyl benzyl ammonium chloride (DDBAC),various salts and acidity etc. on the flotation yield of Cu^{2+} have been investigated. The possible flotation separation mechanism of Cu^{2+} was discussed.The results showed that by controlling pH4.0,in NaCl-NH_4SCN-DDBAC system,the water-insoluble ternary association complex of $(DDBAC)_2[Cu(SCN)_4]$ which produced by Cu^{2+} and SCN^-,DDBAC cation ($DDBAC^+$) floated above water phase and liquid-solid phases were formed with clear interface,while Mn^{2+},Ni^{2+},Fe^{2+} and Al^{3+} could not be floated,so Cu^{2+} was floated quantitatively. Thereby, the quantitative separation of Cu^{2+} from the above metal ions could be achieved. A new spectrophotometric method of determination of trace copper by flotation separation was established.The proposed method has been successfully applied to the determination of Cu^{2+} in various environmental water samples with satisfactory results.

Introduction

Copper is one of the essential microelements for human.Copper deficiency leads to serious medical diseases.However,at higher than normal levels,it turns out to be harmful to the human body,ingesting excessive copper can cause vomiting, nausea, diarrhea, liver or kidney damage or even death. It has been found that copper can accumulate in surface waters.Consequently,it is of great importance and significance for life science to determinate trace copper in environmental samples.Since the content of Cu^{2+} in environment is usually very low, separation and enrichment must be carried out before measurement.There are many other methods to separate and enrich Cu(Ⅱ),such as solvent extraction[1-3], cloud point extraction[4-5],activated carbon absorption[6],liquid membrane extraction[7-8],ion-exchange resin separation[9],HPLC separation[10],ultrasound-assisted extraction[11],solid-phase extraction[12-13].

In this paper we have studied the spectrophotometric determination of trace Cu^{2+} after flotation separation using sodium chloride- ammonium thiocyanate-dodecyl dimethyl benzyl ammonium chloride system. by controlling pH4.0,in the presence of 1.0g NaCl,when the dosage of 0.10 mol/L NH_4SCN was 3.00 mL and 0.010 mol/L DDBAC solution was 2.50 mL respectively, the water-insoluble ternary association complex of $(DDBAC)_2[Cu(SCN)_4]$ which produced by Cu^{2+} and SCN^-,$DDBAC^+$ floated above water phase and liquid-solid phases were formed with clear interface,while Mn^{2+},Ni^{2+},Fe^{2+} and Al^{3+} could not be floated,so Cu^{2+} was floated quantitatively. Thereby, the quantitative separation of Cu^{2+} from the above metal ions could be achieved. A new spectrophotometric method of determination of trace copper by flotation separation using sodium chloride-ammonium thiocyanate-dodecyl dimethyl

benzyl ammonium chloride system was established.The proposed method has been successfully applied to the determination of Cu^{2+} in various environmental water samples with satisfactory results.

Experiment

Equipment and reagents

A model 722S spectrophotometer (Shanghai No.3 Analysis Equipment Plant) was used for photometric measurements.

NH_4SCN solution:0.10 $mol \cdot L^{-1}$.Borax solution:0.1 $mol \cdot L^{-1}$.Dodecyl dimethyl benzyl ammonium chloride:0.010 $mol \cdot L^{-1}$.1.0×10^{-3} $mol \cdot L^{-1}$ of 4-(2-pyridylazo) resorcinol (PAR) ethanol solution was prepared by dissolving 0.1076 g PAR in 500 mL of ethanol solution. A stock of standard solution of Cu^{2+}: 1.000 $g \cdot L^{-1}$.A working standard solution was prepared by appropriately diluting the stock standard solution. Standard solution of other metal ions was prepared by appropriately diluting the stock standard solution.Buffer solutions of different pH was prepared as references[14].

All reagents were of analytical reagent grade.Bidistilled water was used throughout.

Method

50μg of Cu^{2+},a given amounts of 0.10 $mol \cdot L^{-1}$ NH_4SCN solution and 0.010 $mol \cdot L^{-1}$ DDBAC solution were added into a 25 mL ground color comparison tube,then dilute the mixture to 10.00 mL with pH4.0 buffer solution.1.0 g NaCl was added and shaken adequately and they were kept still for a moment.1.00 mL of salt water sample in the lower layer was transferred into another 25 mL ground color comparison tube, and 1.5 mL of 1.0×10^{-3} $mol \cdot L^{-1}$ PAR ethanol solution and 3.0 mL of 0.1 $mol \cdot L^{-1}$ borax solution was added.The solution was diluted to the mark and the absorbance was measured at 510 nm against the reagent blank prepared in the same way. The amount of Cu^{2+} remained in the solution was calculated and the flotation yield of Cu^{2+}(E/%) was calculated according to the determination results. Photometric analysis of other metal ions was referring the reference[15].

Results and Discussions

Effect of DDBAC dosage on the flotation yield of Cu^{2+}

In order to investigate the effect of DDBAC dosage on the flotation yield of Cu^{2+},50μg of Cu^{2+},3.00 mL of 0.10 $mol \cdot L^{-1}$ NH_4SCN solution were applied to the proposed method. It was found that the flotation yield of Cu^{2+} was zero in the absence of DDBAC in the solution. With the increase of DDBAC dosage, the flotation yield of Cu^{2+} increased. When the dosage of DDBAC is up to 2.50 mL or more, the flotation yield of Cu^{2+} was 100%. Hence,2.50 mL of DDBAC was selected for all further studies.

Effect of NH_4SCN dosage on the flotation yield of Cu^{2+}

In order to investigate the effect of NH_4SCN dosage on the flotation yield of Cu^{2+},50μg of Cu^{2+},2.50 mL of 0.010 $mol \cdot L^{-1}$ DDBAC solution were applied to the proposed method.The results showed that the flotation yield of Cu^{2+} was zero in the absence of NH_4SCN in the solution.The flotation yield of Cu^{2+} increased with the increase of NH_4SCN dosage.When the dosage of NH_4SCN was up to 3.00 mL or more, the flotation yield of Cu^{2+} was 100%. So,3.00 mL of NH_4SCN was chosen for subsequent studies.

Flotation separation mechanism

Based on the results above,only in the simultaneous presence of NH_4SCN and DDBAC in the solution,can Cu^{2+} be completed floated.Therefore,the flotation separation mechanism of Cu^{2+} is as follows:

(1) Cu^{2+} reacts with SCN^- to form $Cu(SCN)_4^{2-}$.

$$Cu^{2+} + 4SCN^- \rightarrow [Cu(SCN)_4]^{2-}$$

(Water phase) (Water phase)

(2) $Cu(SCN)_4^{2-}$ reacts with $DDBAC^+$ to form the water-insoluble ternary association complex of $(DDBAC)_2[Cu(SCN)_4]$, so Cu^{2+} was floated quantitatively.

$$[Cu(SCN)_4]^{2-} + 2DDBAC^+ \rightarrow (DDBAC)_2[Cu(SCN)_4]$$

(Water phase) (Flotation phase)

Effect of various salts on the flotation yield of Cu^{2+}

The effects of NaCl,KNO_3,$(NH_4)_2SO_4$ and NaBr on liquid-solid divarication and the flotation yield of Cu^{2+} were investigated.The results showed that liquid-solid divarication could be realized at the presence of each of four salts above. KNO_3, $(NH_4)_2SO_4$ and NaBr decreased the flotation yield of Cu^{2+} in a certain extent. The presence of NaCl speeded up liquid-solid divarication and made the interface more clear between two phases, and consequently Cu^{2+} could be separated quickly and completely. When NaCl dosage was in 0.5 g, 1.0 g, 1.5 g, the flotation yields of Cu^{2+} were 95.1%,100%,100%. When 1.0 g NaCl was added, it could make liquid-solid phase separation perfectly.Therefore,1.0 g NaCl was chosen in the further studies.

Effect of pH on the flotation yield of different metal ions

Under the optimum conditions,the effects of pH on the flotation yield of different metal ions were investigated.The results showed that in the pH range 1.0～7.0,the flotation yield of Cu^{2+} was in the range of 95.7%～100%, it could be considered that Cu^{2+} was floated completely. At pH 4.0, the flotation yield of Mn^{2+},Ni^{2+},Fe^{2+} and Al^{3+} were zero or lesser(all less then 5.0%).Therefore, Cu^{2+} can be separated from Mn^{2+},Ni^{2+},Fe^{2+} and Al^{3+} in the solution by controlling pH4.0.

Separation experiments

Under the chosen conditions,the separations of Cu^{2+} from Mn^{2+},Ni^{2+},Fe^{2+} and Al^{3+} in synthesized samples of binary and polybasic system were studied respectively. The results were shown in Table 1 and Table 2.

Table 1. The separation results of binary-mixed ions (pH=4.0)

Mixed ions	Metal ions added(μg)		Metal ions found in water phase (μg)		Flotation yield(E/%)	
	Cu	Me	Cu	Me	Cu	Me
Cu^{2+}-Mn^{2+}	50	100	0.1	104.7	99.8	-4.7
	50	200	0	197.2	100	1.4
	50	500	0.2	493.9	99.6	1.2
Cu^{2+}-Ni^{2+}	50	100	0	97.4	100	2.6
	50	200	0.2	198.4	99.6	0.8
	50	500	0.3	491.3	99.4	1.7
Cu^{2+}- Fe^{2+}	50	100	0.2	100.0	99.6	0.0
	50	200	0.2	187.7	99.6	6.2
	50	500	0	455.1	100	9.0
Cu^{2+}- Al^{3+}	50	100	0.1	98.3	99.8	1.7
	50	200	0.2	187.6	99.6	6.2
	50	500	0	470.2	100	6.0

Me represents other metal ions except Cu^{2+}.

Table 2. Separation results of Cu^{2+} from polybasic-mixed ions (pH=4.0)

Number of the synthesized samples	1	2	3
Dosage of Cu^{2+} (μg)	100.0	150.0	200.0
Dosage of Me (μg)	50.0	100.0	200.0
Cu^{2+} found in solid phase (μg)	96.8	143.1	196.2
Flotation yield of Cu^{2+} (E/%)	96.8	95.4	98.1

Me represents Mn^{2+},Ni^{2+},Fe^{2+} and Al^{3+}.

Determination of Cu^{2+} in various environmental water samples

500 mL environmental water sample was heated,cooled and filtered to remove insolution suspended substance. Then pH was adjusted to 4.0 with buffer solution.12.00 mL of 0.10 $mol \cdot L^{-1}$ NH_4SCN solution, 10.00 mL of 0.010 $mol \cdot L^{-1}$ DDBAC solution were added into the solution.Aftering stiring for 20 min, the content of Cu^{2+} in filtrate was determined by GFAAS method.Meanwhile, the recovery test of standard addition was performed. The recovery yield of Cu^{2+}(E/%) was calculated. The results were showed in Table 3.

Table 3. The determination results of Cu^{2+} in various environmental water sample (pH=4.0)

Sample	Cu^{2+} added ($\mu g \cdot L^{-1}$)	Cu^{2+} found in filtrate ($\mu g \cdot L^{-1}$)	Cu^{2+} found in solid phase ($\mu g \cdot L^{-1}$)	Cu^{2+} recovered ($\mu g \cdot L^{-1}$)	RSD (%)	Recovery (%)
Well water	0	2.2920	—	—	0.8	—
	20.00	0.5194	21.7726	19.4806	0.9	97.4
	40.00	2.0130	40.2790	37.9870	1.1	95.0
River water	0	1.7070	—	—	0.9	—
	20.00	0.3246	21.3824	19.6754	0.6	98.4
	40.00	2.1428	39.5642	37.8572	1.0	94.6
Tap water	0	0.7404	—	—	0.6	—
	20.00	0.7792	19.9612	19.2208	1.2	96.1
	40.00	3.4416	37.2988	36.5584	1.1	91.4

The results show that the recoveries of Cu^{2+} are 91.4%～98.4%, and the RSD is 0.6%～1.2%.

Conclusion

In this paper,a novel method for the spectrophotometric determination of trace Cu^{2+} after flotation separation using sodium chloride- **a**mmonium thiocyanate-dodecyl dimethyl benzyl ammonium chloride system was reported. The proposed method has been successfully used for the determination of trace Cu^{2+} in various water samples with satisfactory results. It was obvious that this study had certain practical significance on establishing a new methods of separation and determination of trace copper.

Acknowledgement

This work was financially supported by the Guangdong Science and Technology Project (2012A030700007) and Guangdong Nature Science Foundation(S2012010010978).

References

[1] Taskaev,E.;Penev,I.;Kinova,L. J.Radioanal.Nucl.Chem.1988,12(1),83.

[2] Alonso,A.; Almendral,M.-J.; Curto,Y.; Porras,M.-J. Microchim. Acta.2003, 143, 217.

[3] Wei,G.-T.; Chen,J.-C.; Yang,Z. J.Chin. Chem. Soc. 2003, 50, 1123.

[4] Nuray, S.; Cigdem,A. Microchim. Acta.2008, 162, 107.

[5] Ghaedi,M.; Shokrollahi,A.; Niknam,K.; Niknam,E.; Soylak,M. Cent. Eur. J. Chem. 2009, 7(1) , 148.

[6] Sakai,Y.; Tomura,T.; Ohshita,K.; Koshimizu,S. J. Radioanal. Nucl. Chem.1998, 230(1- 2), 261.

[7] Romero,R.; Jonsson,J.-A. Anal. Bioanal. Chem. 2005, 381, 1452.

[8] Prakorn,R.; Kwanta,N.; Ura,Pancharoen. Korean J. Chem. Eng.2004, 21(6), 1212.

[9] Konar,B.; Basu,S. Fresenius J. Anal. Chem.1994,348,281.

[10] Khuhawar,M.-Y.; Lanjwani,S-N. Mikrochim. Acta.1998, 129, 65.

[11] Väisänen,A.; Suontamo,R.; Silvonen,J.; Rintala,J. Anal.Bioanal.Chem.2002, 373,93.

[12] Hu,Q.-F.; Yang,G.-Y.; Zhao,Y.-Y.; Yin,J.-Y. Anal.Bioanal.Chem.2003, 375, 831.

[13] Guo,J.-J.;Su,Q-D.;Gan,W.-E. J.Chin. Chem. Soc.2009, 56, 763.

[14] Chang,W.-B.;Li,K.-A.*Brief Handbook of Analytical Chemistry*;Beijing University Press:Beijing, 1981;a 240,b 262. (in Chinese)

[15] Pan,J.-M.;Chen,Y.-S.;Yan,H.-T. *Chromogenic Agent and Its Application in Metallurgical Analysis*; Shanghai Scientific and Technical Publisher :Shanghai, 1981,116. (in Chinese)