계면활성제를 코팅한 알루미나에 부동화한 2-Mercaptobenzimidazol을 이용한 구리이온의 정량

G. Absalan* and A. Aghaei Goudi

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

(2006. 9. 29 접수)

Determination of Copper Ion with 2-Mercaptobenzimidazol Immobilized on Surfactant-Coated Alumina

G. Absalan* and A. Aghaei Goudi

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

(Received September 29, 2006)

요 약. 2-mercaptobenzimidazol을 착화제로 사용하여 천연수 중 흔적량의 구리를 분리-예비농축-정량하는 과정을 보고한다. 이 방법은 황산소듐도데실과 γ-알루미나를 물속에서 혼합할 때 γ-알루미나 위에 형성되는 계면활성제 응집체에 기반을 두고 있는데, 2-mercaptobenzimidazol이 산성 매질 속에서 생성된 부가미셀 내부의 소수성 부분으로 들어가 구리 이온의 예비농축과 정량에 적합한 조립체가 된다. 수용액으로부터 μg/ml 수준의 구리이온을 흡착제로 흡착하는 최적 실험조건을 알아내었다. 구리 이온은 pH 7.1-8.0 범위에서 흡착제에 정량적으로 흡착되며 설포살리산을 용리액으로 사용하여 정량적으로 탈착할 수 있다. 용액 중의 다른 이온은 구리 이온의 정량을 방해하지 않았으며, 이 방법을 강물 분석에 적용하니 상대표준편차가 4.91%였다.

주제어: 고체상 추출, 원자흡수분광법, 2-Mercaptobenzimidazl, 예비농축, 구리

ABSTRACT. The present paper describes a procedure for separation, preconcentration and determination of trace amount of copper in natural water samples by using 2-mercaptobenzimidazol as the complexing agent. The proposed method is based on the surfactant aggregation formed on γ-alumina by mixing sodium dodecyl sulfate and γ-alumina in water; 2-mercaptobenzimidazol was incorporated into inner hydrophobic part of produced ad-micelles in acidic media to produce an assemble suitable for preconcentration and determination of copper ion. Optimum experimental conditions for adsorption of μg/ml levels of copper ions from aqueous solution by the adsorbent have been reported. The copper ions were quantitively adsorbed by the sorbent over the pH range of 7.1-8.0 and were quantitatively desorbed afterward by using sulfosalycilic acid as the eluent. The determination of copper was not interfered in the presence of common metal ions. The procedure was applied for analysis of river water sample. Relative standard deviation was found to be 4.91%.

Keywords: Solid-Phase Extraction, Atomic Absorption Spectroscopy, 2-Mercaptobenzimidazl, Preconcentration, Copper

INTRODUCTION

Determination of heavy metal ions in natural waters is a task for analytical chemists in order to evaluate and interpret aquatic systems. However, in many cases the available analytical procedures do not show enough sensitivity thus many enrichment procedures have been proposed. The process involving extraction on a solid sorbent has received more acceptances due to a number of possible advantages including the availability of the solid sorbent, obtainment of large preconcentration factors, and

facility for enrichment using systems with continuous flow. Besides, they usually do not need the use of organic solvents, which may be toxic.[1]

Monitoring trace or ultra trace copper in natural, environment, biological and other real samples is very important. It is an essential element not only for life in mammals but also for plants and lower forms of organisms. However, it is toxic above a certain concentration level. Preconcentration procedures for copper determination[2-13] have been developed that involve different analytical techniques. Among them are liquid-liquid extractions using dithiocarbamate[2] and trioctylmethylammonium chloride[3] as complexing agents, copreciptation with magnesium hydroxide as collector,[4] filtration using a membrane filter.[5] Several systems of adsorption that use solid sorbents such as polyurethane foam loaded with diethyldithiocarbamate,[6] activated carbon,[7,8] amberlit XAD resins,[9,10] and naphthalene[11-15] have also been reported. The possibility of chromosorb absorbents for the enrichment of trace copper ion from aqueous solution without using a chelating reagent has been also proposed.[16] Bati et al. used pb-piperazinedithiocarbamate complex as a new solid-sorbent for preconcentration and separation of copper from oil samples.[17] The potential and utility of alumina and admicellar sorbents in chemical speciation, by taking the case of copper (II) in water as example was investigated by Hiraide.[18] Converted copper into the water insoluble complex with the aid of ammonium pyrrolidinedithiocarbamate has allowed a rapid and reliable determination of traces of copper in river and seawater.[19]

2-Mercaptobenzimidazol (MBID) is slightly soluble in water and soluble in alcohol. It reacts with a wide variety of soft metal ions to form insoluble complexes and has been used as an extraction photometric reagent for Bi, Hg and Se.[20] Bagheri et al.[21] reported determination of both Fe^{2+} and Fe^{3+} species in water samples by selective retention of Fe^{2+} complex on a silica gel column loaded with MBID. To the best of our knowledge surfactant-coated alumina has not been used as an adsorbent for the separation and preconcentration of metal ions from aqueous solutions. Surfactant molecules

such as sodium dodecyl sulfate (SDS) are able to form self-aggregate structure called "hemi-micelles" or "ad-micelles" on solid surfaces such as alumina. It gives them a unique ability to immobilize metal complexing agents. Their interior tends to incorporate sparingly soluble metal complexing agents.[22] In this research, MBID was incorporated into inner hydrophobic part of produced ad-micelles when mixture of MBID, SDS, and γ-alumina (Al_2O_3) particles was acidified to produce a sorbent (abbreviated as MBID/SDS/Al_2O_3 in this text) suitable for preconcentration and determination of copper ion.

EXPERIMENTAL

Apparatus

A flame atomic absorption spectrophotometer, FAAS, (PHILIPS PYE UNICAM SP9) with a deuterium lamp background correction was used. A copper hollow-cathode-lamp (VARIAN TECHTRON) was used with an operating current of 5 mA. Wavelength and spectral bandwidth were 324.7 and 0.2 nm, respectively. pH measurements were made with a Metrohm pH meter (model 632) using a combined glass electrode. Vacuum pump was Edwards 2.

Reagents

All reagents were of analytical grades and were used without further purification. Standard copper ion solutions were prepared daily from acidified 1000 μg/ml copper (II) nitrate solution (Fluka). Other reagents were SDS (Fluka), nitric acid (Merck), sulfosalycilic acid (BDH), 2-mercaptobenzimidazol (Merck) and γ-alumina (Merck). Triply distilled water was used throughout the work. A MBID/SDS solution was prepared by dissolving 1 g SDS and 150 mg of MBID in 40 ml of 0.3 M aqueous ammonia diluting to 100 ml with triply distilled water.

Preparation of the sorbent

Ten milliliters of MBID/SDS solution was added into a beaker containing 1.5 g γ-alumina suspended in 50 ml water. The pH of the mixture was adjusted to a value of 2.0 by drop-wise addition of diluted HNO_3 solution. The mixed solution was shaken for

duration of 15 minutes and the produced solid phase (MBID/SDS/AL₂O₃) was filtered with a sintered-glass funnel using the vacuum pump. The product was dried in room temperature and was used as adsorbent for copper throughout the work.

Recommended procedure

A glass column (10×100 mm) packed with 0.20 g MBID/SDS/Al₂O₃ (with a height of 2 mm in the column) was used as the operational column. Aliquot of 5 ml copper ion solution (8 μg/ml) was passed through the column at a flow rate of 1.5 ml/min. The adsorbed copper ion was eluted with 5 ml of 0.15 M sulfosalycilic acid (adjusted at pH 1.5) at flow rate of 2 ml/min. Percent recovery of copper ion was measured by FAAS after analyzing the eluted copper.

RESULTS AND DISCUSSION

γ-Alumina has positively charged surfaces that can strongly adsorb a negatively charged surfactant such as SDS in highly acidic solutions. A concentration of 7×10⁻³ M SDS, below its critical micellar concentration (8×10⁻³ M), was used in order to produce admicelles that could entrap MBID molecules into its produced cores. Above its critical micellar concentration, the excess of SDS would form micelles in the aqueous solution, which were not adsorbed on alumina surfaces and consequently were not suitable for solid-phase extraction purposes.

pH of sample solution

Looking at the chemical structure of MBID[20] shows that it could behave as an amphiprotic substance because it has two basic amines and one acidic –SH (with a pK$_a$ value of 9.97) sites thus its complex formation ability with metal ions is pH dependent. A series of 5 ml of 8 μg/ml copper ion solutions with different pH values were introduced into packed column. Concentrations of copper ions in the effluents were analyzed by FAAS. Fig. 1 shows that copper ions are completely adsorbed in the pH range of 7.1-8.0. A pH of 7.5, in the middle of the optimum pH range, was selected for further
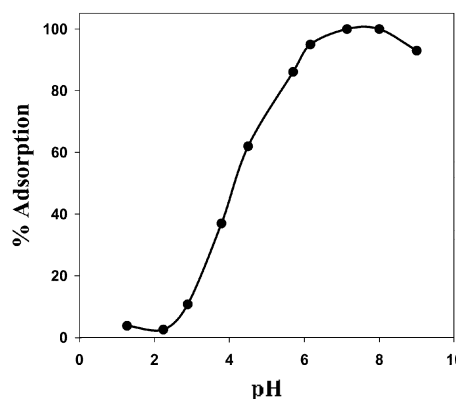
Fig. 1. Effect of pH of the sample solution on percent adsorption of copper ion. Experimental conditions: source: 5 ml of 8 μg/ml copper ion solutions at different pH values, sorbent: 0.2 g MBID/SDS/Al₂O₃.

studies to avoid any abrupt changes in adsorption that may occur due to any changes in pH of the sample. By the way, this could consequently affect the precision of the measurement.

Sample solution flow rate

Percent sorption of 40.0 μg copper ion solution (5 ml of 8 μg/ml) on the surface of 0.2 g of sorbent as a function of sample flow rate was studied. The results (Fig. 2) showed that at flow rates less than 1.5 ml/min, copper ions were quantitatively adsorbed as copper ions and active sites of the sorbent have
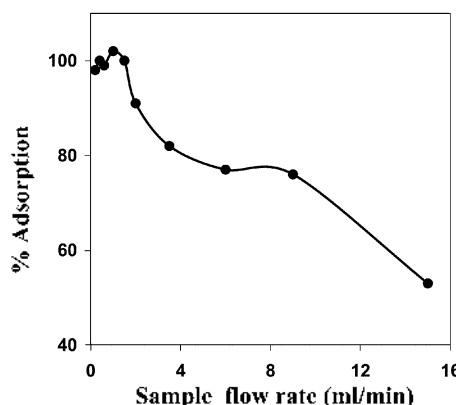

Fig. 2. Effect of sample flow rate on percent adsorption of copper ion. Experimental conditions: source: 5 ml of 8 μg/ml copper ion at pH 7, sorbent: 0.2 g MBID/SDS/Al₂O₃, eluent: 5 ml of 0.15 M soulfosalycilic acid solution at pH 1.5.

enough time for complex formation. Generally, the flow rate of the sample solution is a measure of contact time between the sorbent and copper ion; the lower the flow rate the higher will be the contact time. A flow rate of 1.0 ml/min was chosen for further studies in order to achieve a good precision. Furthermore, the chosen sample flow rate still provided quantitative adsorption with the additional benefit of a decrease in preconcentration time.

Eluent concentration

For desorbing 40.0 μg copper ion, adsorbed on 0.2 g sorbent, different concentrations of the eluent (sulfosalycilic acid) have been used. Percent copper ion recovered is shown as a function of sulfosalycilic acid concentration in *Fig.* 3. As it is shown in this figure, at concentrations more than 0.1 M of sulfosalycilic acid, copper ion was quantitatively desorbed from the sorbent surface. A concentration of 0.15 M of sulfosalycilic acid was selected for further studies.

pH of the eluent solution

To find the optimum pH of the eluent solution for desorbing 40.0 μg of copper ion from sorbent surfaces, a series of eluent solutions with different pH values were used. The results are shown in *Fig.* 4.
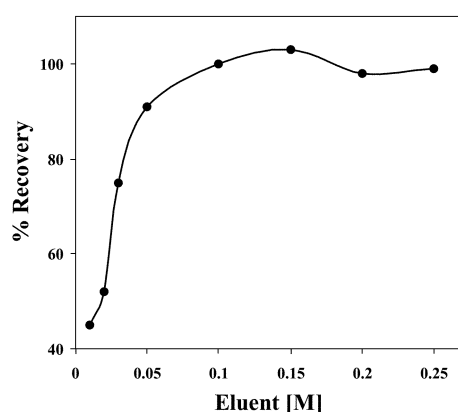

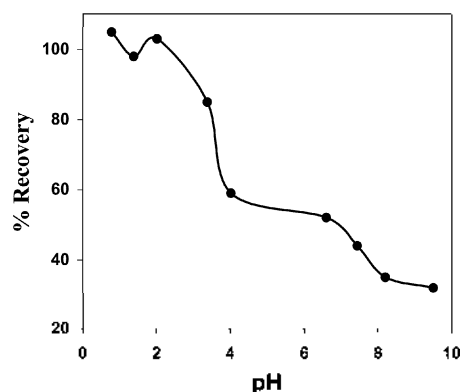*Fig.* 4. Effect of pH of the eluent solution on percent recovery of adsorbed copper ion. Experimental conditions: source: 5 ml of 8 μg/ml copper ion solution at pH 7, sorbent: 0.2 g of MBID/SDS/Al₂O₃, eluent: 5 ml of 0.15 M soulfosalycilic acid with a flow rate of 2 ml/min at different pH values.

As it is seen, the percent recoveries of copper ions at pH ≤ 2 were almost quantitative. A pH of 1.5 for sulfosalycilic acid solution was selected for further research. In another experiment nitric acid solution at pH 1.5 was used as eluent. It was revealed that about 50% of copper ions were recovered. This showed that desorption of copper ion with sulfosalycilic acid is due to complex formation between sulfosalycilic acid and copper ion.

Eluent flow rate

A series of copper ion (40.0 μg) sorbed on sorbent surfaces were eluted at different flow rates of sulfosalycilic acid solution. The percent recovery of copper ion as a function of eluent flow rate is shown in *Fig.* 5. The results showed that copper ion was desorbed almost quantitatively when eluent flow rate was less than 2.4 ml/min. An eluent flow rate of 2 ml/min was considered as the optimum flow rate because it would provide a quantitative recovery with a decrease in analysis time.

Effect of foreign ions on separation of copper ions

The effect of foreign ions present in 10 ml of a binary solution containing 8 μg/ml copper ion with different concentrations of the selected foreign ion, on recovery of copper ion were investigated. Adsorbed copper ions were determined using FAAS after

Fig. 3. Effect of eluent concentration on percent recovery of adsorbed copper ion. Experimental conditions: source: 5 ml of 8 μg/ml copper ion solution at pH 7.0, sorbent: 0.2 g MBID/SDS/Al₂O₃, eluent: 5 ml of soulfosalycilic acid at different concentration.
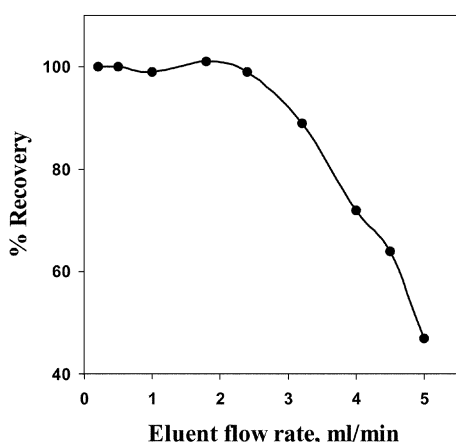
Fig. 5. Effect of eluent flow rate on percent recovery of adsorbed copper ion. Experimental conditions: source: 5 ml of 8 μg/ml copper ion solution at pH 7, sorbent: 0.2 g of MBID/SDS/Al₂O₃ eluent: 5 ml of 0.15 M soulfosalycilic acid solution at pH 1.5.

eluting by sulfosalycilic acid. The results shown in *Table* 1 revealed that there was no serious interference in recovery of copper ion from any of the selected binary solutions.

Selectivity of the method

The ability of the system for separation of foreign ions, under optimum experimental conditions obtained for copper ion is referred as separation selectivity. A multinary solution containing 200 μg/ml each of Ni^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Cr^{2+},

Table 1. Percent recovery of 80 ng/ml copper ion by sulfosalycilic acid in the presence of foreign ions. Experimental conditions: source, 10 ml of 8 μg/ml copper ion containing foreign ions passed with a flow rate of 1.5 ml/min at pH 7.0 through the column; sorbent: 0.6 g of MBID/SDS/Al₂O₃; eluent, 10 ml of 0.15 M sulfosalysilic acid with a flow rate of 2 ml/min at pH 1.5

Foreign ion (μg/ml)	%Recovery of Cu^{2+} (RSD for n=3)
Cr^{2+} (200)	102 (0.09)
Co^{2+} (200)	96 (0.05)
Na^+ (200)	107 (0.15)
Ni^{2+} (200)	114 (0.25)
Hg^{2+} (200)	94 (0.08)
Cd^{2+} (200)	98 (0.06)
Ag^+ (200)	97 (0.20)
Zn^{2+} (200)	94 (0.10)
Fe^{3+} (200)	101.5 (0.07)
Al^{3+} (200)	102.2 (0.10)
SO_4^{2-} (200)	78.6 (0.30)
PO_4^{3-} (200)	101.5 (0.22)
Cl^- (200)	93 (0.19)

Mg^{2+}, Pb^{2+}, Ca^{2+}, Cs^+ and 8 μg/ml of copper ion were prepared. Aliquots of 200 ml of the multinary solution (source solution) were applied into the packed column. After passing through the column, the source solution was analyzed for each cation. Sulfosalycilic acid solution was applied afterward for eluting the possible adsorbed cations. Results, shown in *Table* 2, revealed that the percent eluted of foreign ions made no serious interference in recov-

Table 2. Selectivity of the method (percent recovery of foreign ions). Experimental conditions: source, 200 ml of selected ion solution passed through the column with a flow rate of 1.5 ml/min at pH 7.0; sorbent, 0.6 g of MBID/SDS/Al₂O₃; eluent, 2 ml of 0.15 M sulfosalysilic acid with a flow rate of 2 ml/min at pH 1.5

Foreign ion (μg/ml)	%Ion not adsorbed (RSD for n=3)	%Ion eluted (RSD for n=3)	%Ion on the sorbent (calculated)
Cu^{2+} (8)	0	98 (2.3)	2
Ni^{2+} (200)	22 (1.70)	2.0 (0.05)	76
Fe^{3+} (200)	55 (2.80)	3.1 (0.09)	41.9
Co^{2+} (200)	15 (2.0)	0.5 (0.11)	84.5
Zn^{2+} (200)	14 (1.0)	1.5 (0.07)	84.5
Cd^{2+} (200)	5 (0.90)	2.3 (0.13)	92.7
Al^{3+} (200)	5 (2.3)	0.9 (0.10)	94.1
Cr^{2+} (200)	41 (0.70)	1.8 (0.12)	57.2
Mg^{2+} (200)	10 (2.20)	1.2 (0.04)	88.8
Pb^{2+} (200)	15 (0.09)	1.5 (0.04)	83.5
Ca^{2+} (200)	12 (2.50)	0.8 (0.09)	87.2
Cs^+ (200)	8 (3.70)	5 (1.10)	87

Table 3. Replicate analysis of copper ion spiked in Coar River water (with a pH of 7.5, total hardness of 470 mg/l and a conductivity of 24.4 mS). Experimental conditions: source; 200 ml river water, sorbent; 2.0 g of MBID /SDS/Al₂O₃, eluent; 2 ml of 0.15 M sulfosalycilic acid with a flow rate of 2 ml/min at pH 1.5

Copper ion spiked (μg)	Copper ion found (μg) ±SD(n=3)
8.50	8.63 ±1.21
8.00	8.18 ± 0.87
8.30	8.73 ±1.52

ery of copper ion at the optimum experimental conditions applied for sorption/desorption of copper ion.

Analysis of real samples

In order to assess the applicability of the method to the analysis of real samples, recovery of spiked copper ions from Coar River water (Fars province, Iran) was studied. The results along with the quality of Coar River water are shown in Table 3.

CONCLUSIONS

The proposed method has advantages of good selectivity and simplicity, as there is no need for an additional elution step. It can selectively separate copper ion from other metal ions of much higher concentrations. The method can be successfully applied to the separation and determination of copper in river water samples. The R.S.D. of method was found to be 4.91%.

REFERENCES

1. Christian, G. D.; *Analytical chemistry*, Jhon Wiley & Sons, INC. New York, 1994.
2. Sachsenberg, S.; Klenke, T.; Krumbein, W. E.; Zeeck, E. *Fresenius J. Anal. Chem.* 1992, *342*, 163.
3. Zhang, X. Y.; Keiichi, S.; Satoh, S. A.; Sawada, K.; Suzuki, T. *Anal. Sci.* 1997, *13*, 891.
4. Wu, J.; Boyle, E. A. *Anal. Chem.* 1997, *69*, 2464.
5. Itoh, J. L.; Miyake, T.; Komata, M.; *Nipp on Kagaku Kaishi* 1996, *7*, 645.
6. Atanasova, D.; Stefanova, V.; Russeva, E. *Talanta* 1998, *45*, 857.
7. Santelli, R. E.; Gallego, M.; Valcarcel, M. *Talanta* 1994, *41*, 817.
8. Uzawa, A.; Narukawa, T.; Okutani, T. *Anal. Sci.* 1998, *14*, 395.
9. Elci, L.; Soylak, M.; Dogan, M. *Fresenius J. Anal. Chem.* 1992, *342*, 175.
10. Jain, V. K.; Sait, S. S.; Shrivastav, P.; Agrawal, Y. K. *Talanta* 1997, *45*, 397.
11. Taher, M. A. *J. Anal. Chem.* 2001, *56*, 149.
12. Taher, M. A.; Puri, B. K. *Indian J. Chem. Tech.* 2000, *7*, 168.
13. Taher, M. A. *Microchim. Acta* 2003, *141*, 101.
14. Taher, M. A. *Asian J. Chem.* 2003, *15*, 1266.
15. Taher, M. A.; Bansal, H.; Puri, B. K. *Anal. di Chimica* 2001, *91*, 649.
16. Cui, Y.; Jiang, G.; Lin, J.; He, B. *Anal. Sci.* 2002, *18*, 705.
17. Bati, B.; Cesur, H. *Anal. Sci.* 2002, *18*, 1273.
18. Hiraide, M.; Ishikawa, A. *Anal. Sci.*, 2002, *18*, 199.
19. Hiraide, M.; Itoh T. *Anal. Sci.*, 2004, *20*, 231.
20. Cheng, K. L.; Ueno, K.; Imamura, T. *Handbook of Organic Analytical Reagents*, Vol. 365, CRC Press Inc., 1982; p 484.
21. Bagheri, A.; Gholami, A.; Najafi, A. *Anal. Chim. Acta* 2000, *424*(2), 233.
22. Absalan, G.; Ayatollahi Mehrdjardi M. *Separation and Purification Technology*. 2003, *33*, 95.