

Solid-Phase Extraction of Copper with Lead 4-benzylpiperidinedithiocarbamate on Microcrystalline Naphthalene and its Spectrophotometric Determination

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Received 24.09.2001

Using lead 4-benzylpiperidinedithiocarbamate complex ($\text{Pb}(4\text{-BPDC})_2$), a solid-phase extraction method was developed for pre-concentration and spectrophotometric determination of copper in water samples. In this method, copper in large volume liquid phase quantitatively replaces lead on colorless $\text{Pb}(4\text{-BPDC})_2$ complex and naphthalene solid phase mixture forming Cu-4-benzylpiperidinedithiocarbamate complex ($\text{Cu}(4\text{-BPDC})_2$). The solid phase containing colored $\text{Cu}(4\text{-BPDC})_2$ is dissolved in chloroform and its absorbance is measured at 437 nm against the reagent blank. The range of linearity is 0.4 -10 μgml^{-1} of copper in chloroform, the molar absorptivity of the complex determined from the linear portion of Beer's law plot is $8.197 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and the sensitivity is $0.0013 \mu\text{gcm}^{-2}$ for an absorbance of 0.001.

Key Words: Solid-phase extraction, copper, 4-benzylpiperidinedithiocarbamate, UV-VIS spectrophotometry, microcrystalline naphthalene

Introduction

The dithiocarbamate solvent extraction method is one of the most widely used pre-concentration techniques for trace metal analysis by UV-VIS spectrometry¹⁻³, AAS⁴⁻¹³, HPLC¹⁴⁻¹⁸, NAA¹⁹⁻²¹ and voltametry²². However, in comparison with solvent extraction, solid-phase extraction has some advantages: it is rapid and simple and allows pre-concentration from a larger volume of sample. Thus, the dithiocarbamate solid phase extraction technique has become widespread lately for the pre-concentration of some metals²³⁻³¹. In these works, because ammonium or alkali metal salt of dithiocarbamic acids are used as the reagent, several metals are simultaneously extracted with a solid adsorbent such as activated carbon²³⁻²⁵, microcrystalline naphthalene²⁶⁻²⁸, microfiber filter²⁹ and XAD-2 resin³⁰⁻³¹. Selective extraction of the metal is very important for UV-VIS spectrophotometry due to interferences. It may be achieved by the adjustment of pH or the addition of masking agents. Because of the fast decomposition of dithiocarbamate anions in

acid solutions, the pH should not be reduced extremely and using only masking agents is not successful under certain conditions³².

Dithiocarbamate complexes are more stable in acid solutions and can be successfully used as reagent for the extraction of several metals in liquid-liquid extraction techniques³²⁻³⁴. Recently, using solid metal dithiocarbamate, a new solid-phase extraction method has been described for the determination of copper, cadmium and nickel by FAAS³⁵⁻³⁶.

In this work, a Pb(4-BPDC)₂-naphthalene mixture was used as a new adsorbent for the solid phase extraction of copper in water samples, and UV-VIS spectrometry was selected for the measurement of copper because it is easy and convenient and more economical than AAS. This method is based on the fact that the extraction constant of the Cu(4-BPDC)₂ complex is greater than that of the Pb(4-BPDC)₂ complex. Therefore, Cu(II) in water rapidly exchanges for Pb(II) on Pb(4-BPDC)₂-naphthalene solid phase. Cu(4-BPDC)₂-naphthalene solid phase can be easily dissolved in chloroform and its absorbance can be measured by a UV-VIS spectrophotometer. The aim of this work was to investigate the optimum conditions for the selective pre-concentration of copper in various samples.

Experimental

Apparatus and Reagents

The spectrophotometric measurements were carried out on a UNICAM UV2 spectrophotometer. pH was measured with a JENWAY 3040 model digital pH-meter. The potassium salt of 4-benzylpiperidinedithiocarbamic acid (K4-BPDC) was prepared according to the method given in the literature¹⁷. Cu(II) stock solution (1.000 mgml⁻¹) was prepared by dissolving the appropriate amount of metallic copper (Merck, 99.5%) in a mixture of concentrated nitric acid, evaporating to dryness and dissolving the residue in concentrated nitric acid and completing up to 1000 ml with deionized water. Deionized water was produced by ELGA Maxima Ultra Pure Water Systems. All other reagents were analytical reagent grade.

Preparation of Pb(4-BPDC)₂-Naphthalene Mixture

0.1 mol Pb(4-BPDC)₂ complex was precipitated under stoichiometric conditions using Pb(NO₃)₂ and K4-BPDC solutions in equal volume in water. Naphthalene in acetone was added to the mixture, which was stirred for 24 hours and then filtered, and the solid product was washed with deionized water. In the solid product, the (Pb(4-BPDC)₂-naphthalene ratio was nearly 1/1 (w/w) and it was stored in a flask.

General Procedure

A solution of 1000 ml, containing 1-50 µg of the metals, was placed in a flask and 20 ml of acetate buffer solution (pH ~ 4.5-5) was added. Adding 0.50 g Pb(4-BPDC)₂-naphthalene mixture, the contents were stirred for 10 min, filtered and washed with deionized water. The adsorbent containing copper complex was dissolved in 5.0 ml of chloroform and its absorbance was measured by UV-VIS spectrophotometer.

Results and Discussion

Effect of pH

100 ml solution containing 25 μg of copper solution was obtained and its pH was adjusted with HNO_3 and KOH solutions. The other parameters being constant, the general procedure was applied and the concentration of copper was measured by UV-VIS spectrometer. The results are presented in Fig 1. An optimum pH of 4-5 was selected for extraction.

Effect of Aqueous Phase Volume

Solutions containing 25 μg of copper were diluted from 50 to 4000 ml by deionized water and copper was analyzed by the general procedure. It was observed that the adsorption of copper remained constant up to 4000 ml. The volumes higher than 4000 ml were not studied because of practical difficulties. The volume of aqueous phase is an important factor for the adsorption of metals. They indicated that the exchange reaction of copper is rapid and the efficiency is high.

Effect of Extraction Time

1000 ml solution containing 25 μg copper was extracted for various periods according to the procedure described previously and the absorbance of copper was measured by UV-VIS spectrometry. The results are presented in Fig 2. It was observed that quantitative extraction of Cu was completed in 10 min. An extraction period of 10 minutes was selected.

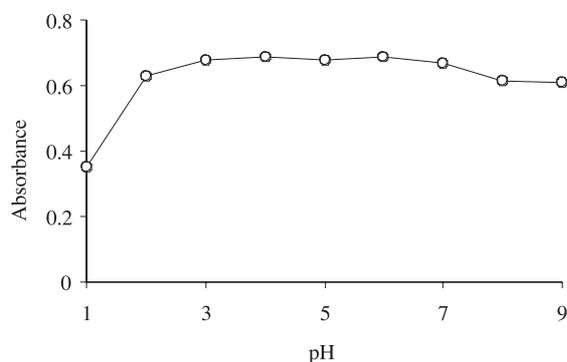


Figure 1. The effect of pH for the extraction of copper

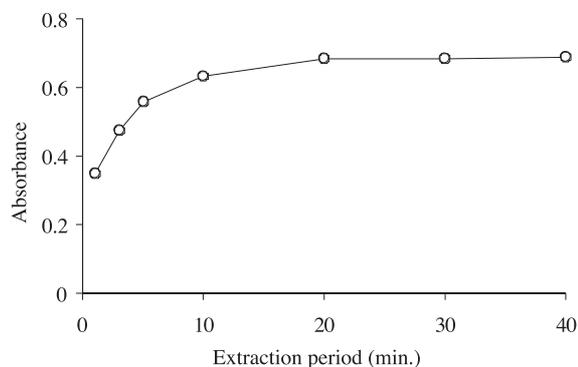


Figure 2. The effect of extraction period for the extraction of copper

Effect of Diverse Ions

100 ml of sample solutions containing 25 μg copper and different amounts of alkali metal or other metal salts were prepared and the determination of copper content was carried out by the general procedure. Tolerance limits were determined as the amount causing an error of $\pm 5\%$ in absorbance. The results are given in Table 1. Many of the salts and metal ions can be tolerated up to gram levels. It is observed that EDTA, cyanide and mercury have interference effects for the determination of copper.

Table 1. Effect of diverse ions for the determination of copper

Diverse ions (mg l ⁻¹)	Tolerance limit*
NaNO ₃ , NaCl, NaBr, NaF, sodium acetate, sodium tartrate, sodium citrate, sodium oxalate	> 50000
NaI	13000
ZnCl ₂ , Cd(NO ₃) ₂ , Co(NO ₃) ₂ , Mn(NO ₃) ₂ , ^a Fe(NO ₃) ₃ , ^b Bi(NO ₃) ₃ , CrCl ₃ , Ni(NO ₃) ₂	> 5000
Bi(NO ₃) ₃ ,	200
Fe(NO ₃) ₃ ,	180
Hg(NO ₃) ₂	30
Na ₂ EDTA	20
NaCN	4

Aqueous phase volume: 100 ml, copper 25 µg, pH 4-5 and 5 ml final chloroform
Tolerance limit was taken as the amount causing an error of ± 5% in absorbance
^aMasked with 5g of NaF, ^bMasked with 5g of sodium tartarate.

Calibration Curve, Linearity and Sensitivity

UV-VIS spectra of Cu(4-BPDC)₂ and reagent blank (Pb(4-BPDC)₂- naphthalene) in chloroform are presented in Fig 3. The calibration graph was constructed with ten standard solutions containing 0.1-20 µgml⁻¹ of copper according to the general procedure. The range of linearity was 0.4-10 µgml⁻¹ of copper in chloroform (the formula for the best line of calibration, $Y = 0.1182X + 0.0164$, and the correlation coefficient was obtained with the method of least squares, $R^2 = 0.9984$). The molar absorptivity of the complex determined from the linear portion of Beer's law plot is $8.197 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and the sensitivity is $0.0013 \text{ µg cm}^{-2}$ for an absorbance of 0.001.

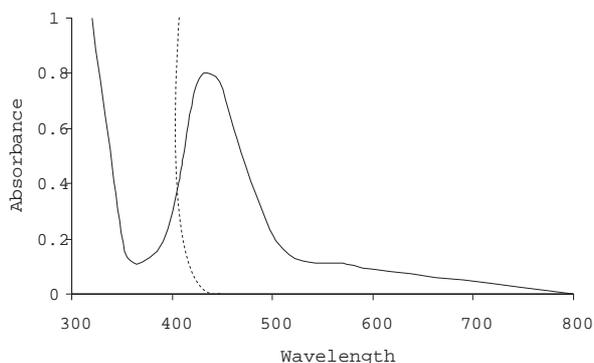


Figure 3. UV-VIS Spectra; (—)Cu(4-BPDC)₂(10⁻⁴mol l⁻¹), (- - -)Pb(4-BPDC)₂ (10⁻² mol l⁻¹) and naphthalene (50.0 g l⁻¹) in chloroform

Determination of Cu in Water Samples

Various water samples were used for the determination of copper. Tap water samples were obtained from Ondokuz Mayıs University and seawater samples were obtained from the coast at Samsun (Black Sea). The samples were filtered and HNO₃ was added to produce a pH below 2 for storage. Prior to analyses, the pH

values were adjusted by acetate buffer and the samples were analyzed by the general procedure. The results are given in Table 2.

Table 2. Determination of copper in water samples

Name of sample	Taken copper (μgl^{-1})	Found* (μgl^{-1})	Recovery (%)
Deionized water	2.00	1.98 ± 0.08	99.0
Tap water	-	0.75 ± 0.13	-
Sea water	-	2.25 ± 0.14	-

*Mean of four determinations with 95% confidence level ($X \pm ts / \sqrt{N}$).

Determination of Cu in Standard Metal Alloys

1.0000 g sample of the alloy was placed in a 100 ml beaker and 10 ml of concentrated HNO_3 was added. The mixture was heated on a hot plate until near dryness. Then 5 ml of concentrated nitric acid was added and the contents were diluted with deionized water to a volume of about 500 ml. The solution was filtered and the volume was completed to 1000 ml in a standard flask. An aliquot of the solution was taken and copper was determined by the proposed method. The results are given in Table 3.

Table 3. Determination of copper in various alloys

Name of the alloy	Certified composition(%)		Taken copper (μgl^{-1})	Found* (μgl^{-1})
C12X3500 Mild steel	C: 0.18 Si: 0.45 S: 0.032 P: 0.029 Mn: 0.70 Ni: 0.18 Cr: 0.31 Mo: 0.10	Co: 0.005 Sn: 0.03 Al: 0.35 W: 0.29 Ti: 0.054 V: 0.02 As: 0.070 Cu: 0.15	15.0	14.8 ± 0.9
C14XHS 50 High speed steel	C: 0.59 Si: 0.30 S: 0.022 P: 0.017 Mn: 0.29 Ni: 0.14	Cr: 3.40 Mo: 3.54 Co: 8.02 W: 6.0 V: 1.37 Cu: 0.13	13.0	13.4 ± 0.7
CX2871830 Inconel type alloy	C: 0.19 Si: 0.38 S: 0.05 P: 0.026 Mn: 0.47 Ni: 54.8 Cr: 0.31	Mo: 3.31 Co: 1.0 Ti: 1.40 Al: 1.77 Fe: Rem. Cu: 0.35	17.5	16.3 ± 1.1

*Mean of four determinations with 95% confidence level ($X \pm ts / \sqrt{N}$).

Conclusion

Dithiocarbamate reagents do not react with alkali or earth alkali metals that are fairly abundant in environmental samples. From this point of view, the proposed method is highly selective for the pre-concentration

of Cu(II) in water samples. Furthermore, because the extraction or stability constants of the Pb(4-BPDC)₂ complex are higher than those of many metal 4-BPDC complexes (such as Co, Fe, Ni, Mn, Tl and Cr), the use of Pb(4-BPDC)₂ complex in the extraction based on replacement is a reason for increased selectivity; on the other hand, the latter is more stable in acidic aqueous solutions. Therefore, the use of the Pb(4-BPDC)₂ complex, for the pre-concentration and UV-VIS spectrophotometric determination of Cu(II) in aqueous solutions, is more suitable than the alkali salt of dithiocarbamic acids. Moreover, the selectivity of the extraction of copper can be increased by using masking agents.

The adsorption mechanism of copper on Pb(4-BPDC)₂ is not known but we estimate that it is similar to the metal-exchange reaction in liquid-liquid extraction as given below:



Consequently, the method is simple, selective and accurate. It can be used for the determination of Cu in water samples, alloys and other materials.

References

1. N. Sing, K. Rostagi, R. Kumar, T. N. Srivastava, **Analyst**, **106**, 599-602 (1981).
2. A. Kumar, M.F. Hussain, M. Stake, B.K. Puri, **Chimica Acta Turcica**, **11**, 337-344 (1983).
3. B. Bati, H. Cesur, H. Bati, M. Özdemir, **Tr. J. of Chemistry**, **19**, 66-72 (1995).
4. K. Kremling, H. Petersen, **Anal. Chim. Acta**, **70**, 35-39 (1974).
5. J.D. Kinrade, J.C. Van Loon, **Anal. Chem.**, **46**, 1894-1898 (1974).
6. K.T. Jan, D.R. Young, **Anal. Chem**, **50**, 1250-1253 (1978).
7. L.G. Danielsson, B. Magnusson, S. Westerlund, **Anal. Chim. Acta.**, **98**, 47-57 (1978).
8. W.K. Bruland, R.P. Franks, **Anal. Chim. Acta**, **105**, 233-245 (1979).
9. B. Magnusson, S. Westerlund, **Anal. Chim. Acta**, **131**, 63-72 (1981).
10. J.M. Lo, J.C. Yu, F.I. Hutchison, C.M. Wai, **Anal. Chem.**, **54**, 2536-2539 (1982).
11. Y. Shijo, T. Shimuzu, T. Tsunoda, T. Shiquan, M. Suzuki, **Anal. Chim. Acta.**, **242**, 209-213 (1991).
12. S. Sachsenberg, T. Klenke, W.E. Krumbein, E. Zeeck, **Fresenius. J. Anal. Chem.**, **342**, 163-166 (1992).
13. H. Segawa, Y. Sohrin, M. Matsu, M. Hojo, M. Kawashima, **Anal. Chem.**, **66**, 1247-1252 (1994).
14. A.M. Bond, G.G. Wallace, **Anal. Chem.**, **55**, 718-723 (1983).
15. H. Irth, G.J. Jong, U.A. Brinkman, R.W. Frei, **Anal. Chem.**, **59**, 98-101 (1987).
16. J.N. King, J.S. Fritz, **Anal. Chem**, **59**, 703-708 (1987).
17. A.M. Bond, T.P. Majewski, **Anal. Chem.**, **61**, 1494-1496 (1989).
18. A.M. Bond, G.G. Wallace, **Anal. Chem**, **53**, 1209-1213 (1981).
19. W.M. Mok, C.M. Wai, **Anal. Chem.**, **56**, 27-29 (1984).
20. P.C. Erkelens, **Anal. Chim. Acta**, **26**, 32-45 (1962).

21. A. Wytenbach, S. Bajo, **Anal. Chem.**, **47**, 2-7 (1975).
22. C.M. Lo, J.D. Lee, **Anal. Chem.**, **66**, 1242-1248 (1994).
23. M. Soy lak, L. Elci, M. Dogan, **Fresenius Envir. Bull.**, **5**, (3-4) 148-155 (1996).
24. G.R. Boaventura, J.D. Hirson, R.E. Santelli, **Fresenius J. Anal. Chem.**, **350**, (10-11), 651-652 (1994).
25. M. Yaman, Ş. Güçer, **Fresenius J. Anal. Chem.**, 350-504 (1994).
26. A. Kumar, M. Jain, B.K. Puri, **Chim. Acta Turcica**, **18**, 155-161 (1990).
27. S. Puri, R.K. Dubey, B.K. Puri, M.F. Hussain, **Anal. Lett.**, **31**, (2), 283-297 (1998).
28. R.K. Dubey, S. Puri, M.K. Gupta, B.K. Puri, **Anal. Lett.**, **31**, (15), 2729-2746 (1998).
29. Z. Aneva, S. Stamo v, I. Kalaydjieva, **Anal. Lab.**, **6**, (2), 67-71 (1997).
30. K. Anezaki, X.Z. Chen, T. Ogasawara, I. Nukatsuka, K. Ohzeki, **Anal. Sci.**, **14**, (3), 523-527 (1998).
31. M. Soy lak, L. Elci, **Int. J. Envir. Anal. Chem.**, **66**, (1), 51-59 (1997).
32. A. Wytenbach, S. Bajo, **Anal. Chem.**, **47**, 1813-1817 (1975).
33. A.R.K. Dapaah, N. Takano, A. Ayame, **Anal. Chim. Acta**, **386**, (3), 281-286 (1999).
34. A.R.K. Dapaah, A. Ayame, **Anal. Chim. Acta**, **360**, (1-3), 43-52 (1998).
35. H. Cesur, B. Bati, **Anal. Lett.**, **33**, (3), 489-501 (2000).
36. H. Cesur, M. Macit, B. Bati, **Anal. Lett.**, **33**, (10), 1991-2004 (2000).