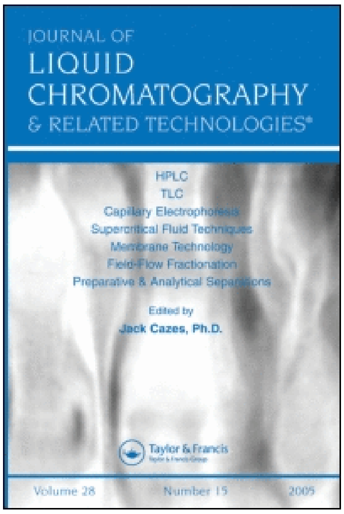

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Liquid Chromatographic Determination of Co(II), Cu(II), Ni(II), and Fe(II) using Di-2-pyridylketon Thiosemicarbazone (DPKT) as Derivatizing Reagent

Bürge Aşçı[a]; Güzin Alpdoğan[a]; Sıdıka Sungur[a]
[a] Department of Chemistry, Yıldız Technical University, Davutpaşa, İstanbul, Turkey

To cite this Article Aşçı, Bürge , Alpdoğan, Güzin and Sungur, Sıdıka(2008) 'Liquid Chromatographic Determination of Co(II), Cu(II), Ni(II), and Fe(II) using Di-2-pyridylketon Thiosemicarbazone (DPKT) as Derivatizing Reagent', Journal of Liquid Chromatography & Related Technologies, 31: 9, 1299 — 1305

To link to this Article: DOI: 10.1080/10826070802019731

URL: http://dx.doi.org/10.1080/10826070802019731

Journal of Liquid Chromatography & Related Technologies®, 31: 1299–1305, 2008

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070802019731

Liquid Chromatographic Determination of Co(II), Cu(II), Ni(II), and Fe(II) using Di-2-pyridylketon Thiosemicarbazone (DPKT) as Derivatizing Reagent

Bürge Aşçı, Güzin Alpdoğan, and Sıdıka Sungur

Department of Chemistry, Yıldız Technical University, Davutpaşa,
İstanbul, Turkey

Abstract: Di-2-pyridyl ketone thiosemicarbazone (DPKT) was examined as a precolumn chelating reagent for high performance liquid chromatographic separation of Co(II), Cu(II), Ni(II), and Fe(II) ions as metal chelates on a 10 μm Bondapak C_{18} (300 mm × 3.9 mm) RP column. A gradient program with a mobile phase of acetonitrile and 0.01 M pH:6.0 acetate buffer is used. Acetonitrile composition is increased from 25 to 40% at 18 min and held at 40% for 18 min. A UV detector was used at 400 nm. The flow rate was 1.5 $\text{mL} \cdot \text{min}^{-1}$. Limit of detection was determined on a 3σ blank basis. Interference effects from other metal ions were also investigated. The method was applied for the determination of Co(II), Cu(II), Ni(II), and Fe(II) ions in drinking and tap water samples.

Keywords: HPLC, Co(II), Cu(II), Ni(II), Fe(II), Thiosemicarbazone

INTRODUCTION

A number of complexing reagents have been used for high performance liquid chromatographic determination of nickel, copper, iron, and cobalt.[1–6] Thiosemicarbazones are interesting reagents for metal ions, because they form highly stable and intensely coloured complexes immediately, by bonding through the sulphur and hydrazine nitrogen atoms, which are used for spectrophotometric,[7–9] HPLC,[10,11] voltammetric,[12,13] determinations and preconcentrations[14–16] for metal ions.

Correspondence: Dr. Bürge Aşçı, Department of Chemistry, Yıldız Technical University, Davutpaşa 34220, İstanbul, Turkey. E-mail: burgeasci@yahoo.de

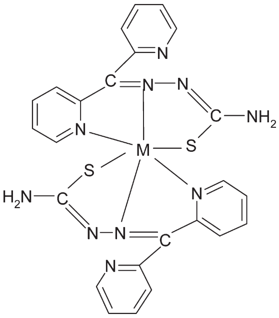

Figure 1. Metal-DPKT complexes.

In the present paper, DPKT (Figure 1) has been assessed for the HPLC determination of Co(II), Cu(II), Ni(II), and Fe(II) ions simultaneously.

EXPERIMENTAL

Reagents and Materials

DPKT was synthetized according to Martinez, Valcarcel, and Pino's method,[17] and its 0.5% solution in ethanol was prepared. This solution was stable for at least a week. Co(II), Cu(II), Ni(II), Fe(II) standard solutions (1000 ppm) (Fluka) were used as suitable dilutions daily. pH 6.0 buffer solutions (0.1 M for precolumn derivatization and 0.01 M for mobile phase preparation) were prepared from CH_3COONa and CH_3COOH in water. Solutions of diverse ions for the interference studies, were prepared by dissolving the calculated amount of each compound in order to give required concentrations of each species. All solutions were prepared with analytical grade chemicals and milliQ water. For mobile phase preparation, HPLC grade acetonitrile and milliQ water were used.

Drinking and tap water samples were collected from markets and the municipial water supplies of Yıldız Technical University Davutpaşa Campus in February 2005. The samples were filtered through a cellulose membrane (Millipore) of pore size 45 μm and stored in 1 liter polyethylene bottles, then they were acidified to 1% with concentrated nitric acid (65%), and were refrigerated at 4°C until analysis.

Apparatus

For spectrophotometric measurements, a Philips 8740 UV/VIS spectrophotometer and 10 mm quartz cells were used. All spectra were recorded from

190 nm to 500 nm with 1 nm slit width, 250 nm min^{-1} scan speed, and very high smooting. Chromatographic analyses were performed using a Shimadzu HPLC system consisting of a model LC-20 AT pump unit, SPD-20A uv-vis dedector, 7725 20 μL sample injection and a computer. A 10 μm alphabond C_{18} (300 mm × 3.9 mm) RP column was used. A gradient program with a mobile phase of acetonitrile and 0.01 M pH:6.0 buffer is used. Acetonitrile composition is increased from 25 to 40% at 18. min. and held at 40% for 18 min. The flow rate was $1.5\ \text{mL} \cdot \text{min}^{-1}$. A UV detector was used at 400 nm.

Analytical Procedure

An aliquat of standard solution containing 0.5–25 μg of Co(II), Cu(II), Ni(II), Fe(II), was transferred to a 5 mL volumetric flask, 1 mL of the reagent solution was added, and the contents were mixed well. This was followed by 1 mL of 0.1 M pH 6 acetate buffer and the volume was adjusted with water. Of this solution, 20 μL was injected onto the column and the complexes were eluted.

For the analysis of drinking and tap water samples various amounts of analyte ions were added to the samples and the above analytical procedure was applied.

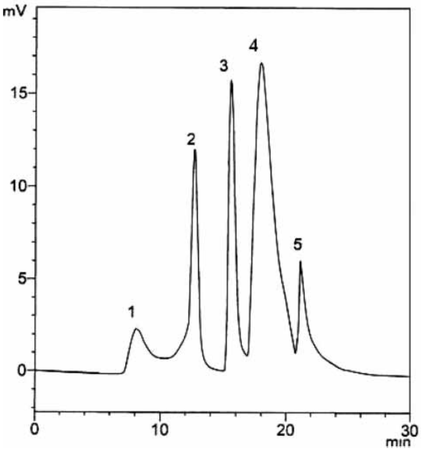

Figure 2. Chromatogram of 1) DPKT, 2) Ni (II), 3) Fe(II), 4) Cu(II), and 5) Co(II) chelates on a 10 μm Bondapak C_{18} column (300 mm x 3.9 mm) with elution of acetonitrile and 0.01 M pH: 6.0 acetate buffer. Acetonitrile composition is increased from 25 to 40% at 18 min. and held at 40% for 18 min. The flow rate was $1.5\ \text{mL} \cdot \text{min}^{-1}$. UV detection was used at 400 nm.

Table 1. Calibration equations for HPLC

Metal	Linearity range (ng)	Correlation coefficient	Dedection limits (ng)
Nickel	2–100	0.9991	0.16
Iron	2–100	0.9999	0.12
Copper	2–100	0.9993	0.11
Cobalt	4–200	0.9990	0.30

RESULTS AND DISCUSSION

Complexation and Spectrophotometric Properties

The reagent reacts with Co(II), Cu(II), Ni(II), and Fe(II), ions in an aqueous ethanolic solution to form water soluble colored complexes in the pH range of 4–10. The maximum colour of metals occured at pH 6. The colours of the complexes are highly stable in ethanolic solution and no change in absorbance was observed for up to 24 hours. Absorption maxima of the chelates were 400 nm for all metals studied. All chelates have a metal to ligand stoichiometry of 1:2.[17]

Separation of the Chelates

Various combinations of acetonitrile and pH 6 acetate buffer were studied for the separation of chelates of Co(II), Cu(II), Ni(II), and Fe(II) ions under

Table 2. Recoveries of analytes spiked into the drinking and top water samples

Analyte	Added (ng)	Found^a (ng) Drinking water	Found^a (ng) Tap water	Recovery (%) Drinking water	Recovery (%) Tap water
Ni	0	N.D	N.D	—	—
	2.0	1.99(0.3)	2.01(0.3)	99	101
	4.0	4.01(0. 2)	40.1(0.3)	100	100
Fe	0	N.D	N.D	—	—
	2.0	1.98(0.5)	2.02(0.6)	99	101
	4.0	4.00(0.4)	4.02(0.5)	100	101
Cu	0	N.D	N.D	—	—
	2.0	1.96(0.4)	1.98(0.5)	98	99
	4.0	3.98(0.3)	39.9(0.3)	99	100
Co	0	N.D	N.D	—	—
	4.0	4.02(0.7)	4.02(0.8)	101	101
	8.0	8.01(0.5)	8.02(0.6)	100	100

^{a}Mean of five measurement (RSD%); ND: Not Detected.

isocratic conditions. However, the best separation was obtained by a gradient elution with acetonitrile and 0.01 M pH:6.0 acetate buffer solution. A typical chromatogram was obtained after injection of 20 ng of Ni(II), Cu(II), and Fe(II), and 40 ng of Co(II). Excess of the reagent added for derivatization, eluted before the metal chelates, and did not interfere with the determinations. The retention times of Ni, Fe, Cu, and Co chelates were 12.7, 15.5, 17.8, and 21.5 min, respectively (Fig. 2).

Calibration and Determination

For the quantitative determination of the mixtures containing Co, Cu, Ni, and Fe ions, calibration graphs were prepared using the external calibration method. Linear calibration ranges and detection limits are shown in Table 1.

Table 3. Tolerance limits of interferents (for ≤ ± 3% error)

Interferent ion	Interferent/ Ni(II) mole ratio	Interferent/ Fe(II) mole ratio	Interferent/ Cu(II) mole ratio	Interferent/ Co(II) mole ratio
Co(II)	50	50	50	—
Fe(II)	50	—	50	30
Cu(II)	50	50	—	30
Ni(II)	—	50	50	30
Cd(II)	50	50	50	30
Hg(II)	50	50	50	30
Zn(II)	50	50	50	30
Bi(II)	50	50	50	30
Pb(II)	50	50	50	30
Mn(II)	250	250	250	250
Al(III)	250	250	250	250
Cr(III)	250	250	250	250
Ca(II)	1000	1000	1000	1000
Mg(II)	1000	1000	1000	1000
Ba(II)	1000	1000	1000	1000
Na(I)	1000	1000	1000	1000
K(I)	1000	1000	1000	1000
Cl^-	1000	1000	1000	1000
F^-	1000	1000	1000	1000
SO_4^{2-}	1000	1000	1000	1000
NO_3^-	1000	1000	1000	1000
$C_2O_4^{2-}$	1000	1000	1000	1000
$C_4H_5O_7^{3-}$	1000	1000	1000	1000
$C_4H_4O_6^{2-}$	1000	1000	1000	1000
HPO_4^{2-}	1000	1000	1000	1000
HCO_3^-	1000	1000	1000	1000

The reproducibility of the method was determined for 5 replicate injections of 20 ng of Ni(II), Fe(II), and Cu(II), and 40 ng of Co(II), and RSD values were found to be 0.3, 0.6, 0.5, and 0.8 for Ni, Fe, Cu, and Co, respectively. The method was applied to the determination of nickel, copper, iron, and cobalt in drinking and top water samples using the standard addition calibration technique. The results are given Table 2.

The results obtained with the proposed method were in good agreement with the indicated value for each sample.

Interferences

Interference effects of various ions found in water samples were tested by adding to the sample the solutions containing Co(II), Cu(II), Ni(II), and Fe(II). A foreign ion was considered as interfering if it produced an error in the peak height of more than $\pm$ 3%. Calculated tolerance limits are shown in Table 3.

CONCLUSION

In this work, a simple and sensitive reversed phase HPLC method has been developed for the determination of Co(II), Cu(II), Ni(II), and Fe(II) ions simultaneously. DPKT has been examined as a precolumn chelating reagent. This reagent can be easily prepared from inexpensive chemicals with a good yield and reacts immediately with a limited number of metal ions to form stable coloured complexes. A number of cations and anions did not interfere with the determination. The applicability of the method for the determination of the above metals in drinking and tap water samples has been tested using the standard addition technique and satisfactory results were obtanined.

REFERENCES

1. Hu, Q.F.; Wu, X.H.; Yang, G.Y. Study on the determination of Cobalt, Nickel, Copper, Zinc and Vanadium in environmental samples by a rapid high-performance liquid chromatograpy. J. Chinese Chem. Soc. **2005**, *52* (2), 277–282.
2. Atanassova, A.; Lam, R.; Zamble, D.B. A high performance liquid chromatograpy method for determining transition metal content in proteins. Anal. Biochem. **2004**, *355* (1), 103–111.
3. Hu, Q.F.; Yang, G.Y.; Li, H.T. Study on determination of seven transition metal ions in water and food by microcolumn high-performance liquid chromatograpy. Bull. Korean Chem. Soc. **2004**, *25* (5), 694–698.
4. Hu, Q.F.; Yang, G.Y.; Yang, J.H. Study on determination of iron, cobalt, nickel, copper, zinc and manganese in drinking water by solid phase extraction and RP-HPLC with 2-2-quinolinylazo-5-diethylaminophenol as precolumn derivatizing reagent. J. Environ, Monit. **2002**, *4* (6), 956–959.

5. Memon, S.A.; Dalziel, J.A.W. Elution of copper(II), nickel(II), cobalt(II), and zinc(II), and the separation of nickel(II), palladium(II), and platinium(II) complexes of quinoxaline-2,3-dithiol, using reversed phase ion-pair HPLC. J. Chem. Soc. Pakistan **2002**, *23* (4), 234–237.
6. Khuhavar, M.Y.; Lanjwani, S.N. High-performance liquid chromatographic Separation and UV determination of cobalt, copper, iron and platinum in pharmaceutical preparations using bis (isovalerylacetone) ethylenediimine as complexing reagent. Mikrochimica Acta **1988**, *129* (1–2), 65–70.
7. Ramanjaneyulu, G.; Redd, P.R.; Reddy, V.K.; Reddy, T.S. Direct and derivative spectrophotometric determination of cobalt with 5-bromasalicylaldehyde thiosemicarbazone. J. İndian Chem. Soc. **2003**, *80* (8), 773–776.
8. Ramanjaneyulu, G.; Redd, P.R.; Reddy, V.K.; Reddy, T.S. Spectrophotometric determination of iron in trace amount using 5-bromo-salicylaldehyde thiosemicarbazone Indian. J. Chem. Sect. A Inorg. Bioinorg. Phys. Theoret. & Anal. Chem. **2002**, *41* (7), 1436–1437.
9. Sarma, L.S.; Ramesh, G.N.; Kumar, C.J.; Reddy, A.V. Sensitive extractive spectrophotometric determination of iron with pyridoxal-4 phenyl-3-thiosemicarbazone. J. İndian Chem. Soc. **2000**, *77* (8), 405–406.
10. Khuhawar, M.Y.; Arain, G.M. Liquid chromatographic determination of cis-platin as platinum(II) in pharmaceutical preparation, serum and urine samples of cancer patients. Talanta **2005**, *66* (1), 34–39.
11. Khuhavar, M.Y.; Lanjwani, S.N. Solvent extraction and HPLC determination of copper, iron, nickel and mercury in water and fishes as 2-pyrrolaldehyde-4-phenyl-3-thiosemicarbazone as derivatizing reagent. J. Chem. Soc. Pakistan **2001**, *23* (3), 157–162.
12. Qu, J.Y.; Liu, M.K.Z. Simultaneous determination of lead and copper by carbon paste electrode modified with pyruvaldehyde bis(N,N′-dibutyl thiosemicarbazone). Anal. Lett. **1999**, *32* (10), 1991–2006.
13. Chang, C.H.; Liu, C.Y. Preconcentration and determination of copper(II) at a chemically modified electrode containing salicylaldehyde thiosemicarbazone. J. Chinese Chem. Soc. **1997**, *44* (3), 231–236.
14. Baytak, S.; Balaban, A.; Turker, A.R. Atomic absorption spectrometric determination of Fe(III), and Cr(III) in various samples after preconcentration by solid-phase extraction with pyridine-2-carbaldehyde thiosemicarbazone. J. Anal. Chem. **2006**, *61* (5), 476–482.
15. Aşçı, B.; Alpdogan, G.; Sungur, S. Preconcentration of some trace metal ions from drinking and tap water samples by sorption on amberilte XAD-4 after complexation with di-2-pyridylketonethiosemicarbazone. Anal. Lett. **2006**, *39*, 997–1007.
16. Khuhawar, M.Y.; Das, P.; Dewani, V.K. Preconcentration and atomic absorptin spectrometric determination of cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc in water samples using 6-methyl-2-pyridinecarboxaldehyde-4-phenyl-3-thiosemicarbazone. J. Chem. Soc. Pakistan **2005**, *27*, 160–162.
17. Martinez, M.P.; Valcarcel, M.; Pino, F. Di-2-pyridyl ketone thiosemicarbazone as an analytical reagent. Anal. Chim. Acta **1976**, *81*, 157–165.

Received December 10, 2007
Accepted December 26, 2007
Manuscript 6246