

## Separation of Copper(II), Nickel(II) and Palladium(II) Complexes of Bis(O-hydroxyacetophenone)ethylenediimine by HPLC

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**Summary:** The separation between copper, nickel and palladium complexes of bis(O-hydroxyacetophenone)ethylenediimine has been achieved, on a stainless steel column (2.6mm x 250mm) packed with aluminium oxide (LiChrosorb Altex T 5 $\mu$ m). The complexes were eluted with 60:40 chloroform:n-hexane solvent system with the flow rate of 1.5ml min<sup>-1</sup> and the absorbance was measured at  $\lambda$  260nm using a UV detector. The linear calibration range with detection limits for copper, nickel and palladium complexes at lower ng levels have been ascertained.

### Introduction

The reagent bis(O-hydroxyacetophenone)ethylenediimine (HAP<sub>2</sub>en) has been widely used as complexing agent for a number of metal ions. The studies were focused at different structural aspects of both, the reagent and its metal complexes, as a useful spectrophotometric reagent and its potential use in solvent extraction of metal ions [1-9].

The metal complexes prepared from tetradentate Schiff bases derived from O-hydroxyacetophenone, have proved to be less useful for gas chromatographic separations of metal ions owing to their insufficient volatility and thermal stability at working temperatures. However, the use of HPLC overcomes such limitations and valuable separations has been produced with these metal complexes, using both, the normal and reverse modes of HPLC systems [10-11].

Thus, in the present work the potential use of the reagent HAP<sub>2</sub>en and its copper, nickel and palladium complexes, on normal phase HPLC has been explored.

### Experimental

The reagent HAP<sub>2</sub>en and its copper and nickel complexes were prepared by the reported method [2], and the palladium complex was prepared following the general procedure of Belcher *et al.* [12].

A Hitachi 655-11 Liquid Chromatograph equipped with a Hitachi 655-A variable wavelength detector, a Rheodyne Sample Injector with 20 $\mu$ l sample loop. The equipment is linked to a Hitachi 056 Recorder, is used throughout the work.

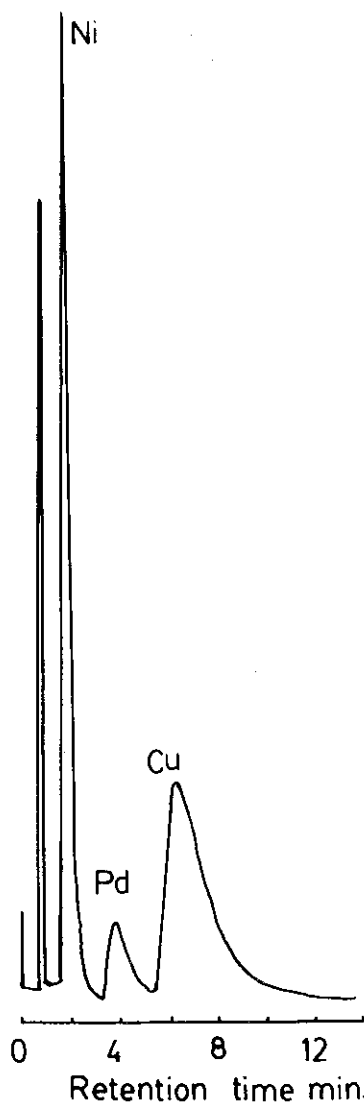


Fig.1: Chromatogram shows the separation of nickel, palladium and copper complexes of HAP<sub>2</sub>en using a 2.6 x 250mm column packed with LiChrosorb Alox T (5 $\mu$ m). The eluent was chloroform:n-hexane mixture (60:40) with  $f_c$ : 1.5 ml min<sup>-1</sup>. Detector: 260nm and 0.16 AUFS. Recorder: 0.1mv FSD with chart speed 5mm min<sup>-1</sup>.

A Stainless Steel Column 2.6 ID x 250mm long was packed with LiChrosorb Alox T 5 $\mu$ m using the balanced density technique [13,14]. Chloroform (containing 1% ethanol as

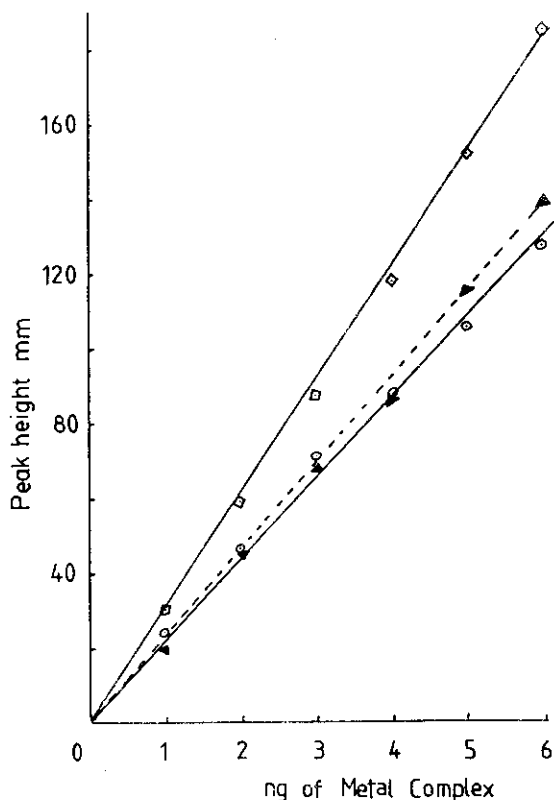


Fig.2: Calibration plots of nickel, palladium and copper complexes of HAP<sub>2</sub>en.

Ni complex x conc x 10<sup>1</sup> ng  
 Cu complex conc x 10<sup>2</sup> ng  
 Pd complex conc x 10<sup>3</sup> ng

a stabilizer) (Fluka) and n-hexane (Merck) as binary mixture (60:40) was used as the eluent.

## Results and Discussion

The chloroform solutions for each of the pure Copper(II), Nickel(II) and Palladium(II) complexes of HAP<sub>2</sub>en were injected on LiChrosorb Alox T 5, m column and eluted with a binary mixture of chloroform in n-hexane in different ratios. The optimum separation with the baseline return between copper, nickel and palladium with the elution order of nickel palladium and copper was achieved using 60:40 chloroform: n-hexane binary mixture

with the resolution factor calculated between nickel/palladium to be 1.8; palladium/copper, 1.4; and nickel/copper, 1.6. The retention volumes calculated for nickel, palladium and copper were 2.62, 4.25 and 9.8 ml respectively, with the flow rate of 1.5 ml min<sup>-1</sup>.

In order to confirm the linearity of the detector response with that of the amount of the complex injected, different amounts of each of the complexes were injected and the average peak heights of triplicate runs, measured at  $\lambda = 260\text{nm}$ , were plotted against concentration in each case. The calibration plots so obtained were linear in the concentration range 10-60ng, 1-6  $\mu\text{g}$  and 100-600ng of nickel, palladium and copper complexes respectively corresponding to 1.7-10ng nickel 0.26-1.6  $\mu\text{g}$  of palladium and 17.8-106ng of copper with the maximum detector sensitivity of 0.16 AUFS and recorder at 0.1mv FSD. The limits of detection measured at least twice the background noise were 0.2ng, 20ng and 2.0ng for nickel, palladium and copper complex respectively. These correspond to 33pg nickel, 5.3ng palladium and 355pg of copper. Thus the nickel complex show the highest sensitivity with lower detection limits of pg levels than the corresponding complexes of both copper and palladium.

### Conclusion

The separation between copper nickel and palladium complexes of bis(O-hydroxyacetophenone) ethylenediimine has been achieved on normal mode of HPLC, with the linear calibration range at ng levels and detection limits at pg levels for metal ions.

### References

1. L.A. Kazitsyna and V.V. Mishchenko, *Vestn. Mosk. Univ., Ser. H, Kim.*, **19**, 22 (1964).
2. S.N. Poddar, N.R. Sengupta and K. Day, *Science Cult. (Calcutta)*, **29**, 257 (1963).
3. S.N. Poddar, M.M. Ray and K. Day, *Science Cult. (Calcutta)*, **29**, 309 (1963).
4. A.N. Sunder Ram, S. Sarasukutty and C.P. Prabhakaran, *Curr. Sci.*, **45**, 514 (1976).
5. J. Agget, A.W. Khoo, R.A. Richardson, *J. Inorg. Nucl. Chem.*, **43**, 1967 (1981).
6. J.P. Tandon, S.R. Gupta and R.N. Prasad, *Monatsh. Chem.*, **107**, 1379 (1976).
7. R.G. Uijay and J.P. Tandon, *Monatsh. Chem.*, **107**, 95 (1976).
8. B.S. Saraswat, G. Srivastave, R.C. Mehrotra, G. Sawhney and J.S. Baljal, *J. Inorg. Nucl. Chem.*, **42**, 805 (1980).
9. G.V. Panova, V.M. Potapov, I.M. Turovets and E.G. Golub, *Zh. Obshch Khim.*, **53**, 1612 (1983).
10. M.Y. Khuhawar, Z.P. Memon, A.G. Bhatti, F.C. Nachnani and S.A. Memon, *J. Pure & Applied Sci. Bhawal. Univ.*, **4**, 35 (1985).
11. M.Y. Khuhawar and S.A. Memon, *J. Res. Bah. Zak. Univ. Multan*, (in press).
12. R. Belcher, R.J. Martin, W.I. Stephen, D.E. Henderson, A. Kamalizad and P.C. Uden, *Anal. Chem.*, **45**, 1197 (1973).
13. J.J. Kirkand, *J. Chromatogr. Sci.*, **9**, 206 (1971).
14. R.E. Majors, *Anal. Chem.*, **44**, 1722 (1972).