*Asian Journal of Chemistry* Vol. 16, No. 2 (2004), 695–698

# Reversed Phase Extraction Chromatographic Studies of Zinc, Cadmium and Mercury

H.R. AHER and S.R. KUCHEKAR*
*Department of Analytical Chemistry and Environmental Science*
*P.V.P. College, Pravaranagar, At Post Loni, Tal. Rahata, Dist. Ahmednagar, India*

A reversed phase paper chromatographic method is developed for separation of zinc, cadmium and mercury. The separations have been performed on a Whatman paper No. 1 using liquid ion exchanger *n*-octylaniline and N-*n*-octylaniline as a stationary phase while various weak acids as the mobile phase. Various experiments were carried out to study the effect of pH (4–9), concentration of mobile phase (0.01–0.1 M) and concentration of stationary phase (0.1–1.5% using chloroform as a diluent) on the $R_f$ values of individual cations. Optimum concentration of *n*-octylaniline, *N-n*-octylaniline and mobile phases were determined. The proposed method is applied for separation and detection of zinc, cadmium and mercury in pharmaceutical samples.

**Key Words: Reversed phase paper chromatography, Zinc, Cadmium, Mercury.**

## INTRODUCTION

In view of its simplicity and better resolution power, the reversed phase chromatography has become a popular separation technique. Earlier, a number of studies have been reported on separation of different metal ions using various mobile and stationary phases[1–8]. But many of the methods reported suffer on account of drawbacks like requirements of high concentration of mobile phase or developing solvent, long separation time, etc. The use of *n*-octylaniline and N-n-octylaniline synthesized in the laboratory as an extractant for some metals was investigated[9–13]. In this communication we describe a reversed phase chromatographic method for separation of mercury from zinc and cadmium and zinc from cadmium on papers impregnated with *n*-octylaniline and N-n-octylaniline and using organic complexing agents as the active mobile phases. The effect of parameters such as concentration of stationary and mobile phases and pH on $R_f$ values have been studied.

Chloroform solution of *n*-octylaniline and N-n-octylaniline were pre-equilibrated with either sodium acetate, sodium salicylate or sodium succinate and were sprayed on whatman paper-1 and used as a stationary phase. Aqueous solutions of sodium acetate, sodium salicylate and sodium succinate adjusted to required pH (using Systronics digital pH-meter 335) with dilute hydrochloric acid and

sodium hydroxide solution, were used as mobile phases. The stock solutions of Zn(II), Cd(II) and Hg(II) were prepared and standardized by standard as described earlier[14–16].

## EXPERIMENTAL

Whatman paper-1 strips (15 × 4 cm) were sprayed with *n*-octylaniline and N-*n*-octylaniline solutions and the desired metal ion solution (200–300 μg) was spotted with microcapillaries. The spot was developed by ascending technique for 10 cm in glass jars (21.5 × 5.2 cm) containing aqueous solution of either sodium acetate, sodium salicylate or sodium succinate of required pH. After development, paper was dried, cations were detected by spraying appropriate colour forming reagent and $R_f$ values were calculated for individual cations by usual procedure.

Zinc and mercury were detected as dark pink and blue coloured spots respectively with 0.1% ethanolic solution of 1-(2-pyridylazo)-2-naphthol[17] and 0.2% solution of diphenylcarbazone[18]. Cadmium(II) was detected as red spot with 0.1% aqueous solution of 4-(2-pyridylazo) resorcinol[19].

## RESULTS AND DISCUSSION

Various experiments were carried out to study the effect of pH (4–9), concentration of mobile phase (0.01 to 0.1 M) and concentration of stationary phase (0.1 to 1.5% using chloroform as a diluent) on the $R_f$ values of individual cations. The results (Table-1) show that $R_f$ values of zinc and cadmium are slightly different at 0.1% *n*-octylaniline, while these are different for mercury in sodium acetate and sodium succinate.

$R_f$ values are different at this concentration of *n*-octylaniline in sodium salicylate for these three cations. A similar trend was also observed in N-*n*-octylaniline. Variation in the concentration of mobile phase (0.01 to 0.1 M) showed that optimum concentration of mobile phase was 0.05–0.1 M.

Liquid ion exchangers in salt form such as acetate, salicylate or succinate undergo anion exchange process on the paper involving metal complexes such as metal acetate, metal salicylate or metal succinate.

$$2[RNH_3^+ \cdot OAc^-] + Zn \text{ or } Cd \text{ or } Hg(OAc)_4^{2} \rightleftharpoons [(RNH_3^+)_2 Zn \text{ or } Cd \text{ or } Hg(OAc)_4^{2}]$$

### Analysis of commercial samples and synthetic mixtures

Proposed method is suitable for the separation of binary mixtures. Mercury and zinc as well as mercury and cadmium are separated at all mobile phases, but zinc and cadmium are separated only in sodium acetate media having 3% concentration of *n*-octylaniline.

This method is also applicable for separation and detection of zinc and mercury in pharmaceutical samples such as Himani Boroplus [Goodman Pharmaceuticals (India) Pvt. Ltd.], Nycil Lavendar [Manisha Pharmaceuticals], Zincovit [Apex Laboratories Ltd.] and Ras Sindur [Shree Baidyanth Ayurvedic Bhavan]. The

dissolution of the samples was done as reported in communication[20] and working procedure outlined above was followed for separation and detection of zinc(II) and mercury(II). Zinc and mercury from these samples show single spot with $R_f$ values 0.64 and 0.04 respectively.

The development time ranges between 40 to 45 min with *n*-octylaniline and N-*n*-octylaniline as the stationary phase.

TABLE 1
EFFECT OF pH AND CONCENTRATION OF STATIONARY PHASE ON $R_f$ VALUES WITH DIFFERENT MOBILE AND STATIONARY PHASES

| Metal ion | Stationary phase | | Mobile Phases | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Na-acetate 0.1 M at pH | | | Na-salicylate 0.1 M at pH | | | Na-succinate 0.1 M at pH | | |
| | Amine | Conc. (%) | 4 | 7 | 9 | 4 | 7 | 9 | 4 | 7 | 9 |
| Zn(II) | *n*-O.A. | 0.1 | 0.79 | 0.56 | 0.50 | 0.34 | 0.37 | 0.35 | 0.92 | 0.52 | 0.53 |
| | | 0.5 | 0.77 | 0.50 | 0.46 | 0.37 | 0.27 | 0.31 | 0.87 | 0.46 | 0.52 |
| | | 1.0 | 0.83 | 0.43 | 0.42 | 0.41 | 0.21 | 0.33 | 0.89 | 0.51 | 0.51 |
| | N-*n*-O.A. | 0.1 | 0.82 | 0.46 | 0.44 | 0.82 | 0.48 | 0.48 | 0.91 | 0.50 | 0.33 |
| | | 0.5 | 0.84 | 0.35 | 0.26 | 0.75 | 0.42 | 0.31 | 0.90 | 0.45 | 0.41 |
| | | 1.0 | 0.87 | 0.30 | 0.25 | 0.78 | 0.40 | 0.28 | 0.91 | 0.46 | 0.45 |
| Cd(II) | *n*-O.A. | 0.1 | 0.86 | 0.49 | 0.53 | 0.39 | 0.32 | 0.23 | 0.92 | 0.71 | 0.48 |
| | | 0.5 | 0.81 | 0.48 | 0.48 | 0.32 | 0.28 | 0.21 | 0.91 | 0.56 | 0.48 |
| | | 1.0 | 0.81 | 0.45 | 0.48 | 0.19 | 0.19 | 0.18 | 0.90 | 0.55 | 0.50 |
| | N-*n*-O.A. | 0.1 | 0.85 | 0.57 | 0.56 | 0.75 | 0.58 | 0.40 | 0.82 | 0.67 | 0.75 |
| | | 0.5 | 0.84 | 0.53 | 0.55 | 0.67 | 0.50 | 0.39 | 0.82 | 0.62 | 0.62 |
| | | 1.0 | 0.80 | 0.50 | 0.50 | 0.52 | 0.48 | 0.30 | 0.81 | 0.46 | 0.46 |
| Hg(I) | *n*-O.A. | 0.1 | 0.27 | 0.23 | 0.27 | 0.26 | 0.26 | 0.21 | 0.19 | 0.08 | 0.07 |
| | | 0.5 | 0.25 | 0.16 | 0.17 | 0.15 | 0.22 | 0.50 | 0.15 | 0.07 | 0.07 |
| | | 1.0 | 0.17 | 0.10 | 0.10 | 0.10 | 0.12 | 0.05 | 0.10 | 0.05 | 0.05 |
| | N-*n*-O.A. | 0.1 | 0.03 | 0.06 | 0.10 | 0.13 | 0.46 | 0.29 | 0.08 | 0.08 | 0.13 |
| | | 0.5 | 0.03 | 0.06 | 0.07 | 0.06 | 0.40 | 0.20 | 0.05 | 0.08 | 0.08 |
| | | 1.0 | 0.02 | 0.05 | 0.03 | 0.05 | 0.27 | 0.10 | 0.04 | 0.07 | 0.05 |

*n*-O.A. = *n*-octylaniline;
N-*n*-O.A. = N-*n*-octylaniline.

## ACKNOWLEDGEMENTS

Authors are thankful to University Grants Commission, New Delhi for financial assistance and to the Management, Pravara Rural Education Society for providing the necessary laboratory facilities.

## REFERENCES

1. E. Cerrai and G. Ghersini, *Chromatography J.*, **16**, 258 (1964).
2. ———, *Chromatography J.*, **18**, 24 (1965).
3. A.K. De and S.K. Sarkar, *Sep. Sci.*, **9**, 431 (1974).
4. C.G. Yeole and V.M. Shinde, *Analyst*, **108**, 1102 (1983)
5. ———, *Indian J. Chem.*, **23A**, 1053 (1984).
6. D.K. Ghosh and U.S. Ray, *Indian J. Chem.*, **30A**, 102 (1991).
7. K. Mitra and S. Roy, *Indian J. Chem.*, **33A**, 961 (1994).
8. K. Saha and U.S. Roy, *J. Indian Chem. Soc.*, **7**, 516 (1998).
9. S.R. Kuchekar and M.B. Chavan, *Talanta*, **35**, 357 (1988).
10. G.N. Mulik, S.R. Kuchekar and M.B. Chavan, *Indian J. Chem.*, **25A**, 1073 (1986).
11. ———, *J. Indian Chem. Soc.*, **64**, 68 (1987).
12. H.R. Aher, P.S. Gunjal, S.R. Kuchekar and M.B. Chavan, *Asian J. Chem.*, **10**, 43 (1998).
13. S.R. Kuchekar, H.R. Aher and M.B. Chavan, *Indian J. Chem.* (in press).
14. A.I. Vogel, Text Book of Quantitative Inorganic Analysis, Longmans-Green, London, pp. 433, 444 (1964).
15. F.J. Welcher, The Analytical uses of EDTA, Van Nostrand, New York, p. 164 (1961).
16. T. Suzuki, *Analyst*, **15**, 666 (1966).
17. G. Ackermann and J. Koethe, *Talanta*, **26**, 693 (1979).
18. J.U. Lurie, Handbook of Analytical Chemistry, Mir Publishers, Moscow, p. 230 (1975).
19. S. Kalyanaraman and S.M. Khopkar, *J. Indian Chem. Soc.*, **6**, 203(1979).
20. V.V. Mudshingikar and V.M. Shinde, *Talanta*, **30**, 405 (1983).

(*Received*: 26 May 2003; *Accepted*: 01 December 2003) AJC-3254