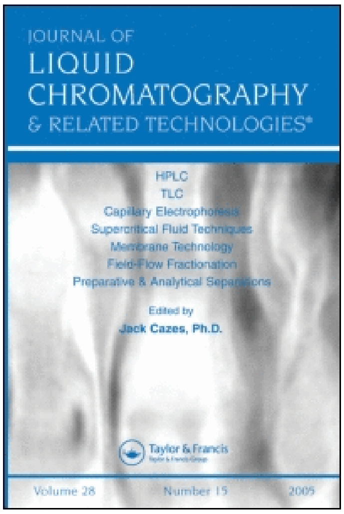

**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Ligand Exchange Chromatography Separations of Some Phenolic Compounds on Zinc Silicate in Fe(III) Form

D. K. Singh[a]; Anjana Darbari[a]
[a] Department of Chemistry, Harcourt Butler Technological Institute, Kanpur, India

**To cite this Article** Singh, D. K. and Darbari, Anjana(1987) 'Ligand Exchange Chromatography Separations of Some Phenolic Compounds on Zinc Silicate in Fe(III) Form', Journal of Liquid Chromatography & Related Technologies, 10: 14, 3235 — 3248

**To link to this Article: DOI:** 10.1080/01483918708068309

**URL:** http://dx.doi.org/10.1080/01483918708068309

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(14), 3235-3248 (1987)

# LIGAND EXCHANGE CHROMATOGRAPHY SEPARATIONS OF SOME PHENOLIC COMPOUNDS ON ZINC SILICATE IN Fe(III) FORM

D. K. Singh and Anjana Darbari
*Department of Chemistry*
*Harcourt Butler Technological Institute*
*Kanpur-208002, India*

## ABSTRACT

The high sorption capacity of zinc silicate for Fe(III) has been utilized for the separation of phenolic compounds on the basis of ligand exchange. The coordination of ligands with the central metal ion occurs through oxygen. Ligand sorption capacity, rate of sorption and break-through capacity have been studied. The distribution coefficients (Kd values) of 21 phenols have been determined in five different systems. Selectivity has been determined on the basis of Kd values of these phenols. On the basis of differences in Kd values various analytically important quantitative binary and ternary separations on columns of zinc silicate in Fe(III) form have been achieved.

## INTRODUCTION

Ligand exchange chromatography (LEC) is a technique used to separate compounds which can form complexes with metal ions. The analytical importance of ligand ion-exchangers is increasing in separation and purification of organic compounds. A number of such ion exchangers have been employed for the determination of amino-acids in sea water (1) and for the determination of non-ionic surfactants (2). Chelating resin in Fe(III) form has been utilized for quantitative trapping of phenolic compounds by ligand exchange process (3) and for the separation of phenol, 2-nitrophenol, 2,4-dichlorophenol and pentachlorophenol (4).

A difficulty with ligand exchange chromatography is that a fraction of metal ions bound to the resin is removed when an eluent with a free cation is used. This fact severely restricted the choice of metal ions. Chelex resins with carboxylic or iminodiacetate group, though safe to use, showed leakage of metal ions into ammonia solution, but the amount was so low that no correction was required (5).

Some inorganic ion-exchangers with high affinity for metal ions have been used for serious LEC studies. Recently zinc silicate in Cu(II) form has been utilized for the separation of some amines (6). There is revived interest towards the ion-exchange properties of silicates in recent years (7,8). However, no such studies for phenolic compounds have been reported with silicate based chelating ion-exchangers, although, Rawat et al. have used zinc silicate for paper chromatographic separation of phenols (9). The ion exchanger in the metal form is superior to the solid sorbents generally employed, on account of its affinity for ligands. Since the coordinating power differs for the various iron-phenol complexes, it is possible to separate the phenols by using a solution containing competing ligand. The high affinity of zinc silicate for iron(III) makes its use as ligand ion-exchanger. The purpose of the present work is to apply the ligand exchange reaction for the separation of phenols retained on the exchanger, by exploiting differences in Kd values.

## MATERIALS AND METHODS

Reagents. Zinc nitrate (BDH), sodium silicate (Merck) and iron(III) nitrate (BDH) were used. The phenolic solutions were prepared by dissolving them either in water or in ethanol depending on their solubilities. The Follins reagent was prepared following the standard method [10] for the spectrophotometric determination of phenols.

Apparatus. An electric rotary shaking machine IEC-56 and Bausch and Lomb Spectronic 20 were used for shaking and spectrophotometric measurements respectively.

Preparation of the Adsorbent. Zinc silicate (7) was prepared by mixing 0.1 M solutions of zinc nitrate and sodium silicate in the ratio of 1:1. The mixture was allowed to stand for 24 hours at room temperature. The precipitate was filtered, washed and dried in an oven at 40°C. The product broke into small particles when immersed in demineralised water. Zinc silicate was finally ground and sized by sieving to 100-150 mesh. Zinc silicate (100-150 mesh) was shaken with 1 M iron(III) nitrate for 12 hours. The dark brown material so obtained due to adsorption of Fe(III) was then washed free of Fe(III) with demineralised water and dried in an oven at 40°C.

## RESULTS AND DISCUSSION

Ligand sorption capacity. To determine ligand adsorption capacity 1 g treated zinc silicate was supported on a glass wool in a column. 10 ml fractions of predetermined amounts of phenols were then passed through the column and the phenol collected in the effluent was determined. The amount initially taken minus the amount found after the passage through the column gave the amount of phenol retained by the exchanger. The process was continued until the amount of phenol in the fraction remained the same before and after passing through the exchanger. The sorption capacity of untreated zinc silicate was also determined for some phenols. The results are presented in Table 1. The results show that only small amounts of phenols are retained on

TABLE 1

Ligand adsorption capacity on treated and untreated zinc silicate

| Sl. No. | Substance | Ligand adsorption capacity, meq/g | |
|---|---|---|---|
| | | Treated Zinc silicate | Untreated Zinc silicate |
| 1 | Phenol | 0.38 | 0.12 |
| 2 | α-Naphthol | 0.50 | 0.21 |
| 3 | o-Cresol | 0.56 | 0.20 |
| 4 | Catechol | 0.88 | 0.26 |
| 5 | Pyrogallol | 1.06 | 0.34 |

the untreated exchanger whereas the capacity of treated zinc silicate for various phenols varies from 0.38 to 1.06 meq/g. The retention of phenols in the latter case occurs by virtue of the ability to form complexes of varying stability with the Fe(III) bound to the exchanger matrix. In some cases of the phenols complex formation could be clearly seen in the form of colored bands. Interaction with the exchanger matrix is possibly responsible for the retention of phenols on untreated zinc silicate.

Metal leakage. Zinc silicate has high affinity for Fe(III). Metal leakage into the eluting solution was determined by shaking 0.5 g of treated exchanger in the desired solutions for four hours at room temperature. The Fe(III) ions eluted into the equilibrating solution were determined with 1,10-phenanthroline(11). The results presented in table 2 show that except in acidic solutions the metal ion retention is sufficiently strong to cause no interference in the determination of eluted phenols. Acidic solutions, however, strip off the metal ions. Hydrochloric acid and oxalic acid having concentration more than 1 M elute iron(III) ions completely leaving the exchanger white.

TABLE 2

Solubility of immobilized Fe(III) in different solvents
Amount of treated zinc silicate taken = 250 mg

| Sl. No. | Solvents | Amount of Fe(III) released in μg |
|---|---|---|
| 1 | Demineralized water | 0.0 |
| 2 | Citric acid, 0.1 M | 0.0 |
| 3 | EDTA , 0.1 M | 0.0 |
| 4 | Sodium hydroxide, 0.1 M | 0.0 |
| 5 | Hydrochloric acid, 0.1 M | 2.5 |
| 6 | Nitric acid, 0.1 M | 2.3 |
| 7 | Oxalic acid, 0.1 M | 15.0 |
| 8 | Ethanol | 0.0 |
| 9 | Ammonium hydroxide 1 M | 0.0 |

Rate of sorption. The rate of sorption was studied by shaking 0.25 g treated zinc silicate with 25 ml of phenol solution. At the intervals of 1, 3, 5, 10, 15, 20, 30 and 40 min the aqueous phase was filtered using Whatman no.4 filter paper and the amount of phenol was determined spectrophotometrically (10) in the filterate. For comparison, similar studies were made on untreated zinc silicate. Equilibrium was attained within 20 min in case of treated zinc silicate whilst 2 hours were required for untreated zinc silicate. Normally fast equilibrium is not expected with inorganic ion-exchangers. Presence of Fe(III) in treated zinc silicate is responsible for such a fast equilibrium rate due to iron(III)-phenol complex formation.

Break-through capacity. The ligand exchange column technique permits continuous operation which is much superior to batch process in terms of time and space. The break-through behaviour of 2,4,6-trinitrophenol and catechol was studied by passing 1 mg $ml^{-1}$ solution of each phenol through a glass column,

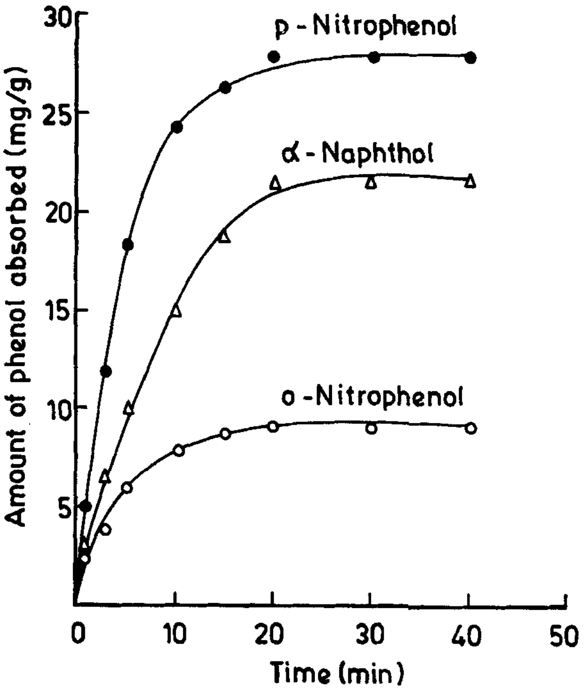

FIG. 1 Rate of Adsorption of Phenols at 25°C.

30 cm x 0.39 $cm^2$ cross-sectional area loaded with 1 g treated exchanger. The flow rate was maintained 0.5 ml $min^{-1}$. For comparison similar studies were made on untreated columns. The results are plotted in figure 2. The results revealed that 8 bed volumes of 2,4,6-trinitrophenol (corresponding to 80 mg retention) can be passed through the treated exchanger without any trace being detected in the effluent against only 1 bed volume (corresponding to 10 mg retention) on untreated columns. Adsorption being relatively a slow process, the break-through in the latter instance occurred in the second bed volume only. Similarly for treated zinc silicate, break-through for catechol occurs after 4 bed volumes (corresponding to 40 mg retention). On the other hand in case of untreated exchanger even the first bed volume

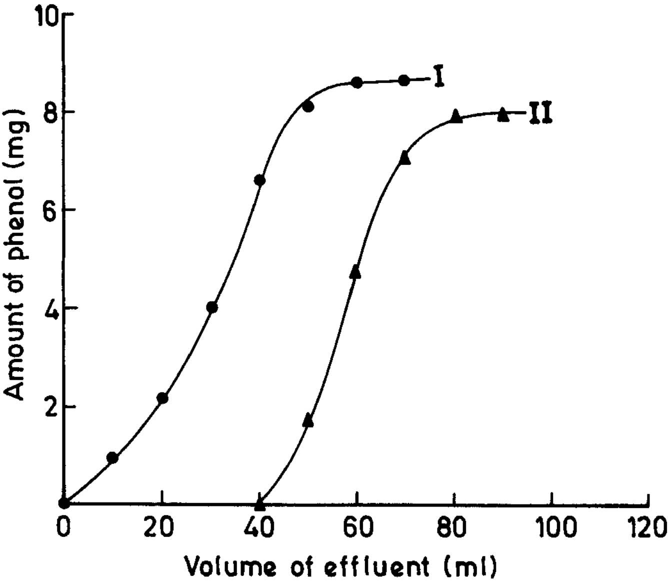

FIG. 2A Break-Through Curve of Catechol.

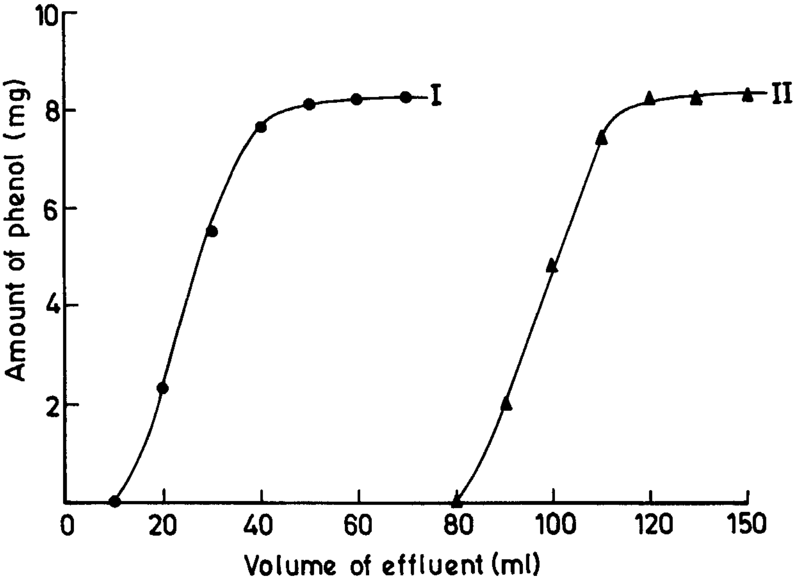

FIG. 2B Break-Through Curve of 2,4,6-Trinitrophenol.
I ( ) Break-Through of Phenol on Untreated Zinc Silicate
II( ) Break-Through of Phenol on Treated Zinc Silicate

did not show instantaneous uptake of phenol. The results of break-through capacity reveal that complexation of phenols with the immobilized Fe(III) in the zinc silicate matrix is, therefore, fairly rapid and can be used with advantage compared to untreated zinc silicate.

Distribution studies. Distribution coefficients (Kd values) of 21 phenols were determined by batch process on treated zinc silicate.

$$Kd = \frac{\text{Amount of phenol in exchanger phase gm}^{-1}}{\text{Amount of phenol in solution phase ml}^{-1}}$$

0.25 g exchanger was shaken with phenolic solutions for four hours. The total volume in all the cases was 25 ml. The amount of phenol remaining in the supernatant liquid was determined by spectrophotometric method (10). The results are shown in Table 3 which indicate that in aqueous media 2,4,6-trinitrophenol, p-nitrophenol, catechol, pyrogallol and o-cresol are strongly retained by the exchanger; α-naphthol, salicylic acid and hydroxyquinone only partially whilst quinol, o- and m-nitrophenol, 2,4-, 2,5- and 2,6-dinitrophenol, β-naphthol, phloroglucinol, gallic acid, resorcinol, m- and p-cresol and phenol are scarcely adsorbed. In non-aqueous media, however, there are some phenols which show higher retention than in aqueous media. The greater solubility of these phenols in acetone and their greater preference for coordination with water than with acetone possibly explains this behaviour. The Kd values in ammonium hydroxide 0.01M are interesting. Barring a few, the phenols show a decrease in Kd values. It is unlikely that decrease in retention is due to the presence of competing amine ligand. Aqueous ammonia only brings about a change in pH of the equilibrating solution resulting in the loss of ligands from central metal ion. This seems to be the reason for the greater retention of the phenols which form complexes with Fe(III). The results of equilibration studies of

TABLE 3

Kd values of phenols on treated zinc silicate

| Phenols | Kd values, ml $g^{-1}$ | | | | |
|---|---|---|---|---|---|
| | DMW | Acetone | $NH_4OH$ 0.01 M | EDTA 0.01M | Sodium citrate 0.01 M |
| o-Nitrophenol | 6.0 | 85.7 | 0.0 | 3.1 | 0.0 |
| m-Nitrophenol | 18.8 | 140.1 | 1.0 | 8.5 | 2.0 |
| p-Nitrophenol | 325.6 | 218.2 | 138.4 | 85.6 | 13.6 |
| 2,4-Dinitrophenol | 34.1 | 19.0 | 2.3 | 32.5 | 2.5 |
| 2,5-Dinitrophenol | 23.5 | 36.4 | 3.0 | 20.6 | 2.3 |
| 2,6-Dinitrophenol | 26.7 | 10.3 | 20.6 | 18.5 | 3.0 |
| 2,4,6-Trinitrophenol | 415.0 | 223.1 | 286.2 | 78.5 | 16.8 |
| α-Naphthol | 180.6 | 133.3 | 112.6 | 28.6 | 11.2 |
| β-Naphthol | 40.6 | 18.2 | 6.5 | 12.6 | 5.6 |
| Quinol | 65.8 | 34.7 | 7.2 | 36.7 | 12.5 |
| Pyrogallol | 336.5 | 566.6 | 405.6 | 183.5 | 18.6 |
| Phloroglucinol | 58.3 | 60.2 | 60.7 | 6.0 | 8.5 |
| Salicylic acid | 173.0 | 16.2 | 140.2 | 7.7 | 10.9 |
| Gallic acid | 43.6 | 6.3 | 2.0 | 8.6 | 8.5 |
| Catechol | 250.0 | 81.8 | 12.6 | 186.5 | 67.6 |
| Resorcinol | 10.0 | 40.6 | 0.0 | 7.5 | 0.0 |
| Hydroxyquinone | 70.1 | 73.5 | 280.0 | 5.6 | 36.8 |
| o-Cresol | 218.0 | 252.6 | 230.6 | 210.5 | 12.6 |
| m-Cresol | 18.8 | 85.8 | 0.0 | 9.4 | 3.0 |
| p-Cresol | 50.0 | 112.5 | 73.6 | 33.3 | 21.2 |
| Phenol | 10.5 | 56.2 | 8.0 | 5.6 | 0.0 |

TABLE 4

Separations achieved on treated zinc silicate columns

| Sl. No. | Mixture | Eluent | Eluate (ml) | Amount loaded (µg) | Amount found (µg) | % Error |
|---|---|---|---|---|---|---|
| 1a | o-Nitrophenol | DMW | 30 | 350 | 350.0 | 0.0 |
| | p-Nitrophenol | Citric acid 0.01 *M* | 40 | 400 | 393.2 | 1.7 |
| 1b | o-Nitrophenol | DMW | 30 | 300 | 298.4 | 0.5 |
| | p-Nitrophenol | Citric acid 0.01 *M* | 50 | 500 | 490.8 | 1.8 |
| 2 | o-Nitrophenol | DMW | 30 | 300 | 301.4 | 0.5 |
| | 2,4-Dinitrophenol | $NH_4OH$ 0.01 *M* | 40 | 360 | 352.4 | 2.1 |
| | 2,4,6-Trinitrophenol | Citric and 0.01 *M* | 50 | 540 | 529.6 | 1.9 |
| 3 | Resorcinol | DMW | 30 | 400 | 398.4 | 0.4 |
| | Catechol | $NH_4OH$ 0.01 *M* | 40 | 525 | 515.6 | 1.8 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 4 | Gallic acid | $NH_4OH$ 0.01 *M* | 40 | 450 | 448.2 | 0.4 |
| | Salicylic acid | EDTA 0.01 *M* | 50 | 400 | 393.4 | 1.6 |
| 5 | Quinol | $NH_4OH$ 0.01 *M* | 40 | 500 | 492.5 | 1.5 |
| | Pyrogallol | Citric acid 0.01 *M* | 50 | 550 | 538.0 | 2.2 |
| 6 | β-Naphthol | $NH_4OH$ 0.01 *M* | 30 | 400 | 391.6 | 2.1 |
| | α-Naphthol | Citric acid 0.01 *M* | 50 | 400 | 391.6 | 1.2 |
| 7 | m-Cresol | $NH_4OH$ 0.01 *M* | 30 | 375 | 371.2 | 1.0 |
| | o-Cresol | Citric acid 0.01 *M* | 40 | 500 | 494.1 | 1.2 |
| 8. | Phenol | DMW | 30 | 350 | 348.0 | 0.8 |
| | Catechol | $NH_4OH$ 0.01 *M* | 40 | 410 | 403.0 | 1.7 |
| | Pyrogallol | Citric acid 0.01 *M* | 50 | 400 | 391.0 | 2.2 |

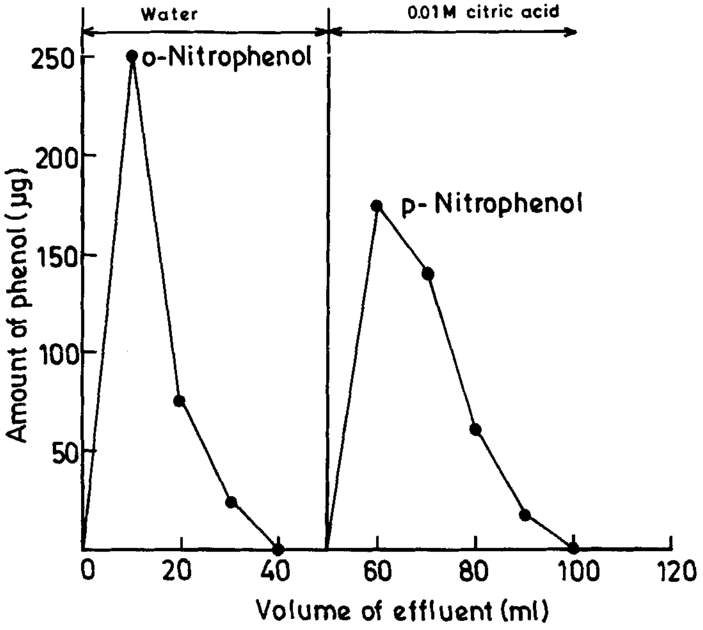

FIG. 3A Separation of o-Nitrophenol-p-Nitrophenol.

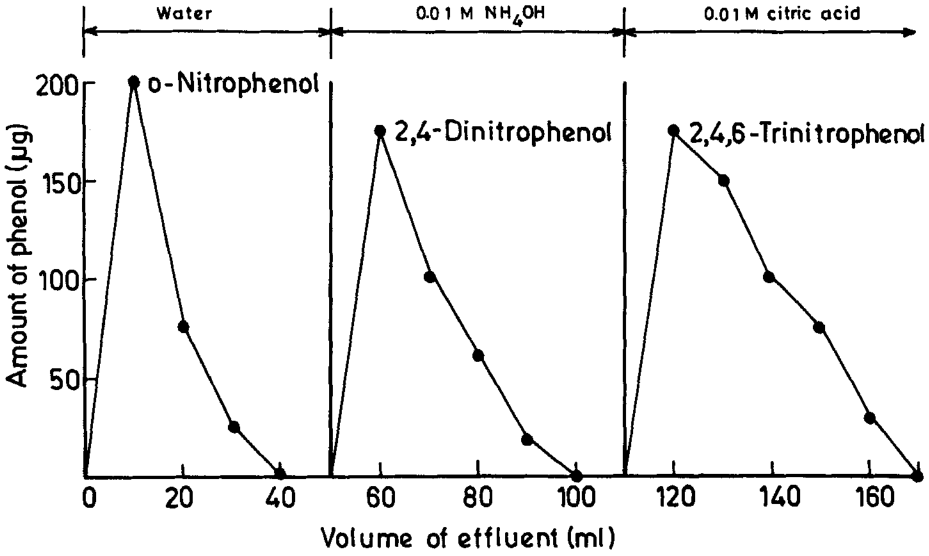

FIG. 3B Separation of o-Nitrophenol-2,4-Dinitrophenol 2,4,6-Trinitrophenol.

phenols in presence of competing ligands such as EDTA and citrate show the appreciable lower retention in all the cases.

Column separations. A glass column 30 cm x 0.39 $cm^2$ cross-sectional area was packed with two grams of the exchanger sorbed with iron(III). The column was washed with 50 bed volumes of demineralised water. The sample solutions containing the desired phenols having the largest differences in Kd values were tried and those whose quantitative separation was achieved are listed in Table 4. The order of elution and eluents are presented in figure 3a-h.

The positional isomers such as o- and p-nitrophenol, o- and m-cresol , α- and p-naphthol and catechol-resorcinol have been easily separated on the columns of treated zinc silicate. Other binary separations are gallic acid from salicyclic acid and quinol from pyrogallol. Some ternary separations are : o-nitrophenol-2,4-dinitrophenol - 2,4,6-trinitrophenol and phenol-catechol-pyrogallol. It is interesting that no significant tailing is observed during the elution of various phenols and only small volumes of eluents were required to give compact chromatograms. Furthermore, the metal adherence to the zinc silicate material is so firm that the same column could be used repeatedly. The method can be utilized to trap trace amounts of these compounds from water and the retained compounds can be separated using an appropriate eluent.

Phenols are among the most common water polluants and this class is included in the list of priority polluants [12). A method is, therefore, needed for low level determination of phenols and for their identification. Zinc silicate in iron(III) form can be utilized for the recoveries of phenols from water by LEC, it is possible to separate the phenols using appropriate eluent (competing ligand).

Acknowledgement. The authors are grateful to Prof. A.K.Vasishtha, Director and Prof. R.S. Tewari, Head, Department of Chemistry, Harcourt Butler Technological Institute, Kanpur-208002, India, for providing research facilities. Financial assistance from U.G.C., India is also gratefully acknowledged.

## REFERENCES

(1) Siegel, A. and Degens, E.T., Science, 151, 1098 (1966).

(2) Carunchio, V., Liberatori, A., Messina, A. and Petronio, B.M., Ann. Chim. Roma, 69, 165 (1979).

(3) Petronio, B.M., Lagana, A. and Russo, M.V., Talanta, 28, 215 (1981).

(4) Petronio, B.M., De Caris, E., and Iannuzzi, L., Talanta, 29(8), 691 (1982).

(5) Shimomura, K., Dickson, L. and Walton, H.F., Anal. Chim. Acta, 37, 102 (1967).

(6) Singh, D.K. and Darbari, A., Chromatographia, 23(2), 93 (1987).

(7) Rawat, J.P. and Iqbal, M., J.Liq. Chromatogr., 3(4), 591 (1980).

(8) Singh, D.K. and Bhatnagar, R.R., Z. Anal. Chem., 325, 195 (1986).

(9) Rawat, J.P., Iqbal, M. and Alam, M., 5(5), 967 (1982).

(10) Snell, F.D. and Snell, C.T., 'Colorimetric methods of analysis', III Edn., Vol.III, D. Von Nostrand Co., Inc. Toronto, N.Y. London, 104 (1953).

(11) Sandell, E.B., 'Colorimetric methods of analysis', Interscience Publisher, Inc. New York, p.537 (1959).

(12) 'Sampling and analysis procedures for screening of industrial effluents for priority pollutants', U.S. Environmental Protection Agency, Environmental and Support Laboratory, Cincinnati, Ohio (1977).