

New surface-modified sorbent layer for the analysis of toxic metals in seawater and industrial wastewater

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ABSTRACT

Thorium nitrate-impregnated silica gel layers were utilized for the separation of zinc, cadmium, thallium and mercury from seawater and industrial wastewater. Some common pesticides, namely malathion, carbaryl, carbofuran and bavistin, do not impair the separation and detection of the above-mentioned toxic metals in seawater and industrial wastewater. Detection limits of these toxic metals are reported.

INTRODUCTION

In recent years, thin-layer chromatography (TLC) has proved to be a convenient technique for the analysis of environmental samples containing inorganic ions. It has been successfully applied for the determination of heavy metals in water and aquatic plants [1], analysis of wastewater for total heavy metal contents [2], characterization of hazardous wastes [3] and quantification of toxic metals in industrial sewage [4]. An enzymatic method has been reported [5] for the detection of copper, mercury, cadmium and silver salts in fresh water after their separation on TLC plates.

In our earlier communication [6,7] we showed that silica gel layers impregnated with inorganic salt solutions are more selective for cations and can provide better separation possibilities than untreated silica gel layers. In continuation, we have now developed a new sorbent phase for TLC analysis of heavy metals, by impregnating silica gel with 0.1% aqueous thorium nitrate solution. The resulting sorbent phase was examined for its possible use in the analysis of seawater and industrial wastewater.

EXPERIMENTAL

Apparatus

A TLC applicator (Toshniwal, India), electrical centrifuge (Remi, India) and pH meter Model LI-10T (Elico, India) were used.

Reagents

Silica gel G (E. Merck, India), thorium nitrate (Riedel De Haen, Germany) and sodium formate (S.D. Fine Chemicals, India) were used. All other reagents were also of analytical grade.

Test solutions

The test solutions (1%) were chloride or nitrate salts of cadmium, mercury, thallium and zinc. Double-distilled water having a specific conductivity (K) of $1.5 \cdot 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C was used to prepare the test solutions.

Alcoholic solutions (1%) of malathion, carbaryl, carbofuran, bavistin, 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid were used.

Detection

The following detection systems were used: (i) dithizone (0.1%) in carbon tetrachloride for Zn^{2+} and Cd^{2+} ; (ii) hydrogen sulphide gas for Tl^{+} and Hg^{2+} .

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Mobile phase

A 1.0 M aqueous solution of sodium formate (pH 7.65) was used.

Stationary phase

The stationary phase was silica gel impregnated with a 0.1% aqueous solution of thorium nitrate.

Preparation of TLC plates

Impregnated TLC plates were prepared by mixing silica gel G with an aqueous solution of 0.1% thorium nitrate in a 1:3 (w/v) ratio. The resultant slurry was mechanically shaken for 10 min, after which it was coated onto glass plates with the help of a TLC applicator to give a layer of 0.25 mm thickness. The plates were air-dried at room temperature and then activated by heating at 100°C for 1 h. After activation the plates were kept in an air-tight chamber until use.

Preparation of spiked water

A 100-ml aliquot of distilled water was spiked with 250 mg each of zinc, cadmium, thallium and mercury salts. The pH of this solution was adjusted to 3 using dilute hydrochloric acid. Hydrogen sulphide gas was passed through the solution till the metal ions present in this solution were completely precipitated. But it was found that zinc could not be precipitated at pH 3. The precipitate was washed with distilled water, centrifuged and dissolved in the minimum possible volume of concentrated nitric acid followed by dilution to 100 ml, using distilled water.

Preparation of spiked industrial wastewater and seawater

A 100-ml volume of industrial wastewater (collected from Link Lock Industries, Aligarh, India) or seawater (collected from Anjuna beach of the Arabian Sea, Goa, India) was spiked with 333 mg each of zinc, cadmium and mercury salts to give a 1% solution. The pH values of the resultant spiked industrial wastewater and seawater were 1.5 and 8.3, respectively.

Procedure

About 0.01 ml of the spiked test solutions (distilled water, industrial wastewater and seawater) was spotted separately on the activated TLC plates.

The spots were air-dried and the chromatograms were developed allowing the solvent to ascend up to 10 cm from the point of application in all cases. After development, the chromatograms were air-dried at room temperature and the Tl^+ and Hg^{2+} spots were visualized by exposing the TLC plate to hydrogen sulphide gas. On exposure to hydrogen sulphide gas, the regions containing Tl^+ and Hg^{2+} turn to blackish brown. When dithizone solution is sprayed onto the TLC plate, Cd^{2+} -containing zones turn yellowish orange, whereas Zn^{2+} -containing zones turn reddish pink. R_L (R_F of the leading front) and R_T (R_F of the trailing front) values for the detected spots were determined. The R_F [$R_F = (R_L + R_T)/2$] and ΔR_F ($\Delta R_F = \text{mean } R_F \text{ on plain silica gel for a particular metal ion minus mean } R_F \text{ on impregnated silica gel for the same metal ion}$) values for the metal ions were calculated. The standard deviation in R_F values was also calculated using the formula

$$S.D. = \sqrt{\frac{\sum (x_i - x)^2}{n}}$$

where x_i is the individual R_F value, x is the mean R_F value and n is the number of observations made for each metal ion.

To study the effect of pesticides on the separation of metal ions present in spiked water, 0.01 ml of spiked distilled water was spotted on the chromatogram followed by the spotting of 0.02 ml of pesticide solution on the same spot. The plates were developed in 1.0 M sodium formate, dried and the spots were detected as described above. The R_F values of the separated metal ions were determined and compared with those obtained in the absence of pesticides.

The limits of detection of the cations were determined by spotting 0.01 ml of cation solutions of various concentrations on the chromatoplates, which were developed in sodium formate, and the spots were visualized using the appropriate detector. This was repeated with successive reduction of the concentration of the cation solution until no detection was possible. This method was carried out three times for each cation. The amount of salt just detectable in the solution was taken as the detection limit.

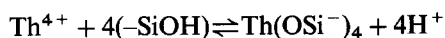
TABLE I

hR_F ($R_F \times 100$), STANDARD DEVIATION IN R_F , ΔR_F AND DETECTION LIMITS OF METAL IONS PRESENT IN STANDARD SAMPLE SOLUTIONS, CHROMATOGRAPHED ON 0.1% THORIUM NITRATE-IMPREGNATED SILICA LAYERS, USING 1.0 M SODIUM FORMATE AS ELUENT

| Sample No. | Metal ion | hR_F | S.D. in R_F | ΔR_F | Detection limit (μg) |
|------------|------------------|--------|---------------|--------------|-----------------------------------|
| 1 | Zn^{2+} | 11 | 0.0047 | +0.76 | 0.23 |
| 2 | Cd^{2+} | 79 | 0.0124 | +0.15 | 6.13 |
| 3 | Tl^+ | 56 | 0.0141 | +0.15 | 7.68 |
| 4 | Hg^{2+} | 93 | 0.0047 | +0.04 | 7.40 |

RESULTS AND DISCUSSION

When silica gel is mixed with an aqueous solution of thorium nitrate, cation exchange takes place at the surface of hydrated silica gel to give a sorbent phase of altered selectivity.



Dugger *et al.* [8] determined some thermodynamic parameters for several such ion-exchange reactions to establish the cation-exchange process.

The positive ΔR_F values (Table I) show that the impregnated silica layers are more selective than the plain silica layers.

Thin layers prepared from impregnated silica gel were of good quality, providing well formed and compact spots for the cations chromatographed. The development time for a 10-cm run was 15 min. The hR_F and ΔR_F values reported are the averages of triplicate observations, hence they are reproducible.

The results of this study are summarized in Tables I and II. It is clear from Table I that the developed chromatographic system is well suited for microgram separation of Zn^{2+} , Cd^{2+} , Tl^+ and Hg^{2+} from their synthetic mixture.

Depending upon the results shown in Table I an attempt was made to establish the applicability of the proposed method in the analysis of spiked water containing zinc, cadmium, thallium and mercury. Three of the metal ions were identified and separated (Table II). Zinc could not be detected because at pH 3 zinc is not precipitated by hydrogen sulphide, and remains in the supernatant liquid. The presence of pesticides in this sample did not show any considerable effect either on the separation or on the R_F values of metal ions, as evident from Table II.

As good results were obtained in the analysis of spiked water (Fig. 1), we made use of this newly developed sorbent phase in the analysis of real environmental samples, namely industrial wastewater and seawater. It is evident from Table II that all the spiked metal ions were readily detectable and separable from these environmental samples.

From the results of this study we anticipate that these metal ions can be easily identified and detected

TABLE II

Zn-Cd-Hg-Tl MIXTURE SEPARATED, CHROMATOGRAPHED ON 0.1% THORIUM NITRATE-IMPREGNATED SILICA LAYERS USING 1.0 M SODIUM FORMATE AS ELUENT

NS = Not spiked; ND = not detected.

| Metal ion | Spiked industrial wastewater | | Spiked seawater | | Spiked distilled water | | Spiked distilled water in the presence of pesticide | |
|------------------|------------------------------|---------------|-----------------|---------------|------------------------|---------------|---|---------------|
| | hR_F | S.D. in R_F | hR_F | S.D. in R_F | hR_F | S.D. in R_F | hR_F | S.D. in R_F |
| Zn^{2+} | 11 | 0.0124 | 10 | 0.0094 | ND | ND | ND | ND |
| Cd^{2+} | 81 | 0.0124 | 79 | 0.0124 | 81 | 0.0124 | 83 | 0.0170 |
| Hg^{2+} | 90 | 0.0094 | 96 | 0.0094 | 93 | 0.0047 | 95 | 0.0124 |
| Tl^+ | NS | NS | NS | NS | 36 | 0.0286 | 52 | 0.0356 |

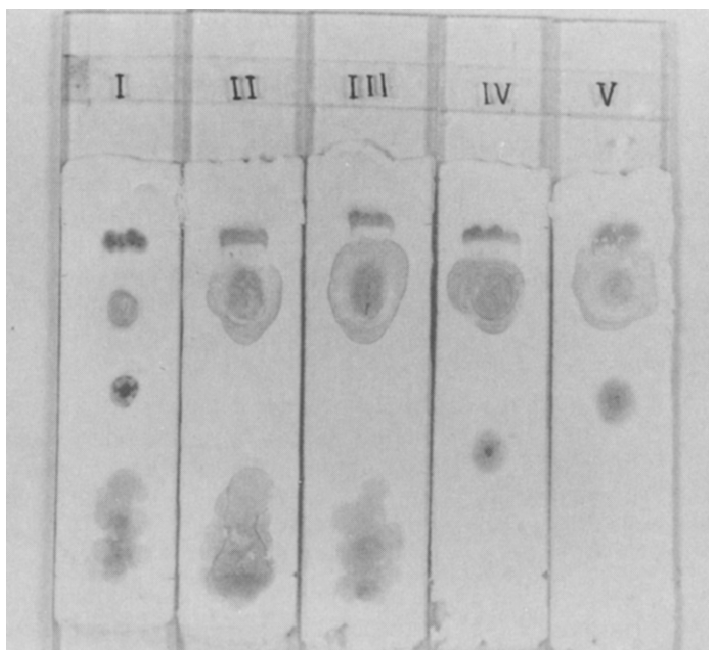


Fig. 1. Separation of a mixture of Zn, Cd, Hg and Tl. (I) Separation in standard sample; (II) separation in spiked industrial wastewater; (III) separation in spiked seawater; (IV) separation in spiked distilled water; (V) separation in spiked distilled water in the presence of pesticides.

if present in river water, using the proposed chromatographic system.

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