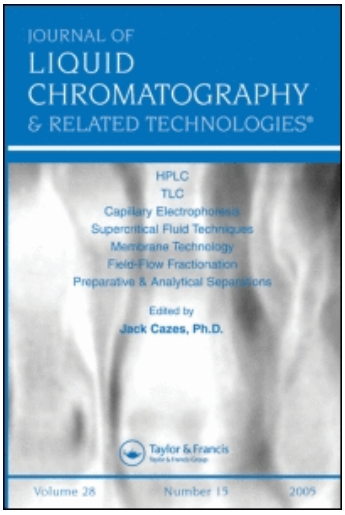

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Separation of Some Herbicides by Two Dimensional Thin Layer Chromatography on Calcium Sulphate

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SEPARATION OF SOME HERBICIDES BY TWO DIMENSIONAL THIN LAYER CHROMATOGRAPHY ON CALCIUM SULPHATE

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Two dimensional thin layer chromatography is being used for the last forty years[1] and now it has became an important tool for the separations of varying complexity. Various coating materials such as alumina, cellulose, kieselgel G, silica gel, silufol and polyamide have been used and studied for the separation of organics such as alkaloids, amino acids, carbohydrates, fatty acids, glycopeptides, glycolipids, lipids, phospholipids, pigments, protiens, peptides, pesticides, steroids and inorganics such as oxy acids of phosphorus, metal ions. Our previous work[2,3,4,5,6] shows that calcium sulphate coated paper and glass plates have a great separation potential for herbicides containing carboxyl group. Therefore now an attempt is made to test the separation potential of calcium sulphate alone and calcium sulphate containing aluminium oxide active neutral, calcium carbonate and p-dimethylaminobenzal-

dehyde for some herbicides by two dimensional thin layer chromatography. The results obtained are discussed in this paper.

EXPERIMENTAL

Apparatus

A Stahl apparatus with a universal applicator (adjustable thickness of the applied layers from 0-2.00 mm) made in India, hot air electric drier (Japan), glass plates (20 x 20 cm), glass jars (25 x 25 x 5 cm) and temperature controlled electric oven were used.

Chemicals

Aluminium oxide active neutral and ethyl acetate (Glaxo Laboratories, India), benzene (S.M. Chemicals, India), Calcium carbonate, calcium sulphate dihydrate, carbon tetra chloride and chloroform (E. Merck, India), p-dimethylaminobenzaldehyde (BDH, India), bromophenol blue, benzoic acid, p-chlorophenoxyacetic acid, citric acid, cinnamic acid, 2,4-dichlorophenoxyacetic acid, gallic acid, indole-3-acetic acid, maleic acid, β-naphthaleneacetic acid, β-naphthoxyacetic acid, oxalic acid, phenoxyacetic acid, sulphamic acid, tartaric acid and trichloroacetic acid (Sigma, USA) were used.

Preparation of Solutions

Solutions (1 %) of benzoic, p-chlorophenoxyacetic, cinnamic, 2,4-dichlorophenoxyacetic, gallic, indole-3-acetic, β-naphthaleneacetic, β-naphthoxyacetic and phenoxyacetic acids were prepared in ethanol. Solutions (1 %) of citric, maleic,

oxalic, sulphamic, tartaric and trichloroacetic acids were prepared in distilled water (DW).

Preparation of plates

A slurry of calcium sulphate was applied on the glass plates with the help of an applicator so that the thickness of the coating would be 0.75 mm. The plates were first allowed to dry at room temperature and then in a temperature controlled electric oven at 110° for 1 hr.

The above procedure was used to prepare the plates of the following coatings.

Coating A : Calcium sulphate (50 g) + DW (110 ml)

Coating B : Calcium sulphate (50 g) + aluminium oxide active neutral + DW (110 ml)

Coating C : Calcium sulphate (50 g) + calcium carbonate (0.5 g) + DW (110 ml)

Coating D : Calcium sulphate (50 g) + ethanolic solution of p-dimethylaminobenzaldehyde (p-DAB) (5 ml of 5 %) + DW (110 ml).

Detection of acids

The acids under study were located on the plates by 1 % ethanolic alkaline bromophenole blue solution.

Spotting of test solutions

Test solutions were spotted on the plates with the help of a fine capillary and the solvent was removed by hot air drier. The plates were developed firstly in a solvent (listed first in the tables) dried at room temperature (30°)

for 15 min and then they were developed in one more solvent (listed at second place in the tables). The ascending direction of the second solvent was arranged perpendicular to that of the first solvent, the solvent was also removed as above and acids were located by treating the plates with the indicator. The distance ascended by the developer was 10 cm in both cases. The R_f values were recorded by assigning the two dimensions coordinates such as (0,0), (0,1), (1,0), (1,1), (0,0.5), (1,0.5) and (0.5, 0.5). For a tailing spot the front limit (RI) and the rear limit (RT) were measured and recorded such as (0-5, 1) and (0.5, 8-10).

RESULTS

The separations achieved are recorded in table I-IO

DISCUSSION

The results obtained (Tables 1-10) show that calcium sulphate layers can be used for the separation of plant growth regulators like cinnamic, β-naphthaleneacetic, β-naphthoxyacetic, benzoic, gallic and indole-3-acetic acids; herbicides like trichloroacetic, 2,4-dichlorophenoxyacetic and p-chlorophenoxy-acetic acids; fungicide like phenoxyacetic acid and organic acids such as citric, maleic, oxalic, sulphamic and tartaric acids which are present in fruit juices (7). It is also clear that the important separations of the aforementioned compounds can be achieved in common solvents such as chloroform and DW. Our previous work shows that calcium sulphate layers can be used by plain thin-layer chromatography for the binary separations. The present study shows that the same materials and solvents can

Table 1 : Separations Achieved on Calcium Sulphate by Two Dimensional TLC in Benzene and DW.

Acids	Separated From
Cinnamic acid (0,1)	Trichloroacetic acid (1,1); and citric, gallic, maleic and tartaric acids (1,0).
Cinnamic acid (0,1)	2,4-Dichlorophenoxyacetic acid (1,1); and citric, gallic, maleic and sulphamic acids (1,0).
β-Naphthaleneacetic acid (0,1)	Benzoic acid (1,1); and citric, gallic, maleic, oxalic and sulphamic acids (1,0).
β-Naphthaleneacetic acid (0,1)	Trichloroacetic acid (1,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
β-Naphthaleneacetic acid (0,1)	2,4-Dichlorophenoxyacetic acid (1,1); and citric, gallic, maleic, oxalic and sulphamic acids (1,0).

be used for many quaternary and ternary separations by the application of two-dimensional thin-layer chromatography. For example, quaternary separation of phenoxyacetic acid (R_f = 1,1) - indole-3-acetic acid (R_f = 0,0) - cinnamic acid (R_f = 0,1) - trichloroacetic or citric or maleic or oxalic or tartaric acid R_f (1,0) and ternary separation of β-naphthaleneacetic acid (R_f = 0,1) - 2,4-dichlorophenoxyacetic acid (R_f = 1,1) or trichloroacetic acid (R_f = 0.8,1) or phenoxyacetic acid (R_f = 0.8,1) which were not possible on plain thin-layer chromatography and now have been achieved by two-dimensional thin-layer chromatography.

Table 2: Separations Achieved on Calcium Sulphate by Two Dimensional TLC in Chloroform and DW

Acids	Separated From
Phenoxyacetic acid (1,1)	Indole-3-acetic acid (0,1); and citric 2,4-dichlorophenoxyacetic, gallic, maleic, oxalic, sulphamic and tartaric acids(1,0).
Trichloroacetic acid (1,1)	Indole-3-acetic acid (0,1); and benzoic, citric, gallic, maleic,oxalic, sulphamic and tartaric acids (1,0).
Phenoxyacetic acid (1,1)	β-Naphthaleneacetic acid (0,1); and benzoic, citric, gallic, maleic, oxalic and sulphamic acids (1,0).
Trichloroacetic acid (1,1)	β-Naphthaleneacetic acid (0,1); and benzoic, citric, gallic, maleic, oxalic , sulphamic and tartaric acids (1,0).
Phenoxyacetic acid (1,1)	β-Naphthoxyacetic (0,1); and benzoic, citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (1,1)	β-Naphthoxyacetic acid (0,1); and benzoic, citric, gallic, maleic, oxalic, sulphamic, and tartaric acids (1,0).

Table 3. Separations Achieved on Calcium Sulphate by Two Dimensional TLC in Ethyl Acetate and DW.

Acids	Separated From
Sulphamic acid (1,0)	Cinnamic acid (0,1); and benzoic, p-chlorophenoxyacetic, 2,4-dichlorophenoxyacetic and gallic acids (1,1) and maleic, phenoxyacetic and trichloroacetic acids (0.8,1).
Sulphamic acid (1,0)	Indole-3-acetic acid (0,1); and benzoic and maleic acids (1,1), and 2,4-dichlorophenoxyacetic acid (0.6,1) and p-chlorophenoxyacetic, gallic, phenoxyacetic and trichloroacetic acids (0.8,1).
Sulphamic acid (1,0)	β-Naphthaleneacetic acid (0,1); and benzoic, p-chlorophenoxyacetic, 2,4-dichlorophenoxyacetic, gallic, phenoxyacetic and trichloroacetic acids (1,1) and maleic acid (0.8,1).
Sulphamic acid (1,0)	β-Naphthoxyacetic acid (0,1); and benzoic and p-chlorophenoxyacetic acids (0.9,1) and 2,4-dichlorophenoxyacetic, gallic, maleic phenoxyacetic and trichloroacetic acids (1,1).

Foot Note - Similar results were obtained on calcium sulphate impregnated with p-DAB coating.

Table 4. Separations Achieved on Calcium Sulphate Containing 0.5 % p-DAB by Two Dimensional TLC in Benzene and DW

Acids	Separated From
2,4-Dichlorophenoxyacetic acid (0.8,1)	Cinnamic acid (0,1); and citric, gallic, maleic and sulphamic acids (1,0).
Phenoxyacetic acid (0.8,1)	Cinnamic acid (0,1); and gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (1,1)	Cinnamic acid (0,1); and citric, gallic, maleic and tartaric acids (1,0).
2,4-Dichlorophenoxyacetic acid (1,1)	β-Naphthaleneacetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Phenoxyacetic acid (0.8,1)	β-Naphthaleneacetic acid (0,1); and gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (0.8,1)	β-Naphthaleneacetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
2,4-Dichlorophenoxyacetic acid (1,1)	β-Naphthoxyacetic acid (0,1); and citric, gallic, maleic, oxalic and tartaric acids (1,0).
Phenoxyacetic acid (0.4,1)	β-Naphthoxyacetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (1,1)	β-Naphthoxyacetic acid (0,1); and citric, gallic, maleic and oxalic acids (1,0).

Table 5. Separations Achieved on Calcium Sulphate Containing 0.5 % p-DAB by Two Dimensional TLC in Chloroform and DW

Acids	Separated From
2,4-Dichlorophenoxyacetic acid (0.5,1)	Cinnamic acid (0,1); and citric, gallic, maleic, sulphamic and tartaric acids (1,0).
Phenoxyacetic acid (0.2,1)	Cinnamic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (0.2,1)	Cinnamic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
2,4-Dichlorophenoxyacetic acid (0.1,1)	Indole-3-acetic acid (0,1); and maleic, oxalic and tartaric acids (1,0).
Phenoxyacetic acid (1,1)	Indole-3-acetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (1,1)	Indole-3-acetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
2,4-Dichlorophenoxyacetic acid (0.8,1)	β-Naphthaleneacetic acid (0,1); and gallic, maleic and tartaric acids (1,0).
Phenoxyacetic acid (1,1)	β-Naphthaleneacetic acid (0,1): and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (1,1)	β-Naphthaleneacetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
2,4-Dichlorophenoxyacetic acid (0.5,1)	β-Naphthoxyacetic acid (0,1); and gallic, maleic and tartaric acids (1,0).
Phenoxyacetic acid (1,1)	β-Naphthoxyacetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).
Trichloroacetic acid (1,1)	β-Naphthoxyacetic acid (0,1); and citric, gallic, maleic, oxalic, sulphamic and tartaric acids (1,0).

Table 6. Separations Achieved on Calcium Sulphate Containing 1 % Alumina by Two Dimensional TLC in Benzene and DW

Acids	Separated From
β-Naphthaleneacetic acid (0,1)	Phenoxyacetic acid (1,1); and sulphamic and tartaric acids (1,0).

Table 7. Separations Achieved on Calcium Sulphate Containing 1 % Alumina by Two Dimensional TLC in Chloroform and DW.

Acids	Separated From
Phenoxyacetic acid (0.5,1)	Indole-3-acetic acid (0,1); and citric, maleic, sulphamic and tartaric acids (1,0).
Phenoxyacetic acid (0.7,1)	β-Naphthaleneacetic acid (0,1); and gallic, maleic, sulphamic, tartaric and trichloroacetic acids (1,0).
Phenoxyacetic acid (1,1)	β-Naphthoxyacetic acid (0,1); and citric, gallic, maleic, sulphamic and tartaric acids (1,0).

Table 8. Separations Achieved on Calcium Sulphate Containing 1 % Alumina by Two Dimensional TLC in Carbon tetra chloride and DW

Acids	Separated From
Phenoxyacetic acid (1,1)	Cinnamic acid (0,1); and indole-3-acetic acid (0,0); and citric, maleic, oxalic, sulphamic, tartaric and trichloroacetic acids (1,0).

Table 9. Separations Achieved on Calcium Sulphate Containing 1 % Alumina by Two Dimensional TLC in Ethyl Acetate and DW.

Acids	Separated From
Sulphamic acid (1,0)	Gallic acid (1,1); and cinnamic, indole-3-acetic, β-naphthaleneacetic and β-naphthoxyacetic acids (0,1).
Sulphamic acid (1,0)	Phenoxyacetic acid (0.7,1); and cinnamic, indole-3-acetic, β-naphthaleneacetic and β-naphthoxyacetic acids (0,1).
Sulphamic acid (1,0)	Trichloroacetic acid (0.8,1); and cinnamic, indole-3-acetic, β-naphthaleneacetic and β-naphthoxyacetic acids (0,1).
Oxalic acid (1,0)	Gallic acid (1,1); and cinnamic, indole-3-acetic, β-naphthaleneacetic, β-naphthoxyacetic acids (0,1).
Oxalic acid (1,0)	Phenoxyacetic acid (0.7,1); and cinnamic, indole-3-acetic, β-naphthaleneacetic, β-naphthoxyacetic acids (0,1).
Oxalic acid (1,0)	Trichloroacetic acid (0.7,1); and cinnamic, indole-3-acetic, β-naphthaleneacetic, β-naphthoxyacetic acids (0,1).
Tartaric acid (1,0)	Gallic acid (0.7,1); and cinnamic, indole-3-acetic, β-naphthaleneacetic and β-naphthoxyacetic acids (0,1).
Tartaric acid (1,0)	Phenoxyacetic acid (0.5,1); and indole-3-acetic, β-naphthoxyacetic acids (0,1).
Tartaric acid (1,0)	Trichloroacetic acid (1,1); and cinnamic and indole-3-acetic acids (0,1).

Table 10. Separations Achieved on Calcium Sulphate Containing 1 % Calcium Carbonate by Two Dimensional TLC in Carbon Tetra Chloride and DW

Acids	Separated From
Indole-3-acetic acid (0,0)	Benzoic acid (0,1); and citric gallic, maleic, tartaric and sulphamic acids (1,0).
Indole-3-acetic acid (0,0)	2,4-Dichlorophenoxyacetic acid (0,1); and citric, gallic, maleic, tartaric and sulphamic acids (1,0).
Indole-3-acetic acid (0,0)	β-Naphthaleneacetic acid (0,1); and citric, gallic, maleic, tartaric and sulphamic acids (1,0).
Indole-3-acetic acid (0,0)	Phenoxyacetic acid (0,1); and citric, gallic, maleic, tartaric and sulphamic acids (1,0).

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REFERENCES

1. Zakaria, M., Gonnord M.F. and Guiochon, G., J. Chromatogr., 1983, 271, 127.

2. Rathore, H.S., Sharma, S.K. and Kumari K. Anal. Letts., 1981, 14, 1327.

3. Rathore, H.S., Kumari, K. and Garg, M., J. Liq. Chromatogr., 1983, 6, 973.

4. Rathore, H.S., Kumari, K. and Agarwal, M., J. Liq. Chromatogr., 1985, 8, 1299.

5. Rathore, H.S. and Kumari, K. Anal. Letts., 1982, 15, 873.

6. Ahmed, S.R., Ali, I., Rathore, H.S. and Gupta, S., J. Liq. Chromatogr., 1984, 7, 1321.

7. Ma, T.S. in S. Patai (Editor), The Chemistry of Carboxylic Acids and Esters, Wilong, London 1969, p. 871.