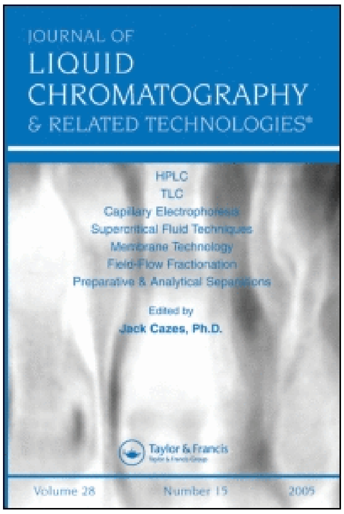

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QUANTITATIVE SEPARATION OF CITRIC ACID FROM TRICHLOROACETIC ACID ON PLATES COATED WITH CALCIUM SULPHATE CONTAINING ZINC OXIDE

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ABSTRACT

Thin-layer chromatographic behaviour of ten acids on coating of calcium sulphate containing ammonium molybdate, aluminium oxide, calcium carbonate, copper sulphate, ferric chloride, magnesium sulphate, phthalic anhydride, titanium oxide, zinc oxide etc. has been studied. Quantitative separation of citric acid from trichloroacetic acids has been achieved on calcium sulphate containing zinc oxide in ethyl acetate. Herbicide, trichloroacetic acid can be separated from plant growth regulators such as indole-3-acetic, β-naphthaleneacetic and β-naphthoxy acetic acids and from other organic acids.

INTRODUCTION

Our previous work[1,2,3] shows that papers impregnated with calcium carbonate, calcium sulphate, aluminium hydroxide and cadmium

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hydroxide have a great separation potential of organic acids. For example, separations such as adipic acid from maleic and malonic acids; citric (CT) or tartaric acids from ascorbic, gallic, malic acids etc; and barbituric acid from hippuric, α-ketoglutaric acids etc can be achieved on papers impregnated with carbonate and sulphate of calcium in aqueous electrolyte solutions. Benzoic or m-nitrobenzoic acids from gallic, β-naphthaleneacetic, β-naphthoxyacetic acids etc; and salicylic acid from CT, malic, tartaric acids etc can be achieved on papers impregnated with hydroxides of aluminium and cadmium in aqueous electrolyte solutions. Glass plates coated with calcium sulphate can be used for the separation of cinnamic, β-naphthaleneacetic and β-naphthoxyacetic acids from adipic, ascorbic, barbituric, hippuric, trichloroacetic (TCA) acids etc in benzene distilled water, and, 1,4-dioxane. Plates coated with calcium sulphate[4] containing charcoal, p-dimethylamino benzaldehyde (p-DAB), fly ash or silica gel can be used to separate cinnamic, indole-3-acetic and β-naphthalene-acetic acids from benzoic, phenoxyacetic and TCA acids in distilled water. However, none of the above mentioned coatings can be used for the separation of CT from TCA. Determination of CT in milk and blood is an important work in order to test the quality of milk and to diagonise certain diseases. TCA is a well known reagent for deproteinizing milk and blood. Most of the methods known for the determination of CT can not be used in presence of large concentration of TCA. As discussed above that TLC is a versatile technique to separate organic acids. Therefore, it was thought to be worth while to search a new coating that can be used to separate CT from TCA. In present study eighteen different coatings have been tested to separate CT from TCA. And it has been found that calcium sulphate containing zinc oxide in ethyl acetate can be used for this purpose. The results obtained are discussed in this paper.

EXPERIMENTAL

Apparatus

Stahl apparatus with applicator (adjustable thickness of the applied layer from 0.5-1.5 mm) (made in India), glass plates (20 x 4 cm), glass jars (25 x 5 cm), temperature controlled electric oven (Tempo, India), magnetic stirrer cum hot plate (Sunvic,U.K.) and Whatman No.40 filter paper (12.5 cm d) (Whatman Limited, England) were used.

Reagents and Chemicals

Bromophenol blue, calcium sulphate and potassium permagnate (Sarabhai M Chemicals, India); aluminium oxide (neutral), calcium carbonate, copper sulphate, diammonium hydrogen phosphate, ethyl acetate, magnesium sulphate, propanol, titanium oxide and zinc oxide (Glaxo Laboratories,India); ferric chloride, nickel sulphate and sodium tungstate (Ranbaxy Limited,India); ammonium molybdate (Koch Light Laboratories,India) and phthalic anhydried (BDH,India) were used. Other chemicals used were of analytical grade.

Aqueous (distilled water, DW) or ethanolic solutions of the acids (0.1N) were used.

Procedure

<u>Preparation of plates</u>. A slurry obtained (coating 1) by mixing calcium sulphate (30 g) with DW (60 ml) was applied on the glass plates with the help of the applicator so that the thickness of coating would be 0.75 mm. The plates were first allowed to dry at room temperature (30 ± 2 °C) for 15 min and then in electric oven at 110 ± 5 °C for 1 h. Similarly plates of variable thickness (0.5-1.5 mm) were made.

The procedure described above was also used to make plates of the following coatings.

Coating ii. $CaSO_4$ (30 g) + $(NH_4)_2MoO_4$ (0.3 g) + DW (60 ml).
Coating iii. $CaSO_4$ (30 g) + Al_2O_3 (0.3 g) + DW (60 ml).
Coating iv. $CaSO_4$ (30 g) + $CaCO_3$ (0.3 g) + DW (60 ml).
Coating v. $CaSO_4$ (30 g) + $CuSO_4$ (0.03 g) + DW (60 ml).
Coating vi. $CaSO_4$ (30 g) + $(NH_4)_2HPO_4$ (0.3 g) + DW (60 ml).
Coating vii. $CaSO_4$ (30 g) + $FeCl_3$ (0.03 g) + DW (60 ml).
Coating viii. $CaSO_4$ (30 g) + $MgSO_4$ (0.3 g) + DW (60 ml).
Coating ix. $CaSO_4$ (30 g) + $NiSO_4$ (0.3 g) + DW (60 ml).
Coating x. $CaSO_4$ (30 g) + $C_6H_4(CO)_2O$ (0.3 g) + DW (60 ml).
Coating xi. $CaSO_4$ (30 g) + Na_2WO_4 (0.3 g) + DW (60 ml).
Coating xii. $CaSO_4$ (30 g) + TiO_2 (0.3 g) + DW (60 ml).
Coating xiii. $CaSO_4$ (30 g) + ZnO (0.3 g) + DW (60 ml).
Coating xiv. $CaSO_4$ (30 g) + ZnO (0.1 g) + DW (60 ml).
Coating xv. $CaSO_4$ (30 g) + ZnO (0.5 g) + DW (60 ml).
Coating xvi. $CaSO_4$ (30 g) + ZnO (1.0 g) + DW (60 ml).
Coating xvii. $CaSO_4$ (30 g) + ZnO (1.2 g) + DW (60 ml).
Coating xviii. $CaSO_4$ (30 g) + ZnO (2.0 g) + DW (60 ml).

Spotting of test solution. Test solution was spotted on the plate with the help of a micro pipette. The plates were kept at room temperature (30 ± 2 °C) for 15 min for the removal of solvent and then developed in a solvent system. For tailing spot, R_f values were calculated by equation (a)

$$R_f = \frac{R_T + R_L}{2} \times \frac{1}{10} \quad \ldots \quad (a)$$

For compact spot, R_f values were calculated by equation (b)

$$R_f = \frac{\text{Distance travelled by substance (cm)}}{\text{Distance travelled by solvent front (10 cm)}} \quad \ldots \quad (b)$$

Detection of acids. Ethanolic alkaline bromophenol blue solution (1%) was used as location reagent for acids on plates.

Effect of CT concentration on its R_f value. A known volume (0.1 ml) of CT solutions of different concentration (0.1-0.5N) were spotted on coating xvi of 1 mm thickness. Then plates were developed in ethyl acetate and R_f values were measured as mentioned above.

Effect of thickness of coating on R_f value of CT. Plates of different thickness (0.5-1.5 mm) of coating xvi were made and 0.1 ml solution of CT (0.5N) was spotted on it. Then plates were developed in ethyl acetate and R_f values were measured as mentioned above.

Effect of concentration of zinc oxide on R_f value of CT. Plates of thickness 1 mm of coatings (xiii-xviii) were made and 0.1 ml of CT (0.5N) was spotted on it. Then plates were developed in ethyl acetate and R_f values were measured as mentioned above.

Quantitative separation of CT from TCA. A known volume of synthetic mixture of CT and TCA was spotted on TLC plates (coating xvi, 1 mm thickness), developed in ethyl acetate and spots were located with the reagent mentioned above. CT spot was scratched from the plates, CT was eluted with 10 ml DW and it was determined[5] with standard potassium permanganate (0.1N) in presence of 10 ml of 4N sulphuric acid.

RESULTS

R_f values obtained on different coatings in different solvent system are recorded in tables I, II and III. Possible separations are listed in table IV. The separations achieved practically are recorded in table V. The results of quantitative separation of CT from TCA are given in table VI. Effect of concentration of CT on its R_f value is shown in Fig 1. A plot of R_f value versus

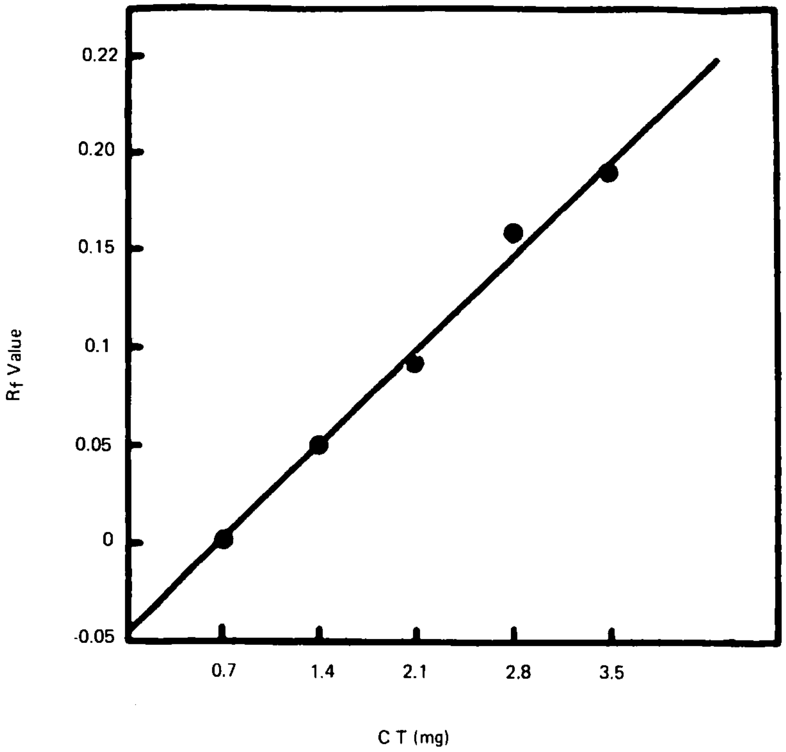

FIGURE 1. Effect of concentration of CT on its R_f value.

thickness of the coating is shown in Fig 2. Effect of concentration of zinc oxide on R_f value of CT is shown in Fig 3.

DISCUSSION

Tables IA and IB show the mobility of ten organic acids in ethanol. On calcium sulphate, acetic and oxalic acids remain at the point of application while other eight acids move. When calcium carbonate is mixed in calcium sulphate CT also remains at the point of application. It is also clear that none of the acids have zero R_f value when neutral or acidic inorganic compounds such as ammonium molybdate, aluminium oxide (neutral), copper sulphate, ferric chloride,

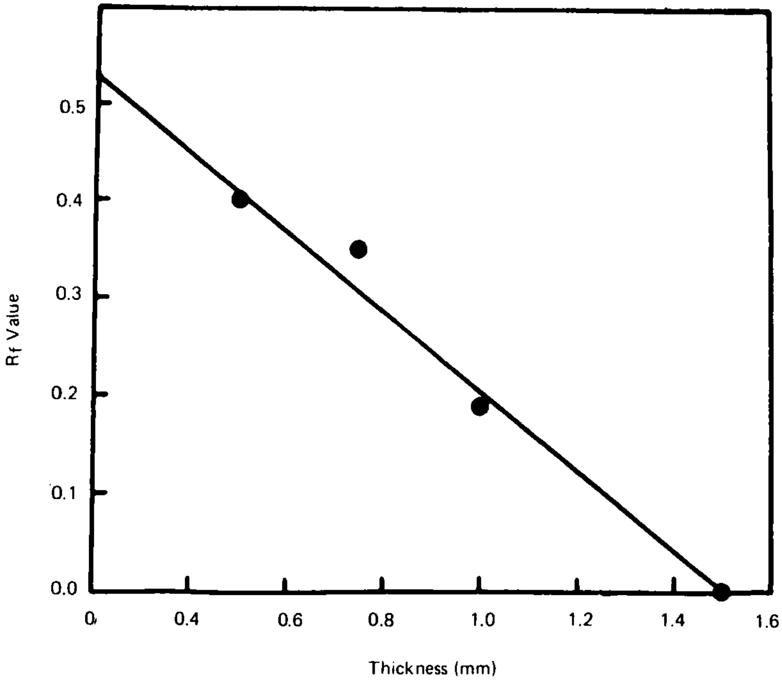

FIGURE 2. Effect of thickness of coating on R_f value of CT.

nickel sulphate, titanium oxide and zinc oxide are mixed in calcium sulphate. These results reflect that calcium sulphate alone and calcium sulphate containing calcium carbonate in ethanol are the selective coatings i.e. acetic and oxalic acids can be separated from other acids on these coatings. Tables IIA and IIB show that calcium sulphate and calcium sulphate containing calcium carbonate are no more specific in DW. On calcium sulphate five acids remain at the point of application and on calcium sulphate containing calcium carbonate none of the acids move. However, in DW other coatings which were inactive in ethanol become specific. For example, calcium sulphate containing aluminium oxide (neutral) can be used to separate CT, oxalic and TCA from other seven acids. Table III

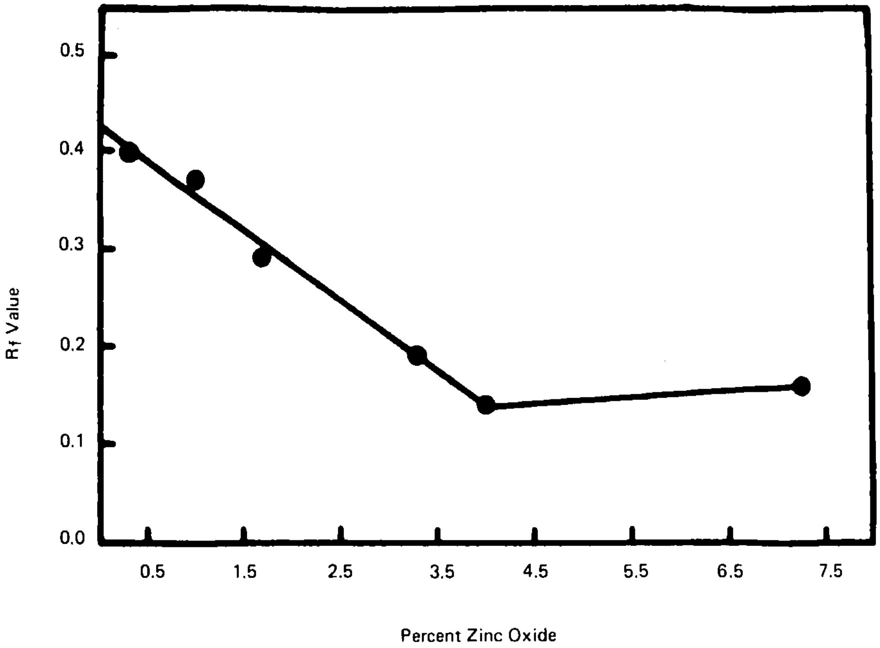

FIGURE 3. Effect of concentration of zinc oxide on R_f value of CT.

shows that calcium sulphate in ethyl acetate can be used for the separation of acetic acid from many acids. Similarly, CT and oxalic acids can be separated from other acids on calcium sulphate containing zinc oxide in ethyl acetate. Acetic and oxalic acids can be separated from many acids on calcium sulphate and calcium sulphate containing zinc oxide in propanol respectively. Table IV shows that many important separations can be achieved on different coatings. Table V shows the practical utility of different coatings for separating organic acids. It is obvious that CT and oxalic acids can be separated from many acids on calcium sulphate and calcium sulphate containing zinc oxide in ethyl acetate and propanol. Herbicide[6], TCA can be separated from plant growth regulators such as

TABLE IA

R_f VALUES OF ACIDS ON PLATES COATED WITH CALCIUM SULPHATE CONTAINING DIFFERENT MATERIALS IN ETHANOL

Acids	Coatings						
	i	ii	iii	iv	v	vi	vii
Acetic	0.00	-	0.00	0.00	-	-	-
Benzoic	1.00	1.00	0.90	1.00	1.00	1.00	1.00
Cinnamic	1.00	1.00	0.90	1.00	1.00	1.00	1.00
Citric	0.50●	1.00	0.50*	0.00	0.50●	1.00	0.50*
Indole-3-acetic	1.00	1.00	0.90	1.00	0.90	1.00	0.90
β-Naphthaleneacetic	1.00	1.00	0.90	1.00	0.90	1.00	0.90
β-Naphthoxyacetic	0.50*	1.00	0.90	1.00	0.90	1.00	0.90
Oxalic	0.00	1.00	0.50*	0.00	0.50●	0.50*	0.50*
Phenoxyacetic	1.00	1.00	0.90	1.00	0.90	1.00	0.90
Trichloroacetic	1.00	1.00	0.50●	0.50*	0.50●	1.00	0.50*

● = Tails, coatings are defined in the experimental section.

TABLE IB

R_f VALUES OF ACIDS ON PLATES COATED WITH CALCIUM SULPHATE CONTAINING DIFFERENT MATERIALS IN ETHANOL

Acids	Coatings					
	viii	ix	x	xi	xii	xiii
Acetic	-	-	-	-	-	0.95
Benzoic	1.00	1.00	1.00	1.00	1.00	0.90
Cinnamic	1.00	1.00	1.00	0.90	1.00	0.90
Citric	1.00	0.50$^{\bullet}$	0.50*	0.80	1.00	0.23*
Indole-3-acetic	1.00	0.90	1.00	0.80	1.00	0.45*
β-Naphthaleneacetic	1.00	1.00	1.00	0.60	1.00	0.50*
β-Naphthoxyacetic	1.00	1.00	1.00	0.90	1.00	0.50*
Oxalic	0.50$^{\bullet}$	0.50*	0.50$^{\bullet}$	0.50$^{\bullet}$	1.00	0.13$^{\bullet}$
Phenoxyacetic	1.00	1.00	1.00	1.00	1.00	0.80
Trichloroacetic	1.00	1.00	1.00	1.00	1.00	0.95

Abbreviations are defined in table IA.

TABLE IIA

R_f VALUES OF ACIDS ON PLATES COATED WITH CALCIUM SULPHATE CONTAINING DIFFERENT MATERIALS IN DW

Acids	Coatings						
	i	ii	iii	iv	v	vi	vii
Acetic	1.00	1.00	$0.50^{\bullet}$	-	1.00	1.00	1.00
Benzoic	0.00	1.00	0.40^{*}	-	0.90	0.75^{*}	1.00
Cinnamic	0.00	$0.50^{\bullet}$	0.00	0.00	0.50^{*}	0.50^{*}	0.50^{*}
Citric	1.00	1.00	1.00	-	1.00	1.00	1.00
Indole-3-acetic	0.00	$0.50^{\bullet}$	0.00	0.00	$0.50^{\bullet}$	0.50^{*}	0.50^{*}
β-Naphthaleneacetic	0.00	$0.50^{\bullet}$	0.00	0.00	0.50^{*}	0.50^{*}	0.50^{*}
β-Naphthoxyacetic	0.00	0.50^{*}	0.00	0.00	0.50^{*}	0.50^{*}	0.50^{*}
Oxalic	1.00	1.00	1.00	-	1.00	1.00	1.00
Phenoxyacetic	0.70	0.70	0.70	-	0.90	0.90	1.00
Trichloroacetic	1.00	1.00	1.00	-	1.00	1.00	1.00

Abbreviations are defined in table IA.

TABLE IIB

R_f VALUES OF ACIDS ON PLATES COATED WITH CALCIUM SULPHATE CONTAINING DIFFERENT MATERIALS IN DW

Acids	Coatings					
	viii	ix	x	xi	xii	xiii
Acetic	1.00	1.00	1.00	1.00	1.00	1.00
Benzoic	0.90	0.85	0.85	1.00	$0.75^{\bullet}$	1.00
Cinnamic	0.00	0.50^{*}	0.50^{*}	0.50^{*}	0.50^{*}	$0.50^{\bullet}$
Citric	1.00	1.00	1.00	1.00	1.00	1.00
Indole-3-acetic	0.00	$0.50^{\bullet}$	$0.50^{\bullet}$	$0.50^{\bullet}$	$0.50^{\bullet}$	0.50^{*}
β-Naphthaleneacetic	0.00	$0.50^{\bullet}$	0.50^{*}	$0.50^{\bullet}$	1.00	$0.50^{\bullet}$
β-Naphthoxyacetic	0.00	0.50^{*}	$0.50^{\bullet}$	0.50^{*}	0.50^{*}	$0.50^{\bullet}$
Oxalic	0.90	1.00	1.00	1.00	1.00	1.00
Phenoxyacetic	0.65	0.70	1.00	1.00	0.65	1.00
Trichloroacetic	0.85	1.00	0.85	1.00	0.75	1.00

Abbreviations are defined in table IA.

TABLE III

R_f VALUES OF ACIDS ON PLATES COATED WITH CALCIUM SULPHATE AND ZINC OXIDE IN DIFFERENT SOLVENTS

Acids	Ethyl acetate		Propanol	
	Coating i	Coating xiii	Coating i	Coating xiii
Acetic	0.00	0.75^*	0.00	0.85
Benzoic	1.00	0.95	0.95	0.95
Cinnamic	1.00	0.95	0.95	0.95
Citric	$0.45^\bullet$	0.00	$0.50^\bullet$	0.05^*
Indole-3-acetic	$0.50^\bullet$	0.50^*	$0.50^\bullet$	0.50^*
β-Naphthaleneacetic	1.00	1.00	0.95	0.95
β-Naphthoxyacetic	1.00	$0.50^\bullet$	0.95	0.95
Oxalic	0.50^*	0.00	$0.50^\bullet$	0.00
Phenoxyacetic	0.95	0.50^*	0.95	0.50^*
Trichloroacetic	1.00	0.90	0.95	0.95

Abbreviations are defined in table IA.

TABLE IV

LIST OF POSSIBLE SEPARATIONS

Acids	Material coated	May be separated from	Solvent system
Citric (0) and oxalic (0)	iv	Benzoic (1), cinnamic (1), indole-3-acetic (1), β-naphthaleneacetic (1), β-naphthoxyacetic (1) and phenoxyacetic (1) acids.	Ethanol
Citric (0.23^*) and oxalic (0.13^*)	xiii	Benzoic (0.9), cinnamic (0.9), phenoxyacetic (0.8) and trichloroacetic (0.95) acids.	-do-
Citric (0) and oxalic (0)	xiii	Benzoic (0.95), cinnamic (0.95), β-naphthaleneacetic (1) and trichloroacetic (0.9) acids.	Ethyl acetate
Citric (0.05^*) and oxalic (0)	xiii	Benzoic (0.95), cinnamic (0.95), β-naphthaleneacetic (0.95), β-naphthoxyacetic (0.95) and trichloroacetic (0.95) acids.	Propanol

TABLE IV (Contd.)

Acids	Material coated	May be separated from	Solvent system
Citric (1), oxalic (1), phenoxyacetic (0.7) and trichloroacetic (1)	iii	Cinnamic (0), indole-3-acetic (0), β-naphthaleneacetic (0) and β-naphthoxyacetic (0) acids.	DW
Cinnamic (0), indole-3-acetic (0), β-naphthaleneacetic (0) and β-naphthoxyacetic (0).	viii	Benzoic (0.9), citric (1), oxalic (0.9), phenoxyacetic (0.65) and trichloroacetic (0.85) acids.	-do-

Abbreviations are defined in table IA.

TABLE V

LIST OF SEPARATIONS ACHIEVED

Acids	Material coated	Separated from	Solvent system
Citric (0) and oxalic (0)	iv	Benzoic (1), cinnamic (1), β-naphthalene-acetic (1.0), β-naphthoxyacetic (1.0) and trichloroacetic (1.0) acids.	Ethanol
Citric (0.23^*) and oxalic (0.13^*)	xiii	Benzoic (0.9), cinnamic (0.9), phenoxy-acetic (0.8) and trichloroacetic (0.95) acids.	-do-
Citric (0) and oxalic (0)	xiii	Benzoic (0.95), cinnamic (0.95), β-naphthaleneacetic (1) and trichloroacetic (0.9) acids.	Ethyl acetate
Citric (0.05^*) and oxalic (0)	xiii	Benzoic (0.95), cinnamic (0.95), β-naphthaleneacetic (0.95), β-naphthoxyacetic (0.95) and trichloroacetic (0.95) acids.	Propanol

TABLE V (Contd.)

Acids	Material coated	Separation from	Solvent system
Citric (1) and oxalic (1)	iii	β-naphthaleneacetic (0) and β-naphthoxyacetic (0) acids.	DW
Phenoxyacetic (0.7)	iii	Cinnamic (0), indole-3-acetic (0), β-naphthaleneacetic (0) and β-naphthoxyacetic (0) acids.	-do-
Trichloroacetic (1)	iii	Indole-3-acetic (0), β-naphthaleneacetic (0) and β-naphthoxyacetic (0) acids.	-do-
Indole-3-acetic (0), β-naphthaleneacetic (0) and β-naphthoxyacetic (0)	viii	Benzoic (0.9), citric (1), oxalic (0.9), phenoxyacetic (0.65) and trichloroacetic (0.85) acids.	-do-
Cinnamic (0)	viii	Phenoxyacetic (0.65) and trichloroacetic (0.85) acids.	-do-

Abbreviations are defined in table IA.

TABLE VI

QUANTITATIVE SEPARATION OF CITRIC ACID (CT)
FROM TRICHLOROACETIC (TCA) ACID

Mixture separated CT (mg) + TCA (mg)	Amount of CT (mg) found	Percent error
0.70 + 1.63	0.49	-30
1.40 + 1.63	1.30	-10
2.10 + 1.63	2.00	-05
2.80 + 1.63	2.63	-06
3.50 + 1.63	3.10	-11

indole-3-acetic, β-naphthalene acetic and β-naphthoxyacetic acids on calcium sulphate containing aluminium oxide (neutral) in DW.

Separation of CT from TCA. It is clear from tables IV and V that CT can be separated from TCA on calcium sulphate containing zinc oxide in ethyl acetate. Table VI shows that CT can be separated from TCA quantitatively. Ratio of CT to TCA is either 1:2 or 2:1 separation can be achieved successfully. Fig 1 shows that the R_f value of CT increases linearly with its increasing concentration. Results plotted in Fig 2 proves the above conclusion because R_f value of CT decreases linearly as the thickness of the coating increases. Fig 3 shows that R_f value of CT decreases as the concentration of oxide increases in calcium sulphate. However, R_f value of TCA remains unchanged by changing the concentration of TCA, thickness of coating and concentration of zinc oxide in calcium sulphate i.e. in all conditions it has R_f value 0.9 to 1.0. Hence it seems that zinc oxide plays a very important role in separating CT from TCA. It may be due to the fact that CT and TCA react with zinc oxide to give zinc citrate and zinc trichloroacetate respectively. It seems that zinc citrate is insoluble in ethyl acetate as it remains at the point of application and zinc trichloroacetate is highly soluble.

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