iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 2 **Issue:** V **Month of publication:** May 2014

DOI:

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

ISSN: 2321-9653

INTERNATIONAL JOURNAL FOR RESEARCH IN APPLIED SCIENCE AND ENGINEERING TECHNOLOGY (IJRASET)

Chromatographic Separation of Phenolic Compounds on Stannic Oxide Layers: Determination of Salicylic acid in Drug Samples

Ajay Gupta

Assistant Professor, Department of Applied Science,S.R Group of Institutions,Jhansi,U.P

Abstract--- Thin layer chromatography of twenty three pharmaceutically important phenolic compounds has been performed on thin layers of stannic oxide ion-exchanger in different aqueous, non-aqueous and mixed solvent systems. A number of useful binary and ternary separations have been achieved on these layers. Resorcinol have been separated selectively from a synthetic mixture of seven commonly used phenols. The method has been utilized for the quantitative separation of salicylic acid from six different multicomponent drug samples.

Key words-----TLC, Stannic oxide ion-exchanger, phenolic compounds and salicylic acid.

I. INTRODUCTION

Thin layer chromatography has found applications for the separation of phenolic compounds using various types of adsorbents[1-3]. Thin layers of inorganic ion-exchange materials have been widely used for the separation of metal ions[4-8]. A survey of literature reveals that very little efforts have been made to utilize such layers for the separation of organic compounds [9-10].Grace et al have reported thin layer chromatographic separation of ortho,meta and para amino phenols on titanium oxide layers[11]. In continuation to the efforts in this direction, separation of phenolic compounds has been performed on thin layers of stannic oxide and their subsequent determinations in synthetic mixtures. Salicylic acid has been separated and quantitatively determined in a number of drug samples.

Phenols have been choosen for the separation study due to their biological,immunological and pharmaceutical importance.Stannic oxide is used as ion-exchange material for the separation of phenolic compounds because it has been found to be quite stable in acids, bases and various organic solvents and has already been used for the separation of pesticides and cephalosporins[12,13]. Moreover,the material exhibits amphoteric ion-exchange behavior depending upon the pH of the medium.The use of such layers without any binder makes it easier to have a clear interpretation about the mechanism of the separation.

II. METHODOLOGY

A. Reagents and Chemicals:

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Stannic chloride pentahydrate(Loba Chemie,India) and ammonia solution (Ranbaxy,India) of A.R grade were used. All other reagents and solvents used were also of A.R grade.

B. Apparatus:

Thin layer chromatographic applicator (Desaga FRG) was used to prepare thin layers on 15x5 cms glass plates. The plates were developed by ascending technique in a large mouth glass chamber.A micropipette was used for the spotting purpose and Systronics-105 spectrophotometer was used for colorimetric studies.

C. Test Solutions:

1% solution of different phenolic compounds were prepared in desired solvents and used as test solutions.

D. Detectors:

The following detectors were used to visualize the phenolic compounds:

(i) 1 ml saturated solution of silver nitrate was added to 20 ml acetone with stirring and the product was treated dropwise with water until the precipitated $AgNO_3$ just dissolved.Spots became intense at about 105 ºC.

(ii) Some of the phenols which were not visualized by the above procedure gave blue to green colored spots with 1-5 % solution of $FeCl_3/K_4Fe(CN)_6$(1:1) in dil.HCl.

(iii) Picric acid, thymol blue, tetrahydroxy anthraquinone(THA) and fluorescein were acted as self detectors.

E. Preparation of ion-exchanger and development of TLC plates:

Stannic oxide ion-exchange material was prepared by adding dilute ammonia solution gradually to 0.5 M stannic chloride solution with constant shaking till the pH of solution raised to 8.5. The resulting precipitate was digested for 24 hours at room temperature and clear supernatant liquid was decanted.The precipitate was washed several times with DMW by centrifugation and decantation till it was free from all chloride ions.The precipitate was filtered under suction and dried completely in an oven at 80 ºC.The ion-exchange material so obtained was cracked in demineralized water,filtered and finally dried in oven at the same temperature.For the preparation of TLC plates,the granules of stannic oxide were well powdered in a mortar. The slurry of this material was prepared in double distilled water and spread over the glass plates with the help of an applicator to obtain uniform thin layers of 0.2 mm thickness. The plates were activated at 80ºC for about one hour in an oven.

F. Solvent systems:

The following solvent systems were used as the developers to observe the movement of various phenols on thin layers of stannic oxide ion-exchanger: 2% formic acid(S_1), 2% boric acid(S_2), 2% sodium borate(S_3),2% boric acid-2% sodium borate(2:1v/v)(S_4), 2% boric acid-2% sodium borate(4:1v/v)(S_5),ethyl acetate-formic acid(1:1v/v)(S_6), acetone-formic acid(1:1v/v)(S_7), acetone-hexane(1:9 v/v)(S_8),acetone-hexane(9:1 v/v)(S_9),1,4 dioxane(S_{10}),dioxane-formic acid(1:1v/v)(S_{11}),benzene-formic acid(1:1v/v)(S_{12}), dimethyl sulfoxide(S_{13}),dimethyl sulfoxide-formic acid(1:1v/v)(S_{14}),cyclohexane-ethyl acetate(3:7v/v)(S_{15}) and ethyl acetate-cyclohexanone (7:3 v/v)(S_{16}).

G. Procedure:

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0.05 ml test solutions of phenolic compounds were applied with the help of micropipette on the plates.After drying the spots, the plates were developed by ascending technique in various solvent systems.The solvents were allowed to ascend upto 10 cm from the point of application in each case.The plates were dried in air and then sprayed with suitable detector.

(i) Quantitative separationof phenolic compounds in synthetic mixtures:

0.05 ml mixture of phenolic compounds containing 50 micro gram each component was spotted with the help of micropipette at the point of application on the glass plate.The plates were developed in the usual manner. The pilot chromatograms were run under the similar experimental conditions to ascertain actual position of the spots on the plates.The same portions of the plates were scratched out and the phenols present in these portions were extracted with 5 ml of absolute alcohol,concentrated and then determined spectrophotometrically.Most of the phenols were determined using titanium sulphate[14].Salicylic acid was spectrophotometrically determined by ferric chloride method[15].

(ii) Quantitative separation of salicylic acid in drug samples:

Salicylic acid was determined quantitatively as a component in six multicomponent drug formulations namely Mycoderm, Pragmatar, Derobin, Keralin, Polyderm and Methazil in which salicylic acid has been used as an antifungal agent. 1 gm(in case of Methazil 1 ml) of each drug sample was dissolved in ethanol or double distilled water in 50 ml of standard flasks. Then 0.05 ml of the standard solutions prepared earlier were put on the TLC plates with the help of micropipette. The plates were developed in desired solvent (i.e 2% formic acid). Pilot chromatograms were run under similar experimental conditions and the actual positions of the spots on the plates were ascertained. The same portions of the spots were scratched out and salicylic acid present in these portions was extracted with absolute alcohol,concentrated on water bath and then determined spectrometro--photometrically by the usual method as above.

The composition of the drug samples as per the labels is given below:

(i) *Mycoderm(FDC):* Each 100 gm contains; salicylic acid 3% w/w, benzoic acid 6% w/w, camphor 0.52% w/w and menthol 0.08 % w/w.

(ii) *Pragmatar(Smithkline):* Each 25 gm contains ; salicylic acid 3 % w/w benzoic acid6% w/w, menthol 0.5 % w/w and camphor 2 % w/w.

(iii) *Derobin(Glaxo):* Each 25 gm contains ; salicylic acid 1.15 % w/w,dithranol 1.15% w/w and coaltar solution 5.3 % w/w.

(iv) *Keralin(East India):* Each 10 gm contains; salicylic acid 6 % w/w ,benzoic acid 12 % w/w and hydrocortisone acetate 0.5 % w/w.

(v) *Polyderm(Chowgle Hind):* Each 25 gm contains; salicylic acid 5 % w/w, iodo--chlorhydroxy quinolin 4 % w/w , prednisolone 0.5 % w/w and mesulphen 40% w/w.

(vi) *Methazil liq.(Bell India):* Each 10 ml contains ; salicylic acid 2.2 % v/v and methanol 6 % v/v.

III. RESULTS AND DISCUSSION

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The cation exchange properties of stannic oxide ion-exchange material exhibit great affinity for phenols which are capable of furnishing hydrogen ions in solution. So such layers offer promising potentialities for various important binary, ternary and multinary separations of phenols as shown in Table-2. It has also been observed that the spots

are compact and well defined in most of the solvent systems. Number of diverse solvent systems have been tried for the separation study of phenols. Among various solvent systems studied, formic acid has been found to be the most effective in the separation of different categories of phenols. It is worthwhile to note that members of the same group of phenols have been conveniently separated from each other e.g. separation of cresols , nitrophenols, naphthols and structural isomers of dihydroxybenzene(viz catechol, resorcinol and quinol). In addition, polyphenols have also been separated from mono and bi-phenols e.g. separations of pyrogallol and resorcinol, phlorogucinol and catechol and of of phenol, pyrogallol and resorcinol etc. Some of the most important and difficult separations achieved on thin layers of stannic oxide are : (i) o- cresol from p-cresol (ii) α-naphthol from β-naphthol (iii) ortho, meta and para phenols (iv) salicylic acid from p-hydroxybenzoic acid (v) catechol from resorcinol and quinol. It has been shown in Table-1 that the addition of formic acid to pure DMSO and 1,4-dioxane results in a decrease in the movement of of majority of phenols. This is due to decrease in the overall polarity of the developing systems. It has also been observed that in acetone-hexane system, R_F value for most of the phenols increases with an increase in acetone content which is due to increased polarizability of these phenols with increased polarity of the system. In the same developing system, resorcinol is strongly held by the stationary phase and remains at the point of application. Its movement is also unaffected on increasing acetone content in the composition.In acetone-formic acid system, a similar trend has been shown by resorcinol , thereby enabling to achieve some multinary separations. R_F values of phenols in certain solvent systems vary with the orientation of hydroxyl groups in isomers

of dihydroxybenzene (DHB) viz ortho DHB (catechol), meta DHB (resorcinol) and para DHB (quinol). In solvent S_1 , S_2, S_{13} and S_{14} , R_F value of dihydroxybenzenes follows the order:

para DHB > meta DHB > ortho DHB

On the other hand, a reverse trend has been observed in S_6 , S_{10} and S_{11} solvent systems where the order is:

ortho DHB > meta DHB > para DHB

This difference in behaviour can only be explained in terms of intramolecular hydrogen bonding in catechol (orth DHB) which is not found in resorcinol and quinol. This might be due to the fact that the affinity of ion-exchanger is more for those phenols which can give more number of hydrogen ions. A remarkable feature of the migration behaviour of phenolic compounds on the layers of this adsorbent is that in diverse solvent systems, certain selective separations of phenols have become possible from synthetic mixture of other common phenols.Therefore, resorcinol has been selectively separated quantitatively from a mixture of phenol, pyrogallol, catechol , o-cresol, p-cresol, α- naphthol and β-naphthol in acetone-hexane (9:1) system.The results are reported in Table-2.

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This method is simple, rapid , selective and applicable to the characterization of phenols over a wide concentration range. The practical utility of the method has been illustrated in separation and determination of salicylic acid as a component in six commonly used multicomponent drug samples. The reproducibility of the method has been checked statistically.The results are summarized in Table-3.

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ISSN: 2321-9653

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Table 1. R_F values of phenolic compounds on stannic oxide layers in different solvent systems

S.N	Phenolic compounds	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}
1.	Phenol	0.48	0.76	0.65	0.70	0.78	0.76	0.88	0.60	0.75	0.85	0.60	0.85	0.85	0.60	0.75	0.60
2.	Pyrogallol	0.65	0.91	0.80	0.83	0.90	0.45	0.50	0.52	0.70	0.92	0.75	0.56	0.70	0.30	0.86	0.28
3.	Catechol	0.62	0.50	0.36	0.51	0.00	0.85	0.81	0.52	0.72	0.78	0.68	0.58	0.53	0.40	0.70	0.62
4.	Resorcinol	0.73	0.63	0.72	0.80	0.62	0.58	0.00	0.00	0.00	0,64	0.52	0.82	0.60	0.51	0.83	0.78
5.	Quinol	0.84	0.76	0.50	0.58	0.60	0.31	0.24	0.20	0.40	0,50	0.35	0.47	0.67	0.62	0.81	0.70
6.	Phloroglucinol	0.90	0.80	0.70	0.78	1.00	0.80	0.57	0.30	0.58	0.95	0.82	0.79	0.62	0.57	0,68	0.45
7.	o-Cresol	0.50	0.84	0.67	0.60	0.30	0.35	0.24	0.78	0.95	0.85	0.16	0.56	0.72	0.62	0.81	0.75
8.	p-Cresol	0.00	0.50	0.86	0.90,	0.88	0.00	0.78	0.86	0.98	0.97	0.51	0.76	0.90	0.70	0.80	0.68
9.	a-Naphthol	0.88	0.77	0.76	0.70	0.68	0.50	0.32	0.25	0.75	1.00	0.30	0.42	0.40	0.42	0.95	0.86
10.	(3-Naphthol	0.50	0.73	0.50	0.62	0.69	0.92	0.40	0.62	0.80	0.85	0.70	0,62	0.58	0.84	0.90	0.82
11.	o-Nitrophenol	0.85	0.72	0.60	0.60	0.56	0.72	0.79	0.60	0.75	0.87	0.80	0.78	0.90	0.78	0.43	0.24
12.	m-Nitrophenol	0.64	0.30	0,45	0.40	0.42	0.78	0.50	0,00	0.00	0.78	0.65	0.69	0.32	0.85	0.95	0.76
13.	p-Nitrophenol	0.21	0.00	0.00	0.20	0.25	0.84	0.31	0,72	0.85	0.94	0.58	0.32	0.00	0.24	0.93	0.44
14.	Salicylic acid	0.90	0.78	0.72	0.75	0.80	0.25	0.47	0.20	0.39	0.93	0.20	0.18	0.69	0.68	0.80	0.60
15.	p-Hydroxybenzoic. acid	0.62	0.76	0.50	0.70	0.75	0.80.	0.64	0.52	0.61	0.90	0.64	0.68	0.41	Q.62	0.88	0.70
16.	Picric acid	0.86	0.78	0.60	0.68	0.68	0.66	0.78	0.31	0.40	0.86	0.69	0.82	0.70	0,38	0.62	0.29
17.	Tannic acid	0.71	0.70	0.55	0.61	0.65	0.60	0.40	0.10	0.24	0.85	0.50	0,35	0.52	0.48	0.26	0.00
18.	Gallic acid	0.73	0.65	0.61	0.64	0.65	0.75	0.54	0.32	0.38	0.81	0.85	0.70	0.68	0.61	0.64	0.20
19.	o-Chlorophenol	0.70	0.62	0.60	0.69	0.70	0.96	0.66	0.70	0.78	0.76	0.48	0.80	0.51	0.47	0.83	0.38
20.	o-Aminophenol	0.38	0.88	0.80	0.85	0.92	0.60	0.25	0.66	0.80	0.78	0.81	0.65	0.40	0.60	0.00	0.76
21.	Tetrahydroxy anthraquinone	0.00	0.50	0.61	0.68	0.75	0.85	0.70	0.08	0.20	0.60	0.72	0.60	0.77	0.62	0.58	0.50
22.	Thymol blue	0.90	0.82	0,73	0.60	0.25	0.92	0.42	0.40	0.68	0.82	0.48	0.49	0.80	0.63	0.78	0.95
23.	Fluorescein	0.34	0.40	0.62	0.48	0.20	0.70	0.64	0.38	0.50	0.94	0.68	0.60	0.52	0.85	0.60	0.00

S_1 = 2% formic acid

S_2 = 2% boric acid

S_3 = 2% sodium borate

S_4 = 2% boric acid-2% sodium borate(2:1 v/v)

S_5 = 2% boric acid-2% sodium borate(4: I v/v)

S_6 = Ethyl acetate-formic acid (1:1 v/v)

S_7 = Acetone-formic acid (1:1 v/v)

S_8 = Acetone- hexane (1:9 v/v)

S_9 = Acetone-hexane (9:1 v/v)

S_{10} = 1.4-dioxane

S_{11} = 1.4-dioxane-formic acid (1:1 v/v)

S_{12} Benzene-formic acid (1:1 v/v)

S_{13} = Dimethylsulfoxide (DMSO)

S_{14}= DMSO-formic acid (1:1 v/v)

S_{15} = Cyclohexane-ethyl acetate (3:7 V/V)

S_{16} = Cyclohexane-ethyl acetate (7:3 v/v)

ISSN: 2321-9653

Table -2. Quantitative separations of phenolic compounds in synthetic mixtures on Stannic oxide thin layer plates

S.N.	Separations achieved	Amount taken (µg)	Amount found (µg)*	% Error	Solvent system
1.	o-Cresol	50	49.75	-0.50	S_1
	p-Cresol	50	49.50	-1.00	
2.	Quinol	50	49.85	-0.30	S_2
	Pyrogallol	50	50.20	+0.40	
3.	o-Nitrophenol	50	50.00	0.00	S_2
	m-Nitrophenol	50	49.70	-0.60	
	p-nitrophenol	50	49.95	-0.10	
4.	α-Naphthol	50	49.90	-0.20	S_6
	β-Naphthol	50	50.40	+0.80	
5.	Salicylic acid	50	50.20	+0.40	S_6
	p-Hydroxybenzoic acid	50	50.15	+0.30	
6.	Catechol	50	49.80	-0.40	S_7
	Resorcinol	50	50.10	+0.20	
7.	Resorcinol from phenol, pyrogallol, catechol, o-cresol, p-cresol, α-naphthol, and (β-naphthol	50	49.65	-0.70	

*Average of five replicate determinations.

S_1 = 2% formic acid

S_2 = 2% boric acid

S_6 = Ethyl acetate-formic acid(1:1 v/v)

S_7 = Acetone - formic acid (1:1 v/v)

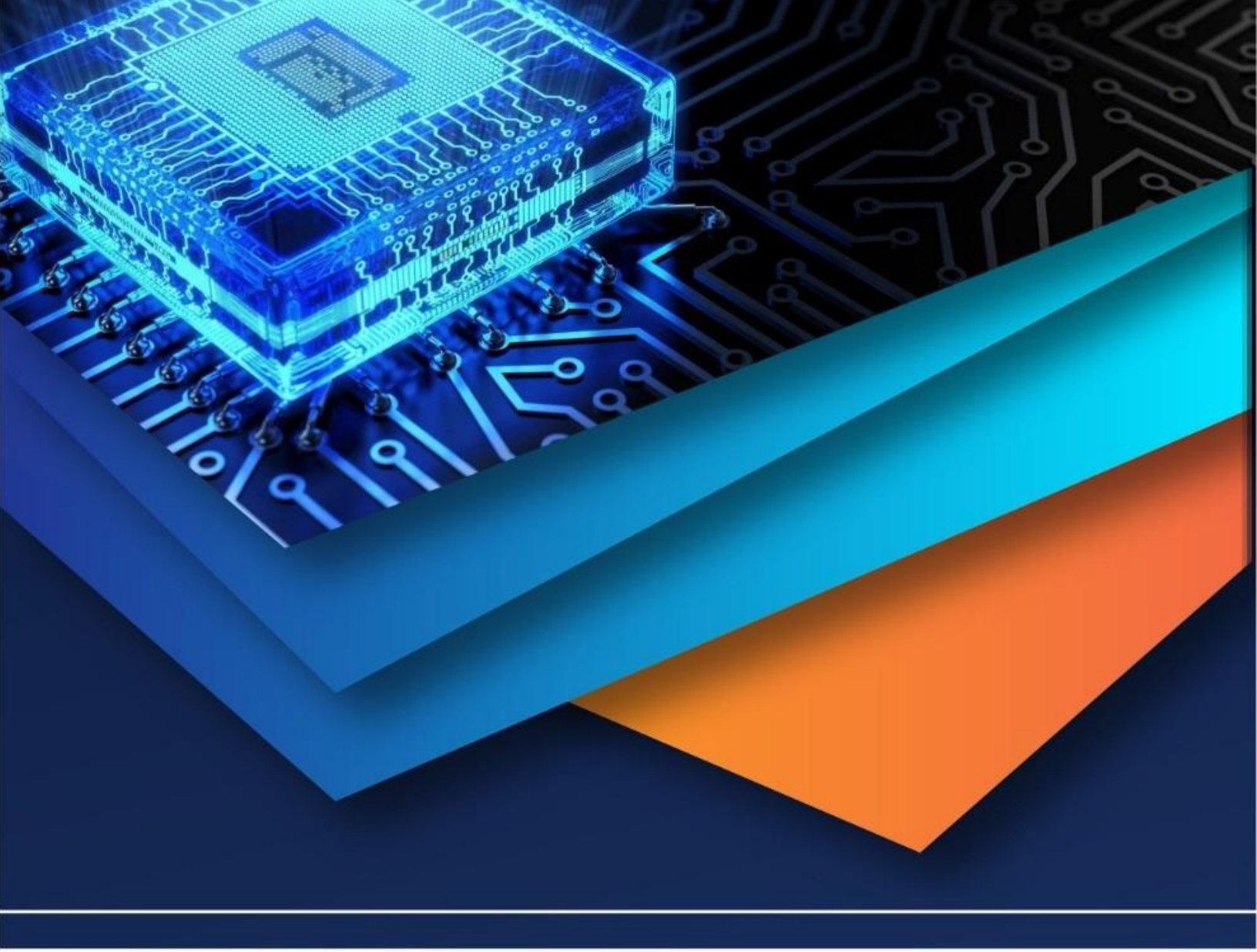
S_9 = Acetone-hexane (9:1 v/v)

ISSN: 2321-9653

Table- 3. Quantitative determination of salicylic acid in drug samples on stannic oxide thin layer plates

S.N.	Commercial name of the drug	Labelled amount of salicylic acid in drug (mg/g)	Amount taken (µg)	Amount found (µg)*	% Deviation from the labelled composition	Solvent system
I.	Mycoderm powder (FDC)	30.0	30.0	29.20	—2.67	S_1
2.	Pragmatar oint. (Smithkline)	30.0	30.0	29.65	—1.17	
3.	Derobin oint. (Glaxo)	11.5	11.5	11.40	-0.87,	
4.	Keralin oint. (East India)	60.0	60.0	60.20	+0.33	
5.	Polyderm oint. (Chowgle Hind)	50.0	50.0	49.15	—1.70	
6.	Methazil liquid (Bell)	22.0	22.0	22.20	+0.91	

*Average of five replicate determinations , S_1=2% Formic acid



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