

THIN-LAYER CHROMATOGRAPHY OF THIOPHENE DERIVATIVES

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While there are several accounts¹⁻⁴ of the application of normal column chromatographic techniques to the separation of thiophene derivatives, there has been no extensive use⁵ of qualitative techniques such as paper chromatography. This is probably due to the lack of suitable methods for the detection of these compounds. Most of the sensitive tests^{6,7} for the presence of thiophenes require the use of conc. sulphuric acid to catalyse a condensation with a carbonyl component. The reaction with isatin to give "indophenines" is typical.

The presence of sulphuric acid in these tests has made the use of paper chromatography difficult but this does not apply to thin-layer chromatography^{8,9} for qualitative separations. The use of aggressive reagents for detection in this method is well known.

In connection with other work in progress, qualitative separations were required and a range of standard thiophenes and derivatives have, therefore, been tested by this technique.

GENERAL PROCEDURE

Thin-layer chromatographic apparatus from Desaga G.m.b.H. was used with Alumina G and Silica G (Merck) as adsorbents in films of 275 μ thickness. The plates were activated by heating at 120° for one hour immediately before use and the thiophenes (ten on each plate) were then added with a micro-pipette in the usual way as solutions in chloroform (50 γ of thiophene derivative in 25 μ l of solvent). After equilibrating in the tank for 30 min the plates were irrigated with petroleum ether (b.p. 40-60°), benzene-chloroform (9:1) or methanol over a period of approximately 30 min at room temperature. Some of the thiophenes tested were volatile under these conditions but this difficulty was overcome by carrying out the complete operation in a cold room at 4°.

When the chromatogram was complete the spots were detected by fluorescence in U.V. light (2450 Å) followed by spraying with a solution of isatin (0.4 %) in conc. sulphuric acid. Other carbonyl reagents (ninhydrin, benzil and phenanthraquinone) were tested and also gave positive results but showed no advantages. After examination the plates were heated for a few minutes at 120° when colour reactions which had not occurred at room temperature were observed and spots already visible at room temperature often showed characteristic colour changes.

RESULTS AND DISCUSSION

We have found that non-polar thiophenes can be separated on alumina by elution with petroleum ether, thiophenes of moderate polarity on silica by elution with benzene-chloroform (9:1) and the very polar thiophene derivatives by methanol on silica. There does not seem to be any characteristic colour produced by the thiophenes tested but there is a predominance of blue and violet colours. Only two thiophenes failed to react with the reagent but this effect was only observed on silica plates; positive reactions were obtained on alumina. There were small variations in the R_F values recorded but variation is often encountered with this technique and was overcome by running a standard compound on all chromatograms. α -Terthienyl was suitable for this purpose.

TABLE I
 R_F VALUES AND COLOUR REACTIONS

Adsorbent: Alumina G		Solvent: Petroleum ether (b.p. 40-60°)		
Compound	Concentration (%)	Colour under U.V.	Colour with isatin	$R_F \times 100$
2-Methylthiophene*	50	—	Yellow → green blue	76
3-Methylthiophene*	300	—	Blue	82
2-Ethylthiophene*	300	—	Deep yellow	92
2,5-Dimethylthiophene*	300	—	Pink	95
2,3,5-Trimethylthiophene*	50	—	Violet → pink	87
2,3-Dimethyl-4-ethylthiophene*	50	—	Brown	84
Tetramethylthiophene*	50	—	Violet → pink	89
Methyl 3-thienyl sulphide*	50	—	Orange	92
n-Decyl 3-thienyl sulphide*	50	—	Pale violet	96
Bithienyl ¹	50	Violet	Blue	80
α -Terthienyl ¹	50	Yellow	Wine red → blue green	57
α -Quaterthienyl ¹	50	Lime green	Pale green	26
5,5'-Dichlorobithienyl ¹⁰	50	Lime green	Violet	89
5,5'-Dimethylbithienyl ¹⁰	50	Violet	Yellow	76
α -Phenyl- α -bithienyl ¹⁰	50	Yellow	Green blue	50
5,5'-Diphenylbithienyl ¹⁰	50	Blue	Wine red → mauve	16
5,5''-Dimethylterthienyl ¹⁰	50	Yellow	Wine red → mauve	48
Adsorbent: Silicagel G		Solvent: Benzene-chloroform (9:1)		
Thiophene-carboxaldehyde	300	Crimson	— (Yellow**)	34 (84)**
2-Nitrothiophene	300	Crimson	— (Pale blue**)	61 (91)**
2-Benzoylthiophene	300	Crimson	Violet (120°)	39
2-Acetylthiophene	300	Crimson	Violet (120°)	25
Adsorbent: Silicagel G		Solvent: Methanol		
Thiophene-carboxylic acid	150	Crimson-violet	Grey → blue (120°)	65
β -(α -Thienyl)-acrylic acid	150	Crimson-violet	Violet	57
4-(α -Thienyl)-butyric acid	150	Crimson-violet	Orange	60
Bithienyl-5-carboxylic acid ¹⁰	50	Deep violet	Yellow	63
2,2'-Bithienyl-methylamine hydrochloride	50	Pale violet	Violet	35

* Volatile samples run at 4°.

** When run at the same concentration on alumina and eluted with benzene-chloroform (9:1) these samples gave the results indicated (e.g. yellow).

The lowest concentrations of the various thiophenes which could be detected on the plates after development varied between different compounds and also depended on the solvent system and the adsorbent being used. The concentrations recorded are those which produce an intense spot and do not represent the lower limits of detection. Later work¹¹ indicates that the silica-gel/benzene-chloroform system is of more general application than is represented by the results given in Table I.

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SUMMARY

A method for the qualitative separation of various thiophene derivatives by means of thin-layer chromatography is described.

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