

PAPER CHROMATOGRAPHY OF POLYPHENYLS  
QUALITATIVE SEPARATION OF SULPHONIC ACID  
DERIVATIVES OF DIPHENYL AND *o*-, *m*- AND *p*-TERPHENYLS

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(Received November 23rd, 1962)

INTRODUCTION

Polyphenyls are a class of compounds the use of which is very promising as moderators and coolants in nuclear reactors.

Some experimental work has appeared in various recent papers on the chromatographic separation of polyphenyls. The separation of isomeric terphenyls on alumina, fuller's earth, silica gel and charcoal has been studied by HELLMANN, ALEXANDER AND COYLE<sup>1</sup> and by WEST<sup>2</sup>.

BARRERA<sup>3</sup> has carried out some separations of terphenyls by chromatography on acetylated paper using the technique described by SPOTSWOOD<sup>4</sup>. Good separations of mixtures of diphenyl and *m*-terphenyl are, however, not possible using the procedure described by BARRERA since for diphenyl  $R_F = 0.64$  and for *m*-terphenyl  $R_F = 0.66$ .

The present paper describes a chromatographic method for separating diphenyl and isomeric terphenyls on untreated paper.

EXPERIMENTAL

*Sulphonation of polyphenyl mixtures*

0.25 g of polyphenyls are mixed with 1.2 ml of concentrated  $H_2SO_4$  ( $d = 1.84$ , Merck analytical reagent grade) and heated in a thermostat at 50° for 4 h. The mixture of sulphonic acids and excess sulphuric acid is diluted with distilled water, poured into a volumetric flask and made up to 25 ml.

*Preparation of the solvent*

The solvent is prepared by mixing *n*-butanol, methanol and 3 *N* aqueous solution of  $(NH_4)_2CO_3$ , in the volume ratio 4:3:2. Some solid ammonium carbonate crystallizes out on mixing the liquids, and is eliminated by centrifugation.

*Chromatographic technique*

The chromatographic separations were carried out by the ascending technique on 23 × 53 cm strips of Whatman paper No. 20.

The solution for the development was put in a glass chromatographic chamber 31 × 21 × 38 cm 20 h before the introduction of the strips. The strips were then

developed with the solvent for 40 h at room temperature (20°). After development, the strips were dried at 70° in an air oven for 30 min, and sprayed with 0.1 % alcoholic solution of methyl red, diluted in the volume ratio 1:5 with phosphate buffer at pH 7.

## RESULTS AND DISCUSSION

The present method of separation takes advantage of the different sulphonation velocities of diphenyl and the isomeric terphenyls under the above-mentioned experimental conditions.

On sulphonation for 4 hours at 50° a mixture of mono- and disulphonic acids is obtained (*viz.* *p*-diphenyl-disulphonic, *o*-terphenyl-monosulphonic and -disulphonic, *m*-terphenyl-monosulphonic and -disulphonic, *p*-terphenyl-monosulphonic acids). With different sulphonation times and different temperatures the composition of the

TABLE I  
RESULTS OF SULPHONATION EXPERIMENTS

Compound	Temp. (°C)	Time (h)	Disulphonic acid	Monosulphonic acid
Diphenyl	50	4	Present ( $R_F$ 0.37)	Not found
	50	5	" "	" "
	100	1-5	" "	" "
	150	5	" "	" "
<i>o</i> -Terphenyl	50	4	" ( $R_F$ 0.23)	Present ( $R_F$ 0.54)
	50	5	" "	Not found
	100	1-5	" "	" "
	150	5	" "	" "
<i>m</i> -Terphenyl	50	4	" ( $R_F$ 0.23)	Present ( $R_F$ 0.50)
	50	5	" "	" "
	100	1-5	" "	" "
	150	5	" "	Not found
<i>p</i> -Terphenyl	50	4	Not found	Present ( $R_F$ 0.44)
	50	5	" "	" "
	100	1-5	" "	" "
	150	5	Present ( $R_F$ 0.23)	Not found

mixture of sulphonic acids is also different. At 150° all the disulphonic acids are formed. In this case the chromatographic separation of *o*-, *m*-, and *p*-terphenyl is not possible. Table I shows the results obtained under various sulphonation conditions. In Table II the composition of the different commercial and synthetic mixtures of polyphenyls, used in the present work, are given.

Figs. 1 and 2 show some paper-chromatographic separations. Good separations and readily discernible spots are obtained from mixtures containing, as lower limits, the quantities of each component given in Table III.

The sensitivity of detection for every sulphonic acid useful for the identification, is shown in Table IV.

When higher polyphenyls (quaterphenyls, quinquephenyls) are present, one or more spots with  $R_F < 0.23$  are obtained, and thus do not interfere with the components of the mixture sought.

TABLE II

COMPOSITION OF THE POLYPHENYL MIXTURES USED FOR THE PAPER CHROMATOGRAPHIC SEPARATIONS

Compound	Commercial mixtures (composition given by the manufacturers)		Synthetic mixtures from purified compounds		
	Santowax R (Monsanto) %	Santowax OMP (Monsanto) %	%	%	%
Diphenyl	1	1	32.95	30.77	31.76
<i>o</i> -Terphenyl	9	12	5.78	30.87	32.54
<i>m</i> -Terphenyl	55	64	30.58	32.69	3.97
<i>p</i> -Terphenyl	15	23	30.67	5.65	31.71
High-boiling fraction (quater- phenyl, quinquephenyl, triphenylene, etc.)	10-20	1	—	—	—

TABLE III

PRACTICAL DETECTION LIMITS OF THE COMPONENTS

The limits for separation (readily discernible spots) are given in weight percent of the mixture.

Compound	wt. %
Diphenyl	0.5
<i>o</i> -Terphenyl	6
<i>m</i> -Terphenyl	4
<i>p</i> -Terphenyl	6

TABLE IV

SENSITIVITY OF DETECTION

Compound	Sensitivity $\gamma$
Diphenyl (as disulphonic acid)	10
<i>o</i> -Terphenyl (as monosulphonic acid)	60
<i>m</i> -Terphenyl (as monosulphonic acid)	25
<i>p</i> -Terphenyl (as monosulphonic acid)	60

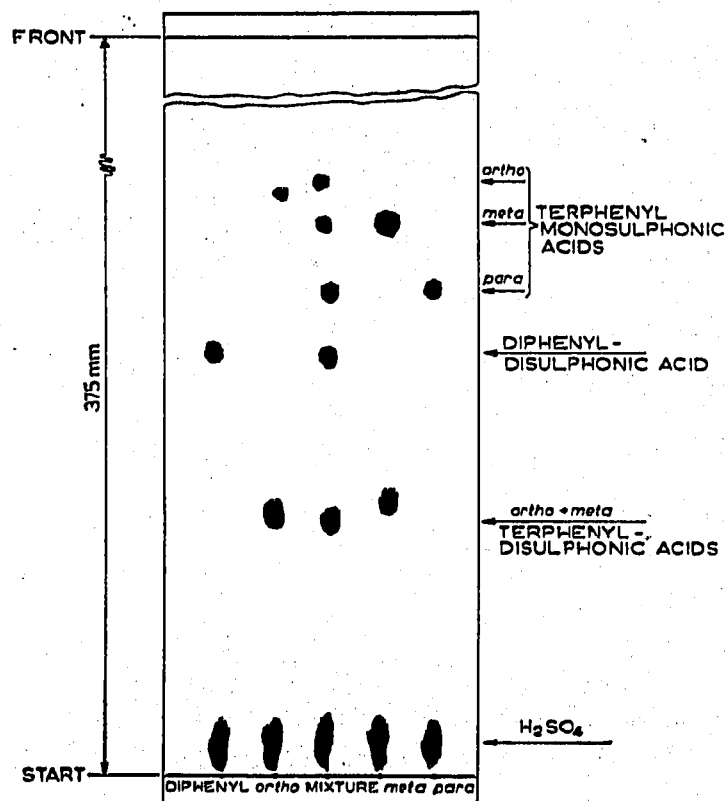


Fig. 1. Paper chromatography of diphenyl, *o*-, *m*-, and *p*-terphenyls and of a synthetic mixture (via the sulphonic acid derivatives).

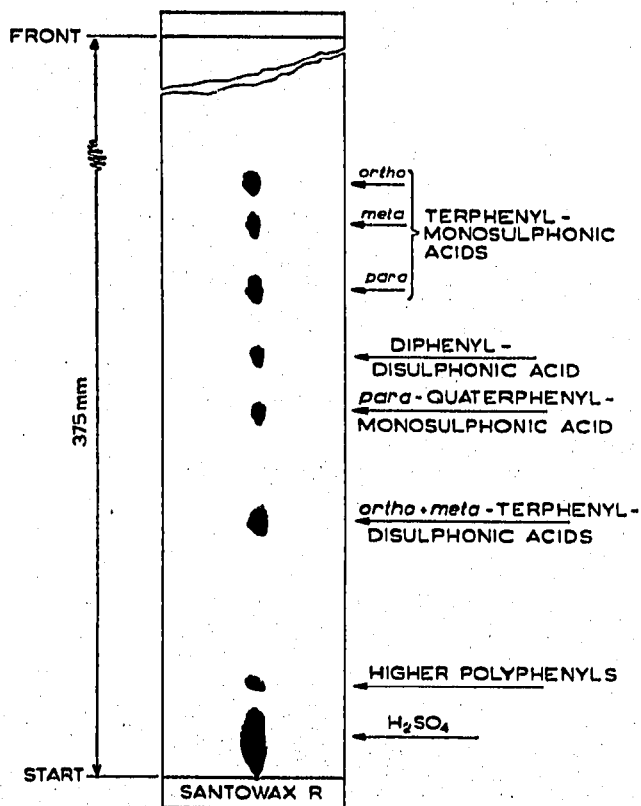


Fig. 2. Paper chromatography of Santowax R (via sulphonic acid derivatives).

## ACKNOWLEDGEMENT

The authors wish to express their appreciation to S.O.R.I.N. for permission to publish this paper.

## SUMMARY

A new paper chromatographic method for separating diphenyl and *o*-, *m*-, and *p*-terphenyls is described, in which the mixture of polyphenyls is first sulphonated under controlled conditions.

The migration velocities of the various sulphonic acids are different, and good separations are obtained by paper chromatography. The acids are located on the chromatographic strips by spraying with an indicator.

## REFERENCES

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