

PAPER CHROMATOGRAPHIC ANALYSIS OF SOME BY-PRODUCTS FROM ALKALINE FUSION OF BENZENESULFONIC ACID

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INTRODUCTION

The alkaline fusion of benzenesulfonic acid or its sodium salt is the oldest commercial method for the synthesis of phenol. This process has been used for many years and is still in use today. Many studies have been carried out in order to determine the operating conditions that will give the greatest yield with the smallest amount of by-products¹⁻³.

The fusion reaction is normally carried out by the addition of benzenesulfonic acid or its sodium salt to molten sodium hydroxide. The temperature of this reaction usually is maintained between 300 and 350° with a slight excess of sodium hydroxide^{1,2}. The desired products of this reaction are sodium phenate and sodium sulfite. The fusion reaction product is normally dissolved in water and acidified to obtain free phenol which is purified by fractionation. The sodium sulfite is recovered from the aqueous phase.

The vigorous conditions of the fusion reaction lead to the formation of a number of interesting by-products. Some of these by-products have been isolated and identified³. The major by-product is *o*-phenylphenol. This compound has a number of commercial applications. Some of the minor by-products are *m*-phenylphenol, *p*-phenylphenol, thiophenol, diphenyl ether, biphenyl, diphenylene oxide, resorcinol, *o,o'*-diphenol, *o,p'*-diphenol and *p,p'*-diphenol. Benzenesulfonic acid usually contains some diphenylsulfone unless it is removed by special means. Therefore, when benzenesulfonic acid is used in the reaction, diphenylsulfone is found in the fusion reaction product. Some of the reported by-products have been found to result from the thermal decomposition of sodium phenate⁴ and others from oxidation of the fusion product¹. Paper chromatographic data have been reported on the phenols known to be present^{5,6}.

The previously reported methods for the separation and identification of the various by-products have all involved laborious and complex procedures. Frequently, the only method available has consisted of repeated extraction, recrystallization and fractionation. This procedure necessitates the use of a large amount of starting material. The process also requires a large amount of time and equipment. This paper describes a paper chromatographic method which greatly simplifies the separation, identification and quantitative estimation of the major phenolic by-products. This method has also shown that five unidentified phenols are present in the fusion reaction product.

EXPERIMENTAL

Sample preparation

A sample of the fusion reaction product is prepared by the method of RHODES *et al.*¹ using benzenesulfonic acid in place of sodium benzene sulfonate. A 300 g sample is dissolved in a minimum of water (about 700 ml) and is then carefully acidified to a pH of 5-6 with 50-60 % sulfuric acid. The solution is transferred quantitatively to a large evaporating dish and evaporated to dryness on a steam bath overnight under a fume hood. Slow agitation will speed the evaporation. The solid residue remaining is finely ground and then extracted repeatedly with 500 ml of boiling acetone until the extracts are colorless. The acetone solutions are combined, filtered and evaporated to dryness. The solid residue from the evaporation of the acetone is extracted again with 200 ml of boiling acetone. The acetone is filtered and evaporated to dryness. The extractions are repeated using 100 ml of acetone until the residue reaches a constant weight, usually requiring a total of three to four extractions. A 1.00 g sample of the final residue is weighed into a 10 ml volumetric flask and diluted to the mark with acetone and a few drops of water to give a clear solution containing 100 $\mu\text{g}/\mu\text{l}$ of solids.

The preceding sample solution can be used for chromatograms that will give qualitative identification of all the phenols known to be present. The same solution can be used for chromatograms that will give quantitative estimation of all the known phenols with the exception of *o*-phenylphenol. Sample preparation for the quantitative estimation of this compound is carried out in the following manner. A 3.00 g sample of the fusion reaction product is weighed into a 10 ml volumetric flask and diluted to the mark with water. This gives a solution containing 300 $\mu\text{g}/\mu\text{l}$ of solids. This solution is then used for quantitative estimation of *o*-phenylphenol.

Reagents

Mineral spirits (Kauri-Butanol value 37-38, aniline point 56-59°) saturated by shaking with distilled water, toluene saturated by shaking with distilled water and anhydrous methanol. In the text, all references to mineral spirits and toluene should be taken to mean water-saturated mineral spirits and toluene. Ceric ammonium nitrate reagent prepared by dissolving 200 g of ceric ammonium nitrate in 500 ml of 2 *N* nitric acid with heating. After standing overnight the clear supernatant liquid is decanted for use as the color developing reagent⁵.

Chromatography

The separation of a complex mixture of products for identification necessitates the use of two-dimensional paper chromatography. Mineral spirits and water or toluene and water are the solvent combinations used for two-dimensional chromatography. The toluene and mineral spirits are kept saturated with water by the presence of a lower water layer in the chamber. The chambers are lined with paper sheets extending into the water layer to insure a saturated atmosphere. The papers are all allowed to equilibrate thirty minutes before immersion unless otherwise specified. All chromatograms are run with ascending solvent travel at 25°. In the case of *p*-phenylphenol and *p,p'*-diphenol, multiple development must be used to achieve quantitative separation.

A 5 μl sample of the prepared acetone solution is applied to a 150 mm square

piece of Whatman No. 1 paper at a point 15 mm from each edge at the lower right hand corner. The first solvent used is mineral spirits. This solvent is allowed to ascend 110 mm and the paper is removed and air dried. The paper is rotated 90° and the second solvent (water) is allowed to ascend 110 mm. The paper is removed and while still wet sprayed with the ceric ammonium nitrate solution. The paper is thoroughly washed with water and air dried. The spots are carefully outlined in pencil.

The preceding process leaves both *p*-phenylphenol and *p,p'*-diphenol on the original spot. In order to locate the *p*-phenylphenol, a second paper must be run in the following manner. The sample is applied as before and mineral spirits allowed to travel up the paper 110 mm. The paper is dried, rotated 90° and water is allowed to travel 110 mm up the paper in the second direction. The paper is again dried and is then rotated back to the original position and toluene is allowed to ascend 110 mm up the paper. The paper is then sprayed and water washed as before. The *p*-phenylphenol spot is carefully outlined in pencil.

To locate any *p,p'*-diphenol present, the following procedure is used. The sample is spotted as before using a 15 μ l sample. The first solvent used is toluene. This solvent is allowed to ascend 110 mm. The paper is air dried and then water is allowed to ascend 110 mm in the same direction. The paper is dried, rotated 90° and anhydrous methanol is allowed to travel 110 mm in the second direction. The paper is dried, sprayed and washed as before. The *p,p'*-diphenol spot is carefully outlined in pencil.

For the quantitative estimation of *o*-phenylphenol, a 10 μ l sample of the aqueous solution of the fusion reaction product is applied to several spots 15 mm from the lower edge of a strip of Whatman No. 1 paper. The paper is dried in the oven 10 min at 100° and then hung in the chamber of mineral spirits for one hour. The paper is immersed and the solvent allowed to ascend 110 mm. The paper is water washed briefly and then sprayed with the ceric ammonium nitrate solution while still wet. The paper is again water washed, dried and the spots carefully outlined in pencil. The average spot area is determined.

In order to obtain quantitative data on the known phenols, calibration curves must be prepared with known samples. The curves are obtained by plotting spot area *versus* sample weight in the usual manner. The sample for determination of the calibration curve for *o*-phenylphenol simulates the aqueous solution of the fusion reaction product. The calibrating solution is prepared by dissolving 6–7 g of sodium phenate, 1–2 g sodium hydroxide, 6–7 g sodium sulfite and 0.15 g of *o*-phenylphenol in water and diluting to 50 ml in a volumetric flask. This gives a solution containing 3.0 μ g/ μ l of *o*-phenylphenol.

In order to gain some additional information on the unknown spots found, the fusion product extract sample is run using toluene in the first direction and water in the second direction.

RESULTS AND DISCUSSION

Qualitative

The R'_F values have been determined in four solvents for the known phenols and in three solvents for the unknown phenols. The R'_F value is the ratio of the spot front to the solvent front⁷. These values are shown in Table I. The reference number in Table I refers to the spot numbers in Figs. 1–4.

TABLE I

 R'_F VALUES OF VARIOUS PHENOLS

Ref. No.	Phenol	R'_F mineral spirits	R'_F toluene	R'_F water	R'_F methanol	Spot color
1	<i>o</i> -Phenylphenol	0.96	0.99	0.61	1.00	rust red
2	<i>m</i> -Phenylphenol	0.77	0.97	0.40	1.00	light tan
3	<i>p</i> -Phenylphenol	0.00*	0.95	0.00	1.00	light gray-green
4	<i>o,o'</i> -Diphenol	0.37	0.83	0.80	1.00	brown
5	<i>o,p'</i> -Diphenol	0.08	0.53	0.52	1.00	light tan
6	<i>p,p'</i> -Diphenol	0.00	0.00	0.00	0.94	light yellow to tan
7	Resorcinol	0.00	0.11	0.78	0.96	light brown
8	Unknown	0.00	0.21	0.31	—	light tan
9	Unknown	0.93	1.00	0.00	—	light pink
10	Unknown	0.79	1.00	0.00	—	light tan
11	Unknown	0.00	0.21	0.00	—	light brown
12	Unknown	0.00	0.00	0.95	—	brown fading to yellow

* Most of the material stays on the spot, but a very small streak extends up to R'_F 0.54.

Both mineral spirits and toluene have been found to be satisfactory for use as the first solvent in the separation. With both of these solvents water is used as the second solvent in a two-dimensional chromatogram. However, for quantitative purposes mineral spirits is preferred since more complete separation occurs. Fig. 1 shows the location of the various spots using mineral spirits and water as the two solvents. Several of the unknown phenols are separated with this solvent combination.

The phenylphenols are not well separated when toluene and water are used as the mobile solvents. However, this combination separates one of the unidentified phenols that was not found by any other method. The *p*-phenylphenol is also separated

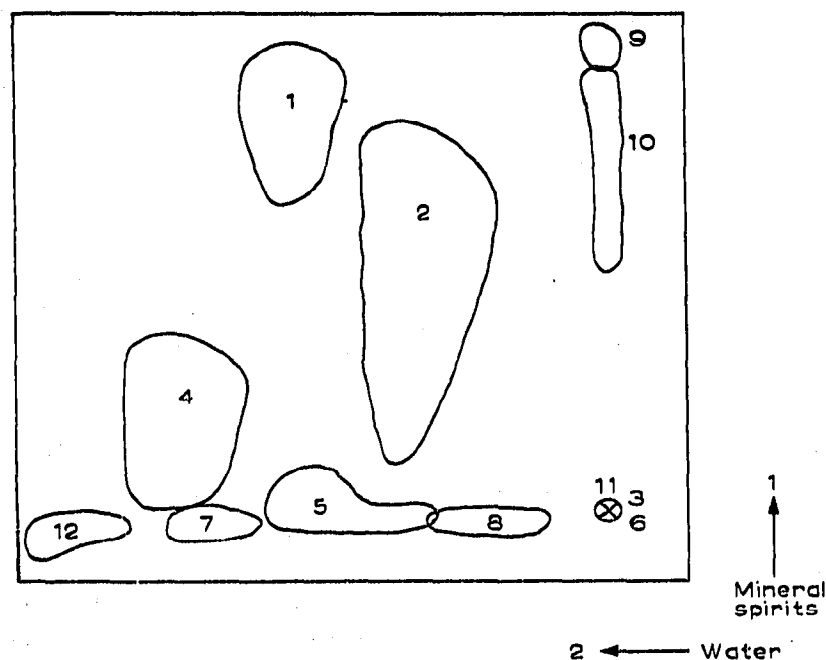


Fig. 1. Two-dimensional chromatogram of fusion product extract using mineral spirits and water.

by this combination although not quantitatively. The location of the spots using this solvent combination is shown in Fig. 3.

In using either mineral spirits or toluene in combination with water to separate the phenols, some material always remains on the original spot. Consequently, it is necessary to resort to a fourth solvent in order to resolve and identify this material and determine the R_f value. Anhydrous methanol separates the material into a single

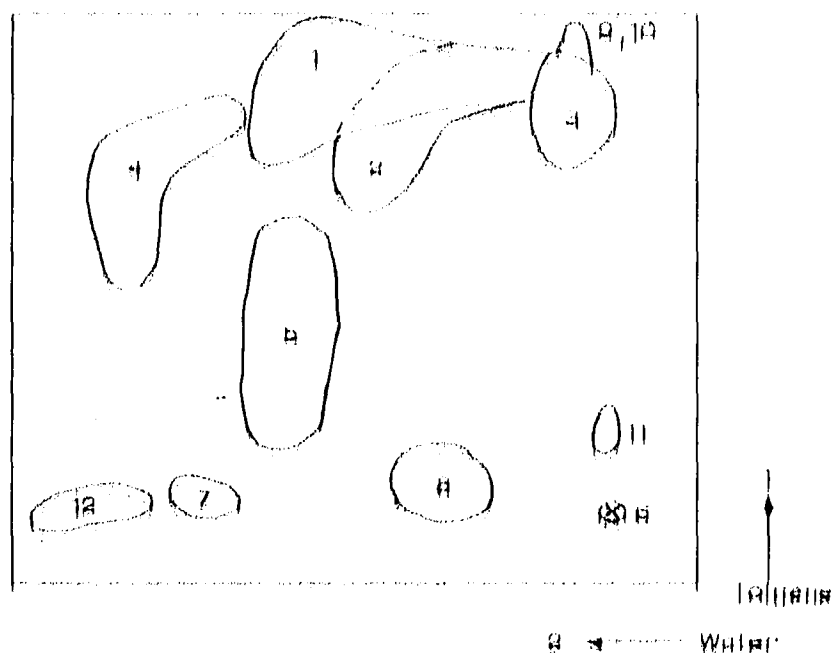
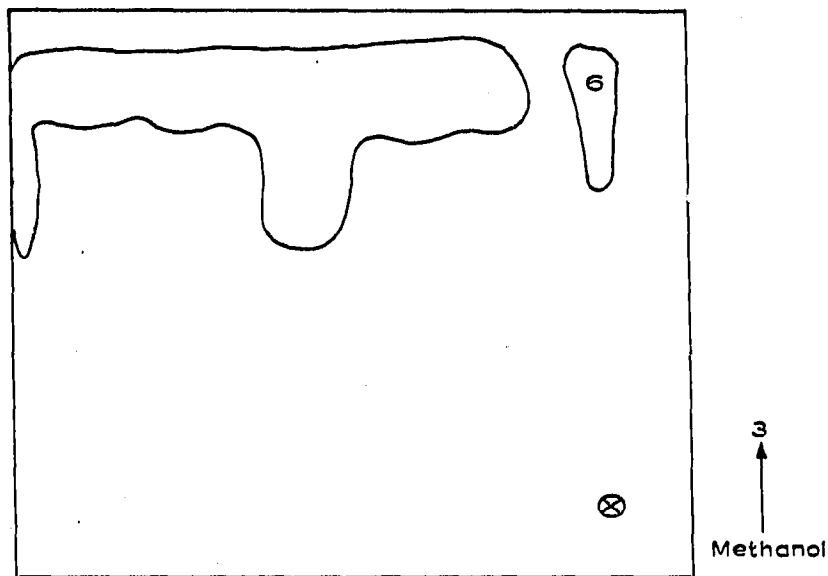


Fig. 3. Two-dimensional chromatogram of fusion product extract using toluene and water.

spot suitable for qualitative and quantitative evaluation. The material was identified as β,β' -diphenol. The location of this spot is shown in Fig. 3. It is still necessary to use both toluene and water in one direction prior to using methanol in the second direction, because both toluene and water remove phenols from the spot. If not removed, these phenols would interfere with the β,β' -diphenol spot. This combination of solvents does not separate the other phenols.

The identification of the various phenols present was simplified by work previously reported on the one-dimensional paper chromatography of the isomeric phenols⁶. In all cases in which spots were identified by means of multi-dimensional chromatography, the results were verified by running known samples in the same manner. All of the known phenols, with the exception of α,β' -diphenol are available from either commercial sources or laboratory supply houses. The authentic sample of α,β' -diphenol was isolated from fusion by products and identified by melting point and infra red analysis.

The presence of the five unknown phenols leads to speculation as to their composition. The chromatographic behavior of some of the phenols gives evidence that is of help in predicting the composition. It is known, for example, that in many compounds there is a definite relationship between the structure and the R_f value^{6,9}. In the case of a series of compounds differing by a single structural unit such as $-COOH$, $-CH_2-$, $-NH_2$, etc. a smooth curve can often be drawn through the spots produced on a two-dimensional chromatogram¹⁰. This same fact appears to be true in



1 ← Toluene
 2 ← Water

Fig. 3. Multiple development chromatogram showing location of *p,p'*-diphenol.

respect to certain isomeric phenols. For example, examination of Figs. 1 and 2 shows that a smooth curve can be drawn between the center points of the three phenylphenol spots. A second curve can also be drawn between the centers of the three known diphenol spots. In this case the curve also passes through or near to spot number 8 which is unknown. Fig. 4 also shows this very clearly for the diphenol spots. Based on this information, it appears that spot number 8 may be a member of the diphenol isomeric series. Three of these are already known to be present, so the

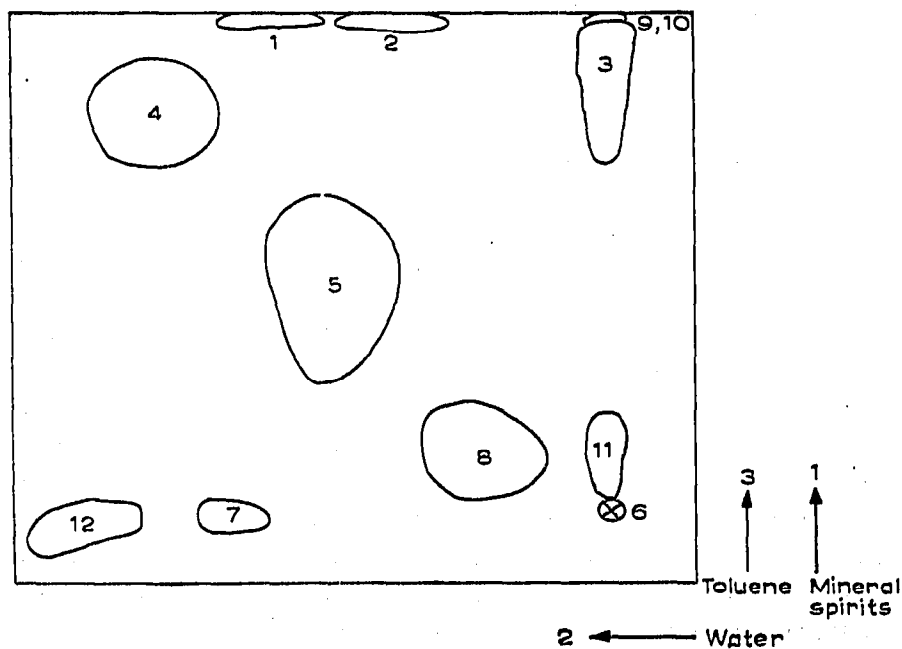


Fig. 4. Multiple development chromatogram showing location of *p*-phenylphenol.

remaining possibilities are *o,m'*-diphenol, *m,m'*-diphenol or *m,p'*-diphenol. Since the *ortho*-substituted phenols tend to have higher R'_F values, it is felt that this spot may be *m,m'*-diphenol or more probably *m,p'*-diphenol.

Unknown spots 9, 10 and 11 may also be members of an isomeric series. These spots show no R'_F value in water, all three show mobility in toluene, while spots 9 and 10 show mobility in mineral spirits. If the assumption is true, then spots 9, 10 and 11 should be *ortho*-, *meta*- and *para*-isomers respectively. It is thought that these phenols may be either isomeric monohydroxydiphenyl sulfones or monohydroxydiphenyl ethers.

Unknown number 12 appears to be a salt of a phenolsulfonic acid. It shows a large R'_F value with water and a zero R'_F value with mineral spirits and toluene. Samples of both phenolsulfonic acid and phenoldisulfonic acid chromatographed with water give spots with an R'_F value identical to that of unknown number 12. Both phenol mono and disulfonic acids have zero R'_F values with mineral spirits and toluene.

When the product of the fusion of benzenesulfonic acid with sodium hydroxide is dissolved in water and acidified, the mixture forms two layers. Unknown number 12 is found in the aqueous layer indicating insolubility in the phenolic phase. This would be expected from a sulfonic acid or its salt.

During the acetone extractions described in the experimental section, a small amount of material is found to be insoluble in acetone during each extraction. This insoluble material has the same R'_F value and spot color as does unknown number 12. This insoluble material, when dissolved in water, reacts with bromine to give 2,4,6-tribromophenol. Both phenol mono and disulfonic acids give 2,4,6-tribromophenol with bromine in water. However, a *p*-toluidine derivative of unknown number 12 is not the same as one prepared from phenolsulfonic acid. A carbon hydrogen analysis shows that the material is neither of the two phenolsulfonic acids. Based on these data, it is felt that unknown number 12 is a phenolsulfonic acid, but is not phenol mono or disulfonic acids. Work is continuing toward the identification of this product.

Quantitative

Examination of the sample preparation procedure described in the experimental section showed that a significant amount of *o*-phenylphenol was lost during evaporation on the steam bath. The relatively high volatility of *o*-phenylphenol was also known from earlier attempts at long equilibration in a chromatographic chamber. During an overnight equilibration, the *o*-phenylphenol would completely disappear from the paper. As a result of these findings, a special technique has been developed for the direct quantitative estimation of *o*-phenylphenol in the fusion product.

Earlier work showed that the sodium salt of *o*-phenylphenol has the same R'_F value as does the free phenol in mineral spirits. However, if sufficient equilibration time in the chromatographic chamber is not allowed, the spot will streak badly. This indicates that during equilibration in the water and mineral spirits saturated atmosphere, hydrolysis of the sodium salt is occurring. An equilibration time of one hour is required to allow complete hydrolysis and avoid streaking. This characteristic of the *o*-phenylphenol allows it to be analyzed directly from the fusion product. None of the other phenols present appear to exhibit this degree of hydrolysis.

Originally some thought was given to the premise that the sodium salt of

o-phenylphenol might have mobility in mineral spirits and become acidified to the free phenol when spraying with the color developer. However, the fact that water washing before color development does not remove the material from the paper shows that hydrolysis to the free phenol has already taken place before spraying. The water washing before color development is not essential but does give a better finished chromatogram. This is because some of the sodium phenate in the fusion product hydrolyzes to give a brown streak on the lower half of the paper when the ceric ammonium nitrate is applied. This streaking is removed by water washing before color development.

In the quantitative determination of *o*-phenylphenol, it is necessary to run a calibration curve with a known sample. It is best to run a calibration curve each time an unknown sample is run. This is required because of the need to reproduce the hydrolysis conditions exactly for both the unknown sample and the calibration sample. Small day to day variations in the calibration curves are caused by slight variations in temperature and humidity conditions in the chromatographic chamber.

The calibration solution for the *o*-phenylphenol analysis is made up by dissolving sodium phenate, sodium sulfite and *o*-phenylphenol in an alkaline solution so that the *o*-phenylphenol content is $3.0 \mu\text{g}/\mu\text{l}$ and the total solids content is about $300 \mu\text{g}/\mu\text{l}$. The minimum amount of *o*-phenylphenol that can be detected on a spot is $6 \mu\text{g}$. The calibration curve normally has samples ranging from $10 \mu\text{g}$ to $35 \mu\text{g}$ of *o*-phenylphenol and is prepared by plotting the spot area *versus* the weight of *o*-phenylphenol in the sample. The amount of *o*-phenylphenol found in a $10 \mu\text{l}$ sample of the fusion reaction product solution is about $25\text{--}30 \mu\text{g}$. The areas of the spots found on the chromatogram are determined with a planimeter and compared to the spot areas found on the calibration curve. The weight of *o*-phenylphenol in the unknown is determined from the calibration curve. When this has been found, the amount of *o*-phenylphenol in the fusion product can be calculated. Table II shows some typical results obtained for the analysis of the fusion reaction product for the various known components.

The analyses for *m*-phenylphenol, *o,o'*-diphenol, *o,p'*-diphenol, and resorcinol can all be run on a single paper simultaneously. The same paper used for qualitative identification can be used for the quantitative estimation of these four materials. As shown in Fig. 1, *o*-phenylphenol does not interfere. A calibration curve must be prepared from each of the known materials in order to determine the weight of the unknown from the spot area. The amount of each unknown in the fusion product can be calculated from the weight determined from the calibration curve since the evaporation residue and starting sample weights are known. Unlike *o*-phenylphenol, the calibration curves for all of these materials do not have to be run at the same time as the unknown. The calibration curves can be prepared at any time, as long as the sample and the calibration curves are run at the same temperature. The calibration curves for all of the phenols other than *o*-phenylphenol are shown in Fig. 5. The lowest detectable amounts of each compound are *m*-phenylphenol $10 \mu\text{g}$, *o,o'*-diphenol $3 \mu\text{g}$, *o,p'*-diphenol $3 \mu\text{g}$, and resorcinol $4 \mu\text{g}$.

The analysis of *p*-phenylphenol requires an extra step in order to isolate the spot. This has been described in the experimental section. When this process has been carried out, the analysis is completed by measurement of the spot area with a planimeter and determination of the weight from the calibration curve. The calibration

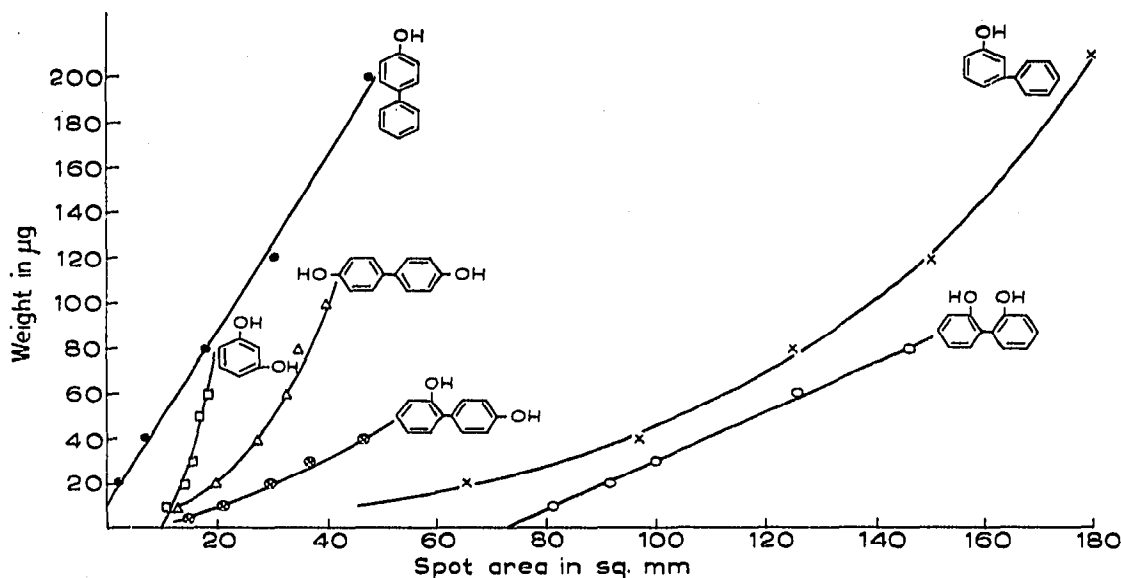


Fig. 5. Calibration curves for the various phenols.

curve for *p*-phenylphenol can be run independently from the sample since a precise degree of control is not necessary as with *o*-phenylphenol. Fig. 4 shows the location of the spots at the completion of this chromatogram. The smallest amount of *p*-phenylphenol that can be determined is about 10 μg .

The analysis of *p,p'*-diphenol also requires an extra step to isolate the desired spot. This was described in the experimental section and shown in Fig. 3. The weight of the *p,p'*-diphenol can be determined from the spot area and the calibration curve. As with the other phenols, the calibration curve can be determined separately. The lower limit of detectability is about 7 μg .

In order to test the entire procedure, a number of different samples of the fusion reaction product have been analyzed by the methods described. The results are shown in Table II.

A synthetic sample was made up from known phenols and analyzed. The results are shown in Table III. The inert material consisted of diphenyl sulfone which was determined by difference. In analyzing a mixture of this type, the sample size must be adjusted so that the proper sample weights are used. A little experimentation determines this quite easily.

TABLE II

ANALYSIS OF DIFFERENT SAMPLES OF THE FUSION REACTION PRODUCT (IN PERCENTAGES)

Run	<i>o</i> -Phenylphenol	<i>m</i> -Phenylphenol	<i>p</i> -Phenylphenol	<i>o,o'</i> -Diphenol	<i>o,p'</i> -Diphenol	<i>p,p'</i> -Diphenol	Resorcinol
A	1.06	0.141	0.202	trace	0.022	0.003	0.005
B	0.75	0.117	0.189	0.004	0.015	0.004	trace
C	0.64	0.075	0.163	0.002	0.007	0.005	0.008
D	0.92	0.091	0.134	0.002	0.008	0.004	0.005
E	0.86	0.089	0.204	trace	0.001	0.004	0.004

TABLE III

ANALYSIS OF A SYNTHETIC SAMPLE MADE UP FROM KNOWN PHENOLS (IN PERCENTAGES)

Product	<i>m</i> -Phenylphenol	<i>p</i> -Phenylphenol	<i>o,o'</i> -Diphenol	<i>o,p'</i> -Diphenol	Inert
Calculated	32.0	47.0	2.0	4.0	15.0
Found	33.0	45.3	2.8	3.7	15.2

A synthetic mixture was made up to contain 18.2% *o*-phenylphenol. This mixture also contained *m*-phenylphenol, *p*-phenylphenol, sodium sulfite, sodium sulfate, *o,o'*-diphenol, phenolsulfonic acid, and was dissolved in a solution of 5% sodium hydroxide. Paper chromatographic analysis for *o*-phenylphenol gave an average value of 17.7%. Triplicate results were all within $\pm 5.0\%$ of the actual value. The sample volume was adjusted as before to give the proper weight of *o*-phenylphenol on the original spot.

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SUMMARY

A number of the known phenolic by-products of the alkaline fusion of benzenesulfonic acid have been analyzed by paper chromatography. The analyses have been carried out both qualitatively and quantitatively. The presence of five unknown phenols has been established. Tentative identifications have been made for some of the unknown phenols and chromatographic conditions established. The R_F values are reported in three solvents for the unknowns. Non-phenolic by-products are not detected by this method.

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