5-31-1957

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## Recommended Citation

Tanner, William Calvert, "Aryl sulfonation in presence of phosphrous trichloride" (1957). *Theses*. 2616.
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# Aryl Sulfonation in Presence of Phosphorus Trichloride

by

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A THESIS

Submitted to the Faculty of
The Department of Chemical Engineering
of
Newark College of Engineering
In Partial Fulfillment of
The Requirements For The Degree
of
MASTER OF SCIENCE
With a Major in Chemical Engineering

Newark, New Jersey

1957

# APPROVAL OF THESIS

for

Department of Chemical Engineering
Newark College of Engineering

by

Faculty Committee

APPROVED: ______________________

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Newark, New Jersey
May 1957

# ACKNOWLEDGEMENTS

The Author wishes to express his indebtedness to Professor Bradley for his invaluable assistance as advisor, and for suggesting the topic for investigation.

The Author wishes to thank his wife, Glenis, for her assistance in preparing the manuscript and for enduring the inconvenience and hardships associated with pushing a husband through evening school.

# ABSTRACT

With sulfuric acid as the sulfonating agent, phosphorus trichloride is demonstrated as being effective in facilitating the sulfonation of some aromatic compounds. Optimum conditions are a molar ratio of 0.5 mole of sulfuric acid: 1.0 mole of aromatic compound with 4 - 5% more phosphorus trichloride than is required to react with the available water in the system, and reaction temperatures between 50°C. and 60°C.

The aromatic compounds studied were benzene, chlorobenzene, bromobenzene, and nitrobenzene.

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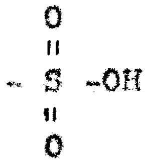
# I. INTRODUCTION

Aryl sulfonation may be defined as the process of replacing a hydrogen of an aromatic nucleus with the sulfo group illustrated.



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

Sulfonation, which is of considerable commercial importance, involves, in addition to sulfuric acid of various concentrations and in the presence of a variety of catalyst, any one of a number of sulfonating agents. A few of the reagents[1,2] employed are chlorosulfonic acid, salts of chlorosulfonic acid, chlorosulfonic anhydride, fluorosulfonic acid, sulfamic acid, sulfur trioxide, and addition products of sulfur trioxide with slightly basic substances as dioxane. The selection or employment of any particular reagent depends upon the aryl to be sulfonated and the degree of sulfonation desired. The catalysts employed in this process may in addition to accelerating the reaction, exercise orienting effects as does mercury[1,2] and its salts. Vanadium salts,[1] vanadium oxides,[1] and alkaline bisulfates[3] accelerate normal sulfonation reactions without orienting effects.

With sulfuric acid as the sulfonating agent, a condensation reaction occurs establishing an equilibrium system; the reaction may be generally represented

$$ArH + H_2SO_4 \rightleftharpoons ArSO_2OH + H_2O. \qquad (1)$$

The reaction is slow at room temperature and even after thirty hours reflux of equal volumes of benzene and sulfuric acid equilibrium is established with only 80 per cent sulfonation. It has been shown that equilibrium is established between 100 and 200 degrees centigrade when the ratio

$$\frac{H_2SO_4}{H_2SO_4 + H_2O} = 0.78^{4,5}.$$

Guyot's work on the sulfonation of benzene substantiates the above ratio. Guyot[6] has shown that sulfonation stops at a definite sulfur trioxide concentration regardless of temperature, agitation, or catalyst employed; this sulfur trioxide concentration, which Guyot designated as the Pi, $\pi$, value is 64 per cent. A sulfur trioxide concentration of 64 per cent corresponds to the hydrate $H_2SO_4 \cdot 1.5\ H_2O$.

The removal of the water formed during sulfonation involving sulfuric acid as the sulfonating agent results in shifting the equilibrium toward the right or increases the yield of the sulfonic acid. Commercially, the water of reaction has been removed by various methods; a few such methods[1] are the use of reduced pressure reactors, azeotropic distillation, and the use of oleum. Reports of the use of boron trifluoride[7] and hydrogen fluoride[8] as sulfonation aids have been published.

Phosphorus trichloride as an aid in mono-aryl sulfonation is reported in this work. It is assumed that the following equation indicates the reaction as it occurs.

$$\text{ArH} + \text{HOSO}_2\text{OH} + 1/3\ \text{PCl}_3 \longrightarrow \text{ArSO}_2\text{OH} + \text{HCl} + 1/3\ \text{P(OH)}_3. \quad (2)$$

The occurrence of the reaction as indicated in equation (2) is substantiated by the reaction products obtained when the reaction temperature is held between 50°C. and 60°C, preferably about 55°C.

Reaction temperatures exceeding 60°C. and excess phosphorus trichloride, around 25 per cent excess, initiate side reactions that result in lower yields of the sulfonic acids. Among the products obtained from these side reactions is sulfone.

$$2\text{ArH} + \text{H}_2\text{SO}_4 \longrightarrow \text{ArSO}_2\text{Ar} + 2\text{H}_2\text{O}. \quad (3)$$

Sulfone is a commonly obtained by-product from most sulfonation reactions; however, its formation in this work, during controlled reactions, was nil.

The following sequence of reactions[9,10] is postulated to describe the other side reactions.

$$6H_2SO_4 + 2PCl_3 \longrightarrow 6[HCl \cdot SO_3] + 2P(OH)_3 \tag{4}$$

$$2[SO_3 \cdot HCl] + 2P(OH)_3 \longrightarrow 2SO_2 + 2H_3PO_4 + 2HCl \tag{5}$$

$$2H_3PO_4 + POCl_3 \longrightarrow 3HPO_3 + 3HCl \tag{6}$$

$$[SO_3 \cdot HCl] + PCl_3 \longrightarrow SO_2 + POCl_3 + HCl \tag{7}$$

$$6H_2SO_4 + 3PCl_3 \longrightarrow 3[SO_3 \cdot HCl] + 3SO_2 + 3HPO_3 + 6HCl \tag{8}$$

$$2H_2SO_4 + PCl_3 \rightarrow [SO_3 \cdot HCl] + SO_2 + HPO_3 + 2HCl \tag{8-A}$$

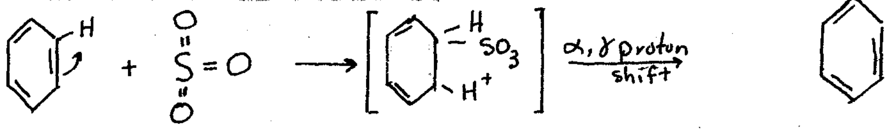
Equation (8-A) represents the overall reaction; the occurrence of this reaction was not conclusively substantiated; however, the phosphorus trichloride was completely consumed in reactions where the sulfonic acid formed was low. This would indicate some reaction, other than sulfonation, was consuming the phosphorus trichloride. Sulfur dioxide was detected in the gas absorption flask included in the apparatus employed for experimentation.

The sulfonation reactions studied were benzene, chlorobenzene, bromobenzene and nitrobenzene.

## II. DISCUSSION OF REACTION

While the purpose of this work is not an elucidation of the mechanism of sulfonation, a brief discussion of the reactions in terms of the Lewis concept of acid and base catalysis as discussed by Luder and Zuffanti[11] will be presented.

The more tenable theories on sulfonation[1,5,12,17] describe the reaction as a cationoid mechanism involving the electrophilic reagent sulfur trioxide. Diagrammatically, the reaction is as follows:



(9)

Equation (9) is postulated as being the probable mechanism involved in sulfonation with sulfuric acid; since it has been shown that the increase in concentration of sulfur trioxide in sulfur acid of less than 100 per cent and the increase in concentration of sulfur trioxide in fuming sulfur acid,[13,14,15] increases the rate of sulfonation.

Luder and Zuffanti[11] using Lewis' conception of acids and bases, have described an acid catalyst as an electrophilic reagent capable of accepting a share in a lone electron-pair, and a base as an electrodotic reagent capable of donating an electron-pair; further, they indicate that any substance can be made to behave as a base providing a sufficiently strong acid is available. This indicates that most substances are amphoteric or capable of behaving as either an acid or a base.

The connotation given above to catalyst is not the classical conception usually accepted; rather, it is a broadened interpretation. Hammett[12] points out that there is no important distinction between a catalyst in the classical sense and the effect produced by a base which appears as the conjugated acid at the end of the reaction.

In this work phosphorus trichloride behaves as an acid catalyst analogous to the behaviour of boron triflouride[7,11] in sulfonation reactions involving sulfuric acid. The action of the phosphorus trichloride may be portrayed in the following equation.

$$1/3PCl_3 + H_2SO_4 \longrightarrow [HCl \cdot SO_3] + 1/3P(OH)_3 \qquad (10)$$

The phosphorus trichloride is electrophilic, or an acid catalyst. In the complex $HCl\ SO_3$ the sulfur trioxide is forcing hydrochloric acid to behave as a base. The subsequent sulfonation occurs in accordance with equation (11).

$$[SO_3 \cdot HCl] + ArH \longrightarrow ArSO_2OH + HCl \qquad (11)$$

In equation (11) the benzene behaves as a base, donating the electron-pair. The summation of equation (10) and (11) gives equation (2), the equation postulated as the overall reaction occurring under controlled conditions previously described.

Evidence supporting the occurrence of equations (10) and (11) is purely circumstantial; however, it is presented for consideration. Sulfur acid[1] is a generic name for a series of solutions of sulfur trioxide in water; endothermically, these hydrates dissociate into sulfur trioxide and water. Sulfonation with sulfuric acid is a mild exothermic reaction. (Mild compared to the exotherm from sulfonation with sulfur trioxide). In this reaction (equation 2) the addition of a solution of phosphorus trichloride in an aryl as chlorobenzene to sulfuric acid initially results in an endothermic reaction; a definite noticeable temperature drop is observed. This initial endothermic reaction is very short in duration, and very little hydrogen chloride is liberated during this stage. The second stage occurs as a violent exothermic reaction with vigorous liberation of hydrogen chloride. This behavior is noted only when reactions are carried out between 50°C. and 60°C.

## III. EXPERIMENTAL PROCEDURE

The conditions of sulfonation are given with each experimental run reported, however, the following procedure was standard for processing each run.

A. Sulfonation was carried out in a three-necked round bottom flask equipped with an agitator, Hopkins condenser, dropping funnel, and agitator. All joints were ground glass.

B. Sulfonation was carried out using Fisher's reagent grade sulfuric acid (94.42%), Fisher's reagent grade aryl compounds and Merck's reagent grade phosphorus trichloride.

C. The phosphorus trichloride was dissolved in the aryl compound and the solution added from the dropping funnel to the agitated sulfuric acid. Standard agitator speeds were used in most runs.

D. When sulfonation was thought to be complete the reaction mix was transferred to a vacuum distillation set-up and distilled to remove any remaining volatile matter.

E. The mixed acids remaining in the distillation residue were poured into cold distilled water. Any insoluble matter was filtered out, air dried and weighed as sulfone. Discolored solutions of the acids were clarified by warming and stirring with Norit-A. The Norit-A was filtered out, washed several times and discarded. The washings were added to the clarified solutions.

F. The clarified filtrate was then diluted to a definite volume in a volumetric flask. Analysis for sulfonic acid, hydrochloric acid and unreacted sulfuric acid were conducted as described under analytical procedures.

## IV. ANALYTICAL PROCEDURES

A. Determination of Sulfonic acids.

An aliquot portion of the mixed acids was diluted with distilled water and neutralized with calcium hydroxide; calcium hydroxide was added until a pH of about 10 was obtained. The precipitated phosphates and sulfate were filtered out, washed several times and discarded. The washings were added to the calcium sulfonate solutions. The filtrate was treated with carbon dioxide to remove excess calcium by bubbling carbon dioxide through the solution, initially, precipitating the calcium as calcium carbonate; carbon dioxide treatment was continued until the precipitate redissolved as the soluble bicarbonate. Upon boiling the carbon dioxide treated solution the soluble bicarbonate converted back to the insoluble carbonate. The solution was evaporated to a small volume before filtering out, and washing the carbonate. The filtrate, calcium sulfonate, was evaporated to dryness, dehydrated and weighed. Corrections for chloride were made, if necessary.

B. The unreacted sulfuric acid was determined by difference.

C. Determination of Chloride

An aliquot of the mixed acids was neutralized with N/10 sodium hydroxide and titrated with standard silver nitrate using potassium chromate as indicator.

D. Preparation of the sulfonamide derivative[16].

Two grams of the anhydrous salt was mixed with four grams of phosphorus pentachloride in a small round bottom flask equipped with a water cooled condenser. The mix was heated with a small flame for several minutes; when the reaction was complete the mix was added cautiously to 15 ml. of ice water. The solution was washed into a separatory funnel and the aqueous layer containing the hydrochloric acid and phosphoric acid was separated from the sulfonyl chloride. The sulfonyl chloride was washed several times before adding it to about 20 ml. of ammonia. The solution was boiled for a few minutes, then cooled and allowed to evaporate slowly. The sulfonamide was used to determine the melting points for verification of the sulfonic acids.

E. Infrared Spectroscopy

Infrared was used to verify most experimental runs after the initial run. A sample of each acid salt prepared in the initial run was converted to the sulfonamide, the melting point determined and verified with that published in literature (Rubber Handbook). An infrared spectrum from the acid salt was then prepared for reference. Visual comparison of spectra with this reference spectrum served to verify products.

## V. EXPERIMENTAL RESULTS AND DATA

### A. Sulfonation of Benzene

Experimental Run 1

Mole Ratios: 0.885 mole of sulfuric acid: 1.770 moles of benzene:0.389 mole of phosphorus trichloride.

Reaction conditions: To the 500 ml. round bottom flask was added 92 gms. of 94.42% sulfuric acid. A mixture of 53.50 gms. of phosphorus trichloride and 138.20 gms. of benzene was added to the dropping funnel and the solution added slowly to the vigorously agitated sulfuric acid. The reaction temperature varied between 30°C. - 35°C.; total reaction time was 3 hours. Reaction product was transferred to a vacuum distillation apparatus for a removal of volatile matter.

| Results: | |
|---|---|
| Sulfone . . . . . . . . . | Nil. |
| Reacted Sulfuric acid(sulfonic acid) . . . . . . . . . . . . . . . | 76.8% |
| Unreacted Sulfuric acid (by difference . . . . . . . . . . . . | 23.2% |

Sulfonamide melting point 153°C.

Sample calculations:

Reactants: (1) Sulfuric acid - 92.00 gms. used.

92 x 0.9442 x 1/98.08 = 0.885 mole

(2) Benzene - 138.20 gms. used (100% excess)

0.885 x 2 x 78.11 = 138.20 gms.

(3) Phosphorus trichloride - 53.52 gms. used

water in the $H_2SO_4$

92.00 - 86.9 = 5.1 gms. = 0.283 mole

The water formed is o.885 moles (1 mole of $H_2O$ formed for each mole of $H_2SO_4$ reacted).

Total $H_2O$ to be consumed by $PCl_3$ is 1.168 moles

1/3 mole $PCl_3$ reacts with 1 mole of $H_2O$.

Total $PCl_3$ required:

1/3 x 1.168 = 0.389 mole = 53.5 gms.

**Product:** 6 gms. of calcium benzene sulfonate isolated from 50.00 ml. of 1000 ml. of the mixed acids.

6 x 1000/50 = 120.0 gms. = 0.339 mole of calcium sulfonate

1 mole of calcium sulfonate = 2 moles of sulfuric acid

reacted sulfuric acid = 0.678 mole

% yield = 0.678/0.885 x 100 = 76.60%

**Chloride correction:**

0.30 ml. of 0.1008 $AgNO_3$ = 5.00 ml. of acid solution

0.30 x .1008 x .03546 = 0.00105 gms. of chloride

50/5 x .001 = 0.01 chloride correction

**Correction** 6.00 - 0.01 = 5.99

5.99 x 1000/50 = 120 gm. = 0.3385 moles = .677 moles of reacted sulfuric acid

0.677/0.885 x 100 = 76.5% yield

**Experimental Run 2**

**Mole Ratios:** 0.477 mole of sulfuric acid: 0.954 mole of benzene: 0.252 mole of phosphorus trichloride. (20% excess).

**Reaction Conditions:** To the 500 ml. flask was added the sulfuric acid. The mixture of phosphorus trichloride and benzene was added from the dropping funnel. The procedure of Run 1 was then followed. The reaction temperature was 25°C. Total reaction time was 14 hours.

**Results:**

| | |
|---|---|
| Sulfone . . . . . . . . . . . . | Nil. |
| Unreacted sulfuric acid . . . | 50.9% |
| Reacted sulfuric acid | 49.1% |

**Experimental Run 3**

**Mole Ratios:** 0.551 mole of sulfuric acid: 1.1 moles of benzene: 0.243 mole of phosphorus trichloride.

**Reaction Conditions:** To the 500 ml. flask was added 57.26 gms. of sulfuric acid and agitation and heating were begun. A mixture of 21.2 ml. of phosphorus trichloride and 97.5 ml. of benzene was prepared and placed in the dropping funnel. When the sulfuric acid was at 60°C, the addition of the phosphorus trichloride and benzene mix was begun. Total reaction time was 1 hour. Volatile matter removed by vacuum distillation.

Results:

| | |
|---|---|
| Sulfone . . . . . . . . . . . . . . . | Nil. |
| Reacted sulfuric acid . . . . . . . | 73.3% |
| Unreacted sulfuric acid . . . . . . | 26.7% |

### Experimental Run 4

Mole Ratios: 0.5072 mole of sulfuric acid: 1.05 moles of benzene: 0.279 mole of phosphorus trichloride (25% excess).

Reaction Conditions: Same as for Experimental Run 3, except for the amount of reactants and the reaction time was 2 hours.

Results:

| | |
|---|---|
| Water insoluble material (sulfone) . . | 11.68% |
| Reacted sulfuric acid . . . . . . . . | 71.8% |
| Unreacted sulfuric acid . . . . . . . | 16.52% |

Melting point 123°C. - 124°C.

### Experimental Run 5

Mole Ratios: 0.50 mole of sulfuric acid: 1.00 mole of benzene: 0.221 mole of phosphorus trichloride.

Reaction Conditions: Same as for Experimental

Run 3 except for the amount of reactants; reaction time was 2 hours and reaction temperature 65°C.

Results:

Sulfone . . . . . . . . . . . . Nil.
Reacted Sulfuric acid . . . 88.70%
Unreacted sulfuric acid 11.3%

Experimental Run 6

Mole Ratios: 0.520 mole of sulfuric acid: 1.04 moles of benzene: 0.228 mole of phosphorus trichloride.

Reaction Conditions: Same as for Run 3, except for amount of reactants and reaction time was 2 hours.

Results:

Sulfone . . . . . . . . . . . Nil.
Reacted sulfuric acid . . . 87.9%
Unreacted sulfuric acid . . 12.1%

Experimental Run 7

Mole Ratios: 0.500 mole of sulfuric acid: 1.0 mole of benzene: 0.229 mole of phosphorus trichloride (4% excess).

Reaction Conditions: To the 500 ml. flask was added 52.00 gms. of sulfuric acid, agitation and heating begun. When the sulfuric acid was at 50°C the solution of 31.5 gms. of phosphorus trichloride and 78.11 gms. of benzene, which had been heated to 50°C. was added from the dropping funnel. Initially, the temperature went down 44°C.; a violent reaction started when the temperature again reached 50°C.; a cold water bath was applied to maintain temperature at 50°C. The cold water bath had to be applied intermittently to maintain an average temperature of 50°C. After one-half hour the temperature was raised to 60°C.; this temperature was maintained, with heat, for 1½ hours. Total reaction time was 2 hours.

<u>Results</u>:

| | |
|---|---|
| Sulfone . . . . . . . . . . . . . . . | Nil. |
| Reacted sulfuric acid . . . . . . . | 99.60% |
| Unreacted sulfuric acid . . . . . | 0.40% |

<u>Experimental Run 8</u>

<u>Mole Ratios</u>: 0.500 mole of sulfuric acid: 1.00 mole of benzene: 0.229 mole of phosphorus trichloride.

<u>Reaction Conditions</u>: To the 500 ml. round bottom flask were added 52.0 gms. of sulfuric acid, 78.11 gms. of benzene, and 31.5 gms. of phosphorus trichloride. Agitation and heating were begun; when the temperature reached 50°C., a violent reaction was occurring and the temperature was rising rapidly.

A cold water bath was now applied and the temperature maintained at 60°C. for the next 2 hours. Heat had to be added during the last 35 minutes to maintain the temperature at 60°C. Total reaction time was 2 hours:

**Results:**

| | |
|---|---|
| Sulfone . . . . . . . . . . . . . | Nil. |
| Reacted sulfuric acid . . . . | 99.60% |
| Unreacted sulfuric acid . . . | 0.40% |

B. Sulfonation of Chlorobenzene

Experimental Run 9

Mole Ratios: 0.490 mole of sulfuric acid: .2097 mole of phosphorus trichloride: 1.0 mole of chlorobenzene.

Reaction Conditions: To the 500 ml. flask was added 50.97 gms. of sulfuric acid, heating and agitation were begun. A mixture of 28.8 grams of phosphorus trichloride and 112.56 gms. of chlorobenzene was prepared and added to the dropping funnel. When the sulfuric acid was at 60°C. the slow addition of the phosphoric trichloride and chlorobenzene was begun. The total reaction time was 1 hour. The reaction mix was then transferred to a vacuum distillation apparatus to remove the volatile matter.

Results:

| | |
|---|---|
| Sulfone . . . . . . . . . . . . | Nil. |
| Reacted sulfuric acid . . . . | 68.8% |
| Unreacted sulfuric acid . . . | 31.2% |

Experimental Run 10

Mole Ratios: 0.500 mole of sulfuric acid: 0.229 mole of phosphorus trichloride: 1.0 mole of chlorobenzene.

Reaction Conditions: To the 500 ml. flask was added 52.0 gms. of sulfuric acid. Heating and agitation were begun; when the acid was at 50°C. a mixture of 112.56 gms. of chlorobenzene and 31.5 gms. of phosphorus trichloride was added slowly. Initially, the temperature declined, then a rapid reaction began and a cold water bath was necessary to control the reaction temperature. The total reaction time was 3 hours.

Results:

| | |
|---|---|
| Sulfone . . . . . . . . . . . | Nil. |
| Reacted sulfuric acid . . . | 88.8% |
| Unreacted sulfuric acid . . | 11.2% |
| Sulfonamide melting point . | 144°C. |

**Experimental Run 11**

**Mole Ratios:** 0.497 mole of sulfuric acid: 0.263 mole of phosphorus trichloride: 0.992 mole of chlorobenzene.

**Reaction Conditions:** To the 500 ml. flask was added 51.46 gms. of sulfuric acid and heating and agitation begun. A mixture of 111.66 gms. of chlorobenzene and 36.08 gms. of phosphorus trichloride was added from the dropping funnel. The procedure of Experimental Run 3 was followed. The reaction temperature was 65°C. and the total reaction time was 2½ hours.

**Results:**

| | |
|---|---|
| Sulfone . . . . . . . . . . . . . | Nil. |
| Reacted sulfuric acid . . . . .. | 74.00% |
| Unreacted sulfuric acid . . . . | 26.00% |

**Experimental Run 12**

**Mole Ratios:** 0.499 mole of sulfuric acid: 0.222 mole of phosphorus trichloride: 0.988 mole of chlorobenzene.

**Reaction Conditions:** To the 500 ml. flask was added 51.87 gms. of sulfuric acid and agitation begun. A mixture of 30.49 gms. of phosphorus trichloride and 112.10 gms. of chlorobenzene was added from the dropping funnel. The procedure of Experimental Run 1 was followed.

Total reaction time was 2.8 hours. Reaction temperature was 23°C.

Results:

Sulfone . . . . . . . . . . . . Nil.
Reacted Sulfuric acid . . . . . 57.00%
Unreacted sulfuric acid . . . . 43.00%

C. Sulfonation of Bromobenzene

Experimental Run 13

Mole Ratios: 0.500 moles of sulfuric acid: 0.231 mole of phosphorus trichloride (5% excess): 0.500 mole of bromobenzene.

Reaction Conditions: To the 500 ml. flask was added 52.00 gms. of sulfuric acid. A mixture of 30.73 gms. of phosphorus trichloride and 78.51 gms. of bromobenzene was added to the hot agitated sulfuric acid. The procedure used in Experimental Run 7 was used.

Results:

Sulfone . . . . . . . . . . . . Nil.
Reacted sulfuric acid . . . . 40.40%
Unreacted sulfuric acid . . . 59.60%
Sulfonamide melting point 165°C.

Experimental Run 14

Mole Ratios: 0.500 mole of sulfuric acid: 0.231 mole of phosphorus trichloride: 0.500 mole of bromobenzene.

**Reaction Conditions:** Same as Experimental Run 13.

**Results:**

Sulfone . . . . . . . . . . . Nil.

Reacted sulfuric acid . . . 42.4%

Unreacted sulfuric acid . . 57.6%

## D. Sulfonation of Nitrobenzene

### Experimental Run 15

**Mole Ratios:** 0.508 mole of sulfuric acid: 0.235 mole of phosphorus trichloride: 1.02 moles of nitrobenzene.

**Reaction Conditions:** To the 500 ml. flask was added 52.8 gms. of sulfuric acid and heating and agitation were begun. A mixture of 32.3 gms. of phosphorus trichloride and 125.90 gms. of nitrobenzene was added from the dropping funnel after the sulfuric acid was heated to 65°C. Total reaction time was 3.5 hours. Steam distillation was used to separate the excess nitrobenzene from the acids.

**Results:**

Sulfone . . . . . . . . . . . Nil.

Reacted sulfuric acid . . . 17.70%

Unreacted sulfuric acid . . 82.30%

## Experimental Run 16

**Mole Ratios:** 0.500 mole of sulfuric acid: 0.267 mole of phosphorus trichloride: 1.44 moles of nitrobenzene.

**Reaction Conditions:** To the 500 ml. flask was added 52.0 gms. of sulfuric acid, heating and agitation were begun. A mixture of 36.2 gms. of phosphorus trichloride and 177 gms. of nitrobenzene was added to the dropping funnel. The procedure used in Experimental Run 15 was followed:

**Results:**

| | |
|---|---|
| Sulfone . . . . . . . . . . . . . | Nil. |
| Reacted sulfuric acid . . . . | 14.4% |
| Unreacted sulfuric acid . . . | 85.6% |

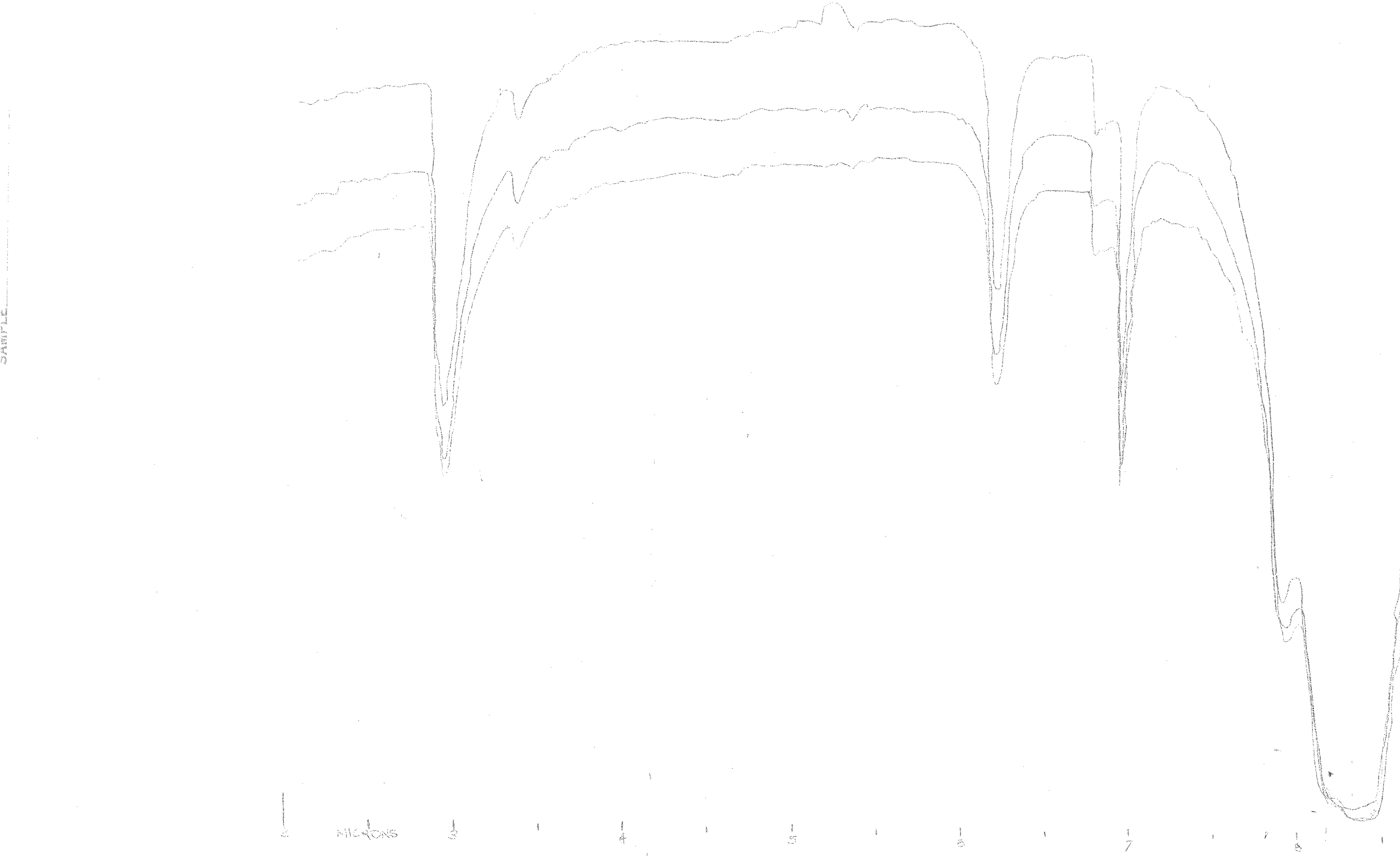
## VI. SUMMARY

| Run | Aryl | Reactants | | | | | Products | | | | | Conditions | | Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $H_2SO_4$ | $PCl_3$ | | ArH | | $ArSO_3H$ | | $H_2SO_4$ | | Sulfone | Reaction | Reaction | |
| | | (moles) | moles | % excess | moles | % excess | moles | % yield | moles | % yield | % yield | time (hrs.) | temp. °C. | |
| 1 | benzene | 0.885 | 0.389 | — | 1.77 | 100 | 0.678 | 76.6 | 0.207 | 23.4 | nil. | 3.0 | 30-35 | — |
| 2 | " | 0.477 | 0.252 | 20 | 0.954 | " | 0.243 | 49.1 | 0.234 | 50.9 | " | 14.0 | 25-30 | — |
| 3 | " | 0.551 | 0.243 | — | 1.1 | " | 0.404 | 73.3 | 0.147 | 26.7 | " | 1.0 | 60 | — |
| 4 | " | 0.507 | 0.279 | 25 | 1.05 | " | 0.364 | 71.8 | 0.143 | 16.52 | 11.68 | 2.0 | 60 | — |
| 5 | " | 0.500 | 0.221 | — | 1.00 | " | 0.444 | 88.7 | 0.056 | 11.30 | nil | 2.0 | 65 | — |
| 6 | " | 0.521 | 0.228 | — | 1.04 | " | 0.458 | 87.9 | 0.063 | 12.10 | " | 2.0 | 65 | — |
| 7 | " | 0.500 | 0.229 | 4 | 1.00 | " | 0.498 | 99.6 | .002 | 0.40 | " | 2.0 | 44-60 | a |
| 8 | " | 0.500 | 0.229 | 4 | 1.00 | " | 0.498 | 99.6 | .002 | 0.40 | " | 2.0 | — | b |
| 9 | chlorobenzene | 0.491 | 0.2097 | — | 1.00 | " | 0.338 | 68.8 | 0.153 | 31.2 | " | 1.0 | 60 | — |
| 10 | " | 0.500 | 0.229 | 4 | 1.00 | " | 0.444 | 88.8 | 0.056 | 11.2 | " | 3.0 | 44-60 | a |
| 11 | " | 0.497 | 0.263 | 20 | 0.992 | " | 0.367 | 74.0 | 0.130 | 26.0 | " | 2.5 | 65 | — |
| 12 | " | 0.499 | 0.222 | 20 | 0.998 | " | 0.284 | 57.0 | 0.215 | 43.0 | " | 2.8 | 23 | — |
| 13 | bromobenzene | 0.500 | 0.231 | 5 | 0.500 | — | 0.202 | 40.4 | 0.298 | 59.6 | " | 2.0 | 44-60 | a |
| 14 | " | 0.500 | 0.231 | 5 | 0.500 | — | 0.212 | 42.4 | 0.288 | 57.6 | " | 2.0 | 44-60 | a |
| 15 | nitrobenzene | 0.508 | 0.235 | 20 | 1.02 | 100 | 0.090 | 17.7 | 0.418 | 82.3 | " | 3.5 | 65 | — |
| 16 | " | 0.500 | 0.267 | 20 | 1.44 | 156 | 0.072 | 14.4 | 0.428 | 85.6 | " | 24 | 65 | — |

NOTES

a. Initially the reaction temperature was 50°C, but declined to 44°C; after one-half hour the temperature was raised to 60°C where it was held for the remainder of the reaction time.

b. All reactants charged into the flask at room temperature then agitation and heating was started, **but** heating was not necessary after 45°C was reached.


SAMPLE
2
MICRONS
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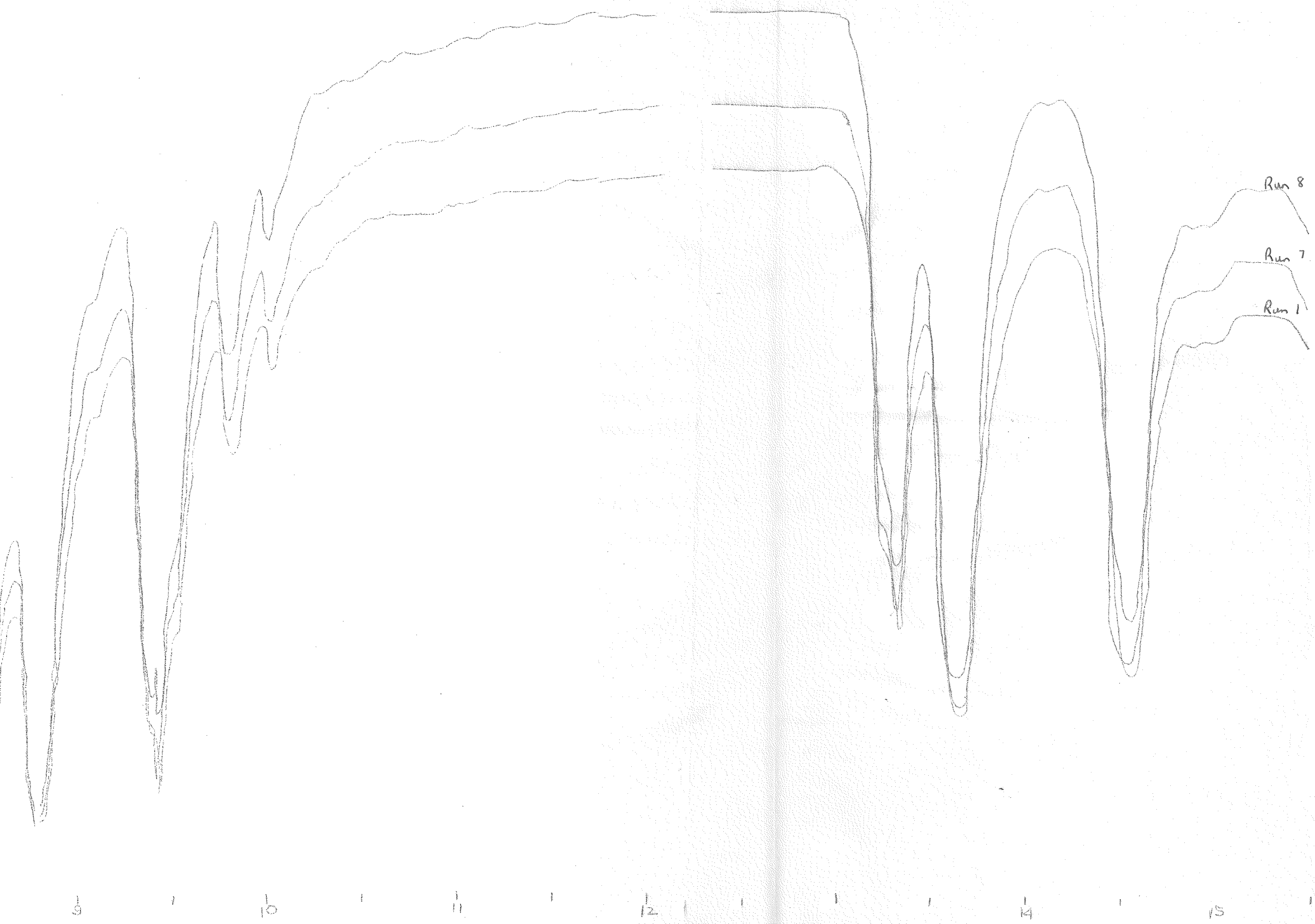
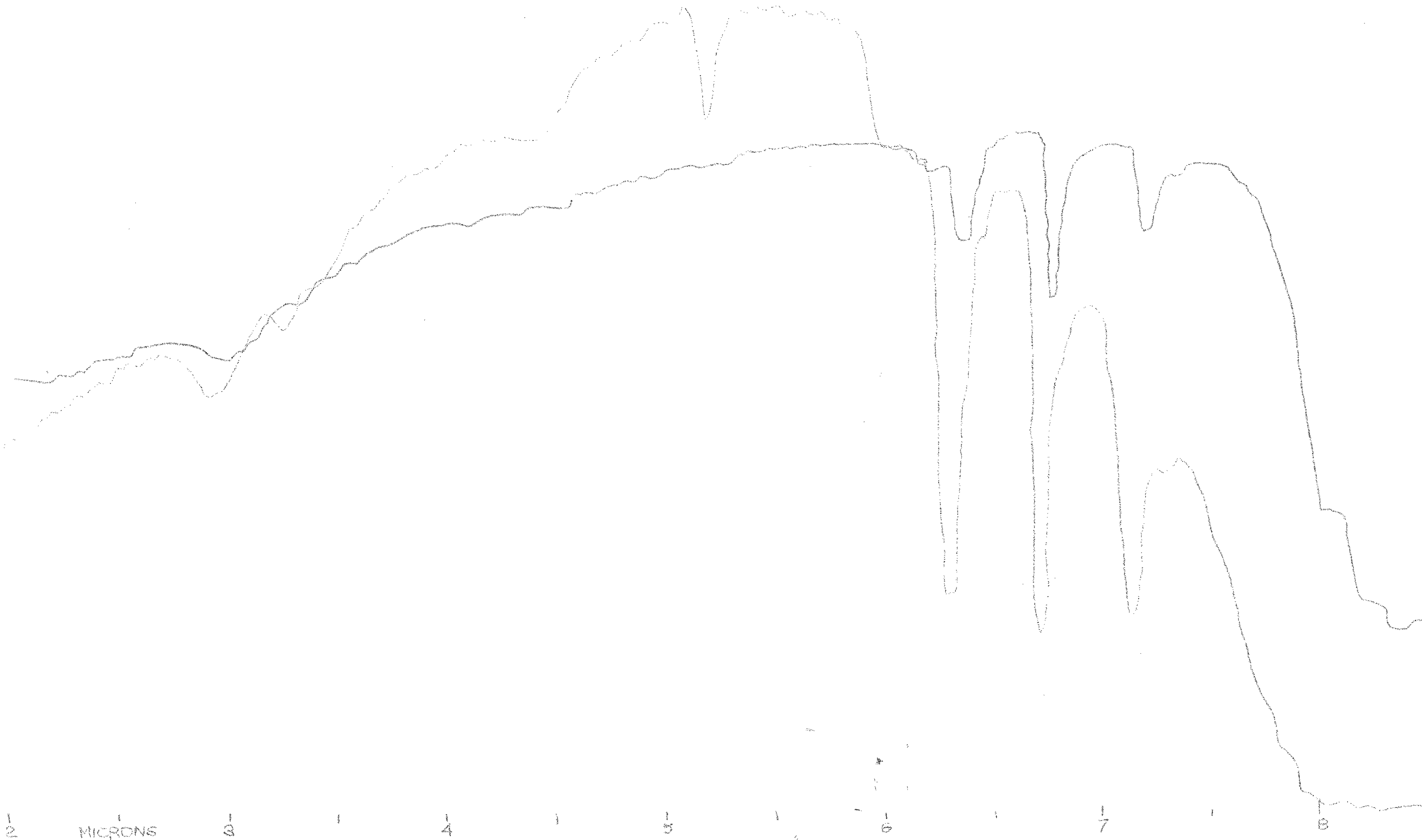


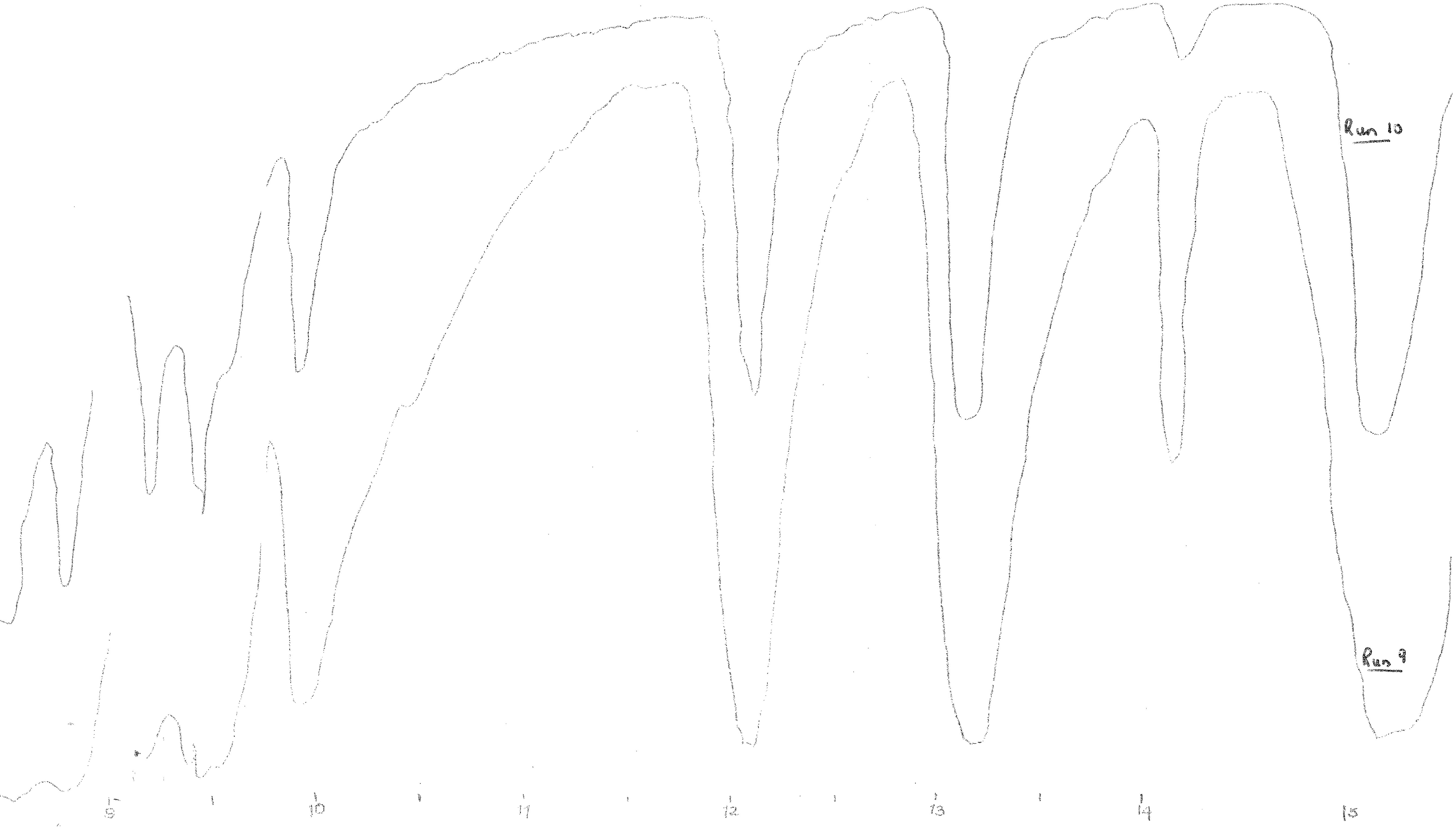
SPECTRUM NO.
SAMPLE Calcium Benzene Sulfonate
ORIGIN
PURITY 100%
PHASE solid
THICKNESS
DATE
OPERATOR
PROBLEM NO.
REMARKS

PRISM NaCl
RESOLUTION 9.27
RESPONSE 1-1
GAIN 4.25
SPEED 4
SUPPRESSION 2
SCALE

THE PERKIN-ELMER CORP.
GLENBROOK, CONN.
NO. C21-6300

SAMPLE

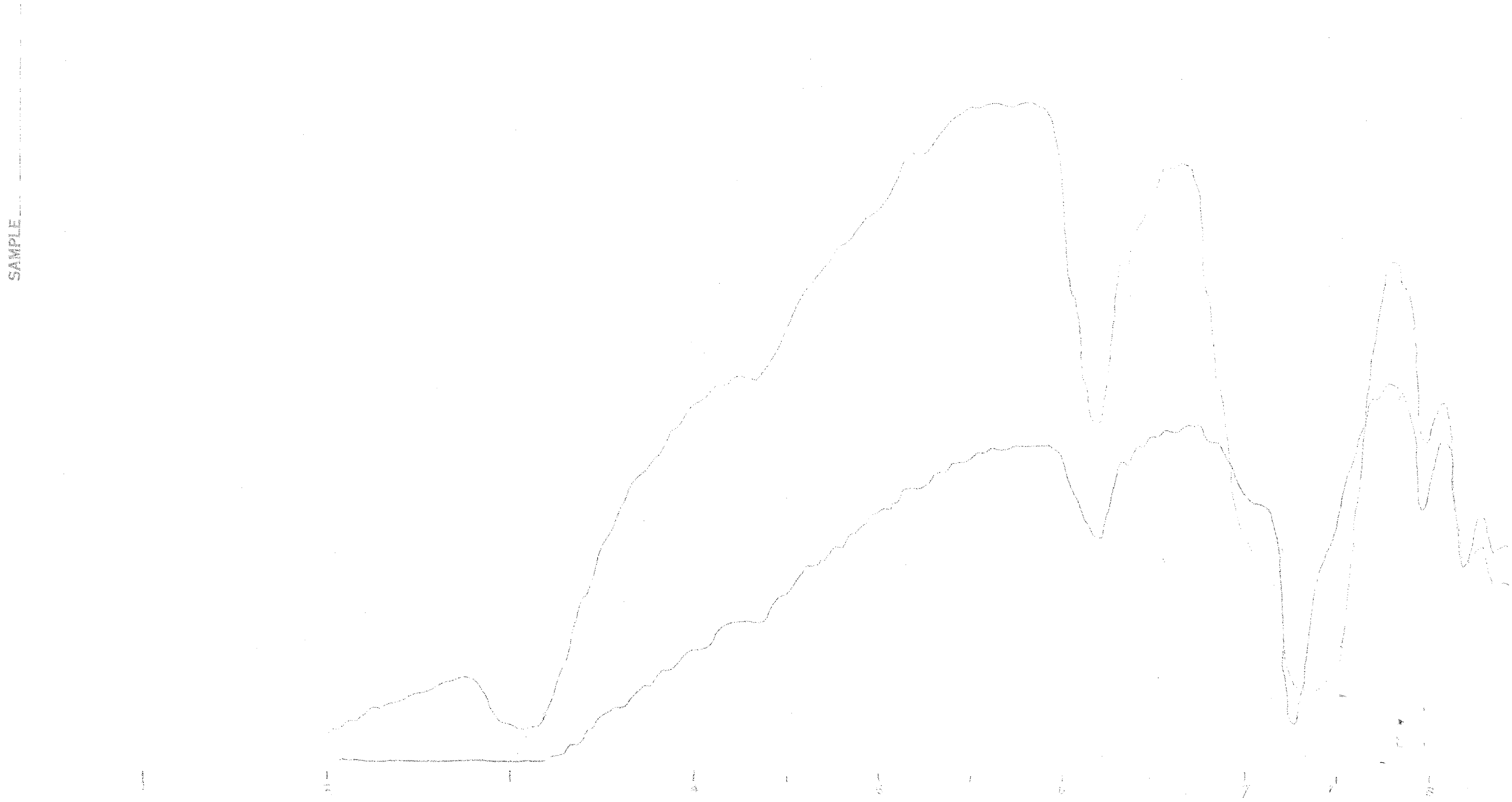




SPECTRUM NO.
SAMPLE Calcium chlorobenzene sulfonate
ORIGIN
PURITY 100%
PHASE solid
THICKNESS
DATE
OPERATOR
PROBLEM NO.
REMARKS

PRISM NaCl
RESOLUTION 9.27
RESPONSE 1-1
GAIN 4.25
SPEED 4
SUPPRESSION 2
SCALE

THE PERKIN-ELMER CORP.
GLENBROOK, CONN.
NO. C21-6300


SAMPLE
2
3
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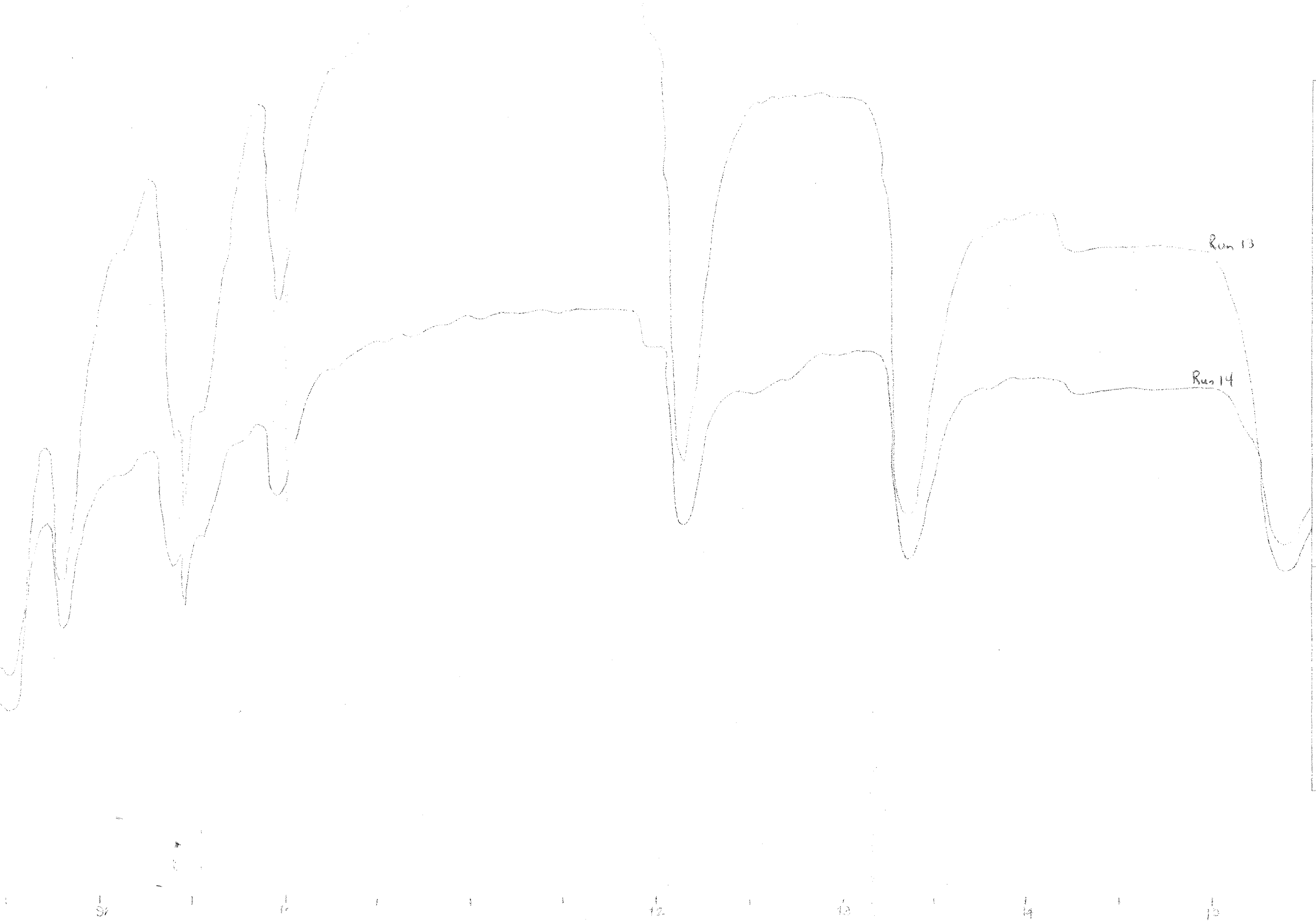

SPECTRUM NO.
SAMPLE Calcium bromobenzene sulfonate
ORIGIN
PURITY 100%
PHASE solid
THICKNESS
DATE
OPERATOR
PROBLEM NO.
REMARKS

PRISM NaCl
RESOLUTION 1
RESPONSE
GAIN
SPEED
SUPPRESSION
SCALE

THE PERKIN-ELMER CORP.
GLENBROOK CONN
NO. C21-6900

# VII. CONCLUSIONS

## A. Sulfonation of Benzene

It may be concluded that the presence of phosphorus trichloride facilitates the sulfonation of benzene. The optimum yields are obtained when molar ratio of reactants is 0.5 mole of sulfuric acid: 1.0 mole of benzene: 0.229 mole (4% excess) phosphorus trichloride, reaction temperature is 50°C.- 60°C, and 2 hours reaction time. Large excesses of phosphorus trichloride result in lower yields of sulfone and the formation of sulfone; reaction temperatures exceeding 60°C. will result in lower yields of sulfonic acid. The formation of sulfone is nil. when reactions are carried out under optimum conditions described above. A yield of 76% sulfonic acid may be obtained from reactions carried out at 30°C. - 35°C.

## B. Sulfonation of Chlorobenzene

The sulfonation of chlorobenzene is facilitated by the presence of phosphorus trichloride. A slight molar excess (4%) with respect to the available water in the sulfuric acid and the water formed. The optimum yields are obtained under conditions described in A. above. The phosphorus trichloride does not alter the normal para sulfonation of chlorobenzene.

## C. Sulfonation of bromobenzene

Bromobenzene is more inert to sulfonation than benzene or chlorobenzene. When molar ratios of 0.500 mole of sulfuric acid: 0.500 mole of bromobenzene: 0.229 mole of phosphorus trichloride are reacted two hours between 50°C. and 60°C. only 43% sulfonation occurs. The melting point of the sulfonamide was 165°C., indicating 100% para substitution; hence, the phosphorus trichloride does not alter the usual para sulfonation of bromobenzene.

## D. Sulfonation of Nitrobenzene

The presence of phosphorus trichloride does not facilitate the sulfonation of benzene. Nitrobenzene is normally extremely inert to sulfonation with sulfuric acid.

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