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GAS CHROMATOGRAPHIC ANALYSIS OF BIPHENYL PYROLYTIC PRODUCTS

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Abstract

Gas chromatographic procedures are presented for the quantitative determination of three hydrocarbon fractions obtained from the pyrolysis of biphenyl.

The low molecular weight hydrocarbons, hydrogen, and carbon monoxide were resolved on a column of silica gel in series with a molecular sieve (Linde 5A) column. The sensitivity, expressed in recorder scale divisions per microliter, of the peak height measurements for the various gases was found to be: hydrogen, 1.72; methane, 24.6; carbon monoxide, 28.4; ethane, 25.8; ethylene, 14.7; propane, 18.0; and propylene, 5.58.

The benzene fraction was analyzed with a column of 30 wt % Apiezon L plus 2 wt % Carbowax 20M on Chromosorb P. The analytical precision of the peak area determinations was $\pm 2\%$ over the range of 35 to 170 micrograms of benzene.

Through the use of temperature programming, the polyphenyl compounds were determined utilizing a stationary phase of 20 wt % LiCl on Chromosorb P. The peak area measurements of the terphenyl isomers were reproducible within $\pm 2\%$, in general, for 10 to 120 micrograms of material. The precision of the quaterphenyl data was also $\pm 2\%$ for 40 to 210 micrograms of the isomers.

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I. INTRODUCTION

A chemical kinetic study of the thermal decomposition of pure biphenyl, one of the components of a prospective organic moderator-coolant (Santowax R^a), requires both the qualitative identification and the quantitative determination of microgram quantities of the pyrolytic products. Of the various analytical techniques available for this purpose, gas chromatography was chosen largely because of the (1) simplicity of sample preparation and of the overall analytical procedure, (2) rapidity of analysis, (3) ability to analyze gases, liquids, and solids with the same type of equipment, and (4) the ability to differentiate readily, in many cases, between isomers.

The gases which were encountered as primary pyrolytic products of biphenyl are hydrogen, methane, ethane, ethylene, propane, and propylene. After passing through a series of cold water and dry ice-acetone traps (Fig. 1), this fraction was collected in a gas sampler (upper right) by an automatic Toepler pump. This was done during two different volatilizations and condensations of the undecomposed biphenyl to prevent the loss of products by entrapment in the solid phase. Products in the condensed state were benzene, the terphenyl isomers, and several of the quaterphenyl isomers. The benzene fraction was passed down through the traps and finally collected in a small tube (right center) cooled with a dry ice-acetone mixture. Acetone containing o-xylene as an internal standard was added to this sample. The bulk of the undecomposed biphenyl remained in the U-tube traps. The high boiling fraction remained behind in the pyrolysis tube (lower left) and was dissolved in benzene.

^aA product of Monsanto Chemical Company containing a mixture of the terphenyl isomers and biphenyl.

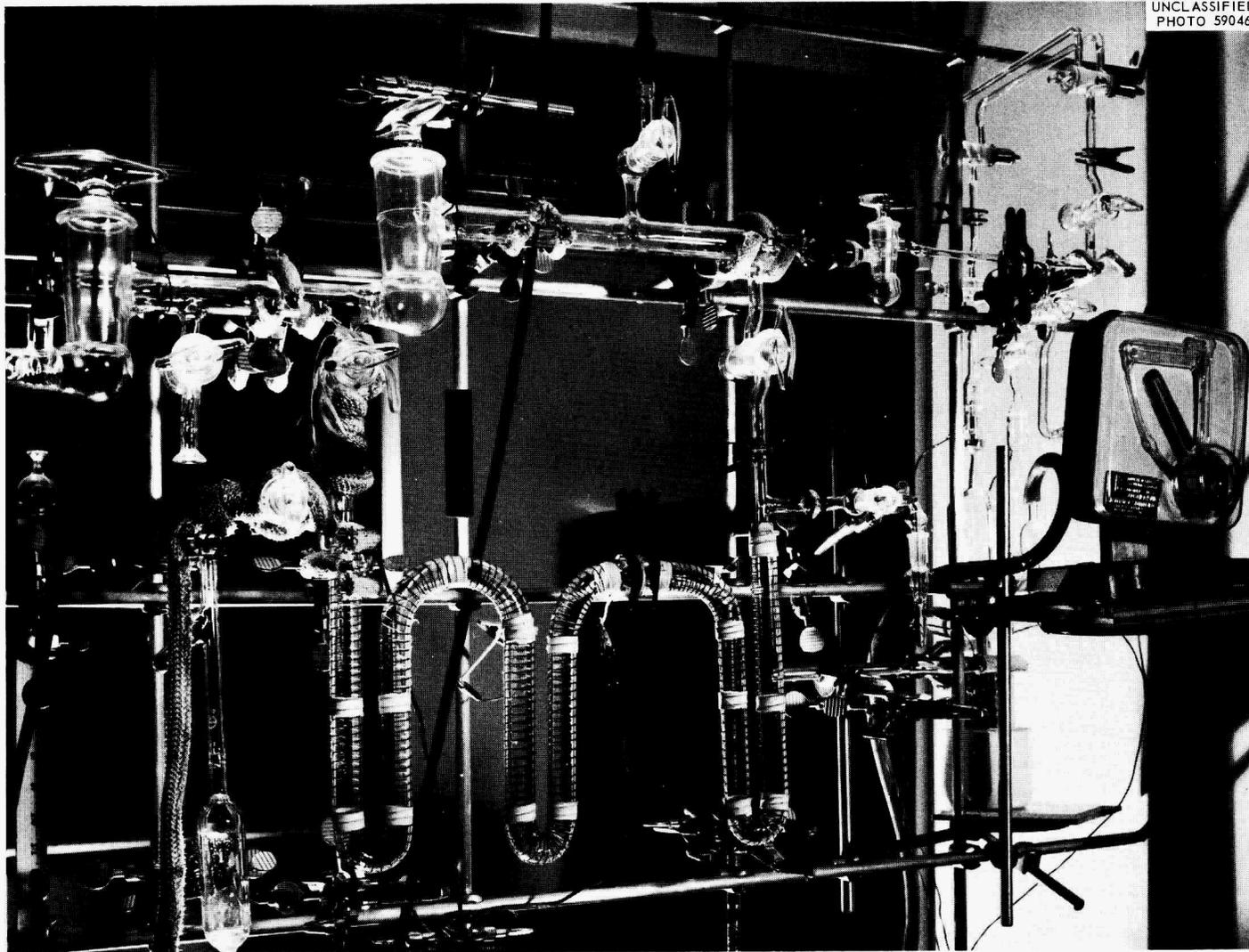


Fig. 1. Fractionation System for Products from Biphenyl Pyrolysis

Reports by Keen et al ¹, Moffat and Solomon², and West³ which might be of interest to the reader deal with the chromatographic analysis of biphenyl radiolytic products, some of which are identical to the pyrolytic products.

II. ANALYSIS OF GASEOUS PRODUCTS

Experimental

West³ and co-workers recommend the use of 2,4-dimethylsulfolane on firebrick to separate the gaseous products other than the permanent gases resulting from the decomposition of biphenyl. However, the authors of this report were unable to achieve the necessary resolution of methane and ethane.

The gas chromatograph used for the analysis of hydrogen and the low molecular weight hydrocarbons was designed and assembled by the Instrument Department of the Instrumentation and Controls Division at Oak Ridge National Laboratory. A schematic diagram of the apparatus is shown in Fig. 2. Tank helium flows through the reference side of the thermistor detection blocks in series before it reaches the gas sampling section. This section may be by-passed by means of an eight-way valve while attaching the gas sampling bulb. In the first column, the 10' x 1/4" OD column of silica gel with 3 wt % squalane, the permanent gases and methane are unresolved and pass on to the 10' x 1/4" OD molecular sieve (Linde 5A) column. The low molecular weight hydrocarbons, resolved on the silica gel column, pass through detector No. 1 and on to the molecular sieve column where they are adsorbed irreversibly. Therefore, it becomes necessary periodically to replace this column. It resolves the permanent gases and methane which are

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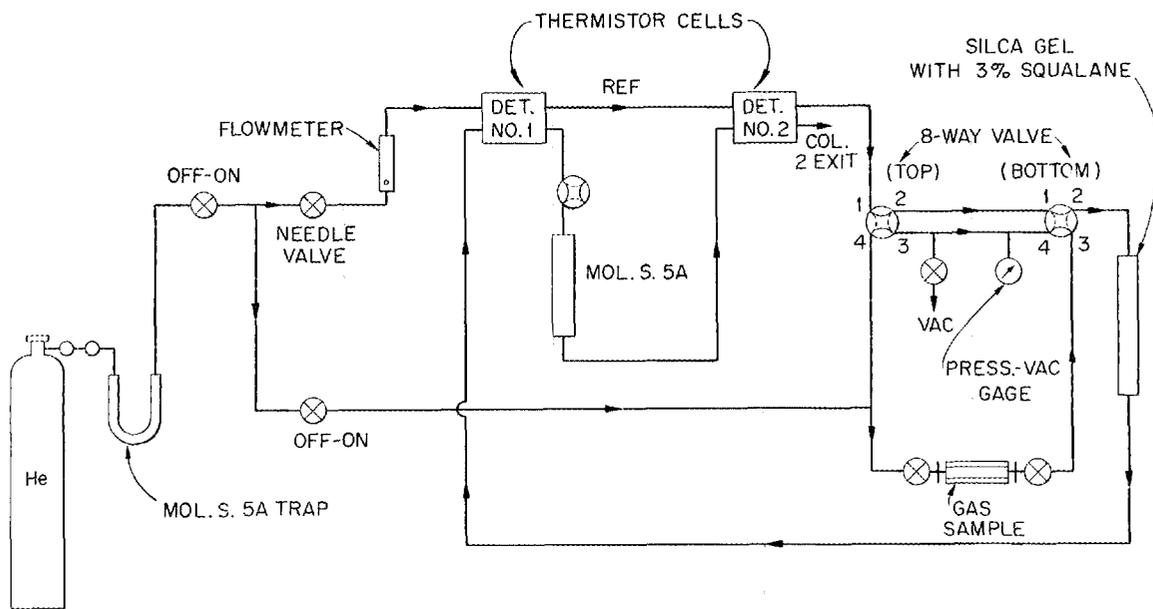


Fig. 2. Gas Chromatograph for Gaseous Products

detected by cell No. 2. A soap-bubble flowmeter was attached when needed to the exit side of the cell.

A typical analysis of helium carrier gas showed 10 ppm hydrogen, 20 ppm water, 25 ppm nitrogen and carbon monoxide, 4 ppm oxygen, and 6 ppm carbon dioxide. The carrier gas was passed through a 1" x 12" stainless steel pipe U-tube filled with molecular sieve (Linde 5A) for clean-up before entering the chromatograph. The eight-way and four-way valves used in the system were stainless steel precision valves with O-ring seals.^b Gow-Mac^c constant current power supplies (Model 9999) were used with the thermal conductivity cells. The latter were detectors which employed matched thermistors with approximately 8000 ohms resistance. The bridge signal was received, attenuated if necessary, and plotted by a 1 mv recorder with a 2 sec full-scale response. All of the electronic equipment was connected to a constant voltage transformer.

Copper tubing (1/4" OD x 10', cleaned with acetone) was used for columns. One was filled with 30-60 mesh molecular sieve (Linde 5A) and purged with dry helium at 300°C for at least four hours before it was put into service. The other column was packed lightly with Burrell's^d intermediate activity silica gel which had been heated overnight at about 250°C and treated with 3 wt % squalane. The columns and detector blocks were completely immersed in a constant

^bCircle Seal Precision Valves, Pasadena, California.

^cGow-Mac Instrument Company, Madison, New Jersey.

^dBurrell Corporation, Pittsburgh, Pennsylvania.

temperature bath regulated at $24^{\circ}\text{C} \pm 0.02^{\circ}$. Detector No. 1 was operated with a bridge current of 4 ma; detector No. 2 at 6 ma. The carrier gas flow rate was maintained at 40 ml/min with a helium back-pressure of 20 psi on the columns.

Results and Discussion

The retention times for the permanent gases and low molecular weight hydrocarbons resolved by this system are given in Table I.

Typical chromatograms produced by these gases are shown in Fig. 3. The unresolved mixture of permanent gases and methane are the first materials eluted from the silica gel column and appear as a single large peak on the chromatogram. The presence of carbon dioxide in a sample is indicated by the shoulder on the propane peak. The unresolved mixture from this column is then resolved on the molecular sieve column. The presence of carbon monoxide and carbon dioxide implies the presence of some oxygen during the pyrolysis of biphenyl. Although the resolution of oxygen and nitrogen is incomplete, it is sufficient to indicate qualitatively the amount of leakage in the vacuum system during sample fractionation.

Standardization curves for these gases were obtained by syringe injection of the pure material. Peak height measurements proved to be more reproducible than peak area measurements. Therefore, plots of volume vs peak height are presented in Figs. 4, 5, and 6. The data for these measurements and their precision are listed in Appendix A.

In general, samples of the products from the pyrolysis of biphenyl contained less than 5 μl of each of the gases except hydrogen and methane. It was not possible in these instances to determine such volumes

Table I. Retention Times for the Permanent Gases and Low Molecular Weight Hydrocarbons

Gas	Silica Gel Retention Time (min)	Molecular Sieve Retention Time (min)
H ₂		4.5
C ₂ H ₆	5.1	
O ₂		6.1
N ₂		6.9
C ₂ H ₄	7.8	
CO		9.7
CH ₄		11.2
C ₃ H ₈	11.5	
C ₂ H ₂	18.4	
C ₄ H ₁₀	31.7	
C ₃ H ₆	33.9	

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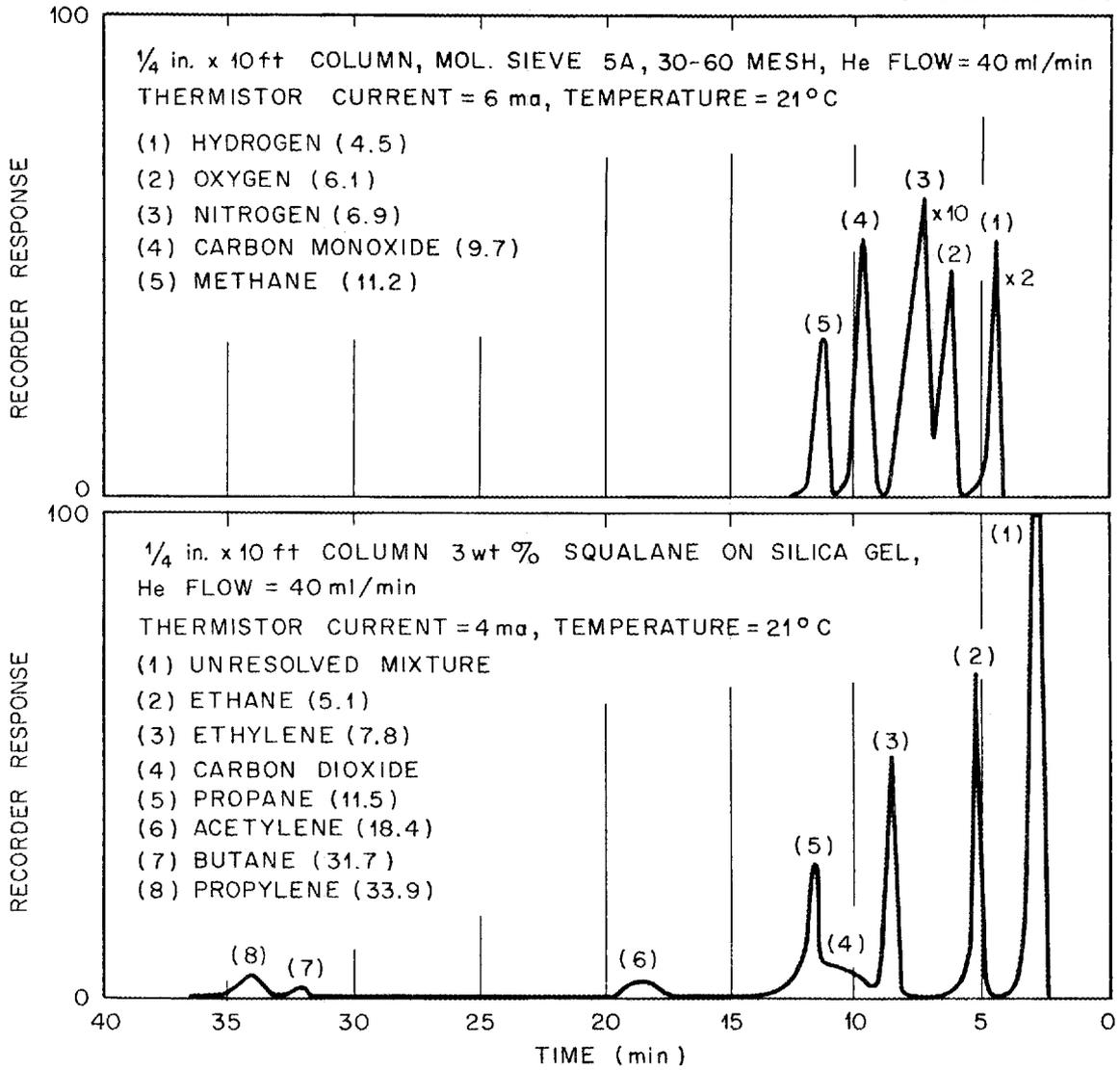


Fig. 3. Chromatograms of Gaseous Products from Biphenyl Pyrolysis

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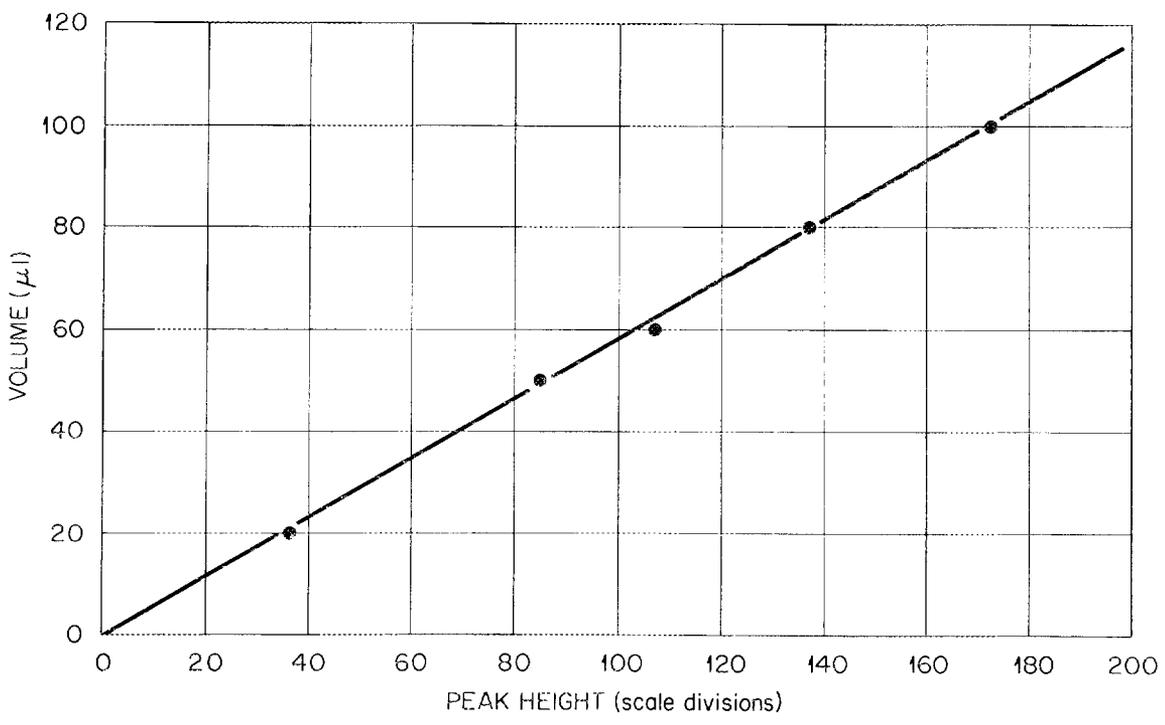


Fig. 4. Standardization Curve for Hydrogen

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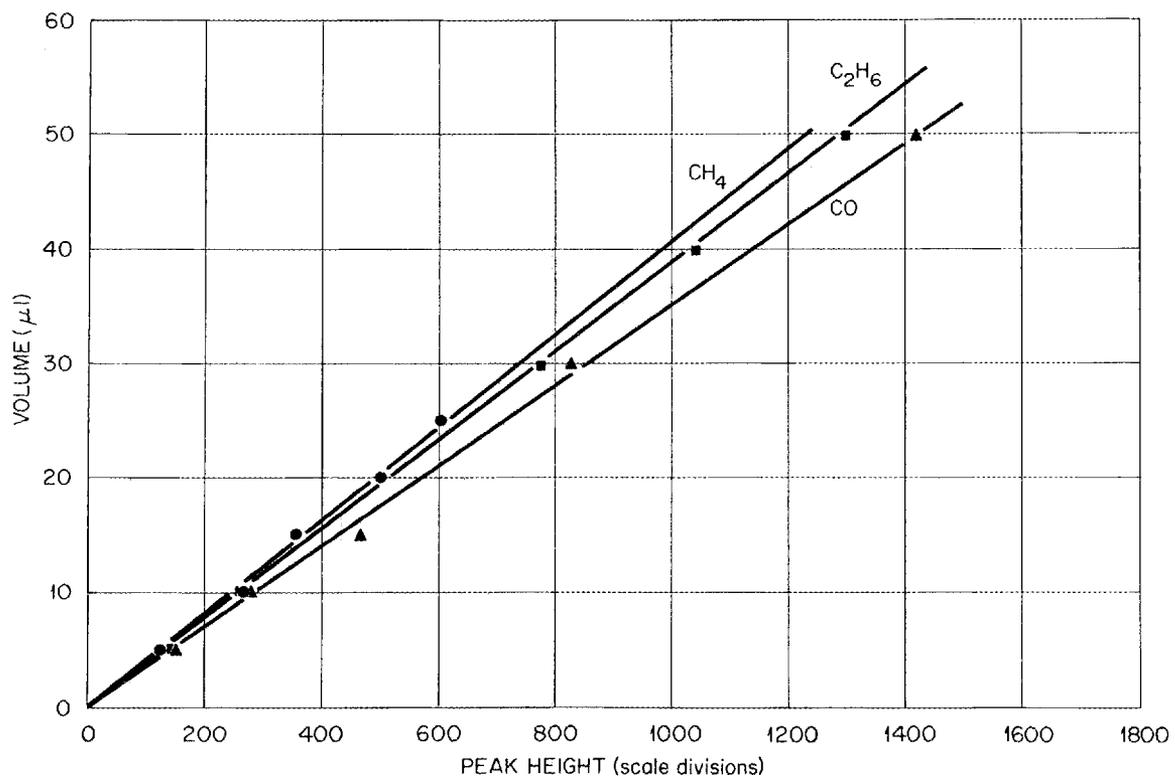


Fig. 5. Standardization Curves for Methane, Carbon Monoxide, and Ethane

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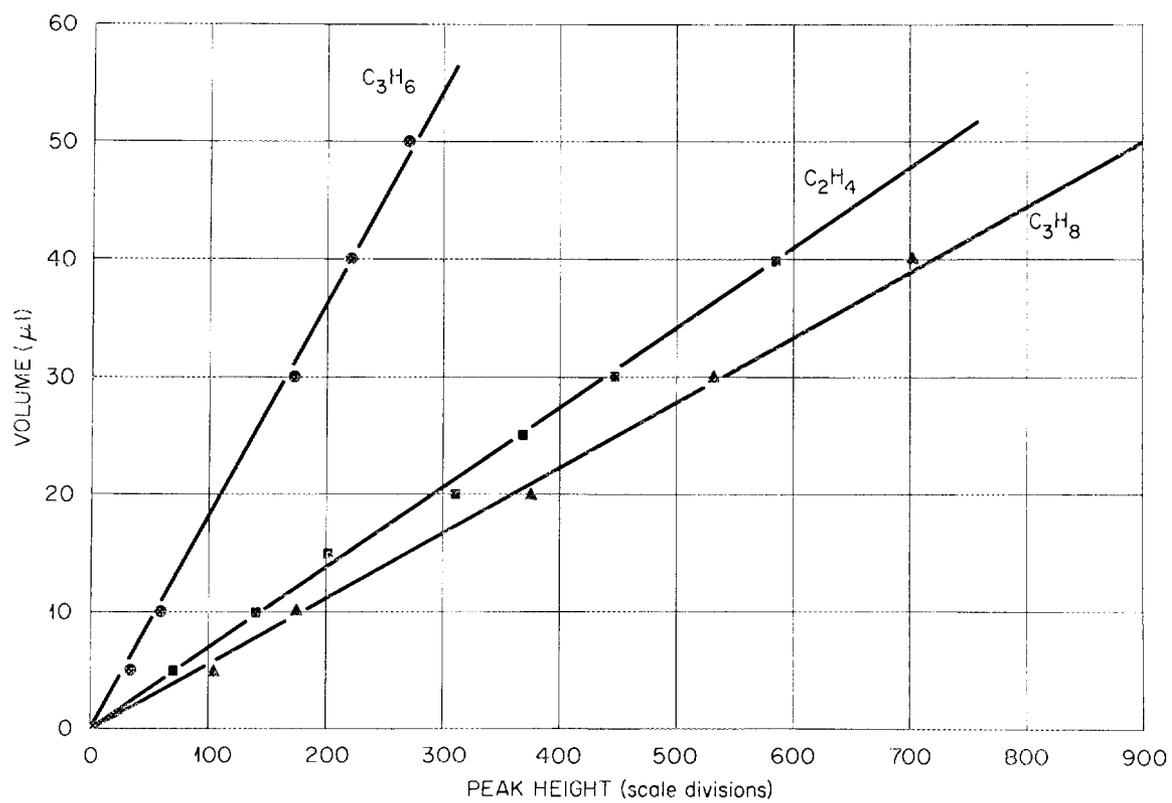


Fig. 6. Standardization Curves for Propane, Ethylene, and Propylene

accurately from the curves shown. Neither was it possible to make accurate sample injections below 5 μl in size in order to extend the curves. Therefore, it was assumed that the straight line function continued to hold at the lower concentrations. Then, the sensitivity of the system, defined as the number of scale divisions per unit volume of gas, is given by the inverse of the slope of the line for the respective gas. These values are listed in Table II.

The sensitivity to hydrogen is low because the thermal conductivities of hydrogen and helium are the same order of magnitude. Substituting argon for helium as the carrier gas resulted in nearly a 50-fold increase in the hydrogen sensitivity, accompanied by a marked decrease in sensitivity for the other gases, of course. By splitting the sample in two, one portion can be analyzed with the maximum sensitivity for hydrogen and the other portion with the maximum sensitivity for hydrocarbon gases. No quantitative data with argon as the carrier gas can be presented at this time.

Table II. Sensitivities of the Low Molecular Weight Hydrocarbons, Hydrogen, and Carbon Monoxide

Gas	H_2	CH_4	CO	C_2H_6	C_2H_4	C_3H_8	C_3H_6
Sensitivity, div/ μl	1.72	24.6	28.4	25.8	14.7	18.0	5.58

III. ANALYSIS OF BENZENE AND RELATED HYDROCARBONS

Experimental

An F and M^e Model 500 gas chromatograph with temperature programming was employed in the chromatographic analysis of benzene

^eF and M Scientific Corporation, Avondale, Pennsylvania.

and related compounds. The filament type thermal conductivity cells were used with a bridge current of 100 ma. The signal with proper attenuation was supplied to a 1 mv, 2 sec full-scale response recorder.

The choice of the stationary phase for a column required speculation of plausible biphenyl pyrolytic products which boil roughly between room temperature and 256°C, the boiling point of biphenyl. From a list of 20 postulated products, the following were chosen to determine column efficiency, stability, and general suitability.

Table III. Plausible Products of Biphenyl Pyrolysis and Their Retention Times on an Apiezon N Column

Product	Boiling Point, °C	Retention Time, min
Benzene	80	14.7
Toluene	111	18.3
Ethylbenzene	136	21.3
Phenylacetylene	142	21.9
n-Propylbenzene	158	24.9
Tert.-Butylbenzene	169	26.6
n-Butylbenzene	183	30.4
Biphenyl (starting material)	256	-

A 2' column of silicone gum rubber did not give the desired resolution of these compounds. A 12' column of about 30 wt % Apiezon N gave better resolution, but "tailing" of the peaks was fairly severe. Carbowax 6000 (2 wt %) was added to reduce this effect. At the same time the solvent for these compounds was changed from tetrahydrofuran to acetone because the former could not be satisfactorily resolved from benzene. These two modifications improved considerably

the geometry of the early appearing peaks. The retention times are given in Table III when using this column with a helium carrier gas flow rate of 30 ml/min and a temperature of 75°C for 5 min, then programming from 75 to 200°C at a rate of 5°C/min. Unfortunately, the components eluted with the longest retention times produced relatively flat peaks. Efforts to reduce the retention times by operating at higher temperatures were unsuccessful due to "bleeding" of the Carbowax. Therefore, work was discontinued with this column. Descriptions of the column and conditions found most satisfactory for the desired purpose follow.

Cleaned copper tubing, 1/4" O.D. x 6' in length, was packed with 35-60 mesh Chromosorb P containing 30 wt. % Apiezon L and 2 wt. % Carbowax 20M as the stationary phases. The column packing was prepared by mixing the solid support with an ethanol solution of the Carbowax 20M, drying under a heat lamp, mixing with a benzene solution of Apiezon L, and redrying with the heat lamp. The tubing was tapped only lightly while filling to prevent the necessity for using a high back-pressure during column operation.

Helium served as the carrier gas with a flow rate of 30 ml/min through the measuring side of the detector and approximately 15 ml/min through the reference side. The injection port and detector block temperatures were about 250°C. The column was temperature programmed from 125 to 250°C at a rate of 11°C/min.

A standard solution of the components dissolved in acetone was stored satisfactorily for weeks in a 25 ml graduate to which a Teflon bore stopcock was sealed. A silicone-rubber septum covered the short

entry arm of the stopcock. The stopcock was opened only during sample removal. Samples of the solutions were introduced to the chromatograph by syringe injection. The reproducibility of sample injection was best when using a gas syringe and measuring the solution volume with all of the liquid in the barrel. A pocket of air between the solution and the plunger permitted complete expulsion of the syringe's contents into the injection port. If this was not done, solution remaining in the needle after injection was partially vaporized in the hot injection port. The fraction vaporized was variable and not measurable, resulting in poor precision.

The sources of chemicals used were: benzene and toluene - Mallinckrodt Chemical Works; o-xylene and tert.-butylbenzene - Matheson, Coleman, and Bell; ethylbenzene, phenylacetylene, n-propylbenzene, n-butylbenzene, and phenylcyclohexane - Eastman Organic Chemicals; purified biphenyl - California Research Corporation.

A Perkin-Elmer printing integrator Model 194 measured the peak areas of the components. It has a printed output of 6000 counts/min.

Results and Discussion

The retention times for benzene and related hydrocarbons on the Apiezon L column under the conditions stated above are listed in Table IV.

A typical chromatogram of these materials dissolved in acetone is shown in Fig. 7.

Benzene was the only one of these compounds produced in detectable amount upon pyrolyzing pure biphenyl at 425°C. o-Xylene was chosen to serve as the internal standard during the determination of benzene.

Table IV. Retention Times for Benzene and Related Compounds on Apiezon L

Compound	Boiling Point, °C	Retention Time, min
Benzene	80	4.0
Toluene	111	6.2
o-Xylene	144	9.0
Phenylcyclohexane	239	20.0
Biphenyl	256	22.7

Therefore, quantitative measurements were made only on standard acetone solutions of these two compounds. The concentration of the o-xylene solution was 10.8 µg/µl; the benzene solution, likewise, was 10.8 µg/µl. Standardization curves for these solutions are presented in Fig. 8.

The curves show that the accuracy of the peak area measurements is somewhat greater than that of the peak height for both compounds. The precision of the data, obtained from the results in Appendix B, also favors the use of peak area measurements as seen in Table V.

Table V. Deviation of Peak Height and Peak Area Measurements for Benzene and o-Xylene

Compound	Deviation, ave.	
	Peak Height	Peak Area
Benzene	+ 2.6	+ 1.2
o-Xylene	+ 1.6	+ 1.2

The area calibration factor for benzene with o-xylene as the standard is defined by:

$$F_b = \frac{W_b A_x}{W_x A_b}$$

where

$$F_b = \text{calibration factor for benzene}$$

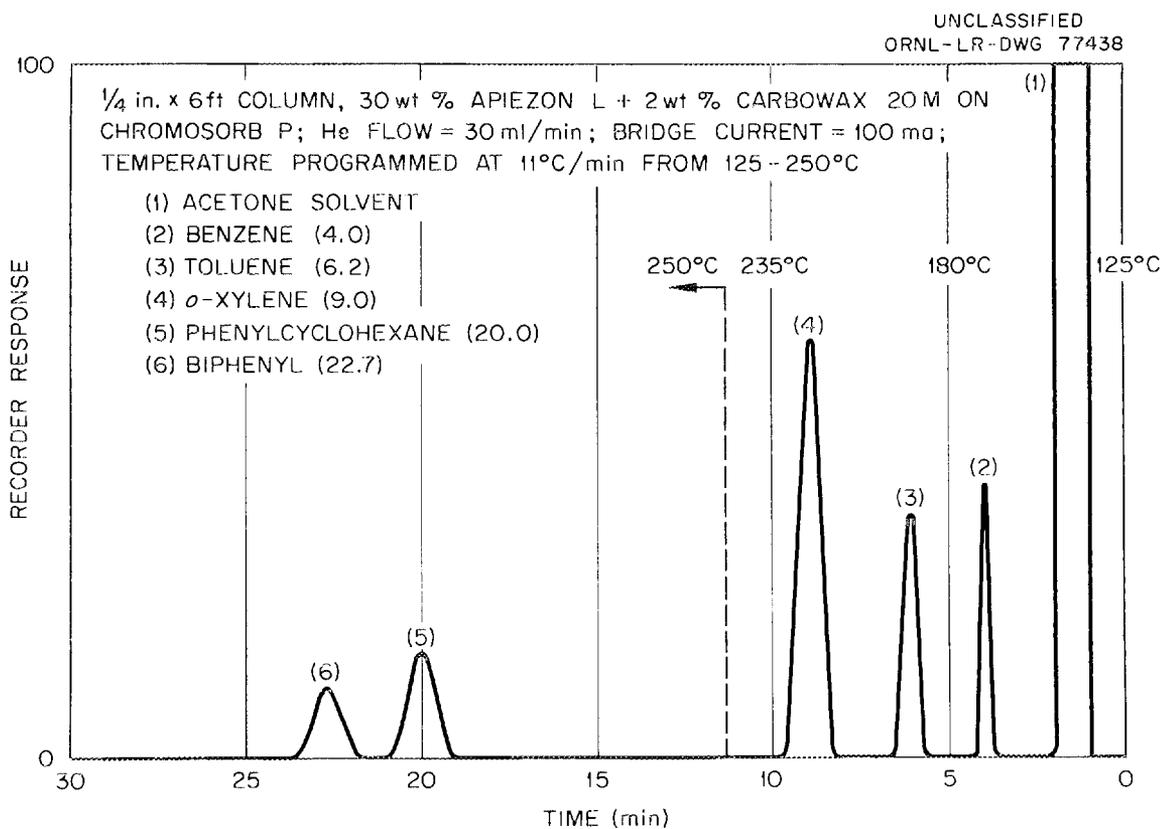


Fig. 7. Chromatogram of Benzene and Related Compounds

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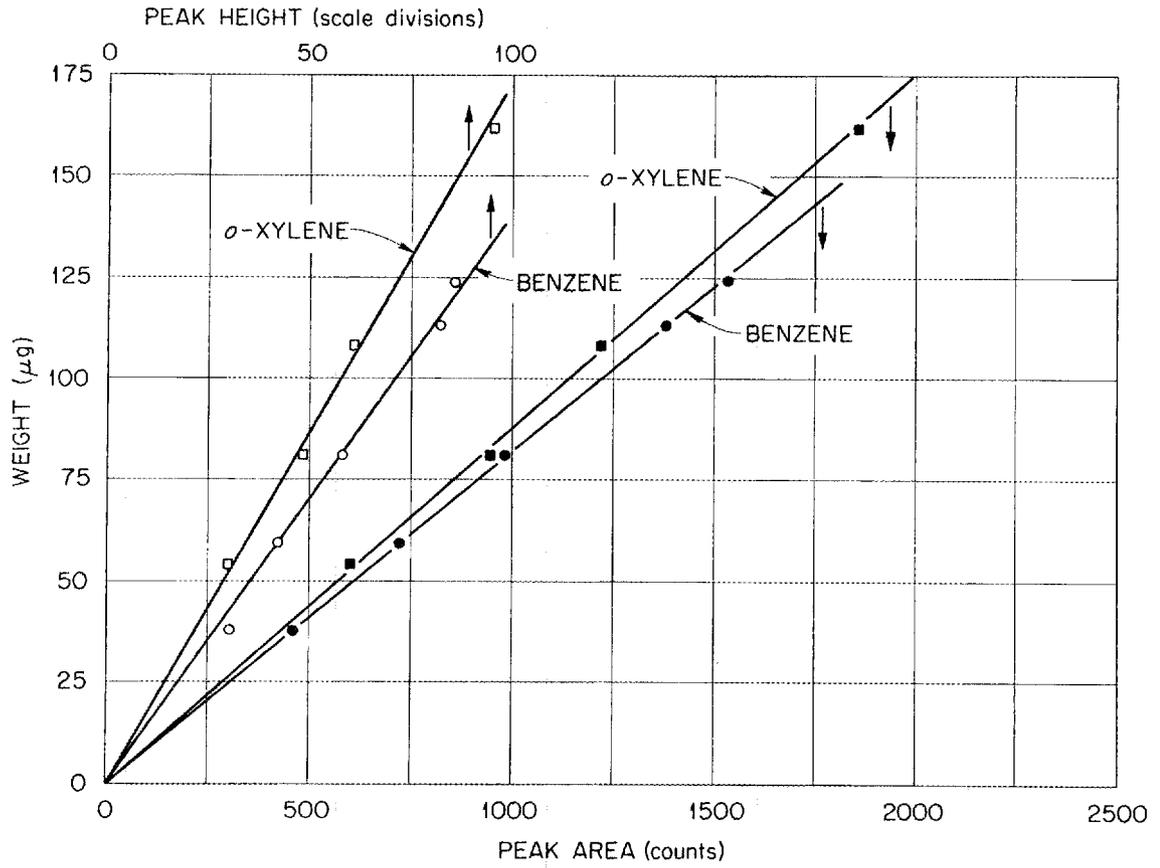


Fig. 8. Standardization Curves for Benzene and o-Xylene

W_b = weight of benzene

A_b = area of benzene peak

W_x = weight of o-xylene

A_x = area of o-xylene peak

From the slopes of the standard curves, $F_b = 0.935$.

IV. ANALYSIS OF POLYPHENYL COMPOUNDS

Experimental

Analysis of the residue or polymeric materials resulting from the radiolysis of terphenyl isomers¹ showed the presence of significant quantities of higher polyphenyl compounds. Therefore, the assumption was made that analogous or identical polyphenyls would be produced during the pyrolysis of biphenyl. The experimental procedure adopted was based on this assumption.

An F and M Model 500 gas chromatograph with temperature programming was the instrument used for these determinations. The filament type thermal conductivity cells were operated at a bridge current of 100 ma. The signal from the cells, properly attenuated, was received and registered by a 1 mv recorder which had a 2 sec full-scale response.

An initial attempt was made to use a high-temperature column consisting of 30 wt % of the eutectic composition of lithium, sodium, and potassium nitrates (18.2:54.4:27.3 wt %) on Chromosorb P. It has been stated⁴ that this column operates satisfactorily above the melting point of the salt eutectic (150°C) to as high a temperature as desired. However, baseline instability and liquid phase decomposition with the evolution of N_2O_4 were encountered at the temperatures required for operation. Therefore, the particular column and operating

conditions subsequently adopted are presented below.

Helium constituted the carrier gas at a flow rate of 30 ml/min through the measuring side of the detector block and approximately 15 ml/min through the reference side. The injection port temperature was about 315°C and the detector block about 350°C. The column was programmed at 11°C/min from 200 to 350°C.

The chromatographic column was a 12' length length of 1/4" OD). stainless steel tubing, freshly cleaned, packed with 20 wt. % lithium chloride on 35-80 mesh Chromosorb P. The packing was prepared by dissolving the desired quantity of lithium chloride in water, intimately mixing the solution with the solid support, drying under a heat lamp, and finally heating in a muffle furnace at 750°C for about one hour to fuse the salt onto the support.²

Standard solutions of the polyphenyl compounds were prepared with benzene as the solvent and stored in containers described in the previous section. Samples were injected into the chromatograph, also, as described earlier.

Eastman Organic Chemicals was the source of supply for o-, m-, and p-terphenyls. K and K Laboratories, Inc. was the supplier for o-quaterphenyl, and 1,3,5-triphenylbenzene. m,p-Quaterphenyl was obtained through the courtesy of F. L. Howard, Pure Substances Section of the National Bureau of Standards.

A Model 194 Perkin-Elmer printing integrator with a printed output of 6000 counts/min was used for peak area measurements.

Results and Discussion

The retention times for several polyphenyl compounds on a 12'-20 wt. % LiCl column, operated under the conditions given above, are

presented in Table VI.

Table VI. Polyphenyl Retention Times on a LiCl Column

Compound	Formula	M. Pt., °C	R.T., min
Biphenyl	$C_6H_5-C_6H_5$	71	4.5
o-Terphenyl	$C_6H_5-C_6H_4-C_6H_5$	56-7	8.4
o-Quaterphenyl	$C_6H_5-(C_6H_4)_2-C_6H_5$	117.8	11.0
m-Terphenyl	$C_6H_5-C_6H_4-C_6H_5$	86-7	11.6
p-Terphenyl	$C_6H_5-C_6H_4-C_6H_5$	212-3	12.6
1,3,5-Triphenylbenzene	$(C_6H_5)_3-C_6H_3$	150-9	18.3
m-Quaterphenyl	$C_6H_5-(C_6H_4)_2-C_6H_5$	87	18.3
m,p-Quaterphenyl	$C_6H_5-(C_6H_4)_2-C_6H_5$	167	20.3

It should be pointed out that only small quantities of o-quaterphenyl and m-terphenyl were resolved on this column. Mixtures of these two compounds containing more than about 80µg of o-quaterphenyl appeared on the chromatogram as a single sharp peak. The order in which these two compounds were eluted from the column was opposite that reported by Moffat and Solomon.² The order of elution was established in our case by increasing the concentration of m-terphenyl in an acetone solution of the two compounds and noting which peak height increased during analysis.

A chromatogram of the polyphenyl fraction of biphenyl pyrolytic products is shown in Fig. 9. Peak (3) was shown to be due to the presence of m-terphenyl since analysis of small samples indicated the absence of o-quaterphenyl. Although the difference between the retention times of m- and p-terphenyl was relatively small, there was

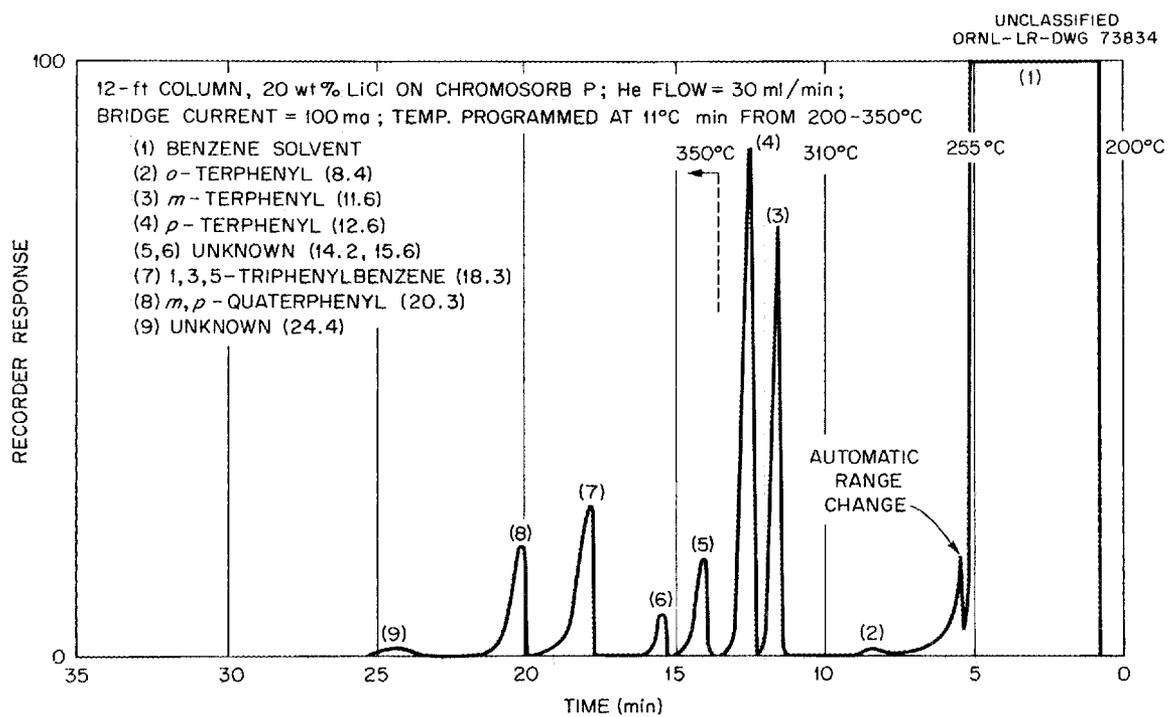


Fig. 9. Chromatogram of Polyphenyl Compounds

sufficient time for complete resolution of these peaks under the operating conditions used. However, the retention times for m-quaterphenyl and 1,3,5-triphenylbenzene were such that it was not possible to resolve these two compounds on this column. Hence, it cannot be stated unequivocally at this time that peak 7 was due to the presence of 1,3,5-triphenylbenzene. The retention times for the unidentified peaks suggested the presence of additional quaterphenyl isomers, but the inability to procure these isomers prevented definite identification.

The preparation of two different standard solutions of the polyphenyls was dictated by the similarity in retention times for some of the compounds. The composition and concentration of these solutions are given in Table VII.

Table VII. Standard Solutions of Polyphenyls in Benzene

Solution A		Solution B	
Component	Conc., $\mu\text{g}/\mu\text{l}$	Component	Conc., $\mu\text{g}/\mu\text{l}$
Biphenyl	4.5	p-Terphenyl	5.2
o-Terphenyl	4.8	m-Quaterphenyl	5.1
1,3,5-Triphenylbenzene	10.1	m,p-Quaterphenyl	2.4
m-Terphenyl	7.1		

Standardization curves for these solutions are presented in Figs. 10 and 11. The curves in Fig. 10 show that the accuracy of the peak area measurements was better than that of peak height. As a consequence, peak height vs. component weight was not plotted in Fig. 11. The data for these measurements, listed in Appendix C, showed, oddly enough, the precision of the peak height data to be better in most instances than that of the area measurements.

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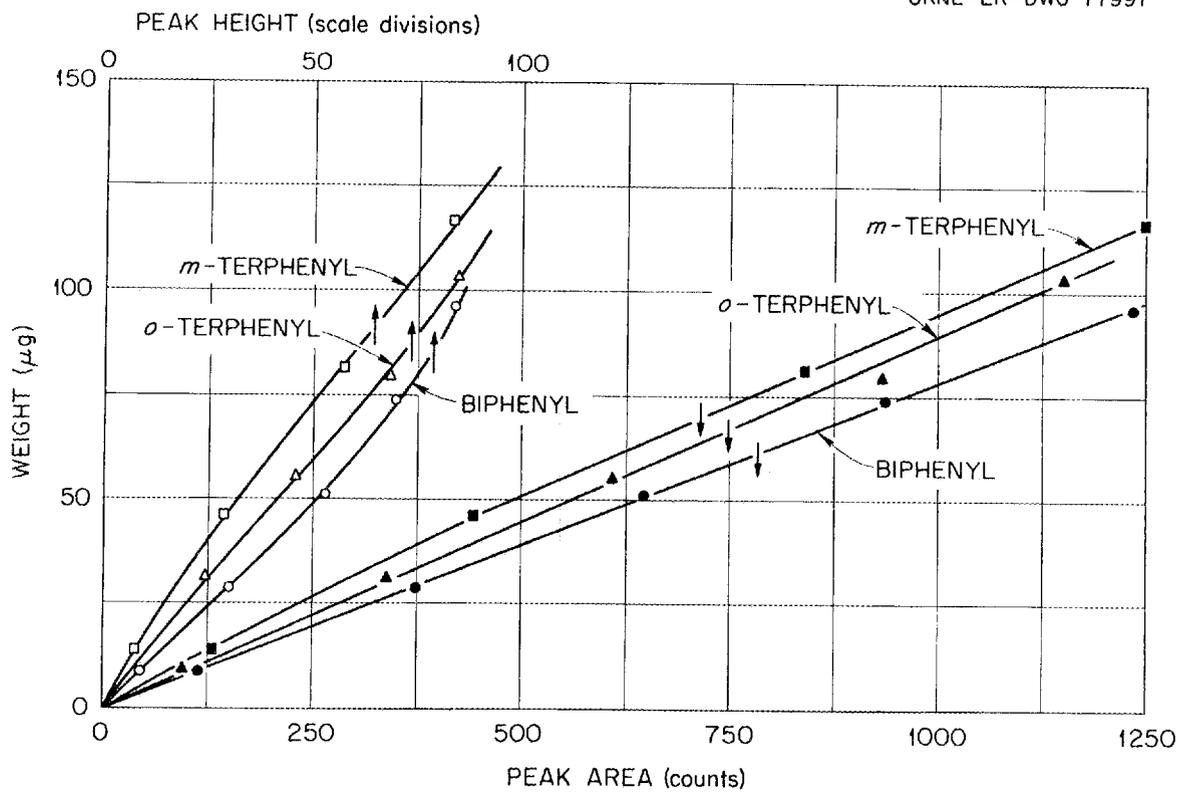


Fig. 10. Standardization Curves for Biphenyl, o-Terphenyl, and m-Terphenyl

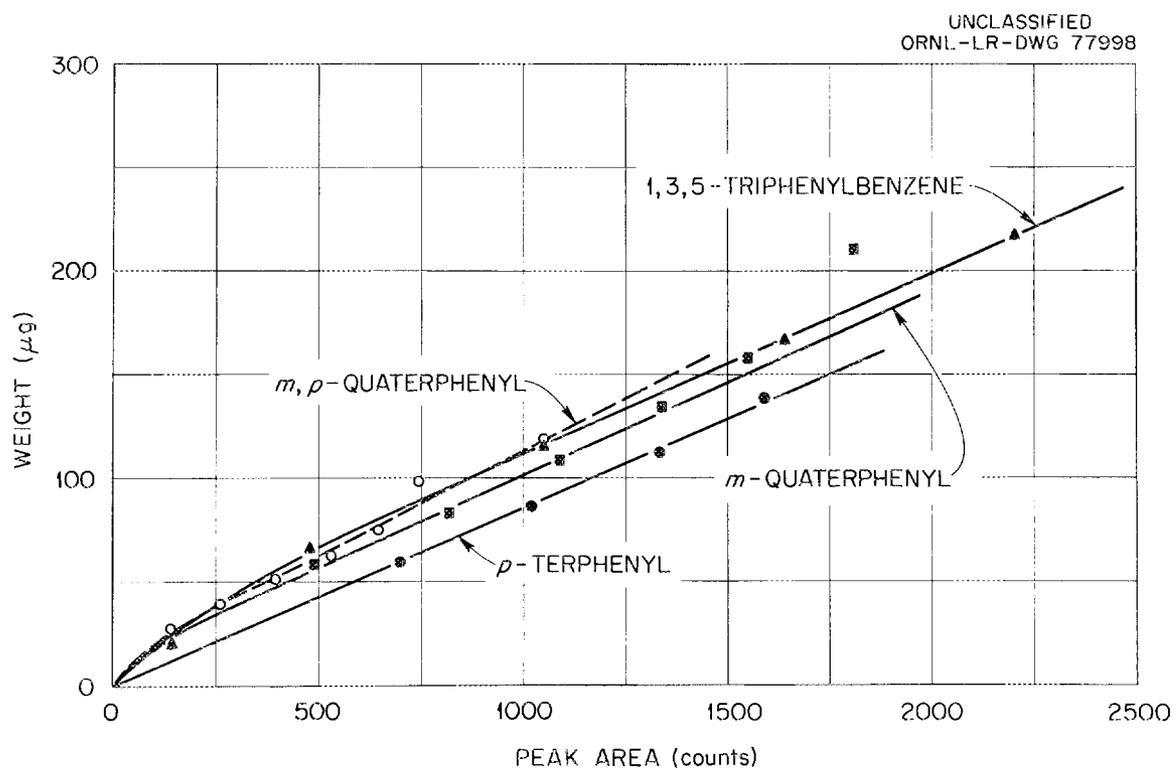


Fig. 11. Standardization Curves for *p*-Terphenyl and Three Quaterphenyl Isomers

In general, the curves drawn from area measurements are much nearer a straight line relationship than is found for the peak height data. This is in agreement with Johns'⁵ findings. No explanation can be given for the deviation from linearity which occurs at low concentrations in the area plots for some of the polyphenyls.

The area calibration factors for the polyphenyls, relative to biphenyl, are listed in Table VIII. They were calculated as indicated previously (p. 19).

Table VIII. Polyphenyl Area Calibration Factors

<u>Compound</u>	<u>F</u>
Biphenyl	1.00
o-Terphenyl	1.14
m-Terphenyl	1.12
p-Terphenyl	1.09
1,3,5-Triphenylbenzene	1.11
m-Quaterphenyl	1.14
m,p-Quaterphenyl	1.30

It should be understood that these factors can be applied only where a linear relationship exists between peak area and amount of the particular polyphenyl.

V. SUMMARY

Gas chromatographic procedures are given for the quantitative determination of hydrocarbon products obtained upon pyrolyzing biphenyl.

The low molecular weight hydrocarbons, hydrogen, and carbon monoxide were resolved on a 10' column of silica gel, with 3 wt % squalane, in series with a 10' column of 30-60 mesh molecular sieve

(Linde 5A). The columns and thermistor detector blocks were maintained at $24^{\circ}\text{C} \pm 0.02^{\circ}$. At a helium flow rate of 40 ml/min, the determination of hydrogen, carbon monoxide, methane, ethane, ethylene, propane, and propylene was complete in 35 min. Calibration curves from peak height measurements were established for these gases over the range of 5 to 50 microliters, except for hydrogen where the range was 20 to 100 microliters. The analytical precision of the results was generally within $\pm 5\%$.

Benzene and o-xylene were analyzed on a 6' column of 30 wt. % Apiezon L plus 2 wt. % Carbowax 20M on Chromosorb P. Filament type thermal conductivity cells were used with helium serving as the carrier gas at a flow rate of 30 ml/min. The injection port and detector block temperatures were about 250°C while the column was temperature programmed at $11^{\circ}\text{C}/\text{min}$ from 125 to 250°C . Calibration curves are drawn from peak area determinations covering 35 to 170 micrograms of material. The reproducibility of results was $\pm 2\%$.

The polyphenyl compounds were resolved on a 12' column of Chromosorb P with a stationary phase of 20 wt. % LiCl. Helium, at a flow rate of 30 ml/min, served as the carrier gas and the detectors were the filament type thermal conductivity units. The column was temperature programmed at $11^{\circ}\text{C}/\text{min}$ from 200 to 350°C while maintaining the injection port and detector block temperatures above 300°C . Approximately 20 min was required to resolve a mixture of biphenyl, o-terphenyl, m-terphenyl, p-terphenyl, 1,3,5-triphenylbenzene, m- quaterphenyl, and m,p-quaterphenyl. Peak area determinations were used to construct standardization curves for these compounds over the

range of 10 to 120 micrograms for the terphenyls and 40 to 210 micrograms of the quaterphenyls. The precision of the data was $\pm 2\%$, in general.

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Figure Captions

1. ORNL-PHOTO-59046, Fractionation System for Products from Biphenyl Pyrolysis.
2. ORNL-DWG-73832, Gas Chromatograph for Gaseous Products.
3. ORNL-DWG-77992, Chromatograms of Gaseous Products from Biphenyl Pyrolysis .
4. ORNL-DWG-77993, Standardization Curve for Hydrogen.
5. ORNL-DWG-77994, Standardization Curves for Methane, Carbon Monoxide, and Ethane.
6. ORNL-DWG-77995, Standardization Curves for Propane, Ethylene, and Propylene.
7. ORNL-DWG-77438, Chromatogram of Benzene and Related Compounds.
8. ORNL-DWG-77996, Standardization Curves for Benzene and o-Xylene.
9. ORNL-DWG-73834, Chromatogram of Polyphenyl Compounds.
10. ORNL-DWG-77997, Standardization Curves for Biphenyl, o-Terphenyl, and m-Terphenyl.
11. ORNL-DWG-77998, Standardization Curves for p-Terphenyl and Three Quaterphenyl Isomers.

VII. APPENDIX A

Standardization Data for Low Molecular Weight Hydrocarbons, Hydrogen, and Carbon Monoxide

Compound	Volume, μ l	Peak Height, scale divisions	Peak Height/ μ l	Deviation
Hydrogen	20.0	36.0	1.80	0.06
	50.0	91.0		
		87.5		
		75.0		
	Average	84.5	1.69	0.05
	60.0	107	1.78	0.04
	80.0	143		
		135		
		134		
	Average	137	1.72	0.02
100	172	1.72	0.02	
		Average	1.74	\pm 0.02
Methane	5.0	123	24.6	0.2
	10.0	272		
		260		
		Average	266	26.6
	15.0	330		
		340		
		368		
		370		
	Average	355	23.5	1.3
	20.0	480		
520				
Average	500	25.0	0.2	
25.0	580			
	630			
	Average	605	24.2	0.6
		Average	24.8	\pm 0.08

Compound	Volume, μl	Peak Height, scale divisions	Peak Height/ μl	Deviation	
Carbon Monoxide	5.0	145	29.0	0.3	
	10.0	270	27.8	0.9	
		285			
	Average	278			
		15.0	456	30.9	2.2
	470				
	Average	463			
		30.0	825	27.5	1.2
	50.0	1420	Average	28.3	0.4
		1430			
1396					
Average	1419				
			Average 28.7	± 1.0	
Ethane	5.0	142	28.6	2.1	
		144			
	Average	143			
		10.0	252	26.1	0.4
	270				
	Average	261			
		30.0	790	25.8	0.7
	758				
	Average	774			
		40.0	1040	26.0	0.5
50.0	1296	Average	26.0	0.5	
	1300				
	Average				1298
		Average 26.5	± 0.8		

Compound	Volume, μl	Peak Height, scale divisions	Peak Height/ μl	Deviation	
Ethylene	5.0	65.4			
		77.0			
		Average	71.2	14.2	0.3
	10.0	159			
		130			
		130			
		146			
		Average	141	14.1	0.4
	15.0	203		13.5	1.0
	20.0	305			
		317			
		Average	311	15.6	1.1
25.0	350				
	386				
	Average	368	14.7	0.2	
30.0	443				
	450				
	Average	447	14.9	0.4	
40.0	597				
	570				
	Average	584	14.6	0.1	
			Average	14.5 \pm 0.5	
Propane	5.0	105	21.0	2.5	
	10.0	180			
		170			
		Average	175	17.5	1.0
	20.0	376	18.8	0.3	
	30.0	520			
546					
	Average	533	17.8	0.7	

Compound	Volume, μl	Peak Height, scale divisions	Peak Height/ μl	Deviation	
Propane (cont.)	40.0	735			
		690			
		705			
		686			
		Average	704	17.6	0.9
		Average	18.5	± 1.0	
Propylene	5.0	34.5			
		32.5			
		Average	33.5	6.70	0.82
	10.0		60.0	6.00	0.12
	30.0		172	5.73	0.15
	40.0	208			
		235			
		Average	222	5.55	0.33
	50.0	268			
		273			
	Average	271	5.42	0.46	
		Average	5.88	± 0.38	

VIII. APPENDIX B

Standardization Data for Benzene and o-Xylene Using Apiezon L Column

Compound	Weight, μg	Peak Height, scale divisions	Peak Area, counts	
o-Xylene	54.0	29.8	594	
		29.6	593	
		31.0	617	
		Average	31.0 ± 0.6 ($\pm 2\%$)	601 ± 10 ($\pm 1.7\%$)
	81.0	49.9	962	
		47.7	931	
		48.3	952	
		Average	48.6 ± 8.3 ($\pm 1.7\%$)	948 ± 12 ($\pm 1.3\%$)
	108.0	61.3	1210	
		60.6	1246	
62.1		1211		
59.8		1216		
	Average	61.0 ± 7.5 ($\pm 1.2\%$)	1221 ± 13 ($\pm 1.1\%$)	
162.0	95.6	1871		
	97.8	1835		
	94.0	1865		
		Average	95.8 ± 1.3 ($\pm 1.4\%$)	1857 ± 15 ($\pm 0.81\%$)
Benzene	37.8	31.6	464	
		27.6	453	
		31.7	471	
		Average	30.3 ± 1.8 ($\pm 5.9\%$)	463 ± 6 (1.3%)
	59.4	42.0	710	
		42.4	734	
		42.1	722	
		Average	42.2 ± 0.2 ($\pm 0.47\%$)	733 ± 8 ($\pm 1.1\%$)
	81.0	56.8	977	
		60.5	949	
59.2		1013		
58.0		998		
-		960		
57.1		992		
	Average	58.3 ± 1.2 ($\pm 2.1\%$)	982 ± 20 ($\pm 2.0\%$)	

Compound	Weight, μg	Peak Height, scale divisions	Peak Area, counts	
Benzene (cont.)	113.4	80.4	1390	
		82.9	1385	
		84.2	1379	
		Average	82.5 ± 1.4 ($\pm 1.7\%$)	1385 ± 4 (0.29%)
	124.2	83.8	1522	
		83.4	1497	
		87.0	1568	
		91.4	1548	
		85.4	1535	
		Average	86.2 ± 2.4 ($\pm 2.8\%$)	1534 ± 20 ($\pm 1.3\%$)

IX. APPENDIX C

Standardization Data for Polyphenyl Materials Using LiCl Column

Compound	Weight, μg	Peak Height, scale divisions	Peak Area, counts
Biphenyl	8.96	9.0	115
	29.1	29.9	370
		29.9	373
		30.0	376
		Average	29.9 ± 0.03 ($\pm 0.1\%$)
	51.5	52.8	649
		52.7	650
		53.7	653
		52.2	641
	Average	52.9 ± 0.5 ($\pm 0.95\%$)	648 ± 4 ($\pm 0.62\%$)
	73.9	69.7	944
		69.8	916
		69.6	946
		70.2	942
	Average	69.8 ± 2 ($\pm 0.29\%$)	937 ± 11 ($\pm 1.2\%$)
96.3	83.8	1248	
	84.2	1243	
	84.8	1211	
	Average	84.3 ± 4 (0.47%)	1234 ± 15 ($\pm 1.2\%$)
o-Terphenyl	9.62	-	96
	31.3	24.6	342
		24.1	329
		24.9	350
	Average	24.5 ± 0.3 ($\pm 1.2\%$)	340 ± 8 ($\pm 2.4\%$)
	55.3	46.6	615
		46.6	600
		44.4	612
		45.7	606
		47.0	613
Average	46.1 ± 1 ($\pm 2.2\%$)	609 ± 3 ($\pm 0.5\%$)	

Compound	Weight, μg	Peak Height, scale divisions	Peak Area, counts	
o-Terphenyl (cont.)	79.4	69.0	940	
		67.3	896	
		68.9	960	
		68.7	937	
		Average	68.4 ± 6 ($\pm 0.9\%$)	933 ± 19 ($\pm 2.0\%$)
	103.4	85.1	1165	
		85.6	1197	
		85.4	1137	
		83.3	1115	
		85.3	1140	
	Average	84.9 ± 7 ($\pm 0.8\%$)	1151 ± 24 ($\pm 2.1\%$)	
m-Terphenyl	14.1	7.4	131	
	46.0	29.0	456	
		27.5	421	
		28.1	-	
		28.5	451	
		29.7	-	
		Average	28.5 ± 0.6 ($\pm 2.1\%$)	443 ± 14 ($\pm 3.2\%$)
	81.3	57.5	838	
		57.2	844	
		57.4	831	
		57.5	845	
		Average	57.4 ± 1 ($\pm 1.7\%$)	840 ± 5 ($\pm 0.6\%$)
	116.7	85.4	1306	
		84.2	1313	
84.4		1325		
		Average	84.7 ± 0.5 ($\pm 0.6\%$)	1315 ± 7 ($\pm 0.5\%$)
		84.1	1260	
		82.8	1243	
	Average	83.5 ± 0.7 ($\pm 0.8\%$)	1252 ± 9 ($\pm 0.7\%$)	

Compound	Weight, μg	Peak Height, scale divisions	Peak Area, counts
1,3,5-Triphenylbenzene			
	20.2	3.3	146
	65.8	14.0	-
		14.4	498
		-	467
		14.5	483
		14.4	481
	Average	14.3 ± 0.2 ($\pm 1.4\%$)	483 ± 8 ($\pm 1.7\%$)
	116.4	31.3	1039
		32.8	1086
		31.7	1000
		30.9	1096
		31.7	1023
	Average	31.7 ± 0.5 ($\pm 1.6\%$)	1049 ± 34 ($\pm 3.2\%$)
	167.0	48.2	1694
		48.3	1600
		47.8	1625
	Average	48.1 ± 0.2 ($\pm 0.4\%$)	1640 ± 36 ($\pm 2.2\%$)
	217.6	59.8	2139
		62.3	2285
		61.1	2188
		62.1	2231
		61.0	2188
	Average	61.3 ± 0.6 ($\pm 1.0\%$)	2206 ± 41 ($\pm 1.9\%$)
p-Terphenyl			
	59.8	42.4	680
		41.5	695
		41.5	682
		42.6	691
	Average	42.0 ± 0.5 ($\pm 1.2\%$)	687 ± 6 ($\pm 0.9\%$)
	85.8	65.0	1031
		65.0	1017
		65.0	990
		64.9	1045
	Average	65.0 ± 0.03 ($\pm 0.05\%$)	1021 ± 17 ($\pm 1.7\%$)

Compound	Weight, μg	Peak Height, scale divisions	Peak Area, counts
p-Terphenyl (cont.)	111.8	84.8	1343
		84.7	1318
		-	1319
		83.4	1358
		83.2	1321
	Average	84.0 ± 0.7 ($\pm 0.8\%$)	1332 ± 15 ($\pm 1.1\%$)
	137.8	92.5	1589
m-Quaterphenyl	58.1	14.9	490
		-	495
		13.4	493
		13.3	471
		Average	13.9 ± 0.7 (± 5.0)
	83.3	26.6	811
		26.1	820
		27.3	832
	Average	26.7 ± 0.4 ($\pm 1.5\%$)	821 ± 7 ($\pm 0.9\%$)
	108.6	38.3	1096
		37.0	1082
		37.4	1094
	Average	37.6 ± 0.5 ($\pm 1.3\%$)	1091 ± 6 ($\pm 0.5\%$)
	133.8	46.4	1341
159.1	-	-	1528
		52.4	1580
		52.0	1462
		55.1	1606
		Average	53.2 ± 1.3 ($\pm 2.4\%$)
	209.6	63.9	1850
		62.0	1780
		63.6	1800
	Average	63.2 ± 8 ($\pm 1.3\%$)	1810 ± 27 ($\pm 1.5\%$)

Compound	Weight, μg	Peak Height, scale divisions	Peak Area, counts
m,p-Quaterphenyl	27.5	3.2	167
		3.1	136
		2.8	112
		2.7	142
		2.6	
	Average	2.9 ± 0.2 ($\pm 6.9\%$)	139 ± 15 ($\pm 10.8\%$)
	39.4	6.2	294
		5.8	235
		5.5	231
		6.4	281
			Average
	51.4	9.9	407
		8.4	385
		9.9	400
	Average	9.4 ± 0.7 ($\pm 7.4\%$)	397 ± 8 ($\pm 2.0\%$)
	63.3	12.7	531
	75.3	15.6	620
		14.9	635
		14.3	-
		16.1	682
			Average
	99.2	19.2	771
		18.6	731
		19.2	737
	Average	19.0 ± 0.3 ($\pm 1.6\%$)	746 ± 16 ($\pm 2.1\%$)
	118.3	24.8	1038
		26.3	1079
		27.1	1044
		25.9	1052
			Average

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