UNCLASSIFIED

AERE - M 820

United Kingdom Atomic Energy Authority

RESEARCH GROUP

Memorandum

A SIMPLE APPARATUS FOR THE GAS CHROMATOGRAPHY OF POLYPHENYLS

R. W. WILKINSON J. A. WINTER

Chemistry Division,

Atomic Energy Research Establishment,

Harwell, Berkshire.

1961

Available from H.M. Stationery Office

PRICE 2s. 6d. NET

U.D.C.
547.621 : 543.544.25
543.544.25 : 547.621

UNCLASSIFIED
(Approved for Sale)

AERE - M.820

A SIMPLE APPARATUS FOR THE GAS CHROMATOGRAPHY OF POLYPHENYLS

by

R. W. Wilkinson and J. A. Winter

ABSTRACT

A simple and cheap gas chromatography apparatus for the analysis of polyphenyls has been developed. It has been designed to deal with both solid and semi-liquid samples. The apparatus makes use of model engine glow plugs for the detectors and a column of alumina with no liquid phase. The normal running temperature is 425°C.

Chemistry Division,
U.K.A.E.A. Research Group,
Atomic Energy Research Establishment,
Harwell.

February, 1961

HL 61/1004 (SC 2)

CONTENTS

		Page No.
1.	Introduction	1
2.	Furnace	1
3.	Detector Unit and Column	1
4.	Detector Circuit	2
5.	Sample Injection	2
6.	Qualitative use	2
7.	Quantitative use	3
8.	Acknowledgements	3
9.	References	3
10.	Results	4
Tables		
I	Analysis of Santowax-R (Batch 1) by Gas Chromatography	4
II	Analysis of various Synthetic Polyphenyl mixtures containing High boiling fractions	5

1. Introduction

A simple laboratory gas chromatography apparatus suitable for routine determinations of polyphenyls, and especially for the analysis of Santowaxes has been developed in the Radiation Chemistry Group. The apparatus is constructed from readily available components, is cheap to assemble, robust, and simple to operate.

The sample injection system has been designed to deal with solid and semi-liquid samples, since these are the two forms in which polyphenyl mixtures are most commonly available. Irradiated samples especially are prone to be semi-liquid.

Basically the apparatus consists of a laboratory furnace on end maintained at about 425°C, a Felton (1) glow-plug detector, and a ¼" stainless steel column packed with ordinary chromatographic alumina using helium as carrier gas.

2. Furnace

The furnace consists of a 3" I.D. stainless steel tube wound with insulated 20 SWG nichrome wire and enclosed in the usual lagged Sindanyo box; steady temperature conditions are obtainable by means of a 2 kw. Variac run directly from the mains. Our apparatus runs at a very steady 425°C at 95 volts, the only adjustment to the Variac being very slight to cope with seasonable variations in the ambient temperature. The temperature variation over the length of the column-detector unit, which occupies 15" of the furnace length, is 10°C, and the temperature quoted is that of the central portion of the column. The helium inlet tube is preheated with a standard heating tape run off D.C. mains voltage.

3. Detector Unit and Column

The detector is basically the same as that described by Felton (1) and employs hot wires in the usual manner, the novelty being the use of model aircraft glow plugs as the hot wires. It is essential to use ceramic insulated plugs (e.g. Champion V.G. -2) and not fibreglass insulated (such as K.L.G. Miniglow) as the insulation burns away in the latter. The layout of the detector block and gas connections is shown in Figs. 1 and 2. The connections to the glow plugs are by end silver soldering 20 S.W.G. silver wires on to the top terminal of the plugs, after which they must be boiled in water for an hour or so to remove all traces of flux. If any flux remains the joint will last only a short time. The plug connections are covered in ceramic beads and are taken out through holes in the top Sindanyo cover plates. They are taken well away from the furnace before good soldered connections to the bridge circuit are made. The entire detector block and gas inlet tubes are packed thickly round with wet asbestos pulp, and the whole top plate on the outside of the furnace is covered with more asbestos pulp which will dry quite hard and strong. It is essential that the top plate should be well insulated thermally, especially where the detector leads are brought out from the furnace. The leads too must be well insulated, since a really good baseline will not be obtainable if these simple precautions are not taken to eliminate variations in the resistance of the leads.

The detector block itself consists of a 2" by 1" by 3" stainless steel block cut from standard 2" by 1" bar and bored to take ¼" O.D. stainless steel stubs, welded in. The glow plugs are screwed ¼" by 32 t.p.i. and are fitted in their holes so as not to project into the gas stream. The most satisfactory ¼" unions are 'Simplifix' stainless steel fittings inside the furnace, and brass 'Simplifix' fittings outside. For the fittings inside the furnace, the use of anti-scuffing compound on the threads will assist dismantling whenever replacement of the column is desired, the fittings inside the furnace being used once only, as leaks occur if fittings are "second-hand". The columns are constructed from standard bending quality ¼" O.D. stainless steel tube, and are packed with B.D.H. Chromatographic alumina, the ends of the column being plugged with tufts of silica wool. The columns are highly retentive, and the retention times are quite sensitive to column length. We have found 22-24" to be a good compromise between satisfactory resolution of the terphenyls and time of analysis. The column is wound with thick asbestos tape from the detector block downwards to assist even temperature distribution.

4. Detector Circuit

The detector circuit is extremely simple (Fig. 3) and consists of a straightforward Wheatstone net fed by 2 volt 150 A-H accumulator, the unbalance voltage being taken to a 5 or 10 mV recorder, the accumulator being trickle charged during use. The Honeywell Brown 2.5 mV recorder fitted with 10, 5 and 2.5 mV ranges has been found to be very satisfactory. The detector is not highly sensitive, as one would expect, the output being of the order of 2.0 mV/mg for biphenyl, and somewhat lower for the higher polyphenyls. However, since a sample of the order of 15-18 mg is required to give peak areas on the linear part of the calibration graph, the sensitivity is quite satisfactory for normal use. Also, with these mixtures, the composition of very small samples might not be accurately representative of the whole mixture.

5. Sample Injection

A sample of about 10 to 15 mg is pushed into the small hole at the base of the sample injector (Fig. 4) which can be weighed before and after; a thread is provided to screw into the silver steel rod. The rod is then pushed through the silicone rubber washer (Fig. 1) and the brass tap turned to the open position. The injector rod can then be inserted to a point directly over the column. The silicone washer ensures a gas tight seal round the silver steel bar. The whole operation should be carried out without unnecessary force as a hard push may dislodge a portion of the sample, thereby giving an incorrect result for quantitative analysis.

6. Qualitative use

A large range of stable hydrocarbons give identifiable peaks; up to para quater-phenyl. Retention time for a given substance is not a constant, but for a given unknown mixture spiking with known substances gives a first indication of the identity of unknown peaks. This method is very simple and with biphenyl and the terphenyls very rapid (see Fig. 5), but the quaterphenyls take some time,

about one hour for p-quaterphenyl. The peaks from the quaterphenyls are much flatter than the corresponding terphenyls, but are easily observed (see Figs. 6 and 7). Some work has been done on mixtures of naphthalene, anthracene and phenanthrene and these were resolved as shown in Fig. 8. Higher polyphenyls such as m-sexiphenyl have not as yet been observed as peaks but a hump in the base line occurs when a sexiphenyl is passed through the column and the base line requires some time to return to normal. The polyphenyl hydrocarbons used have given no evidence of decomposition, such as multiple peaks. The type of chromatogram produced is shown in Fig. 5.

7. Quantitative use

The peak area from a given component depends on the mass present but is also affected by the presence of other components. However, a known weight of a given mixture will always produce the same peak areas under the same conditions and the quantitative use is based on this. The peak areas are measured with an Amsler planimeter. To calibrate the apparatus a polyphenyl wax of known composition was prepared by weighing out accurately various polyphenyls, well mixing and melting very carefully. An excellent wax can be made up from 5% by weight of Biphenyl, 10% of o-Terphenyl, 40% of m-Terphenyl, and 45% of p-Terphenyl. Varying known weights of this wax can be placed in the sample injector and passed through the column. The areas of the peaks produced for each polyphenyl can be plotted against weight in mg. and then used as calibration graphs.

A note of the pressure of the helium flow and the detector volts must be taken to ensure that conditions may be reproduced, also the column temperature must be fixed at 425°C. The helium flow through the column is never turned off but left flowing night and day, and this enables one to use the apparatus without unnecessary delay.

When an analysis has been made on a polyphenyl mixture a check on the accuracy can be made by making up a known mixture with the composition of the polyphenyl mixture upon which the analysis was done. This mixture is then run through the column and the peak areas measured as before. Thus if necessary a correction can be made to the original analysis. It has been observed that with mixtures of higher boilers and biphenyl/terphenyl mixtures the difference between the amount of high boilers present and those indicated increases with increase of high boilers (Fig. 9). By successive approximation it is possible to make a known mixture with same peak areas as the unknown, thus taken to have the same composition. Table I shows a typical analysis on Santo-Wax R polyphenyl wax.

8. Acknowledgements

The authors are grateful to Dr. W. G. Burns for much helpful advice and to Mr. B. Morris for many practical suggestions. Thanks are also due to Dr. J. Cade for the supply of pure quaterphenyls.

9. References

1. Felton H. R. Gas Chromatography. Chapter XV. Academic Press New York. 1958, page 131 - 143.

10. Results

TABLE I

Analysis of Santowax-R (Batch 1) by Gas Chromatography

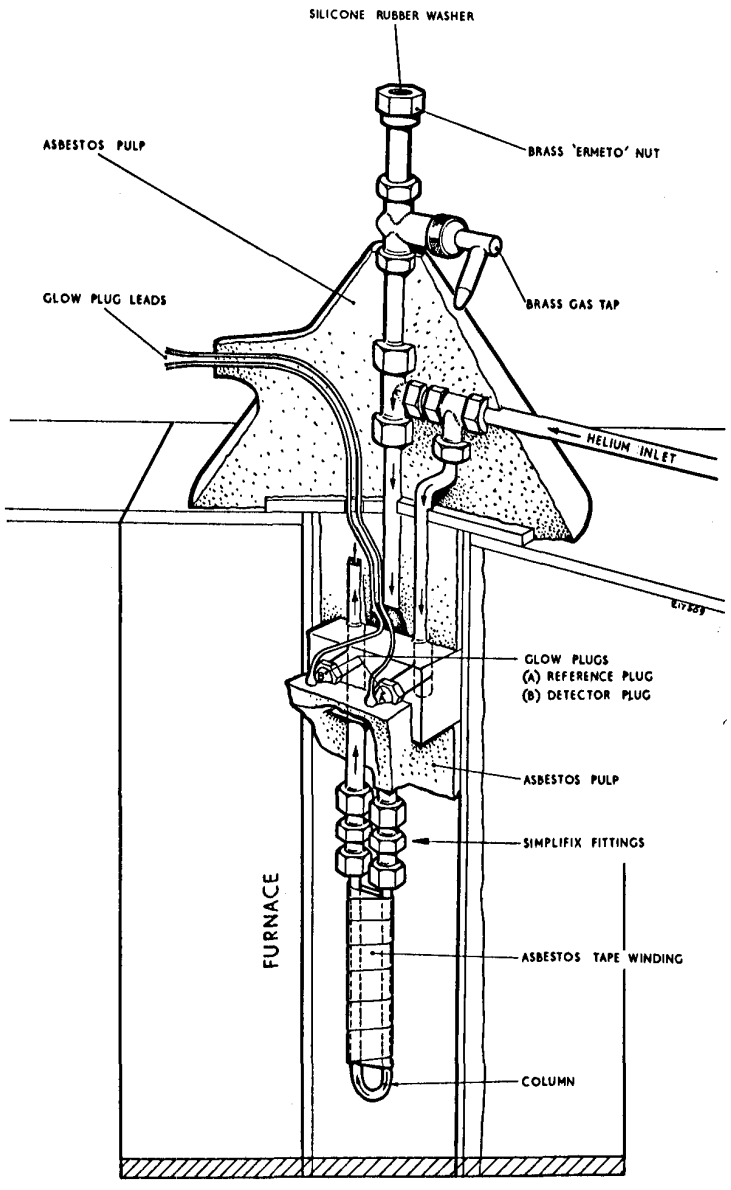
No. of Run	1	2	3	4	5	6	7	8	MEAN	Standard Deviation
Weight of sample mgs	12.6	16.1	14.0	14.0	11.3	15.0	12.0	12.4	-	-
Biphenyl Weight %	1.27	1.18	1.28	1.29	1.15	1.28	1.10	1.21	1.22	0.07
o-Terphenyl Weight %	10.3	9.0	8.6	10.0	9.15	8.6	8.5	9.0	9.14	0.66
m-Terphenyl Weight %	56.4	58.2	56.0	55.0	53.0	53.0	55.0	54.2	55.10	1.76
p-Terphenyl Weight %	23.0	23.0	26.0	24.2	26.5	25.3	22.6	23.8	24.30	1.47
H.B.s. by difference	9.03	8.62	8.12	9.15	9.90	11.82	12.8	11.79	10.24	1.71

TABLE II

Analysis of various Synthetic Polyphenyl mixtures containing High boiling fractions

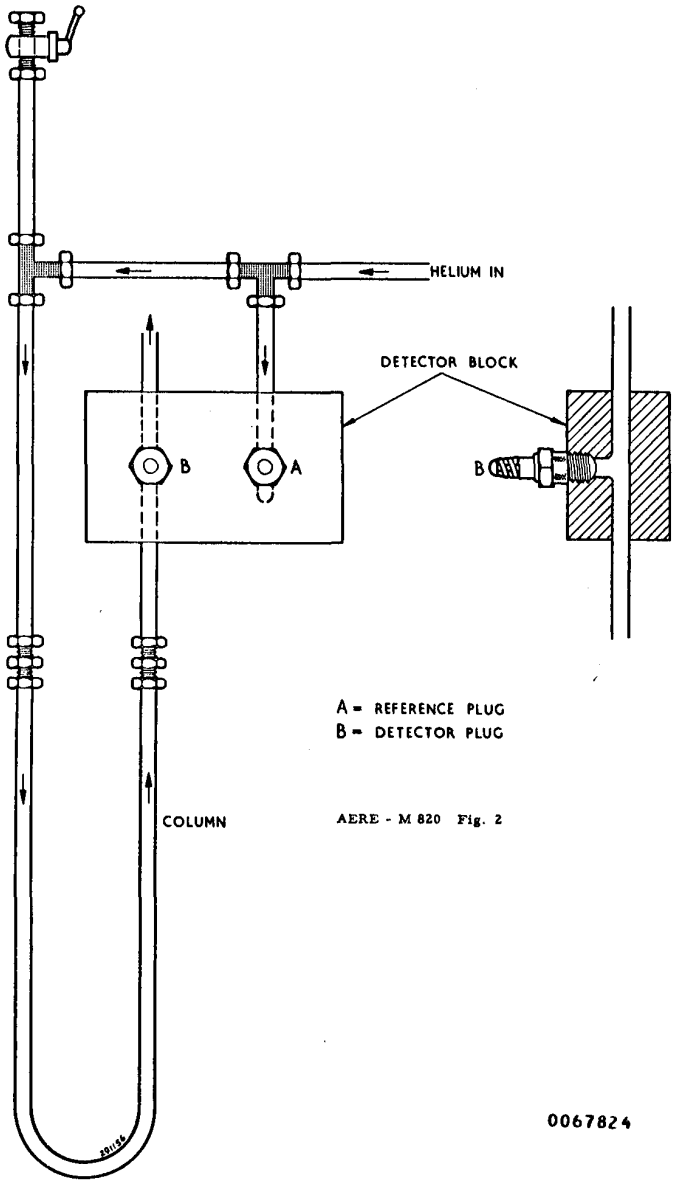
Run No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Weight of sample in mgs	14.5	12.0	12.8	15.3	14.5	14.8	18.4	17.0	19.0	18.2	18.2	20.0	18.2	20.0	19.4
Biphenyl found %	1.4	1.2	1.3	3.2	1.3	1.3	0.95	0.89	1.10	2.70	2.70	2.50	1.3	1.3	1.3
Biphenyl present %	1.22	1.22	1.22	3.9	1.5	1.5	1.0	1.0	1.0	2.97	2.97	2.97	1.5	1.5	1.5
o-Terphenyl found %	9.0	9.0	9.2	7.6	8.0	8.1	6.4	7.05	6.85	5.30	5.80	5.40	5.2	5.4	6.2
o-Terphenyl present %	9.14	9.14	9.14	7.9	8.5	8.5	7.0	7.0	7.0	6.01	6.01	6.01	6.5	6.5	6.5
m-Terphenyl found %	54.4	55.4	54.8	29.0	45.5	45.2	40.5	39.0	40.5	20.50	20.50	20.35	16.7	16.9	18.0
m-Terphenyl present %	55.14	55.14	55.14	31.0	45.0	45.0	42.0	42.0	42.0	23.58	23.58	23.58	22.0	22.0	22.0
p-Terphenyl found %	24.0	23.8	24.0	35.6	21.0	22.4	18.5	18.0	17.55	24.5	24.5	24.65	18.1	18.4	15.5
p-Terphenyl present	24.3	24.3	24.3	35.9	25.0	25.0	20.0	20.0	20.0	27.31	27.31	27.31	20.0	20.0	20.0
High Boilers found % difference	11.2	10.5	10.7	24.6	24.2	23.0	33.65	35.06	34.0	47.0	46.5	47.1	58.7	58.0	59.0
High Boilers present*	10.2	10.2	10.2	21.3	20.0	20.0	30.0	30.0	30.0	40.13	40.13	40.13	50.0	50.0	50.0
Excess Mean % High Boilers found		0.8			3.50			4.25			6.73			8.56	

* High Boiler Content made up with p-quaterphenyl.



0067823

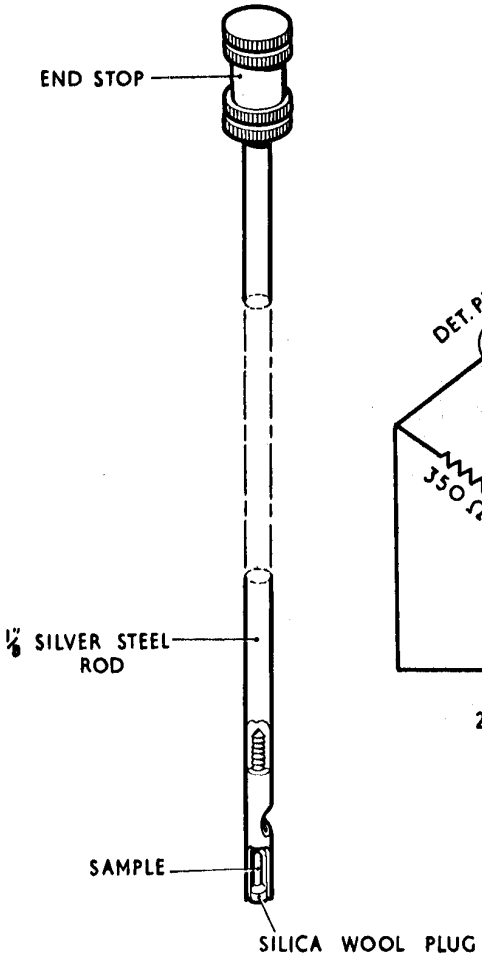
AERE - M 820 Fig. 1



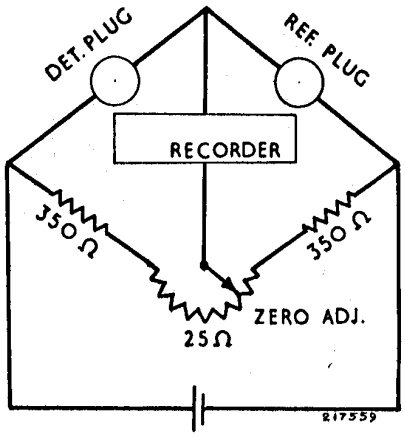
A = REFERENCE PLUG
B = DETECTOR PLUG

AERE - M 820 Fig. 2

0067824



AERE - M 820 Fig. 4 SAMPLE INJECTOR

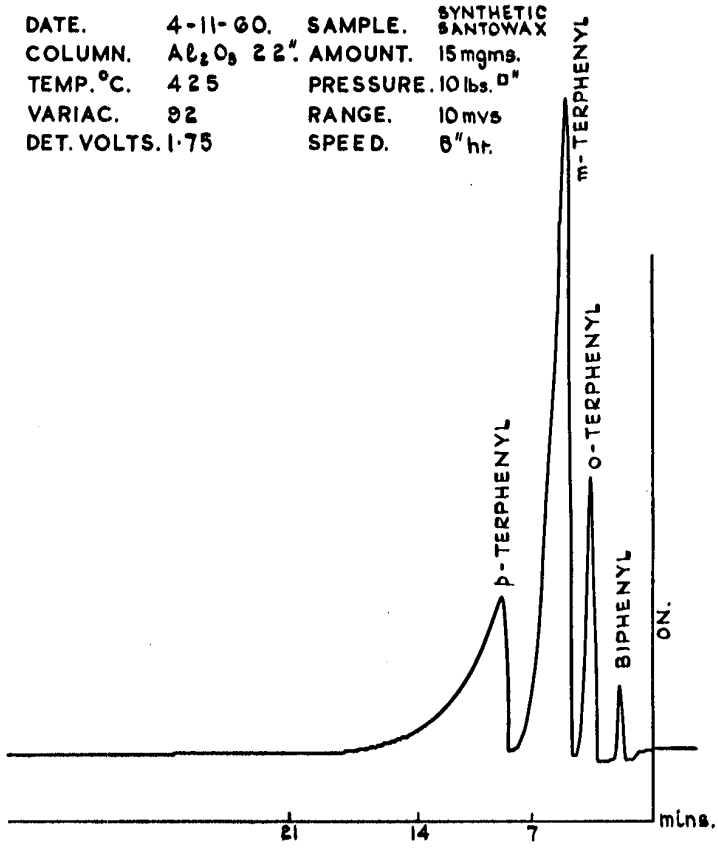


BRIDGE CIRCUIT

AERE - M 820 Fig. 3

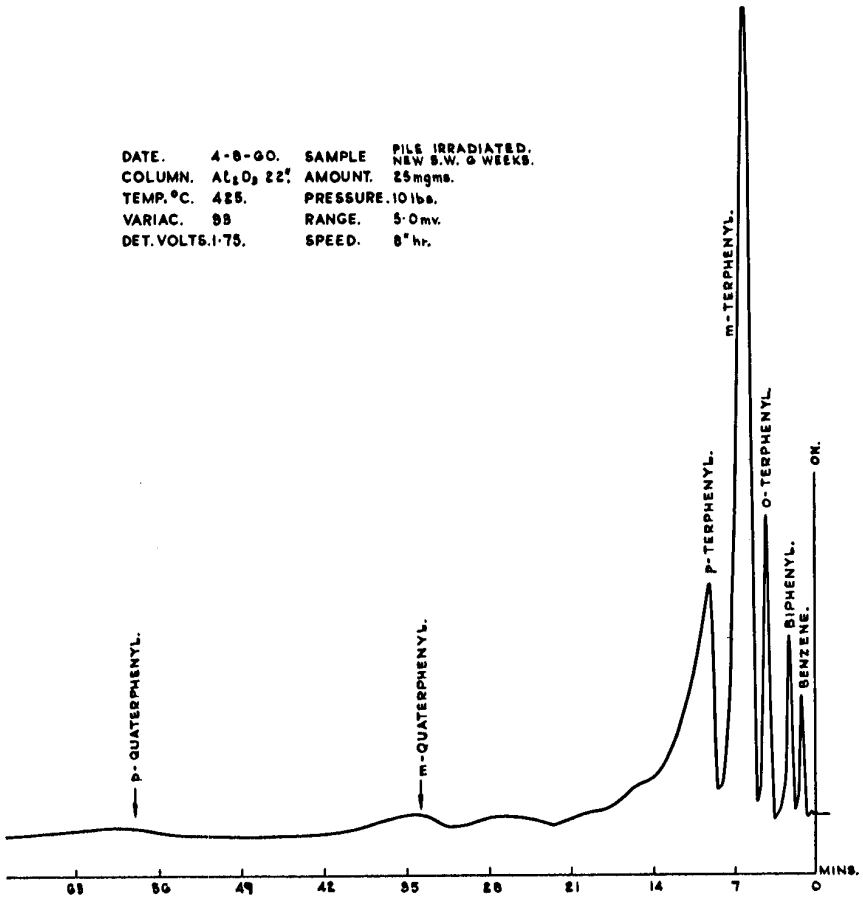
0067825

DATE.	4-11-60.	SAMPLE.	SYNTHETIC SANTOWAX
COLUMN.	Al_2O_3 22".	AMOUNT.	15 mgms.
TEMP. °C.	425	PRESSURE.	10 lbs. 0"
VARIAC.	92	RANGE.	10 mvs
DET. VOLTS.	1·75	SPEED.	6"/hr.



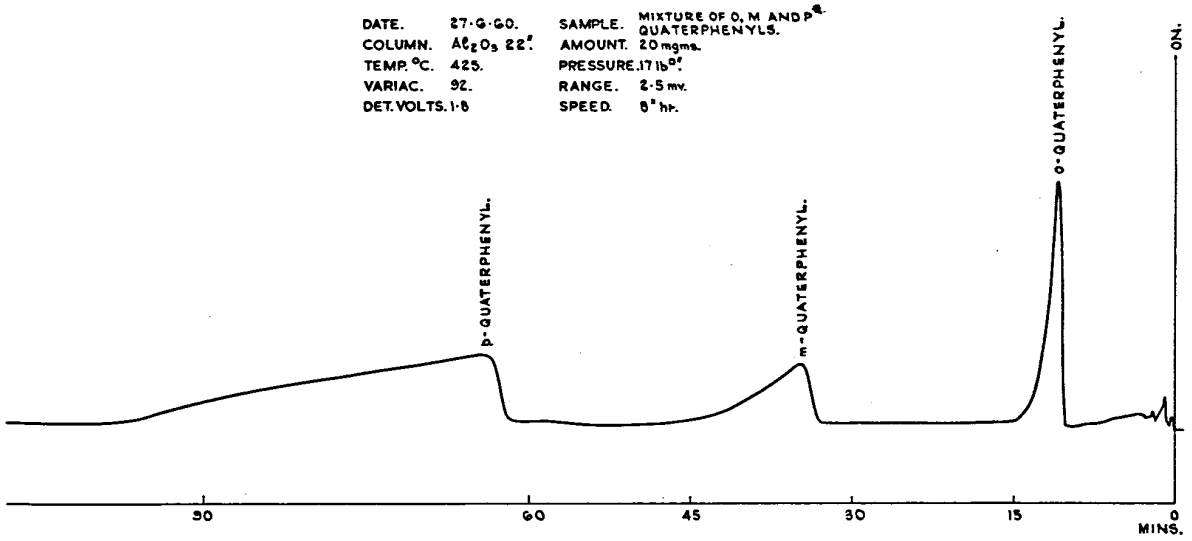
AERE - M 820 Fig. 5

0067826



AERE - M 820 Fig. 6

0067827

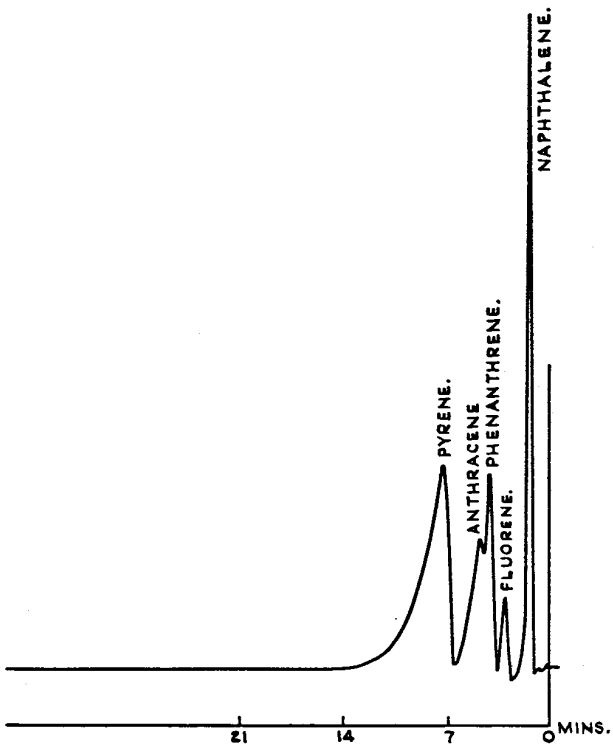


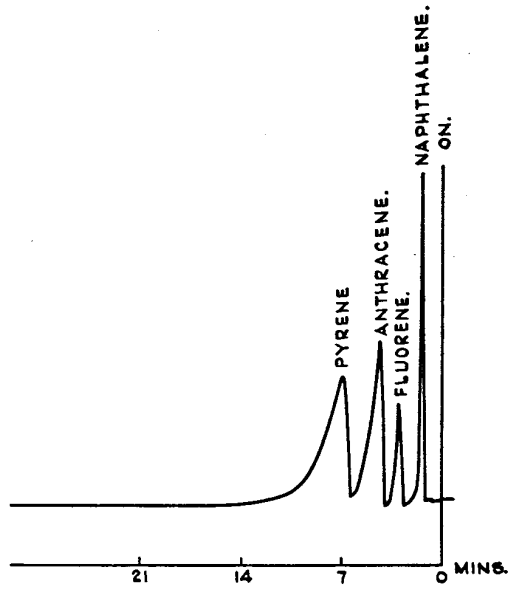
AERE - M 820 Fig. 7

*THE QUATERPHENYLS INJECTED ARE THOSE LINKED IN THE O, M AND P POSITIONS.

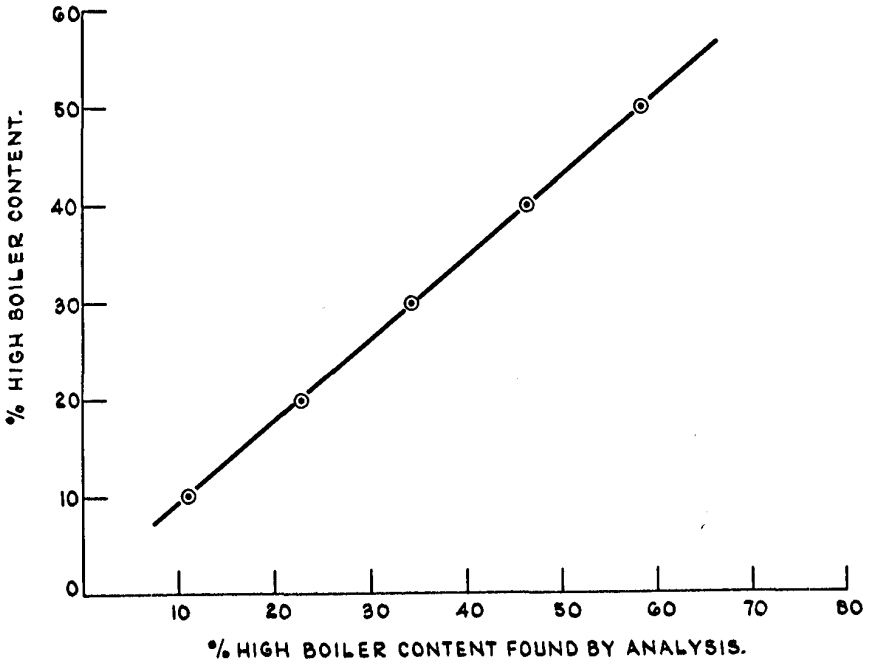
0067829

DATE. 9-12-60. SAMPLE.
COLUMN. Al_2O_3 22". AMOUNT. 10mgms
TEMP. °C. 425. PRESSURE. 10 lbs 0"
VARIAC. 92. RANGE. 5mv.
DET. VOLTS. 1·6. SPEED. 8"/hr.





AERE - M 820 Fig. 8



AERE - M 820 Fig. 9

0067830

Available from
HER MAJESTY'S STATIONERY OFFICE
York House, Kingsway, London W.C. 2
423 Oxford Street, London W. 1
13a Castle Street, Edinburgh 2
109 St. Mary Street, Cardiff
39 King Street, Manchester 2
50 Fairfax Street, Bristol 1
2 Edmund Street, Birmingham 3
80 Chichester Street, Belfast
or through any bookseller.

Printed in England

S. O. Code No. 91 - 3 - 10 - 61