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Environmental Protection Technology Series

SYNTHESIS AND PURIFICATION OF CARCINOGENIC POLYNUCLEAR AROMATIC HYDROCARBON STANDARDS

Office of Research and Development

U.S. Environmental Protection Agency

Washington, DC 20460

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EPA-650/2-74-040

SYNTHESIS AND PURIFICATION OF CARCINOGENIC POLYNUCLEAR AROMATIC HYDROCARBON STANDARDS

by

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Morristown, New Jersey

Contract No. 68-02-0545
Project No 26 AEK, 42
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July 1974

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ABSTRACT

This report details the experimental work performed under Phase I of Contract 68-02-0545 which called for the preparation of samples of the following six condensed polycyclic aromatic hydrocarbon compounds at a purity exceeding 99.9+%:

(1) Benzo(a)pyrene - (20 g.)
(2) Benzo(a)anthracene - (10 g.)
(3) Benzo(e)pyrene - (10 g.)
(4) Chrysene - (10 g.)
(5) Benzo(b)fluoranthene - (10 g.)
(6) Benzo(k)fluoranthene - (10 g.)

Due to termination of the contract before completion, only the chrysene compound was completed to the required purity and quantity. Four of the other compounds were completed only partially through the steps in their syntheses. The efforts of a subcontract on the sixth compound, Benzo(a)-anthracene, were unsuccessful.

Experimental details as well as analytical methods and safety procedures developed during the course of this work are described herein.

1.0 INTRODUCTION

This report details the experimental work performed under Phase I of the contract #68-02-0545, based on Technical Proposal No. DU-72-8312 to the Environmental Protection Agency. Phase I called for the preparation, in purity exceeding 99.9%, of samples of the following six condensed polycyclic aromatic hydrocarbons:

(1) Benzo(a)pyrene - (20 g.)
(2) Benzo(a)anthracene - (10 g.)
(3) Benzo(e)pyrene - (10 g.)
(4) Chrysene - (10 g.)
(5) Benzo(b)fluoranthene - (10 g.)
(6) Benzo(k)fluoranthene - (10 g.)

Due to termination of the contract before completion of Phase I, not all of the above compounds are available for shipment under the terms of the contract. The available compounds and intermediates will be shipped in bulk, according to the latest instructions from the contracting authority.

2.0 SUMMARY

2.1 Benzo(a)pyrene

The second step of the eight step synthetic sequence was completed and pyrene-1-carboxaldehyde is ready for shipment. However, difficulties encountered in step 3 prompted us to propose an alternate approach, discussed in more detail in section 4.0 of this report.

2.2 Benzo(a)anthracene

Initial plans called for the obtainment of commercial material and development of purification and analytical methods. Materials ordered from Princeton Organic and Aldrich Chemical were not delivered at termination of the contract by the E.P.A.

2.3 Benzo(e)pyrene

Four out of five synthetic steps have been completed. Sufficient quantities of the immediate precursor for compound (3) have been prepared and this compound will be shipped.

2.4 Chrysene

Sufficient quantities have been prepared in adequate purity and the compound will be shipped.

2.5 Benzo(b)fluoranthene

Sufficient quantity has been prepared and in a purity which may be sufficient, but has not been clearly demonstrated.

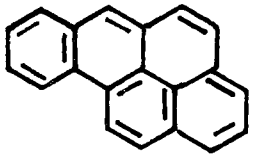
2.6 Benzo(k)fluoranthene

The synthesis of this compound has been completed. Since only one run of the last synthetic step has been completed, the amount of material prepared is only 9 g. However, sufficient synthetic precursor is available to prepare additional amounts of compound 6. Purification procedures have also been developed. The available amount of compound 6 in impure state, plus its immediate precursor, will be shipped.

3.0 PROPOSED SYNTHESES OF COMPOUNDS IN PHASE I (from T.P. No. DU-72-8312)

Phase I will consist of the synthesis of the following compounds:

3.1 Benzo(a)pyrene



Pyrene (I), the starting material, will be of the purest commercial grade (zone refined). Prior to use, the purity of the starting material is checked by a combination of chromatographic and fluorometric techniques (and further purification if necessary). Previously published[1-3] Friedel-Crafts synthesis of benzo(a)pyrene from pyrene will not be used because of the lack of selectivity of these conditions for 1-substitution on pyrene. Instead, the Vilsmeier-Haack synthesis[4,5] of pyrene-1-carboxaldehyde (II) will be effected. The aldehyde (II) is freed from pyrene as much as possible by distillation and

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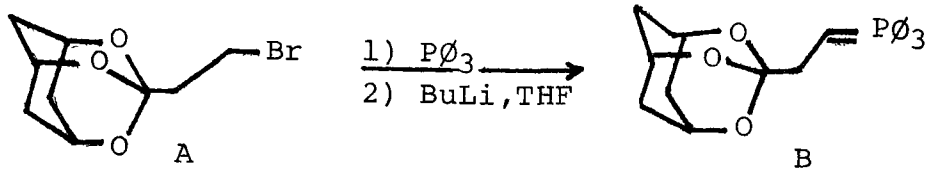
1 J. W. Cook et.al., J. Chem. Soc., 1933, 398.
2 W. Winterstein et.al., Ber., 68, 1082 (1935).
3 H. Vollmann et. al., Ann. 531, 48 (1937).
4 M. deClercq and R. H. Martin, Bull. Soc. Chim. Belges, 64, 367 (1955).
5 N. P. Buu-Hoi et.al., J. Chem. Soc., 1958, 48.

crystallization (Pyrene will be completely removed later before it can be involved in side reactions). If impurities beside traces of pyrene are present, these are removed by chromatographic absorption.

2-(2,4,10-Trioxa-3-adamantyl)-ethyl bromide (A) is prepared by the procedure of Stetter[6,7] from 2-bromopropionitrile and the phosphorane (B), prepared by the reaction of the phosphonium salt from A and triphenylphosphine and n-butyl lithium in tetrohydrofuran, is allowed to react with aldehyde II. The product, 1-(1-pyrenyl)-3-(2,4,10-trioxa-3-adamantyl)-propene-1 (III) is



A B

reduced to 1-(1-pyrenyl)-3-(2,4,10-trioxa-3-adamantyl)-propane (IV) with platinum catalyst in a hydrogen atmosphere (slight hydrogenation of the polycycle at this stage will be inconsequential but will be prevented by careful control of the amount of hydrogen absorbed). The ortho ester IV is hydrolyzed with acid to 4-(1-pyrenyl)-butyric acid (V) which can be freed of any traces of pyrene by continuous extraction of an aqueous solution of the sodium salt. The acid is cyclized to 7,8,9,10-tetrahydrobenzo(a)pyrene (VII) which is carefully dehydrogenated with palladium on alumina (charcoal contains hydrocarbon impurities) in specially purified mesitylene as solvent in a nitrogen atmosphere to give the desired benzo(a)pyrene (VIII). If dehydrogenation is not absolutely complete, the dehydrogenation process is repeated and, if necessary, chromatographic absorption is applied.

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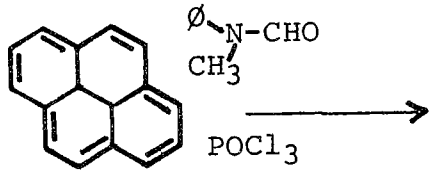
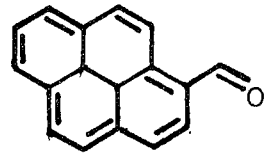
6 H. Stetter and K. H. Steinacker, Ber. 85, 451 (1952).
7 H. Stetter and K. H. Steinacker, Ber. 87, 205 (1954).

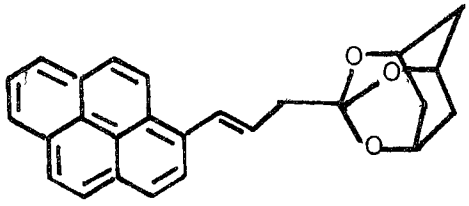


I



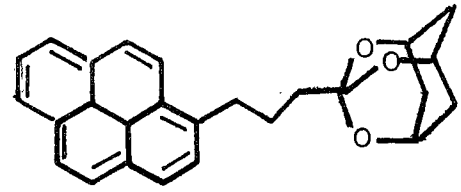
II

B
(page 3)



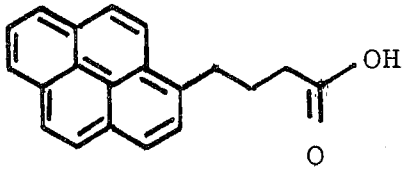
III

H_2
PtO



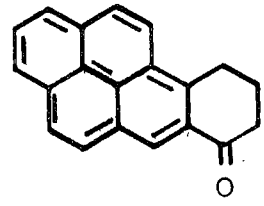
IV

H_3O^+



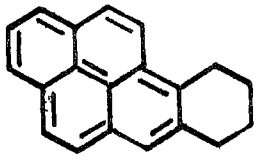
V

HF
press.



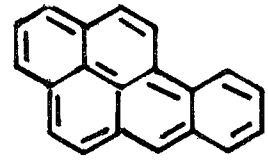
VI

W.K.



VII

Pd, Al_2O_3
mesitylene



VIII

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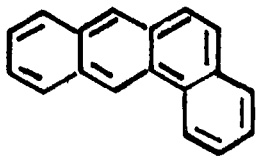
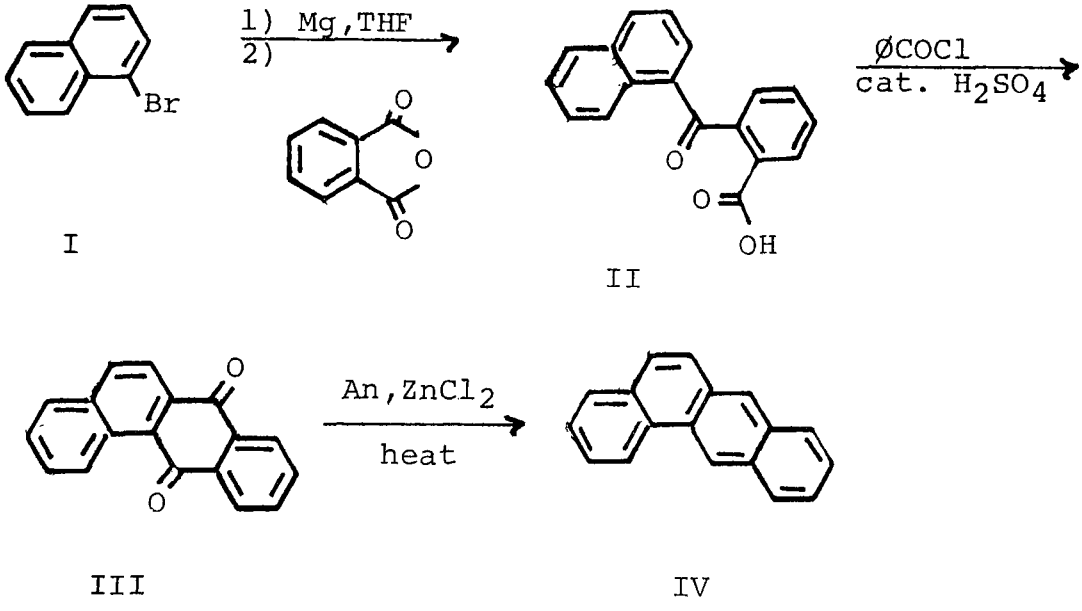
* Wolff-Kishner reduction

3.2 Benz(a)anthracene



The starting material, 1-bromonaphthalene (I), will be of the highest purity available and will be further purified by fractional freezing and low temperature crystallization after a careful distillation. The Grignard reagent from I in tetrahydrofuran is reacted with high purity phthalic anhydride (particularly free of quinones and of benzoic acid) to give the keto acid II which is cyclized with benzoyl chloride containing a trace of sulfuric acid to 7,12-dihydrobenz(a)-anthracene-7,12-dione (III) which is purified by distillation and, if necessary, chromatographically purified to give purest material. The quinone is reduced to the hydrocarbon benz(a)anthracene (IV) by zinc dust melt and subsequently chromatographically purified[1-4].



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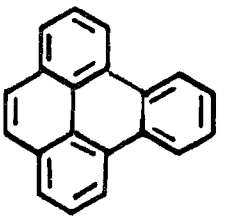
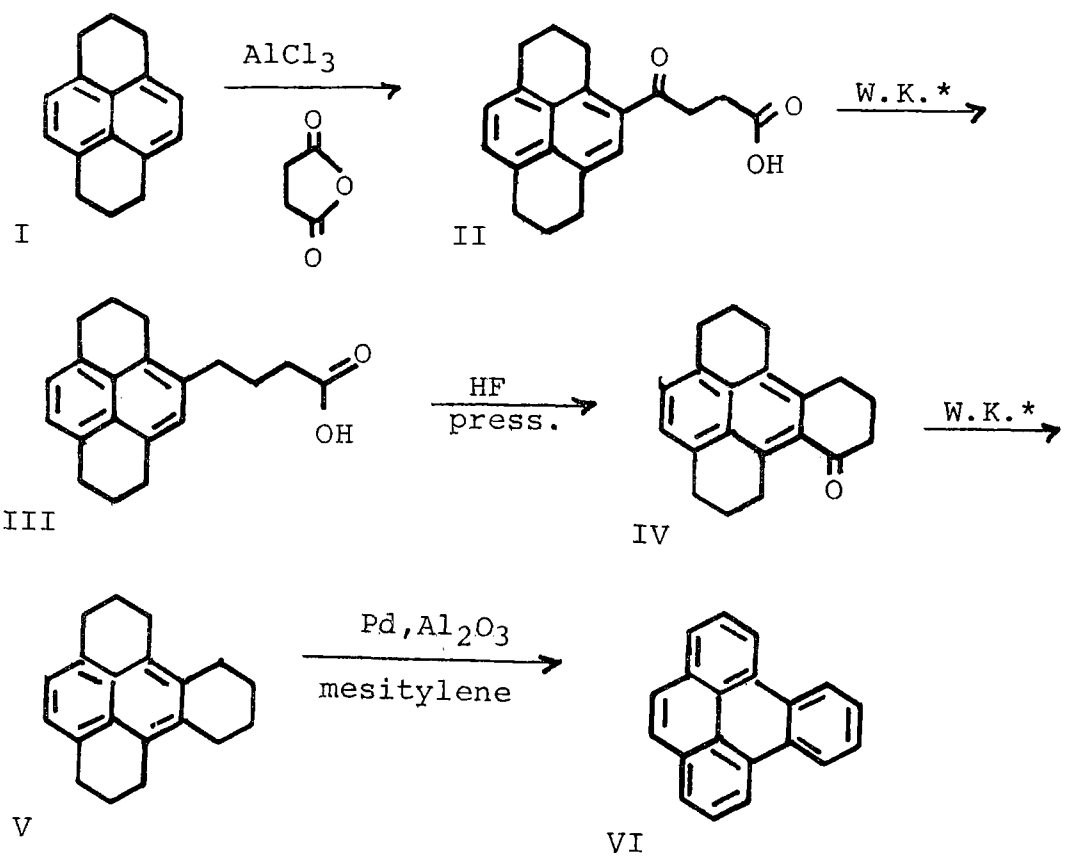
1 K. Elbs, Ber. 19, 2209 (1886).
2 S. Gabriel and J. Coleman, Ber. 33, 446 (1900).
3 G. Heller and K. Schulke, Ber. 41, 3627 (1908).
4 C. Graebe, Ann. 340, 254 (1905).

3.3 Benzo(e)pyrene



Reduction of pyrene[1-3] results in the formation of mostly 1,2,3,6,7,8-hexahydropyrene (I) under controlled conditions. The commercially available material must be freed of other isomers by recrystallization followed by zone refinement and/or chromatography. The synthesis I through VI is then applied during which the ketone IV is chromatographically purified. (Steps III - VI are substantially the same as V - VIII in 3.1.)



* Wolff-Kishner reduction

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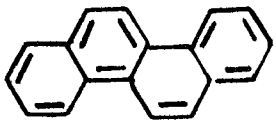
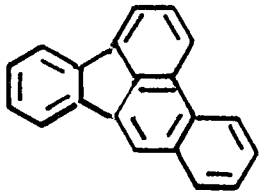
1 J. W. Cook and C. L. Hewett, J. Chem. Soc., 1933, 401.
2 I. Kagehira, Bull. Chem. Soc. Japan, 6, 241 (1931).
3 W. Treibs and G. Meuer, Ber. 91, 1910 (1958).

3.4 Chrysene

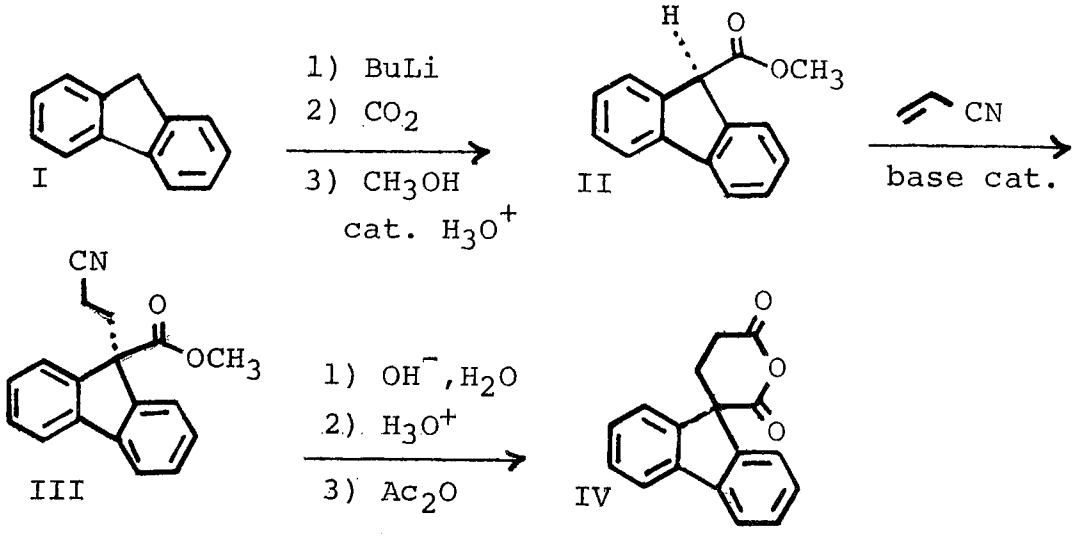


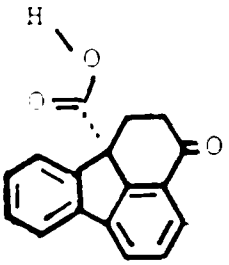
Purest commercial chrysene contains benzo(b)carbazole as the main impurity. This can be removed by KOH fusion, followed by potassium fusion and distillation from potassium (repeated twice). Final purification is done by column chromatography. If anthracene or higher annulated analogues are suspected impurities, they will be removed by maleic anhydride fusion and caustic extraction prior to final purification.

3.5 Benzo(b)fluoranthene

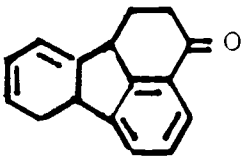


Fluorene (I) (highest commercial purity--e.g., zone-refined) is converted to methyl 9-fluorene carboxylate (II) by literature procedure, then cyanoethylated (III) with acrylonitrile and base catalyst. Compound 3 is saponified and dehydrated to the anhydride (IV) with acetic anhydride. This compound is isomerized to the keytone V by heating with $AlCl_3$ (nitrobenzene) and decarboxylated to VI by heat (Cu catalyst). Synthesis to this stage is analogous to literature procedure. (A. Campbell and S. H. Tucker, J. Chem. Soc. 1949, 2623) The synthesis of the final product VI - X follows the general procedure given in 3.1, Steps II - VIII.



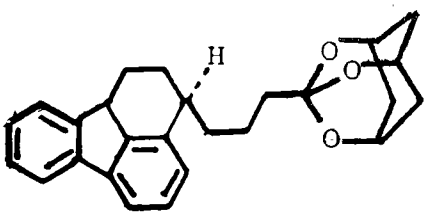


heat
Cu cat.

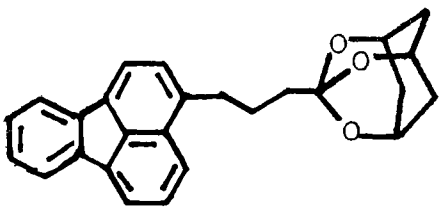


1) B (page
2) H_2PtO

V VI

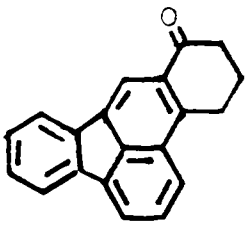


Pd,Al_2O_3
mesitylene

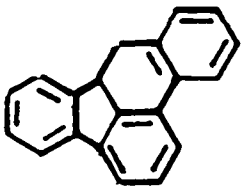


1) H_3O^+
2) HF
press.

VII VIII



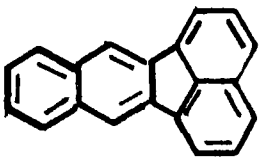
1) W.K.*
2) Pd,Al_3O_3
mesitylene



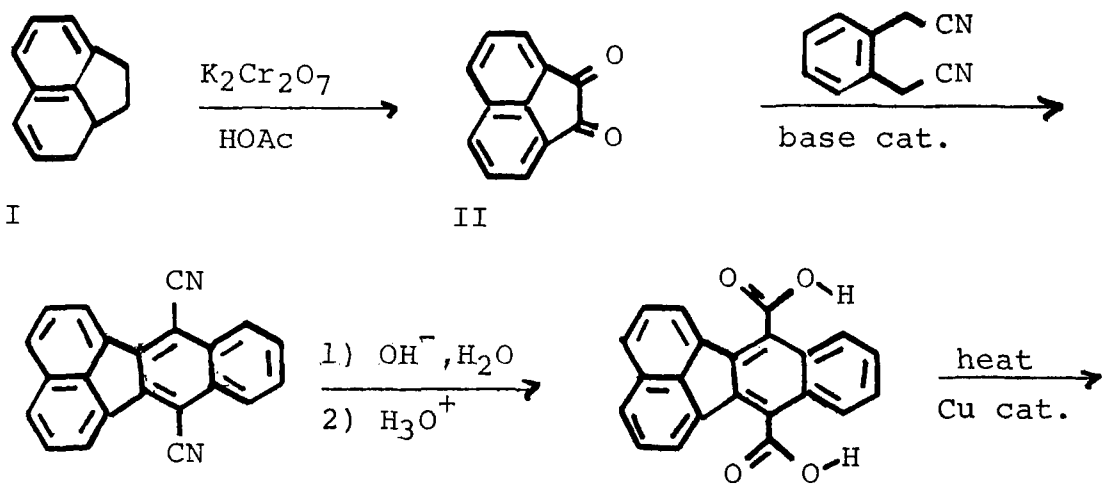
IX X

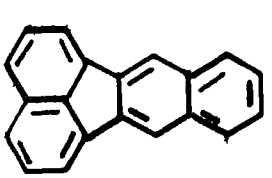
* Wolff-Kishner Reduction

3.6 Benzo(k)fluoranthene



The synthesis of benzo(k)fluoranthene is effected via literature[2] procedures (I - V). The starting material, acenaphthene (I), is highest purity, zone-refined material.





V

Literature references are as follows:

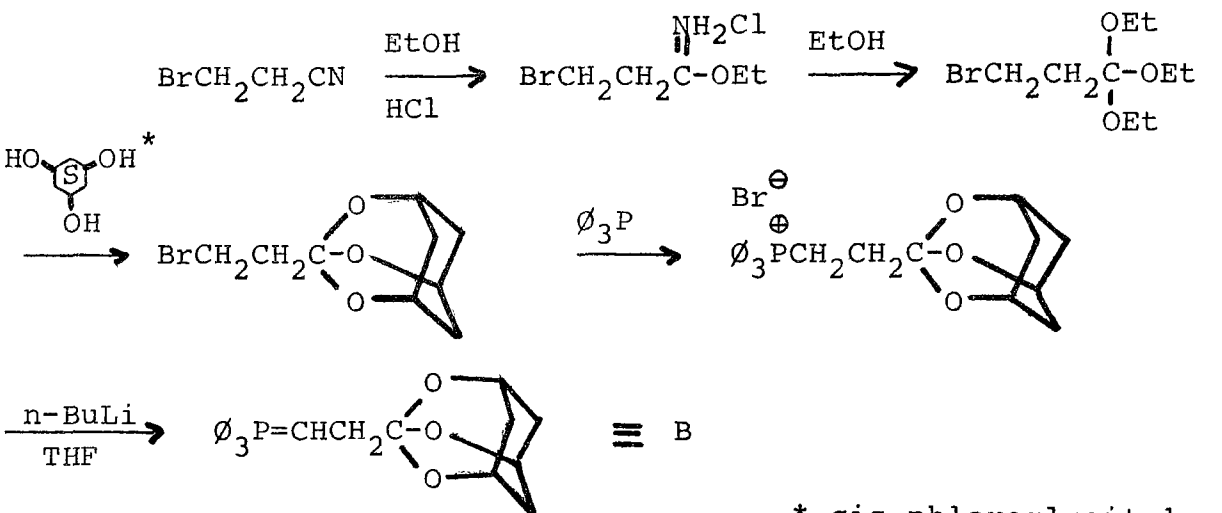
1 Steps I - II, Org. Synth. Coll., Vol. III, p. 1.
2 Steps II - V, H. Maurev et.al., C. R. Acad. Sci. Paris, 223, 951 (1946).

The following sections detail the work performed and final status of each of the six compounds listed above. Experimental details as well as analytical procedures and results are given in Sections 5 and 6 of this Report.

4.0 DISCUSSION OF EXPERIMENTAL RESULTS

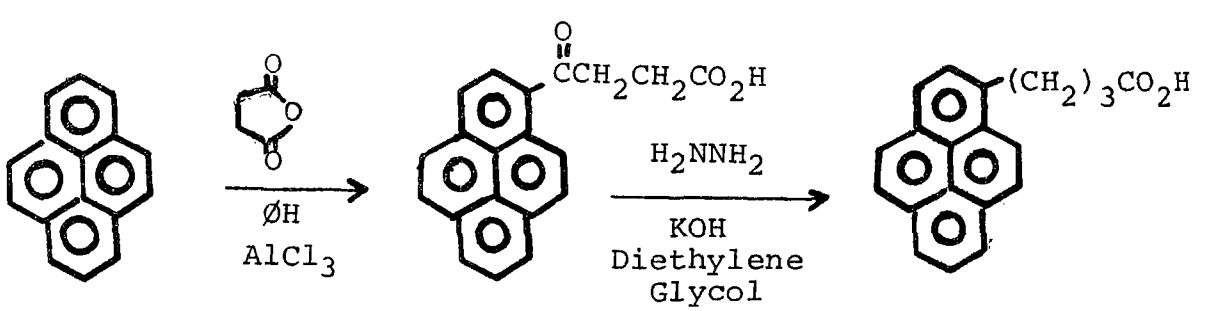
4.1 Benzo(a)pyrene

The synthesis originally proposed by F. Goetz (see below) called for condensation of pyrene-1-carboxaldehyde with a Wittig reagent, (B), prepared by a separate 6-stage synthetic sequence, as follows:



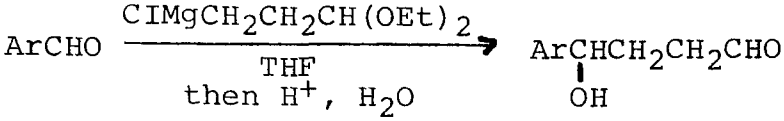
* cis-phloroglucitol from hydrogenation of phloroglucinol

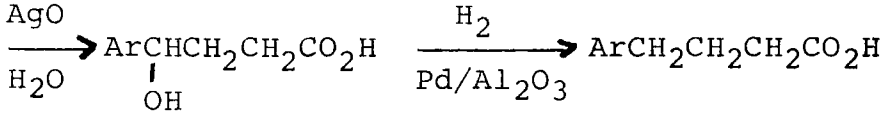
Pyrene was purified and formylated by two different procedures, only one of which, the Villsmayer-Haack synthesis using N-methylformanilide and $POCl_3$, afforded sufficiently pure pyrene-1-carboxaldehyde. The preparation of the previously unreported reagent (B) was found to involve unexpected difficulties, and the synthesis was discontinued. Before termination of the contract, a different approach, based on direct Friedel-Crafts acylation with succinic anhydride under conditions which afford high selectivity toward 1-substitution, was planned as outlined below:



The rest of the synthesis would be as outlined in the original proposal. The commercial availability of compound VI, Aldrich 18,061-0, presents another alternative if it can be adequately purified.

Alternatively, pyrene-1-carboxaldehyde might be utilized to synthesize compound V in the following way:





VI

The pyrene-1-carboxaldehyde was found to contain no impurities detectable by thin layer chromatography and is available for shipment.

4.2 Benzo(a)anthracene

Benzo(a)anthracene, with guaranteed purity of 99.9%, was ordered from Princeton Organics, Inc. Shipment of this material was not made by the time that work on the present contract was terminated, so the order was cancelled. This compound, in 99% purity, was also ordered from Aldrich Chemical Company, but also not received before contract termination.

4.3 Benzo(e)pyrene

1,2,3,6,7,8-Hexahydropyrene was purified by recrystallization from abs. ethanol and the resulting material was found to contain no TLC-detectable impurities. Friedel-Crafts acylation with succinic anhydride and aluminum chloride in purified nitrobenzene by a modified procedure based on the method of Cook and Hewett (J. Chem. Soc. 398(1958)) produced a good yield of 1,2,3,6,7,8-hexahydro-4-pyrenoylpropionic acid which was recrystallized from benzene. Wolff-Kishner reduction (Huang-Minlon modification) gave the corresponding hexahydropyrenylbutyric acid in very good yield. The product was purified via its sodium salt, then by recrystallization (twice) from methanol. Friedel-Crafts cyclization with anhydrous hydrofluoric acid at 25°

gave a very good yield of 1,2,3,6,7,8,9,10,11,12-decahydrobenzo(e)pyrene-9-one which was purified by recrystallization first from ethanol and methanol, then from ethanol alone. Further purification by column chromatography on silica gel (benzene elution) followed by recrystallization from ethanol gave material free of impurities detectable by thin-layer chromatography.

Reduction to the corresponding decahydrobenzo(e)pyrene was accomplished by the Huang-Minlon modification of the Wolff-Kishner reduction, which afforded a very good yield of product purified by recrystallization from benzene. Further purification was necessary to remove a colored impurity, and a satisfactory chromatographic scheme was developed. However, contract termination prevented further work at this point. The impure 1,2,3,6,7,8,9,10,11,12-decahydrobenzo(e)pyrene is available for shipment.

4.4 Chrysene

Chrysene with guaranteed minimum purity of 99.9% was purchased from Princeton Organics, Inc., and analytical methods based on thin-layer, high-pressure liquid, and gas-liquid partition chromatographies were developed for purity determination. Three volatile impurities, totaling 0.2% by peak area on GLPC (flame ionization detection), were observed, and the material was returned to the supplier. A sample of Chrysene obtained from Aldrich Chemical Company and found to be ~ 96% pure by GLPC was sent to Prof. A. R. McGhie at the University of Pennsylvania for zone-purification. The purified material was analyzed by the same methods and found to be of > 99.9% purity. This material is available in sufficient quantity and is ready for shipment.

4.5 Benzo(b)fluoranthene

The synthesis originally outlined in the contract proposal was abandoned when a simpler alternative synthesis was found to be satisfactory. The condensation of fluorene with 2-chlorobenzaldehyde was performed by the Method of Hammer, Stauner and Chardonnens (Helv. 49, 1723 (1966)) in methanolic sodium methoxide. The resulting 9-[2-chlorobenzylidene]-fluorene was obtained in good yield and recrystallized from ethanol. Although the product displayed a lower melting point than the literature value, it was found to afford benzo(b)fluoranthene in a form readily purified to the level required. The dehydrohalogenative ring closure was based on British Patent 459,108 (1/1/37), example 1, and the

method of Badger and Spotswood (J. Chem. Soc. 1959, 1635). Benzo(b)fluoranthene was obtained in high yield and recrystallized from benzene/ethanol. Chromatography on silica gel afforded material free of any TLC-detectable impurities. Further purification by zone-refining (Prof. McGhie) produced material with one TLC-detectable impurity. The determination of the absolute amount of this impurity was not undertaken due to contract termination. This material is available for shipment, as is a large quantity of relatively crude benzo(b)-fluoranthene which was recrystallized from ethanol/benzene, but neither chromatographed nor zone-refined.

4.6 Benzo(k)fluoranthene

This synthesis followed the general outlines of that originally proposed. Acenaphthenene quinone (Aldrich) was purified by recrystallization from glacial acetic acid and condensed with o-phenylenediacetonitrile (Aldrich) in piperidine solution as described by Orchin and Reggel JACS, 73, 436 (1951)). The resulting 7,12-dicyanobenzo(k)fluoranthene was purified by recrystallization from N,N-dimethylacetamide and then hydrolyzed to the corresponding dicarboxamide with potassium hydroxide in 2-ethoxyethanol containing a small amount of water. The benzo(k)fluoranthene-7,12-dicarboxamide was purified by recrystallization from N,N-dimethylformamide. Conversion to benzo(k)fluoranthene by means of heating with 100% phosphoric acid at 200° was complicated by foaming, and a low yield of crude product was obtained. Sufficient precursor dicarboxamide remains to produce enough crude material for final purification to obtain the required amount for the contract by an improved procedure (see experimental). An apparently satisfactory purification procedure has also been developed for the crude benzo(k)-fluoranthene. Contract termination precluded further work in this area.

5.0 EXPERIMENTAL

5.1 Purification of Pyrene

The sample of Aldrich pyrene had a light yellow color and contained a number of components detected by thin layer chromatography (TLC). Analysis by gas chromatograph (GC) indicated 99.0% purity by peak area. A method was developed by column chromatography to purify the pyrene.

A column 4.0 cm x 26.0 cm was packed with basic aluminum oxide, and carbon tetrachloride as a solvent. A concentrated solution of 200 g pyrene in carbon tetrachloride was passed down the column and washed with additional carbon tetrachloride. The flow rate was not controlled as the process was similar to a filtration. The impurities were adsorbed at the top of the column where a dark brown area formed. A brown cast developed over the column as the pyrene moved down, the effluent however was colorless. A greenish-yellow color appeared in the eluent after short exposure to air and light. The solvent was removed by vacuum distillation and the pyrene obtained was white. The recovery was nearly quantitative.

GC analysis indicated 99.9% pyrene and only trace impurities present. TLC analysis showed no impurities present.

This technique was repeated twice using a fresh column each time and over 600 gm of pyrene was purified.

5.2 Pyrene-1-carboxaldehyde

The method of Vollman, Becker, Corell and Streeck (Ann., 531, 107 (1937)) was used. To a solution of 266 g. Eastman N-methylformanilide in 200 ml. dry o-dichlorobenzene kept under dry Nitrogen, was added dropwise, over two hours with stirring and external cooling (to maintain T $\leq$ 25°C), 266 g. of B & A phosphorous oxychloride. To the resulting clear, dark red solution was added 197 g. of purified pyrene (see above) and the mixture was heated and stirred at 90 - 95°C for 2 hours. Upon cooling, a precipitate formed, and it was collected by suction filtration, washed well with benzene and then added to distilled water to afford the crude aldehyde which was collected by filtration and recrystallized from ethanol. A first crop of 101.0 g., M.P. 126.8 - 127.6° (lit. 126°), a second crop of 8.2 g. M.P. 126.5 - 127.0°, and a third crop of 4.3 g., M.P. 123 - 124.5° were obtained. Total yield was 51%. Crops I and II were free of impurities detectable by thin layer chromatography.

5.3 Purification of Hexahydropyrene

The sample of hexahydropyrene from Aldrich Chemical Company was analyzed by thin layer chromatography (TLC) which revealed the presence of two impurities. The product has the largest R_f (Chromatogram XXIV, analytical section). Due to the large quantity of reagent required, a chromatographic purification procedure was not developed.

It was found that the impurities could be removed by a slow recrystallization of the sample from absolute ethanol. A 500 g. sample of hexahydropyrene was dissolved in one liter of absolute ethanol at 70°C. The solution was then allowed to cool slowly over a 12-hour period in an insulated container. TLC analysis of material recrystallized in the above manner indicated that both impurities had been removed.

5.4 3-[1,2,3,6,7,8-Hexahydro-4-pyrenoyl]-propionic acid (HPPA)

The procedure of Cook and Hewett (J. Chem. Soc., 398 (1933)) was employed with a modified work-up as follows: A solution of 43 g. Eastman succinic anhydride in 415 ml. Aldrich nitrobenzene was slowly treated with 120 g. B & A anhydrous aluminum chloride with stirring and cooling. Then 90 g. of purified (see above) S-hexahydropyrene was added gradually with stirring, and the mixture was stirred overnight at room temperature. The mixture was then poured into ice and water and concentrated hydrochloric acid was added to dissolve the aluminum salt precipitates. The mixture was then extracted three times with a total of 2 liters chloroform, and the combined extracts were washed with water and evaporated to leave a thick slurry of the crude product in nitrobenzene. This was thinned with benzene, cooled, suction-filtered and the residue washed well with cold benzene. Recrystallization from benzene afforded, after drying in vacuo, 88.2 g. (66%), M.P. 176.5 - 178°C (lit. 173.5°). Another crop of 12.0 g., M.P. 176.0 - 178°, was obtained (total 75% yield) from the mother liquors. No TLC analysis was deemed feasible at this stage.

5.5 4-[1,2,3,6,7,8-Hexahydropyrenyl]-butyric acid (HPBA)

A mixture of 77 g. (0.25 mole) of HPPA, 33 g. B & A 85% KOH, 16.9 g. Eastman 95% hydrazine and 250 ml. Eastman diethylene glycol was heated gently until the KOH went into solution and then refluxed for 1 hour (T = 155°C). Water was then distilled off until the temperature reached 205°C, and refluxing was maintained for 4.5 hours during which time the temperature was 218 - 224°C. The mixture was cooled, poured into water, acidified to pH2 with HCl, filtered, and the residue washed well with water. After drying in vacuo, 75.2 g. crude material was obtained, wich afforded, after two recrystallizations from methanol, 32.9 g. M.P. 130-133°. The mother liquors yielded 37 g. which was converted to the sodium salt with 5% sodium bicarbonate solution.

The salt was filtered, washed with water, benzene, water again, and then acidified with HCl and extracted into benzene. The benzene solution was extracted twice with water, dried over anhydrous magnesium sulfate, and evaporated to yield 34.8 g. Recrystallization from 200 ml. methanol afforded 27.7 g. M.P. 132 - 134°C. This was combined with the other crop to afford 60.6 g. (82.4%). One more recrystallization from ~500 ml. methanol afforded 58.2 g., M.P. 130 - 133°C. Again, TLC analysis was not deemed feasible and the material was carried through the next step of the synthesis.

5.6 1,2,3,6,7,8,9,10,11,12-decahydrobenzo(e)pyrene-9-one (DBPO)

To 58.0 g. (197 mmol) HPBA in a 1 liter polyethylene bottle, was added 340 g. Matheson anhydrous liquid hydrogen fluoride, and the resulting mixture was stirred magnetically until the starting material was completely dissolved. The purple solution was left standing at room temperature for 70 hours and the HF was then removed by purging with N_2 into a solution of potassium hydroxide in water. The residue was treated with aqueous potassium carbonate and then taken to pH 11 with potassium hydroxide. The resulting mixture was extracted three times with a total of 1500 ml. diethyl ether, and the combined extracts were washed twice with water, dried over $MgSO_4$, and evaporated to leave 50.8 g. (93%) of the crude ketone as a dark orange solid. This was recrystallized from 700 ml. ethanol-methanol (2:1) to afford 44.8 g. dark orange crystals, M.P. 147 - 148.5°C. Another recrystallization as above gave 40.7 g., M.P. 147.5 - 148.5° lighter orange crystals.

Thin layer chromatographic (TLC) results indicated the material contained several components with lower R_f values than the product. Since the sample was very soluable in benzene and had good resolution from the impurities on silica gel, a method of purification was developed by column chromatography.

A column 8 cm x 40 cm was packed with silica gel and benzene. A solution of 39.2 g. sample in 150 ml benzene was placed on the column and washed with additional benzene. The flow rate was maintained at 5 cc per minute. As the sample moved down the column, an orange colored band moved ahead of the main component. This material had not been detected by TLC as its concentration in the sample was very low. (This material was isolated.) The other impurities remained near the top

of the column. Movement of the components on the column was checked periodically by examining the column with long-wave ultraviolet light.

The product was isolated as it eluted from the column and the solvent was removed by vacuum distillation. The recovery was 99%. After recrystallization from absolute ethanol, TLC analysis indicated the absence of any impurities.

5.7 1,2,3,6,7,8,9,10,11,12-decahydrobenzo(e)pyrene

A mixture of 35.4 g. (128 mmoles) purified (DBPO), 27.4 g. B & A 85% potassium hydroxide, 13.5 g. Eastman 95% hydrozine and 200 ml. Eastman diethylene glycol were heated gently to dissolve the KOH, then refluxed for one hour (T = 150°C). Water was distilled off until the temperature reached 210°C, and reflux was maintained for four hours, during which time some condensation of product accumulated on the condenser. The mixture was cooled, poured into water and extracted with benzene. Some solid remained undissolved at this stage. The benzene solution was washed with water, dried over $MgSO_4$, and evaporated to leave 11.9 g. yellow solid. The undissolved solid was rinsed out of the separatory funnel, washed with methanol and dried to afford 22 g. This was combined with the 11.9 g. and recrystallized from benzene to afford 27.1 g. (81%) of large yellow prisms, M.P. 190 - 195° (lit 196 - 197). A second crop of 1.8 g., M.P. 187 - 193° was obtained by recrystallization of 5.1 g. material left upon evaporation of the mother liquors. Sublimation of the second crop was not effective for purification. The 27.1 g. first crop was set aside while a purification scheme was worked out as follows:

Analysis of the material by thin layer chromatography (TLC) revealed the presence of three components. The product was separated from two impurities by large R_f differences in the system used (Chromatogram XXVIII, analysis section).

A method to purify this material was developed by column chromatography. A column 2.0 cm x 20.0 cm was packed using Mallinckrodt CC-7 silica gel in hexane, toluene (1:1). To this column 100 mg of the sample was applied in the above solvent system, and the flow rate set at 0.2 ml per minute. The movement of the bands was monitored by briefly exposing the column to long wave ultraviolet light (360 mμ), the bands appearing as fluorescent areas. The product was eluted from the column and the solvent distilled off under vacuum. The solid obtained was colorless, and TLC analysis revealed no impurities.

Plans were made to purify the entire sample using a 10 cm x 50 cm column, however, the contract was terminated before this could be completed.

5.8 Chrysene

See Section 6.

5.9 9-[2-chlorobenzylidene]-fluorene (CBF)

In two separate preparations a total of 93 g. (0.66 mole) Aldrich 2-chlorobenzaldehyde, 33.2 g. (0.60 mole) fluorene, 250 ml. MC & B 4.35 M (1.11 mol) sodium methoxide in methanol, and 1425 ml. B & A anhydrous methanol were refluxed for eight hours. The yellow oil which precipitated was separated, and the methanol layer was reduced about two-thirds on the rotary evaporator. The newly precipated yellow oil was added to the previous quantity and the total was triturated with dilute aqueous HCl, then with water to afford 155.1 g. (91%) of a clear yellow oil which resisted attempts at crystallization but crystallized spontaneously after standing at -10°C for several days. Several recrystallizations from anhydrous ethanol failed to give material with the reported melting point of 71°C. A main crop of 96.9 g. M.P. 57 - 61°C was obtained along with several smaller crops. A small sample of this material was carried through the next step of the synthesis (see below) and was found to afford benzo(b)fluoranthene in good yield and in a form readily purified by column chromatography, so no further purification or analysis was undertaken on the impure CBF.

5.10 Benzo(b)fluoranthene

A 96.5 g. (0.33 mole) sample of CBF, 400 g. B & A 85% KOH, and 1000 ml. Aldrich quinoline were refluxed (T = 230°C) with good stirring for 3 hours. The mixture was cooled to 130°, poured into a mixture of 1800 ml. conc. HCl and 20 kg. ice in a large glass carboy. The resulting mixture was filtered, and the residue was washed with water, dissolved in ~1300 ml. warm benzene, quickly extracted with water and the benzene solution evaporated. The residue was dried in vacuo overnight, then recrystallized from 2.5 liters benzene-ethanol (1:2) to afford 51.0 g. (61%) of fine, shiny, grey-brown needles, M.P. 167.5 - 168.0°C (lit. 167°, Badger and Spotswood).

Details of final purification will be found in Section 6.

5.11 Purification of Acenaphthenequinone

Thin layer chromatographic analysis of an Aldrich Chemical sample of acenaphthenequinone revealed the presences of several impurities. The material was purified by recrystallization from glacial acetic acid. Long brown needles were obtained, M.P. 260 - 261°C. TLC analysis of this material revealed one black spot on a purple background in the presence of ultraviolet light, 254 mμ (Chromatogram XXIX, analytical section).

5.12 7,12-dicyanobenzo(k)fluoranthene (DCBF) (F. Goetz)

At 10°C, separate solutions of 60 g. (0.33 mole) purified 1,2-acenaphthenequinone in 250 ml. freshly distilled piperidine and of 70 g. (0.45 mole) purified o-phenylenediaectonitrile in 350 ml. of the same solvent were prepared. The acenaphthenequinone solution was added over 20 min. with stirring at 10 - 15°C to the solution of the dinitrile. Then 150 ml. more piperidine was added, and the temperature was allowed to rise to 40°C with stirring. At this point precipitation of the product made stirring difficult, and the mixture was left standing at room temperature for two days. The mixture was then diluted with 1000 ml. "Spectrograde" DMF and filtered. The residue was carefully washed with four 1000 ml. portions of DMF, then with methanol, and finally dried to yield 90.2 g. (89%) of a light yellow solid (see below).

Due to the limited solubility and high melting point of this compound, thin layer and gas chromatographic analysis were not attempted. From the crude material, a 100 g. sample was recrystallized from eight liters of N,N-dimethylacetamide, then washed with N,N-dimethylformanide, methanol, and diethyl ether. 88 g. of small yellow needles were obtained which decomposed at 358 - 360°C.

5.13 7,12-benzo(k)fluoranthenedicarboxamide (BFDC)

An 87 g. sample of DCBF was added to a solution of 1.8 kg B & A 85% KOH in 9 l. Aldrich 2-ethoxyethanol and 720 ml. water at 100°C and the resulting mixture was refluxed with stirring for 48 hours. The mixture was cooled to 100°C diluted with 6 l. water and allowed to cool to 30°C with constant stirring. The off-white product was filtered, washed first with a mixture of 4 l. H_2O and 2 l. 2-ethoxyethanol then with 6 l. methanol, and air dried.

Limited solubility and decomposition at higher temperature hindered the analysis of this intermediate. Purification was accomplished by recrystallization from N,N-dimethylformamide. (Glacial acetic acid was not used due to insufficient solubility.) Three crops of crystals were obtained:

Crop 1, 35.1 g., M.P. 419 - 421°C
Crop 2, 28.1 g., M.P. 418°C
Crop 3, 2.3 g., M.P. 413°C

5.14 Benzo(k)fluoranthene

To 1300 ml. (2.8 kg) 100% H_3PO_4, (prepared from 1190 ml. (2006 g.) 85% H_3PO_4 and 791 g. P_2O_5) in a two liter r.b. flask was added 35.0 g. BFDC (batch 1). The mixture was stirred magnetically and heated. When the temperature reached 160° much foaming occurred. (Suggestion for better results: Add dicarboxamide gradually to well stirred (mech.) H_3PO_4 at ~160° then heat to 200° for 8 hours.) The foam that overflowed was collected, washed well with water, 5% sodium bicarbonate, water again, and dried to leave 7.4 g. solid. The remainder of the main reaction mixture was heated to maintain 220° for 4 hours with frequent swirling (since magnetic stirring was inefficient). The mixture was quenched by pouring onto excess ice and the aqueous suspension extracted with a total of 2.5 l. benzene. The benzene solution was washed with water, 5% $NaHCO_3$, and then dried over $MgSO_4$ and flashed to leave 17.1 g. solid. This was recrystallized from benzene (hot filtration to remove insoluble material) to afford 5.9 g. M.P. 214.5 - 215°C. The 7.4 g. material obtained from overflow above was recrystallized in the same way to afford 1.4 g. M.P. 215.5 - 215.5°C. The benzene mother liquors from both crops were combined and concentrated to afford a third crop of 2.2 g. M.P. 214.5 - 215°C.

See Section 6 for purification scheme.

6.0 ANALYSIS AND PURIFICATION OF FINAL PRODUCTS

6.1 Introduction

Analysis of the aromatic hydrocarbons and their intermediates listed in this report was accomplished by three techniques, liquid (L.C.), gas (G.C.) and thin layer chromatography (T.L.C.). T.L.C. was used as the main screening technique in detecting impurities. When a final product or intermediate was found to contain an impurity, methods of purification were developed by recrystallization, column chromatography or zone refining.

The purified final products in each synthesis were analyzed by all the T.L.C. systems listed in Table I and by the liquid and gas chromatographic techniques developed to analyze the crude materials. The application of these techniques insures that all the detected impurities have been removed by the purification procedure and the material has a minimum purity of 99.9%.

Table I lists the adsorbents and solvent systems used in the screening program. All of the chromatographic adsorbents with the exception of magnesium hydroxide[1] and Porapak[2] T were obtained from Brinkmann Instruments, Inc.[3]. Eastman[4] chromagram silica gel sheets were also used.

Layers of magnesium hydroxide, Porapak T, acetylated cellulose and acetylated polyamide were prepared in the laboratory using Chromaflex T.L.C. plates[5]. This technique gave the best and most reproducible layers in the shortest period of time. The other adsorbents used were obtained in a prepared state from the suppliers.

The charge transfer systems were prepared by soaking the plate for three minutes in an acetone solution of the complexing agent; the plate was then air dried for 12 hours and kept in a dark area. It was found that prolonged exposure to light, and possibly air, cause the layer to darken, decreasing the sensitivity of the analysis.

All T.L.C. plates were developed in Chromaflex developing tanks[5], then air dried until no odor of solvent could be detected. The plates were then analyzed in the presence of long and short wave ultraviolet light (360, 254 mμ) and with an iodine vapor chamber. A small

walk-in dark room was constructed on the lab bench, and long and short wave ultraviolet lamps were mounted 45° to the bench surface. A black cloak of polyethylene was worn to prevent the reflection of fluorescent light onto the plate. This light is created by the interaction of the ultraviolet light and the normal laboratory clothing; its presence hinders the analysis.

Liquid chromatographic analysis was carried out using an 830 DuPont liquid chromatograph[7] equipped with an ultraviolet detector (254 mμ). Many problems were noted with this equipment, and excessively long equilibration times were required before reproducible data could be obtained.

Gas chromatographic analysis was done on a Packard 7400 gas chromatograph[8] equipped with glass columns, on-column injection, and a flame ionization detector.

All zone refining of the crude final products were done by Professor Andrew McGhie at the University of Pennsylvania.

Table IV lists the order in which copies of the chromatograms appear.

TABLE I

T.L.C. Screening Systems

Adsorbents:	Solvent Systems:
Alumina	Carbon Tetrachloride Benzene, Heptane, Chloroform (1:1:1)
Silica Gel.	Benzene Methylene Chloride, Benzene (1:1) Toluene
Magnesium Hydroxide	Toluene Methylene Chloride Tetrahydrofuran Methyl Ethyl Ketone
Microcrystalline Cellulose	Dimethylformamide, Water (1:1)
Porapak T	Methanol Acetone
Cellulose 10%, 20%, 50%, 40% Acetylated	Ether, Methanol, Water (4:4:1) Toluene, Ethanol, Water (4:17:4) Tetrahydrofuran, Dimethylformamide, Water (1:1:1)
Polyamide 11, 6, 6.6	Tetrahydrofuran, Diethyl ether, Hexane (2:7:4) (1:2:2)
Polyamide 11, 6, 6.6 Acetylated	Toluene, Ethanol, Water (4:17:4)

Charge Transfer System

Silica Gel 0.2% Caffeine 0.3% 2,4,7,-Trinitro-9-fluorenone 0.3% 1,3,5-Trinitrobenzene	Benzene, Heptane (1:1)

TABLE II

Suppliers of Equipment and Chromatographic Materials

1 Fisher Scientific Co.
52 Tadem Road
Springfield, New Jersey 07801

2 Waters Associates, Inc.
61 Fountain Street
Framingham, Massachusetts 01701

3 Brinkmann Instruments, Inc.
Canteague Road
Westbury, New York 11590

4 Eastman Kodak Company
Rochester, New York 14650

5 Kontes
Vineland, New Jersey 08360

6 Ultra-Violet Products, Inc.
San Gabriel, California

7 E. I. DuPont Company, Inc.
Wilmington, Delaware 19898

8 Packard Instruments Company, Inc.
2200 Warrenville Road
Downers Grove, Illinois 60515

TABLE III

Conditions for Liquid and Gas Chromatographic Analysis

of

Aromatic Hydrocarbons

Liquid Chromatography:

830 DuPont Liquid Chromatograph

Column - One Meter ODS

Solvent System - Methanol, Water (6:4)

Flow Rate - One milliliter per minute

Pressure - 1000 P.S.I.

Temperature - 50°C

Detector - Ultraviolet 254 mμ

Attenuator - 4x, 0.04 OD full scale

Chart Speed - 0.2 inch per minute

Gas Chromatography:

Packard 7400 Gas Chromatograph F.I.D.

Column - 6 ft. Chromasorb G Coated with 1.0% OV-17

Carrier Gas - Helium 60 cc per minute

Detector Temperature - 210°C

Injector Port. Temperature - 210°C

Chromatogram IV - Isothermal 235°C, Chart Speed 0.5 inch per minute

Chromatogram V - Program 10 minutes at 205°C then 2° per minute to 235°C then held 10 minutes

6.2 Purification and Analysis of Chrysene

Two samples of commercial grade chrysene from Aldrich Chemical Company and Eastman Organic Chemicals were obtained and analyzed by T.L.C., L.C., and G.C. A specially purified sample from Princeton Organics was also included in the analysis. The chromatograms of these analyses are presented in Chromatograms I thru V. The results of this analysis show the Eastman sample to be the poorest of the group, containing two impurities. The Aldrich sample contains the same two impurities, but one is present in only trace amounts. The Princeton sample was by far the cleanest. However, it did not meet the purity specifications stated in its purchase contract, and the sample was returned.

Attempts to effect a preliminary purification by column chromatography on Mallinkrodt CC-7 silica gel with toluene as a solvent showed only a minor improvement (see Chromatogram VI for T.L.C. analysis of the three fractions collected). The only impurity that was removed from the bulk of the sample was the one producing the white colored spot with the lowest R_f.

A fresh sample of Aldrich Chemical Company chrysene was submitted to Professor Andrew McGhie for zone refining. The sample was successfully purified by the following procedure:

(1) Approximately 50 gms of the chrysene supplied (Aldrich Chemical Co.) was sublimed and charged into a 15 mm O.D. zone melting tube. The sample was then given 25 zone passes on a Sloan-McGowan zone melter. After zoning, the tube was cut up and seven samples taken for L.C. and G.C. analyses. A green band was observed at the top of the Z.R. tube and a red band at the bottom, indicating impurities with $K<1$ and $K>1$.

(2) A center section of this zone melting tube was recast and rezone melted in a 12 mm O.D. tube for 70 zone passes. This tube was sectioned and analyzed by L.C. A persistent impurity was observed throughout the tube which was removed only slowly by zone melting.

(3) Approximately 16.5 gms of the purest material from this tube was then continuously chromatographed under Argon through a 50 mm O.D. tube of Woelm neutral alumina using benzene (A.C.S. certified, Fisher) as eluant.

After 21 hours, the chrysene had been eluted completely leaving a 4 cm band of blue violet fluorescent impurity at the top of a 50 cm Column. Chromatography was carried out in the dark, using DuPont Kapton sheet as light shield. The apparatus used was a modified Sangster and Irvine unit. After this treatment, the chrysene was recrystallized from the benzene eluant.

The purified sample received from Professor McGhie was analyzed by all the T.L.C. systems listed in Table I and the L.C. and G.C. procedures listed in Table III. No impurities have been detected by these techniques, and, thus, all of the detectable impurities in the crude material have been removed. These analytical results indicate this material to have purity of 99.9%. (Refer to Chromatograms VII thru XVI).

6.3 Analysis and Purification of Benzo(b)fluoranthene

The synthesized sample of benzo(b)fluoranthene was analyzed by a number of T.L.C. systems. The most effective systems appear in Chromatogram XVII. This chromatogram reveals the presence of at least three impurities in the crude material.

A purification method based on the best T.L.C. system was developed for column chromatography. A column 4.0 cm x 25.0 cm was packed with Brinkmann[3] neutral silica gel and toluene. The solvent was purified by passing it through a precolumn of neutral alumina. A 1.0 g. sample of crude benzo(b)fluoranthene was applied to the column as a solution in toluene. It was then eluted with toluene and the movement of the bands was monitored by exposing the column to long-wave ultraviolet light. The exposure time was kept to a minimum to prevent photochemical reactions from taking place. After the product was eluted from the column, the solvent was distilled off under vacuum and the material analyzed by T.L.C., L.C. and G.C. techniques. T.L.C. analysis (Chromatogram XVIII) revealed the presence of one spot for the product; no impurity spots were detected. The L.C. and G. C. techniques developed were not capable of resolving the impurities in the crude material and were not thought to be of value here. This purification was then scaled-up as described below.

A column 7.5 cm x 33.0 cm was packed in the same manner as above; 25.9 g. of benzo(b)fluoranthene was dissolved in 750 cc of toluene and applied to the

column. The toluene had been purified by passing it through a precolumn of neutral alumina. A total of 25.2 g. of the applied sample was collected over five fractions, a 97.3% recovery. The solvent was distilled off under vacuum and the fractions analyzed by T.L.C.

T.L.C. analysis (Chromatograms XIX, XX) showed fractions one and two to contain one spot for the product. The combined weight for these fractions is 5.8 g. The chromatograms of fractions three and four show that they might contain a trace impurity with a lower R_f than the product. It was difficult to determine if any impurity was present in this area due to the tailing of the product. For this reason the fractions were combined (18.9 g.) and submitted to Professor McGhie for zone refining. The chromatogram of fraction five showed that it contained the impurities of the crude material (0.5 g.). This was expected as all the impurities in the crude material have lower R_f's than the product in this system. (Fractions 3 and 4)

The column purified benzo(b)fluoranthene was zone refined in the following manner:

> Approximately 20 g. of benzo(b)fluoranthene was pumped extensively for 2 days on a high vacuum line to remove the occluded chromatographic solvent (alcohol). The sample was then melted under 0.5 atmos. Argon into a 10 mm O.D. Pyrex zone melting tube to give an ingot ~ 35 cm long. The tube was sealed under ~ 0.75 atmos. Argon and given 60 zone passes on a Sloan-McGowan zone melter (zoning speed 1"/hr., ℓ/L = 1:20). The upper two-thirds of the ingot was taken as pure product.

Analysis of the zone refined benzo(b)fluoranthene by T.L.C. (Chromatograms XXI, XXII) revealed the presence of an impurity spot just under the product spot. Zone refining of the sample did not improve its purity. The nature and concentration of this impurity have not been determined as no quantitative techniques have been developed that are capable of sufficiently resolving the impurity. Further work on the analysis and possible purification of this material was stopped due to the termination of the contract.

6.4 Analysis and Purification of Benzo(k)fluoranthene

(see Section 5.14)

Three recrystallization fractions of benzo(k)fluoranthene were submitted for analysis and purification. The fractions were analyzed by T.L.C. (Chromatogram XXIII) and found to contain several components. A method of purification based on the T.L.C. separation was developed for column chromatography:

A column 7.5 cm x 33.0 cm was packed with Mallinckrodt CC-7 silica gel and hexane-toluene (3:1). All solvents were distilled before use. The three fractions were to be combined totaling 11.5 g., dissolved in the solvent system and applied to the column. The product would have been eluted from the column and the solvent distilled off under vacuum.

The above purification method was not applied to the sample due to the termination of the contract.

TABLE IV

List of Chromatograms of Analysis Section

Chromatogram	Title
I thru V	Crude Chrysene
VI	Column Purified Chrysene
VII thru XVI	Pure Chrysene
XVII	Crude Benzo(b)fluoranthene
XVIII thru XX	Column Purified Benzo(b)fluoranthene
XXI and XXII	Zone Refined Benzo(b)fluoranthene
XXIII	Crude Benzo(k)fluoranthene
XXIV	Pyrene
XXV	Pyrene-1-Carboxyaldehyde
XXVI	Hexahydropyrene
XXVII	Decahydrobenzo(e)pyrenone
XXVIII	Decahydrobenzo(e)pyrene
XXIX	Acenaphthenequinone

Chromatogram I

Crude Chrysene

Solvent front

Solvent System:

X
Toluene

Y
Pentane
Diethyl Ether
(19:1)

Adsorbent:

Silica Gel
Eastman

Detection:

U.V. 254 mμ
Iodine Vapor

Quantity:

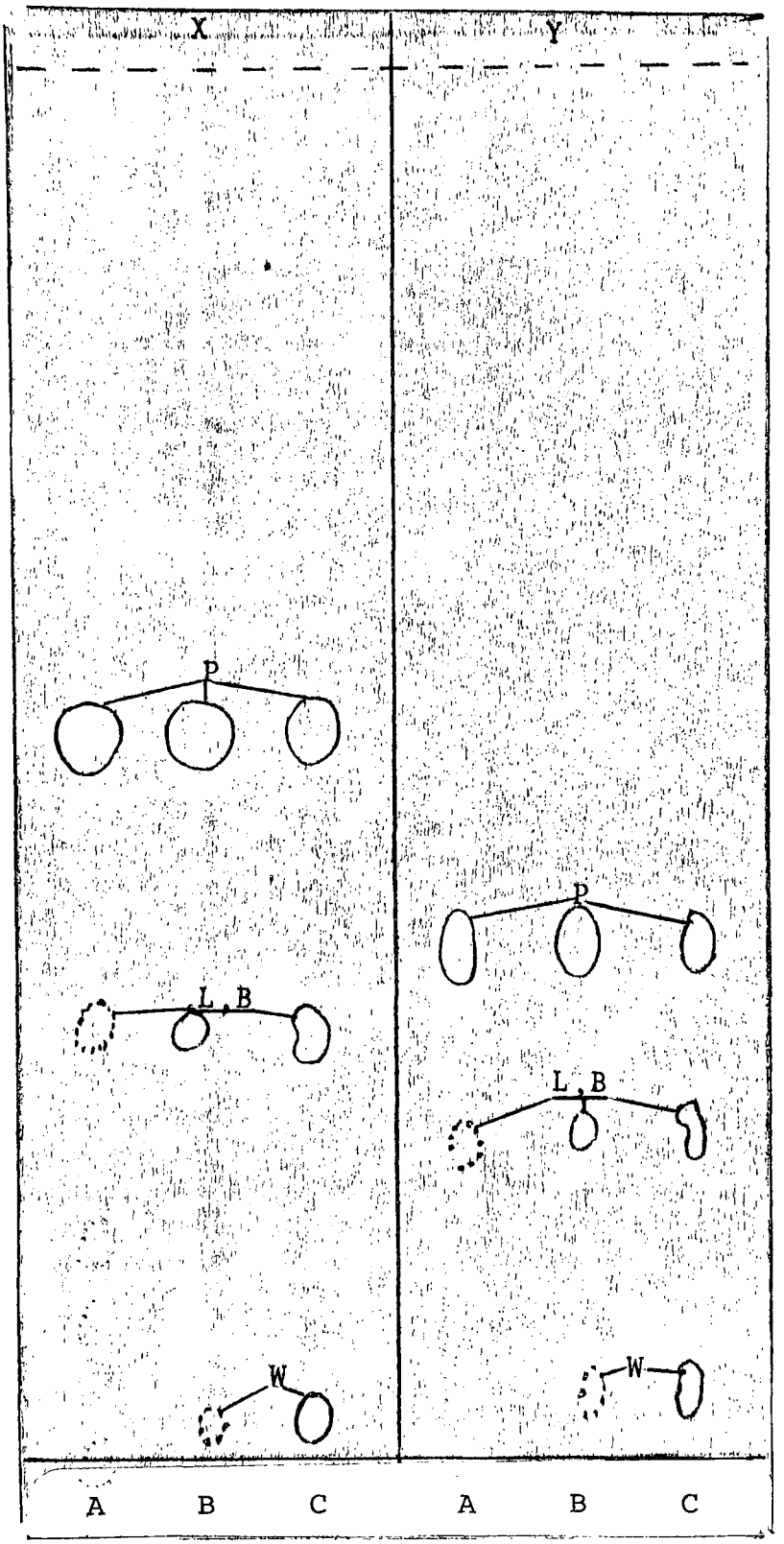
4γ as 0.4% solution
Methylene Chloride

Code:

A - Princeton Organic
B - Aldrich Chemical
C - Eastman Organic

P - Purple
L,B - Light Blue
W - White

Dotted line indicates
trace amounts

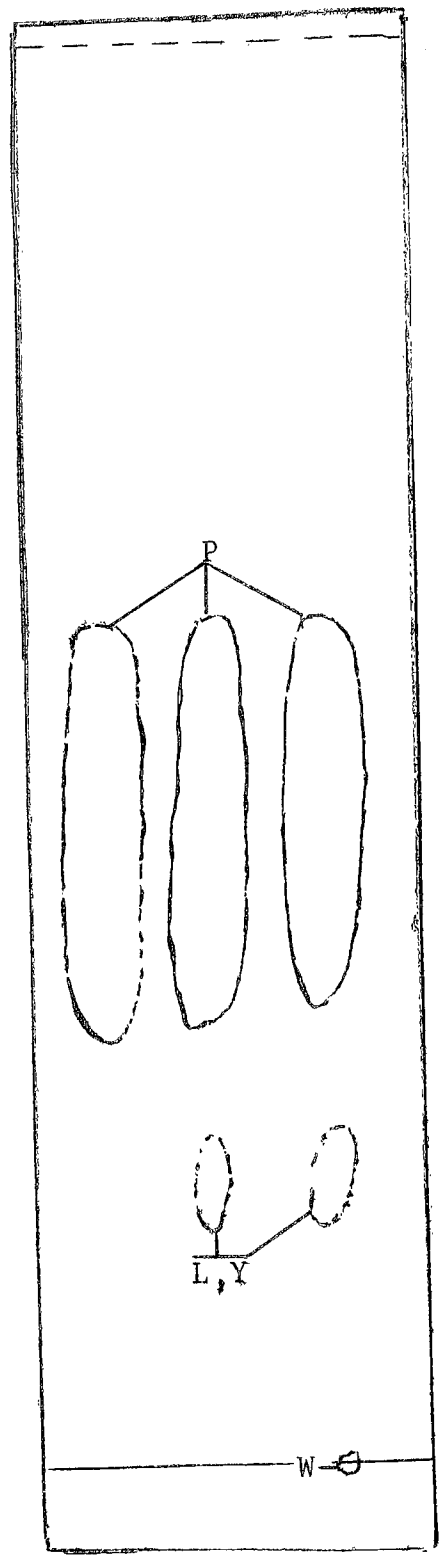


Starting Spots

Chromatogram II

Crude Chrysene

Solvent Front



Starting Spots

Solvent System:

Tetrahydrofuran
Diethyl Ether
Hexane (1:1:1)

Adsorbent:

Polyamide 11
Brinkmann

Detection:

U.V. 254 mμ

Quantity:

8γ as 0.4% Solution
Methylene Chloride

Code:

A - Princeton Organic

B - Aldrich Chemical

C - Eastman Organic

P - Purple
L,Y - Light Yellow
W - White

Chromatogram III

Crude Chrysene

Solvent Front

Solvent System:

Toluene
Ethanol
Water (4:17:4)

Adsorbent:

Cellulose 40%
Acetylated
Brinkmann

Detection:

U.V. (360,254 mμ)

Quantity:

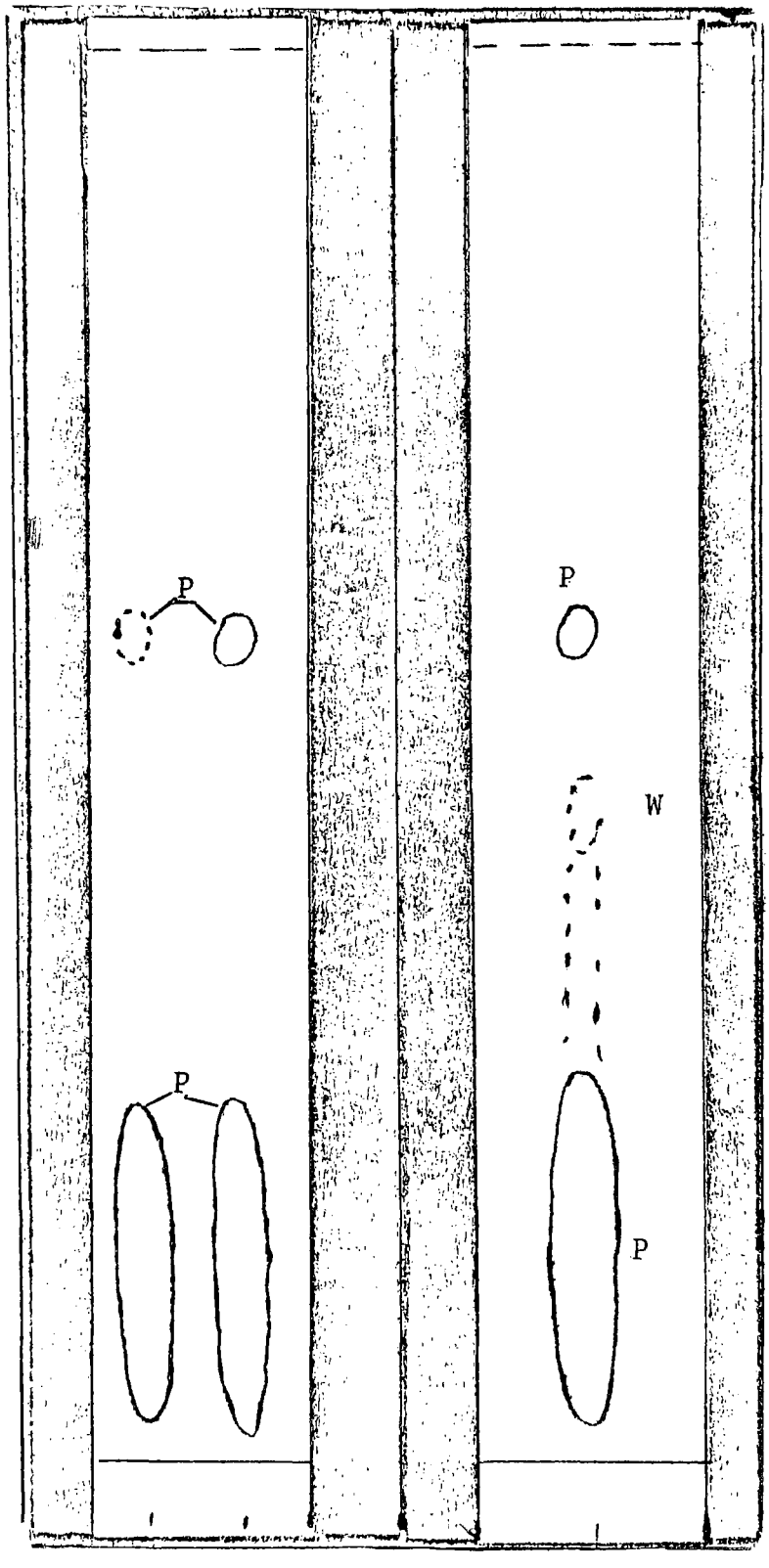
16γ as 0.4% Solution
Methylene Chloride

Code:

A - Princeton Organic
B - Aldrich Chemical
C - Eastman Organic

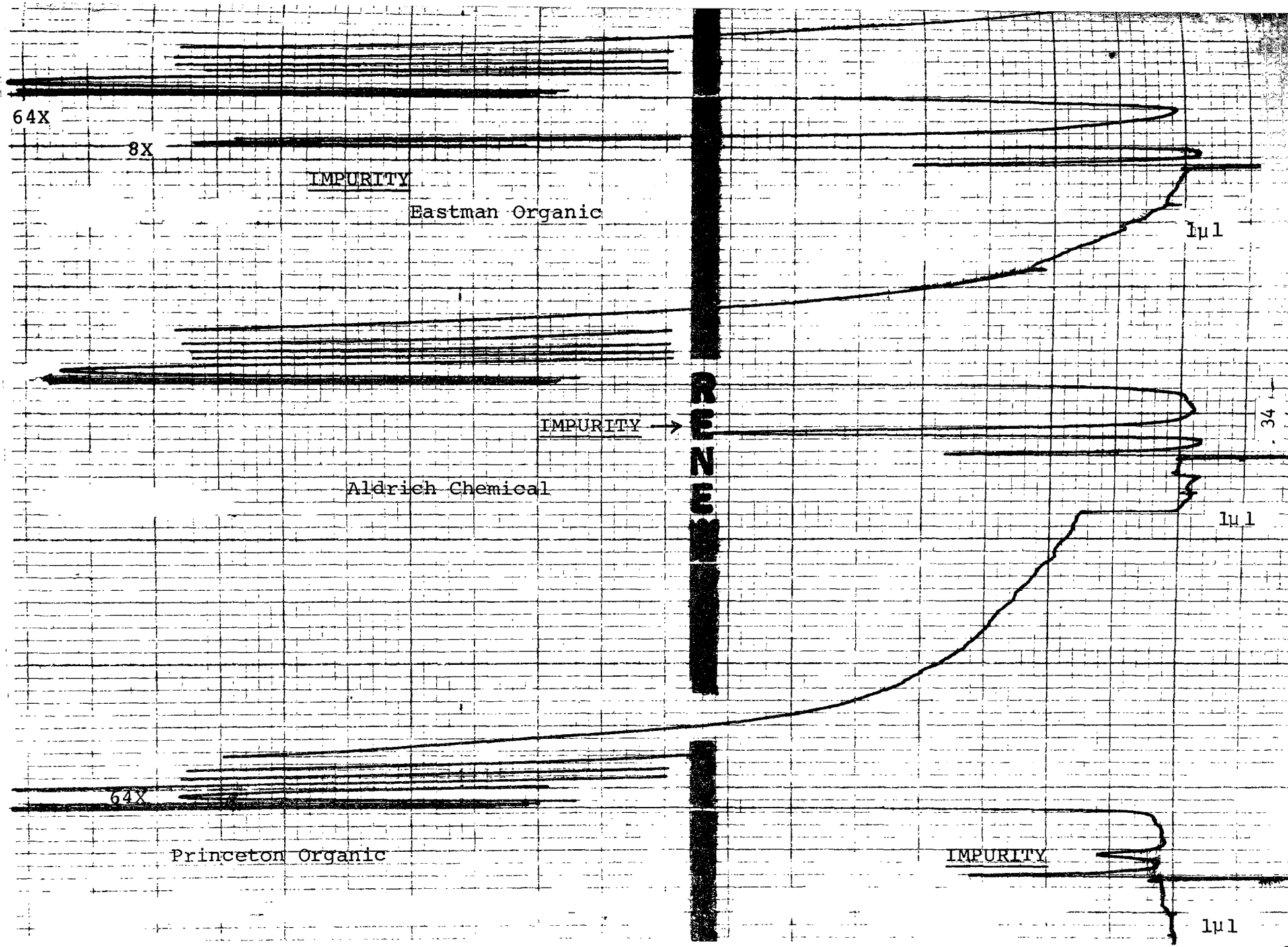
P - Purple
W - White

Dotted line indicates
trace amount and tailing.



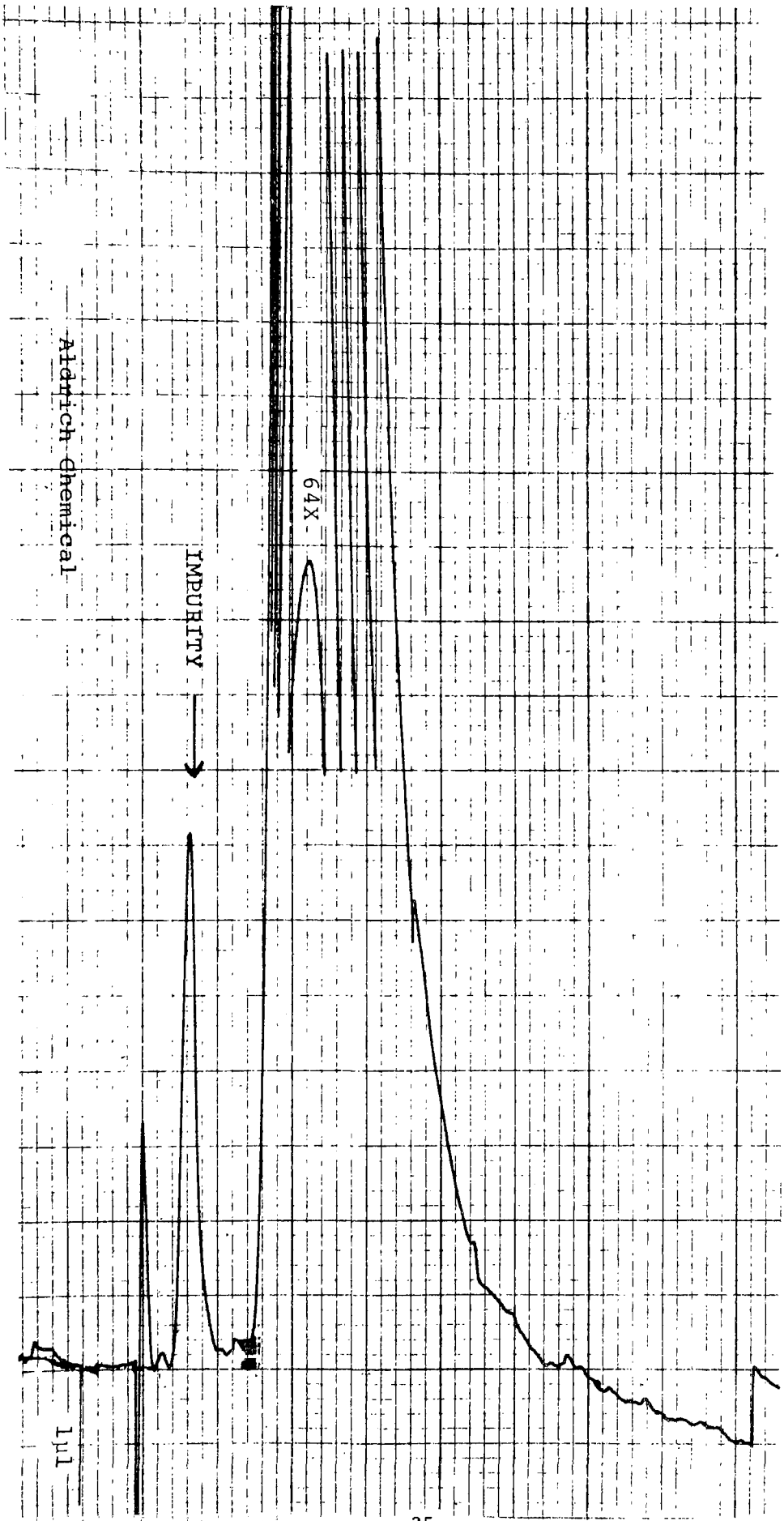
Starting Spots

A B C


64X
8X
IMPURITY
Eastman Organic
1µl
IMPURITY
RENEX
34
Aldrich Chemical
1µl
64X
Princeton Organic
IMPURITY
1µl

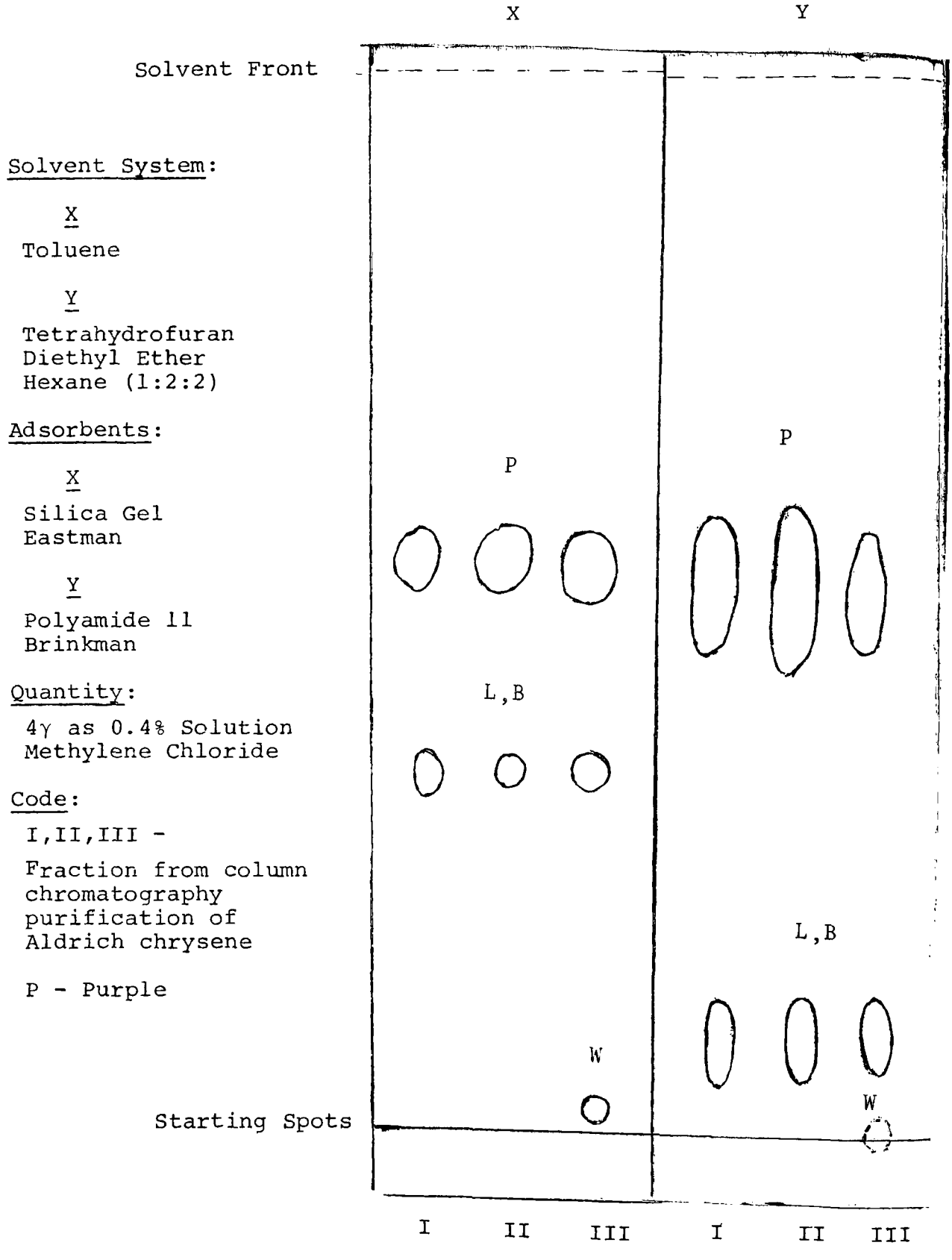
Chromatogram V

L.C. Analysis of Aldrich Chemical Chrysene



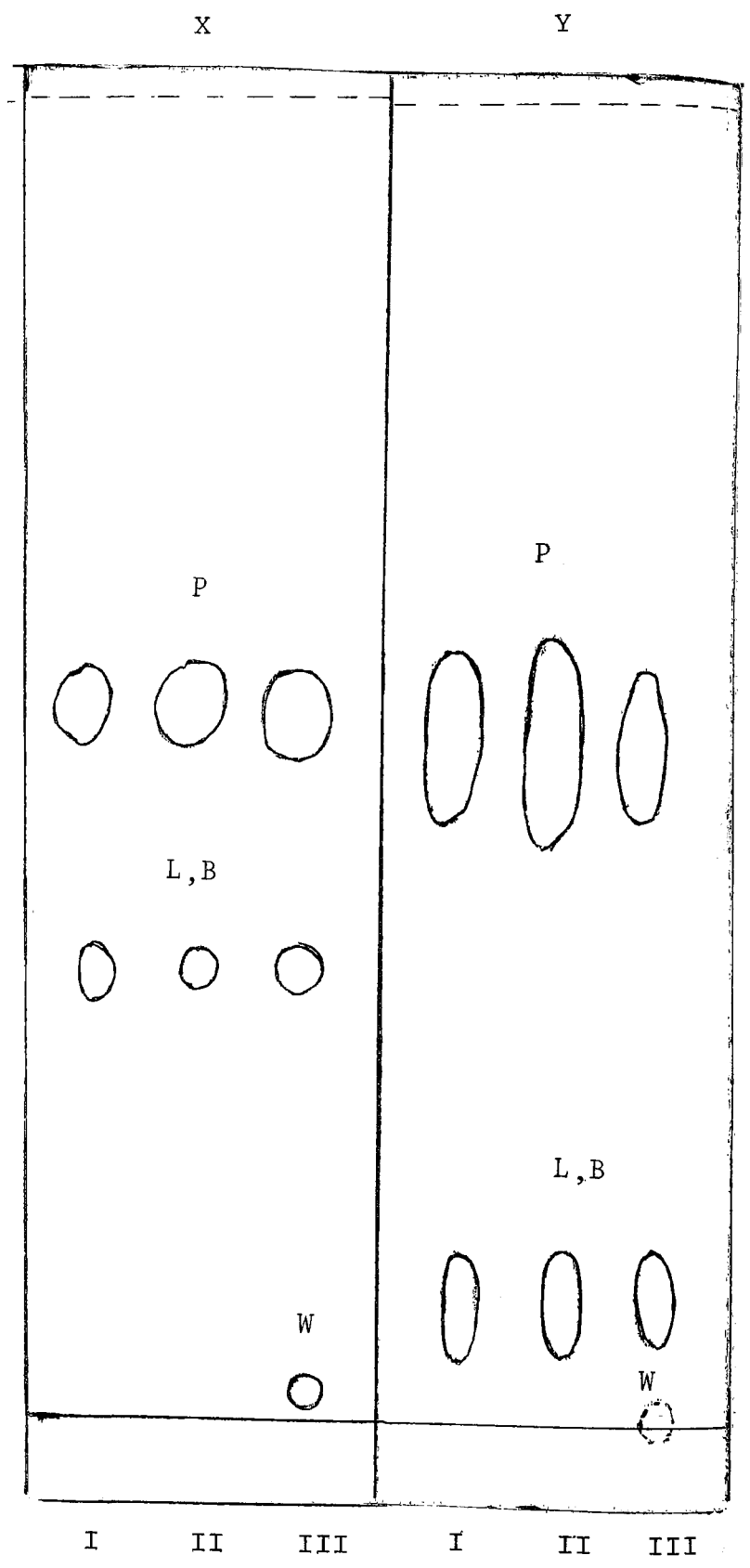
Chromatogram VI

Column Purification of Chrysene



Chromatogram VI

Column Purification of Chrysene



Solvent System:

X

Toluene

Y

Tetrahydrofuran
Diethyl Ether
Hexane (1:2:2)

Adsorbents:

X

Silica Gel
Eastman

Y

Polyamide 11
Brinkman

Quantity:

4γ as 0.4% Solution
Methylene Chloride

Code:

I,II,III -

Fraction from column chromatography purification of Aldrich chrysene

P - Purple

Chromatogram VII

Pure Chrysene

Solvent Front

Solvent System:

Toluene

Adsorbent:

Silica Gel.
Eastman

Detection:

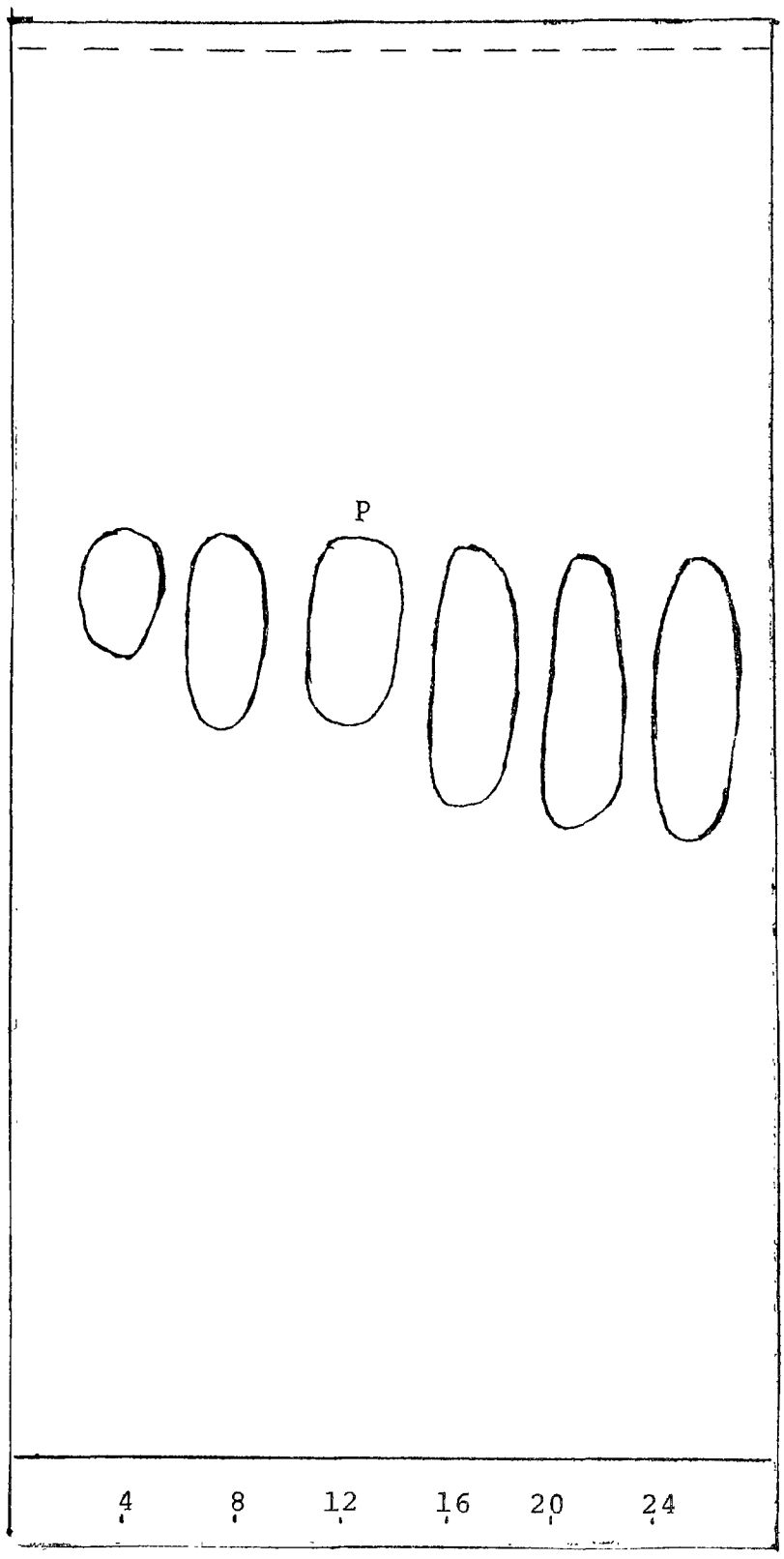
U.V. (360,254 mμ)
Iodine Vapor

Quantity:

Numbers refer to γ/spot
as 0.4% Methylene
Chloride Solution

Color:

Purple



Starting Spots

Pure Chrysene

Solvent Front

Solvent System:

Tetrahydrofuran
Diethyl Ether
Hexane (1:2:2)

Adsorbent:

Polyamide II
Brinkmann

Detection:

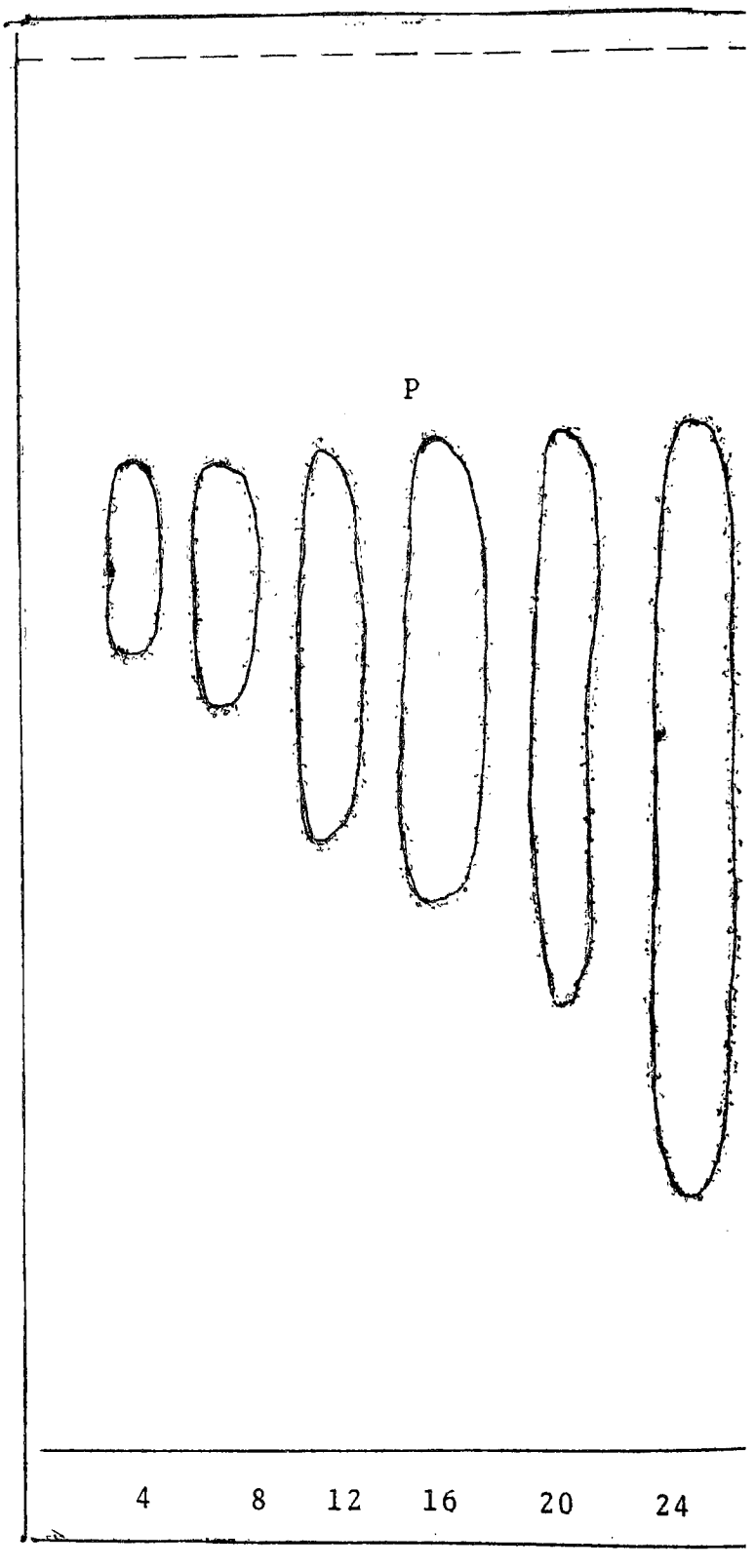
U.V. (360, 254 mμ)
Iodine vapor

Quantity:

Numbers refer to γ/spot
as 0.4% Methylene
Chloride Solution

Color:

Purple



Starting Spots

Chromatogram IX

Pure Chrysene

Solvent System:

X

Acetone

Y

Methanol

Adsorbent:

Porapak T
Waters Assoc.

Direction:

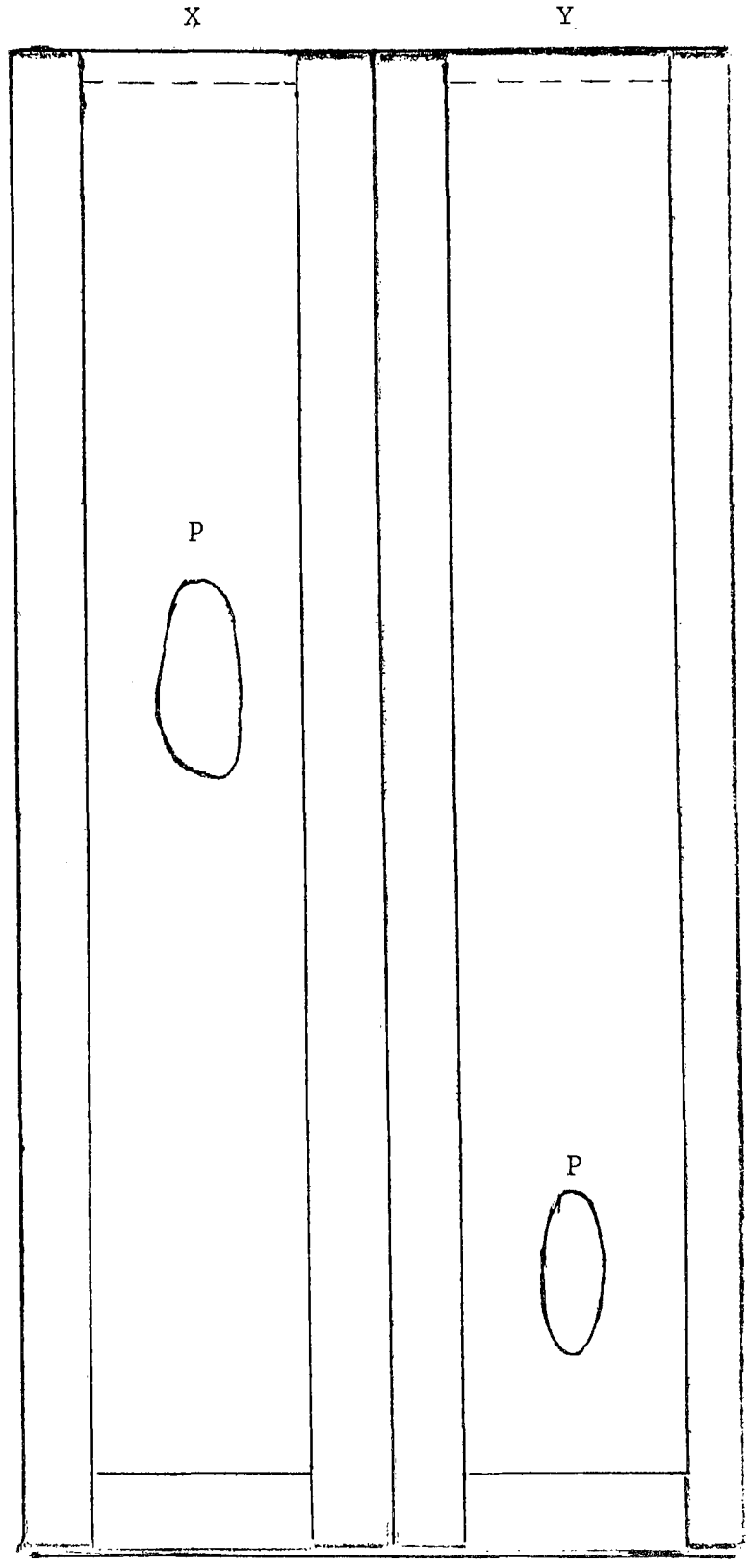
U.V. (360,254 mμ)
Iodine vapor.

Quantity:

4γ as 0.4% Solution
Methylene Chloride

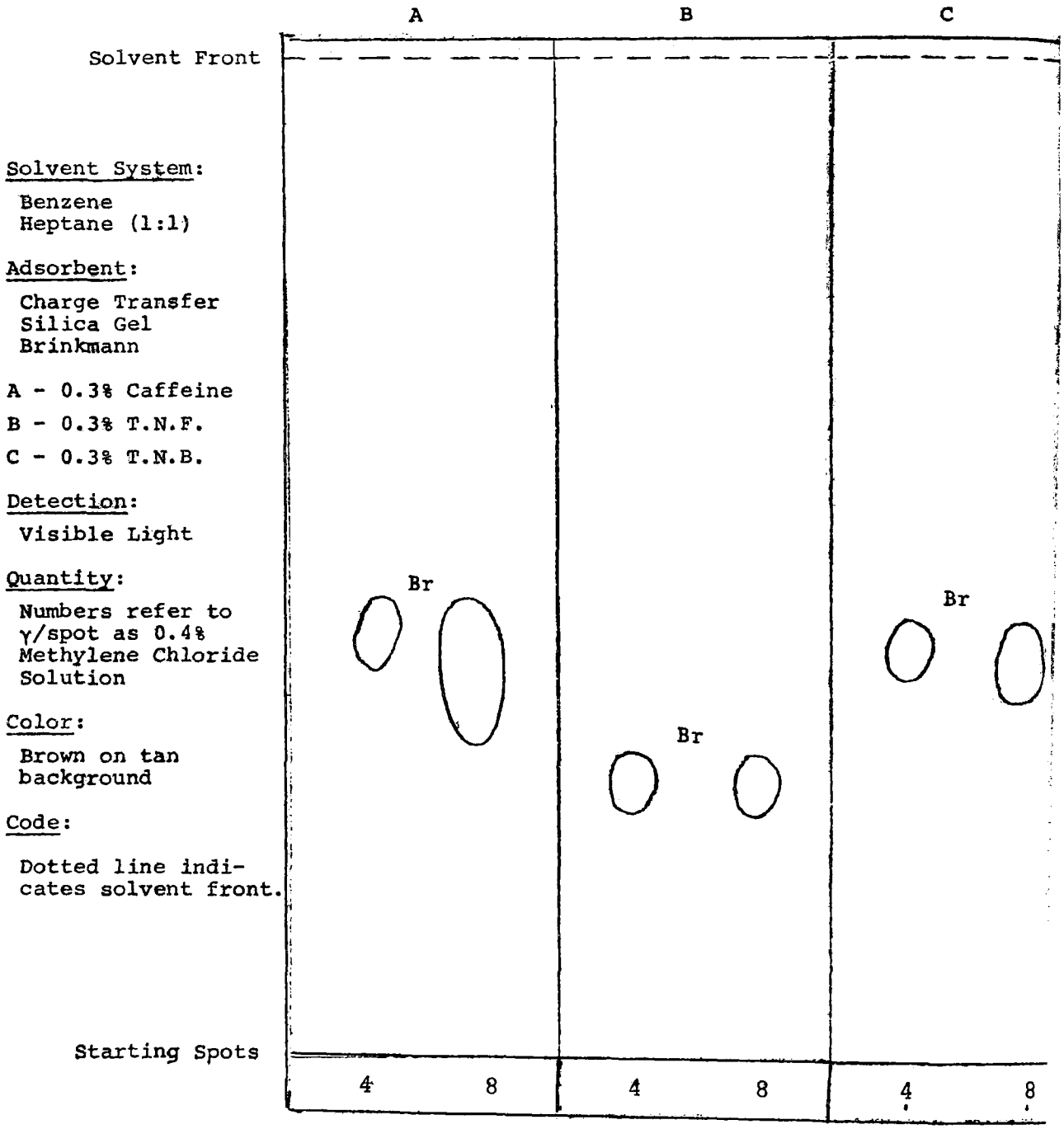
Color:

Purple



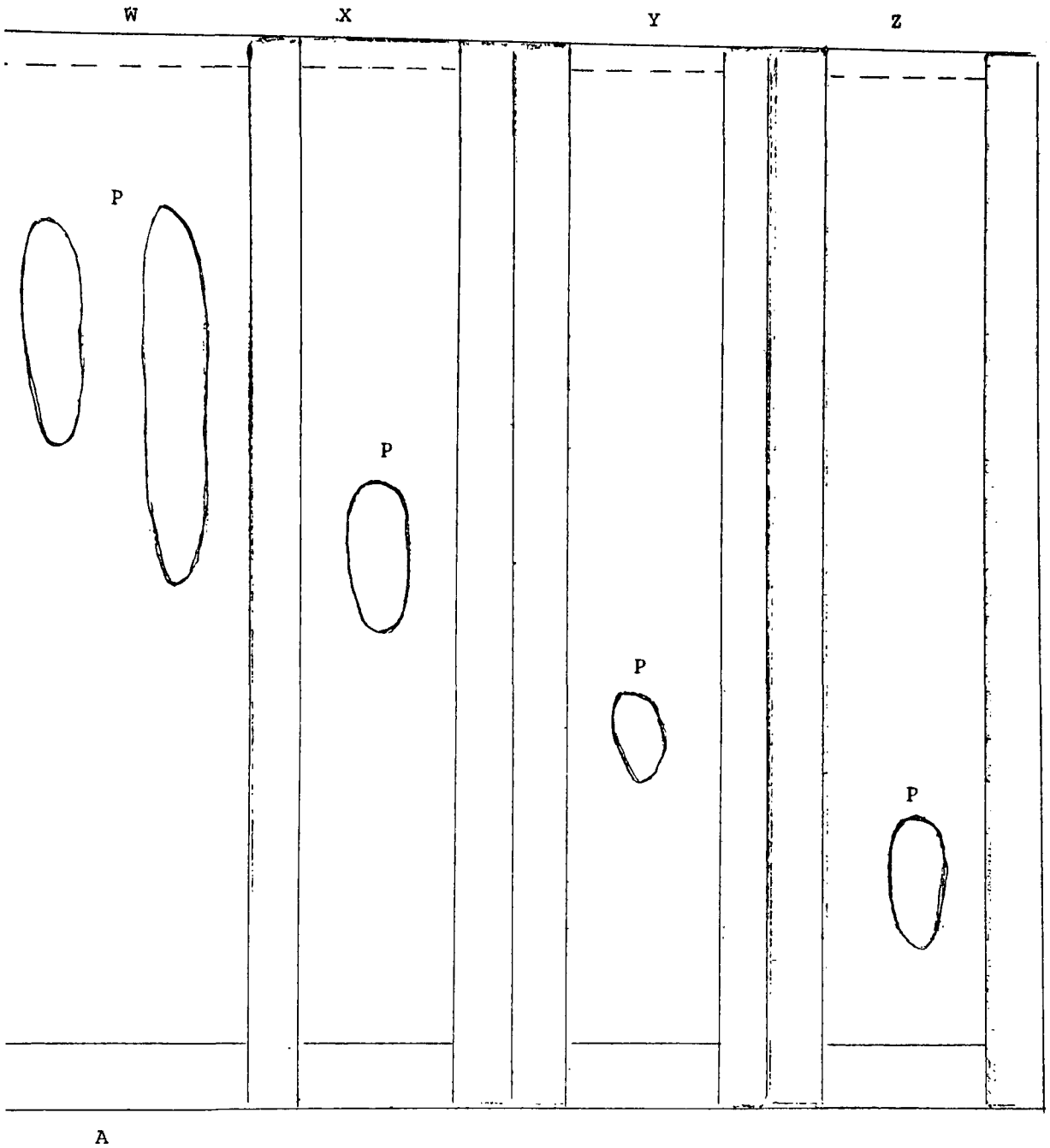
Chromatogram X

Pure Chrysene



Chromatogram XI

Pure Chrysene



Solvent System:

Diethyl Ether
Methanol, Water
(4:4:1)

Quantity:

A - 8γ
All other 4γ
per spot 0.4%
Methylene Chloride
Solution

Adsorbent:

Cellulose

W - 10% Acetylated
X - 20% "
Y - 30% "
Z - 40%

Brinkmann

Detection:

U.V. (360, 254 mμ)
Iodine Vapor

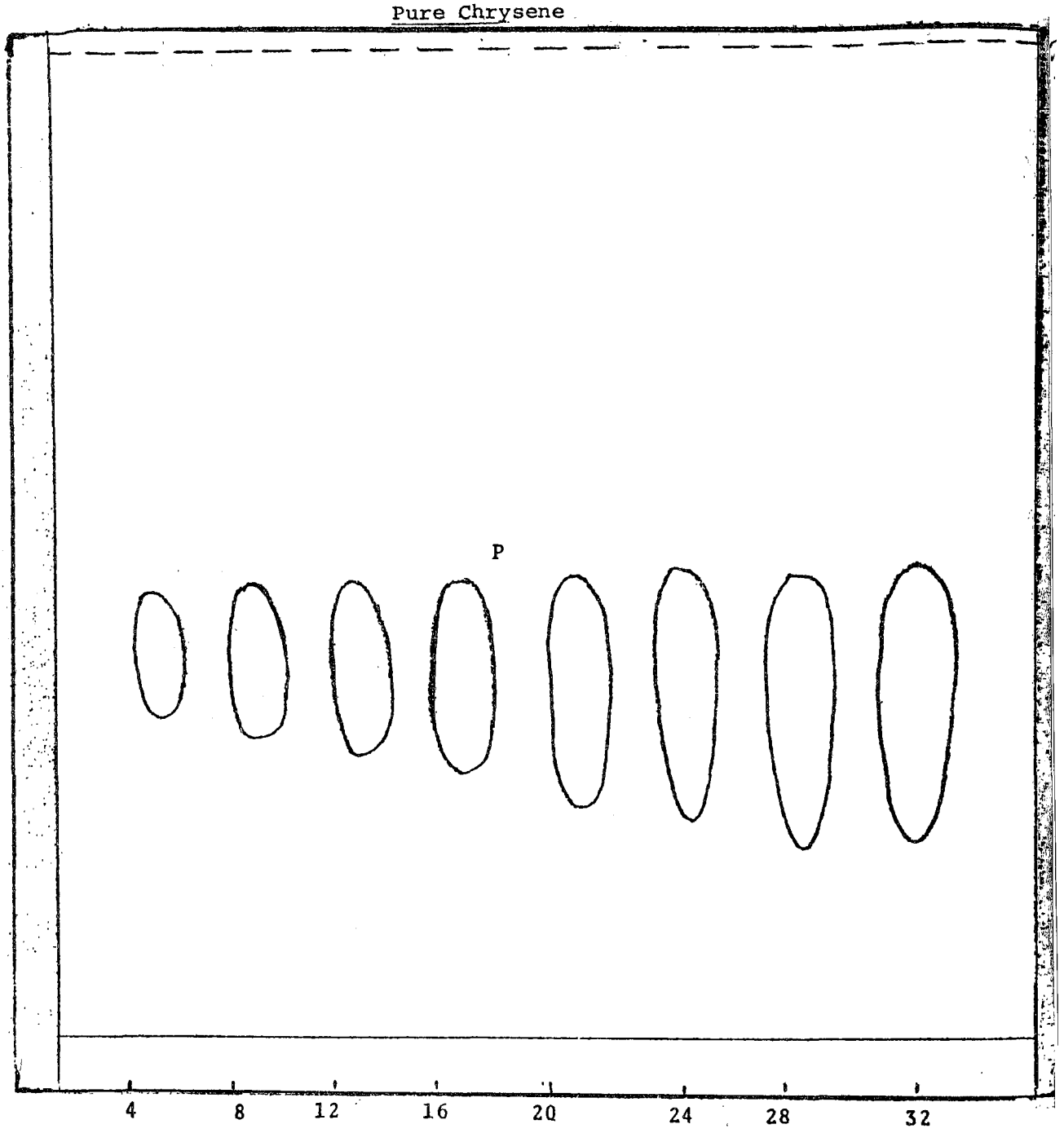
Color: Purple

Code: Solid line indicates starting spots.

Dotted line indicates solvent front.

Chromatogram XII

Pure Chrysene



Solvent System:

Diethyl Ether, Methanol, Water (4:4:1)

Adsorbent:

Cellulose 20% Acetylated

Detection:

U.V. (360,254 mμ)
Iodine Vapor

Quantity:

Numbers refer to γ/spot as 0.4% Solution Methylene Chloride

Color: Purple

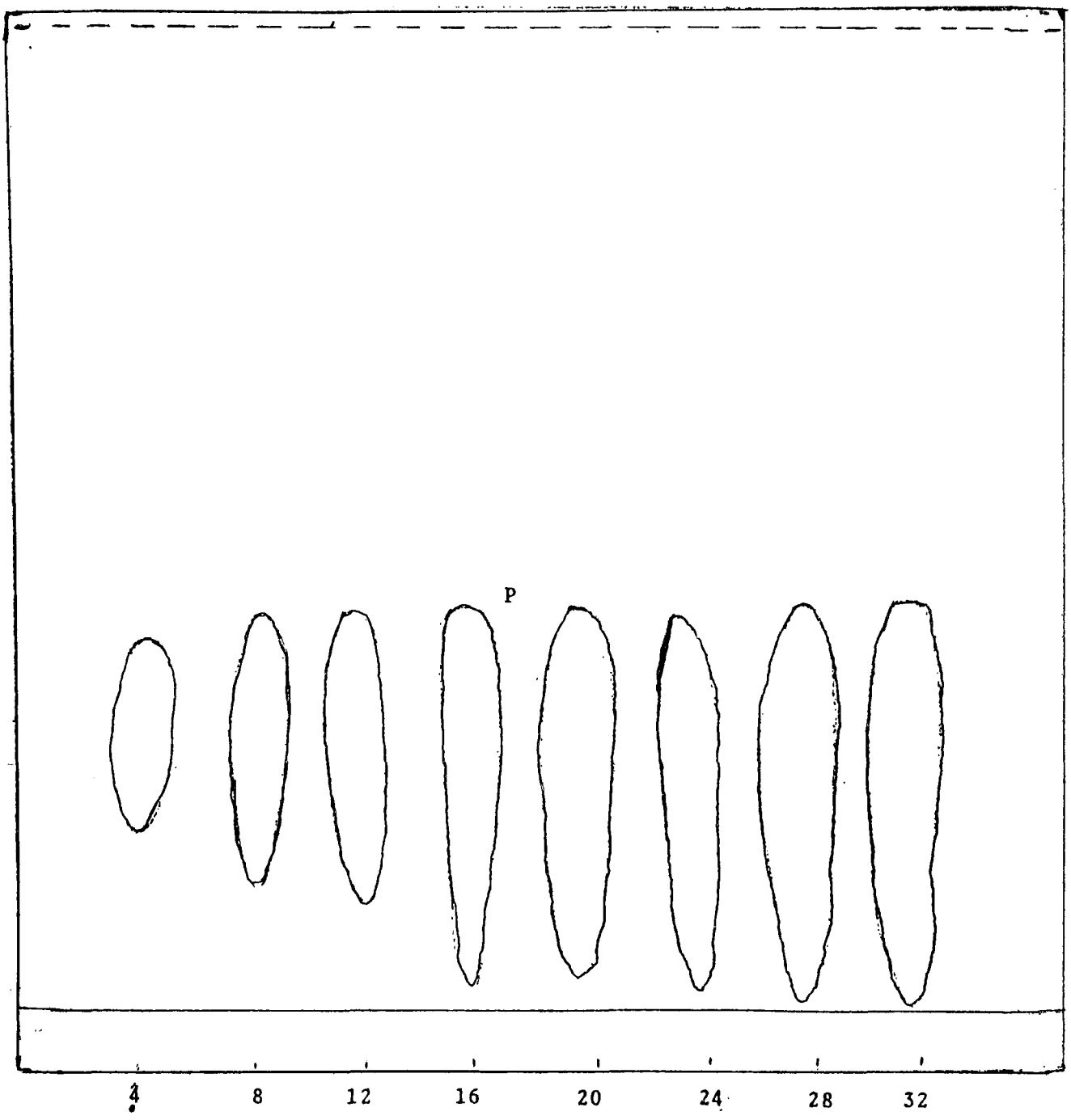
Code:

Solid line indicates starting spots.

Dotted line indicate solvent front.

Chromatogram XIII

Pure Chrysene



Solvent System:

Toluene, Ethanol
Water (4:17:4)

Adsorbent:

Cellulose 30%
Acetylated

Detection;

U.V. (360, 254 mμ)
Iodine Vapor

Quantity:

Numbers refer to γ/spot
as 0.4% solution
Methylene Chloride

Color: Purple

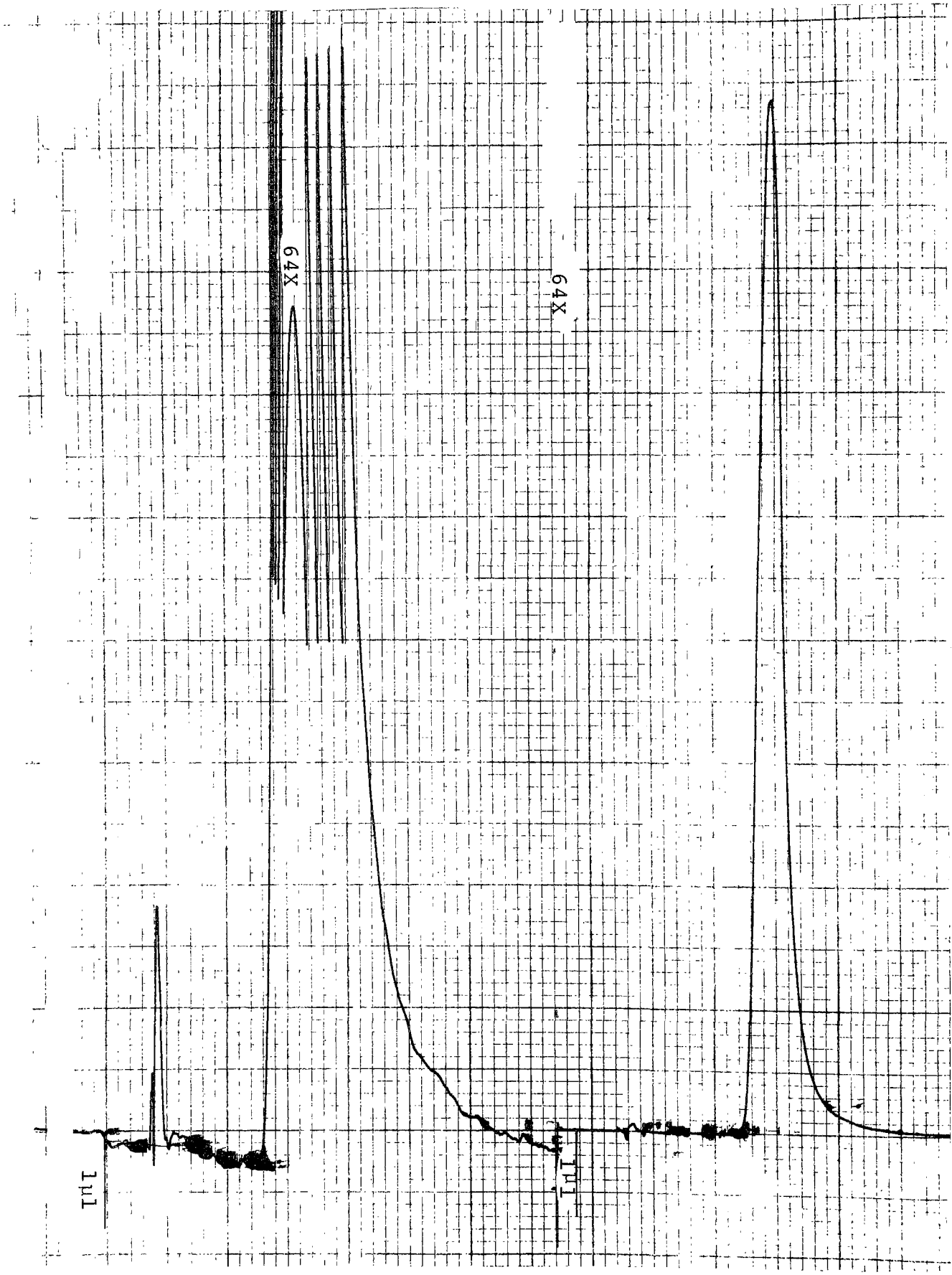
Code:

Solid line indicates
starting spots.

Dotted line indicates
solvent front.

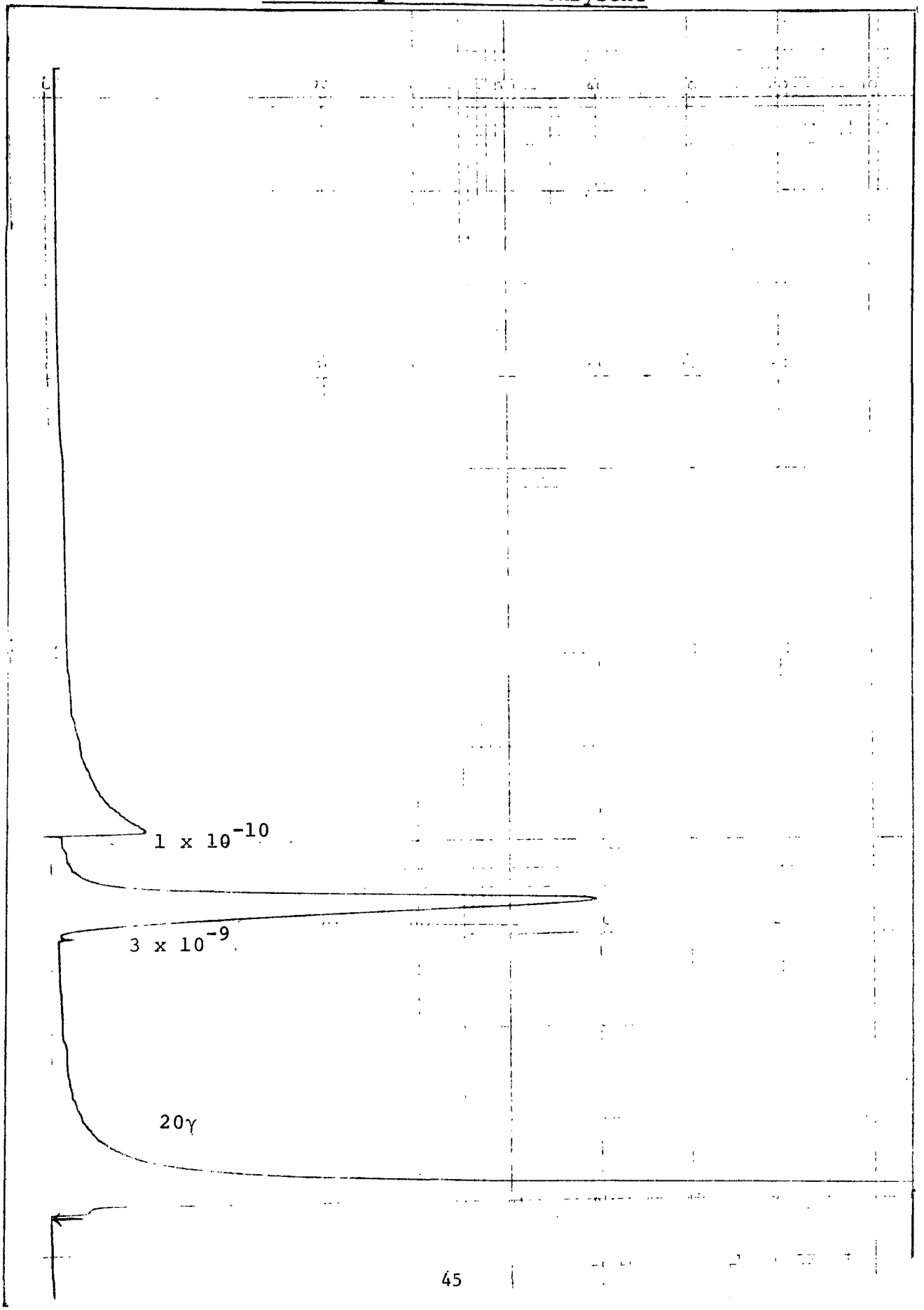
Chromatogram XIV

L.C. Analysis of Pure Chrysene

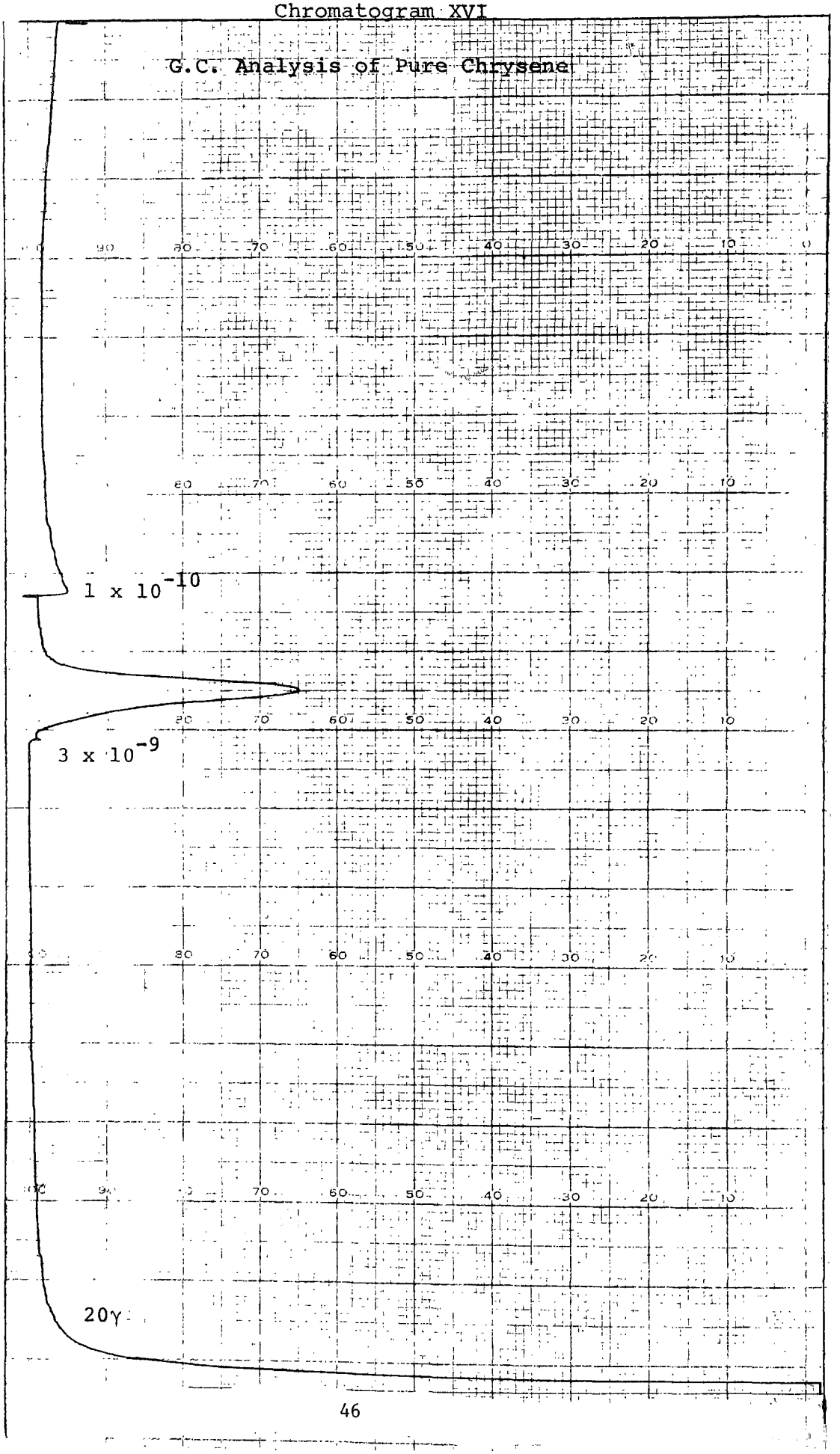


Chromatogram XV

G.C. Analysis of Pure Chrysene



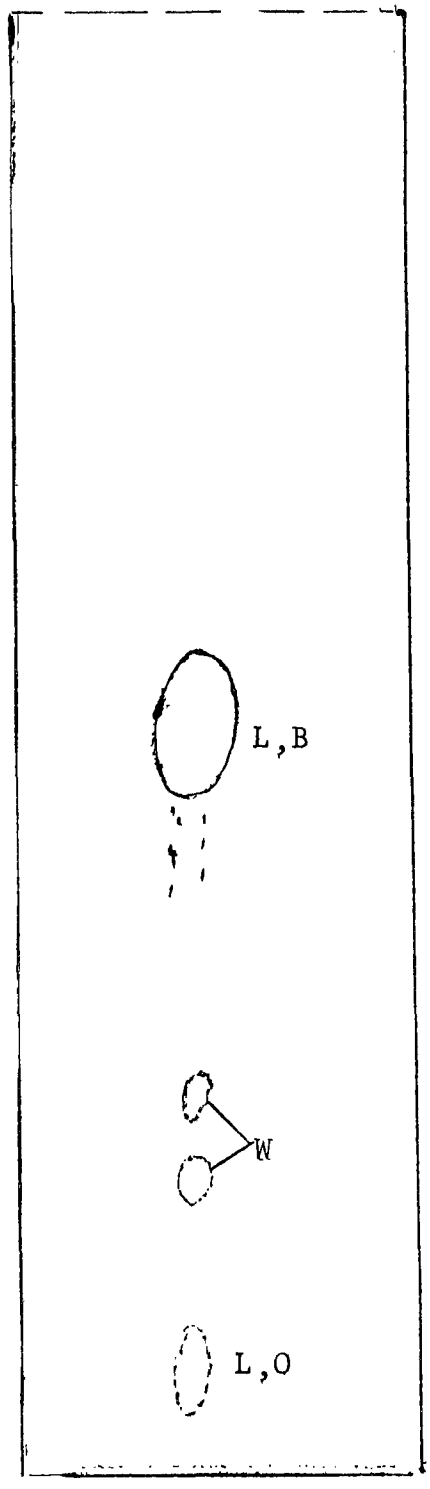
Chromatogram XVI



Chromatogram XVII

Crude Benzo[b]Fluoranthene

Solvent front



Starting spot.

Solvent System:

Toluene

Adsorbent:

Alumina
Brinkmann

Detection:

U.V. (360,254 mμ)

Quantity:

4γ per spot as 0.4% Solution
Methylene Chloride

Color:

L,B - Light Blue

W - White

L,O - Light Orange

Dotted line indicates slight tailing.

Chromatogram XVIII

Purified Benzo[b]Fluoranthene - Small Column

Solvent System:

Toluene

Adsorbent:

Alumina
Brinkmann

Detection:

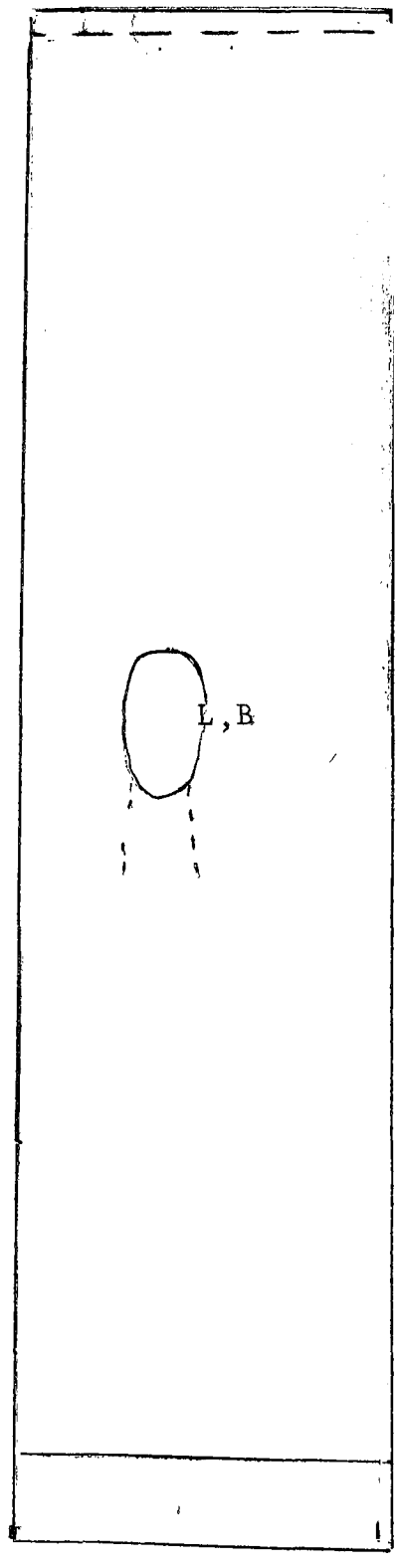
U.V. (360,254 mμ)

Quantity:

4γ per spot as 0.4% Solution
Methylene Chloride

Color:

L,B - Light Blue



Chromatogram XIX

Purified Benzo[b]Fluoranthene - Large Column

Solvent front

Solvent System:

Toluene

Adsorbent:

Alumina
Brinkmann

Detection:

U.V. (360,254 mμ)
Iodine Vapor

Quantity:

4γ per spot as 0.4%
Solution
Methylene Chloride

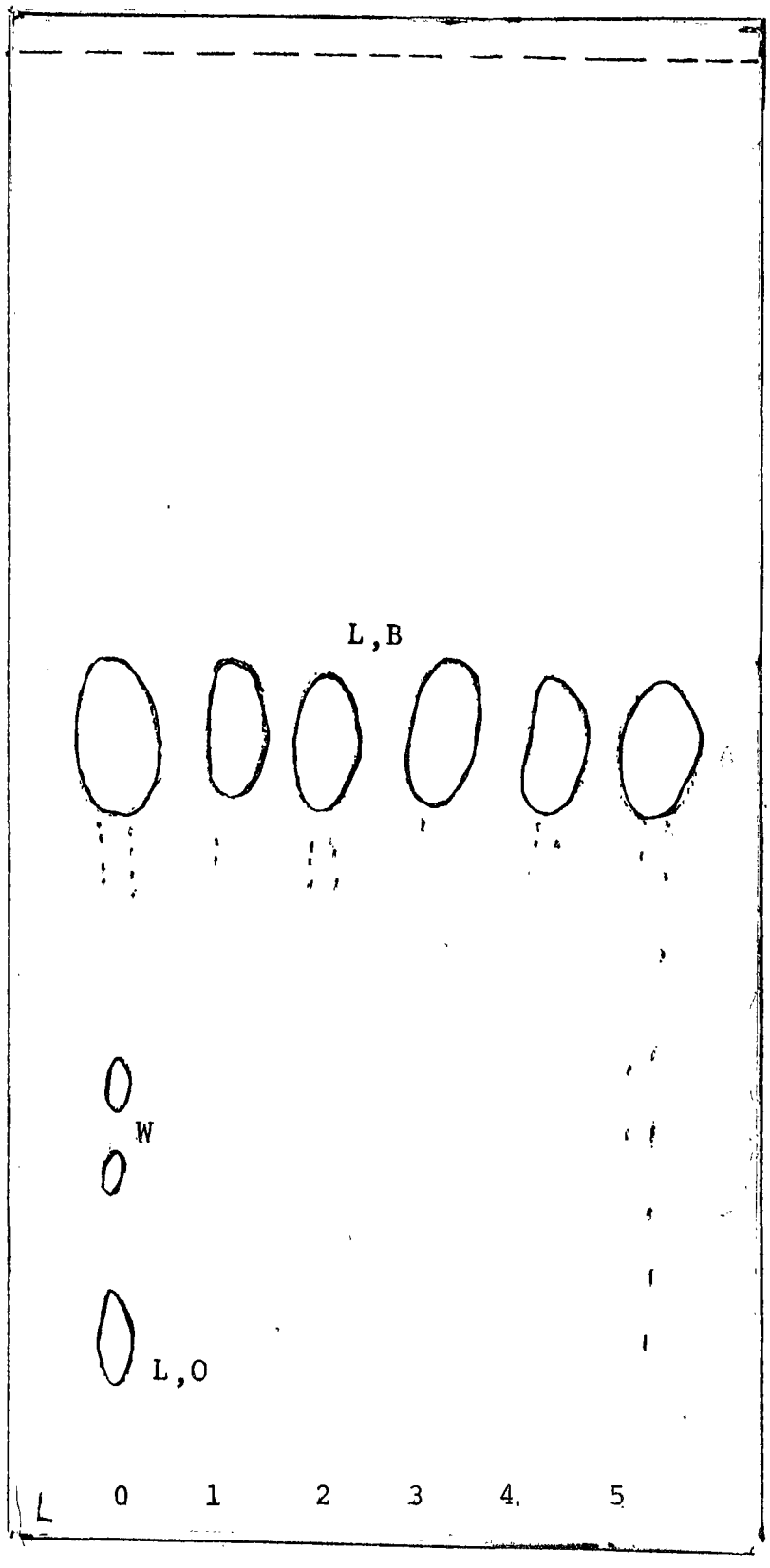
Color:

L,B - Light Blue

W - White

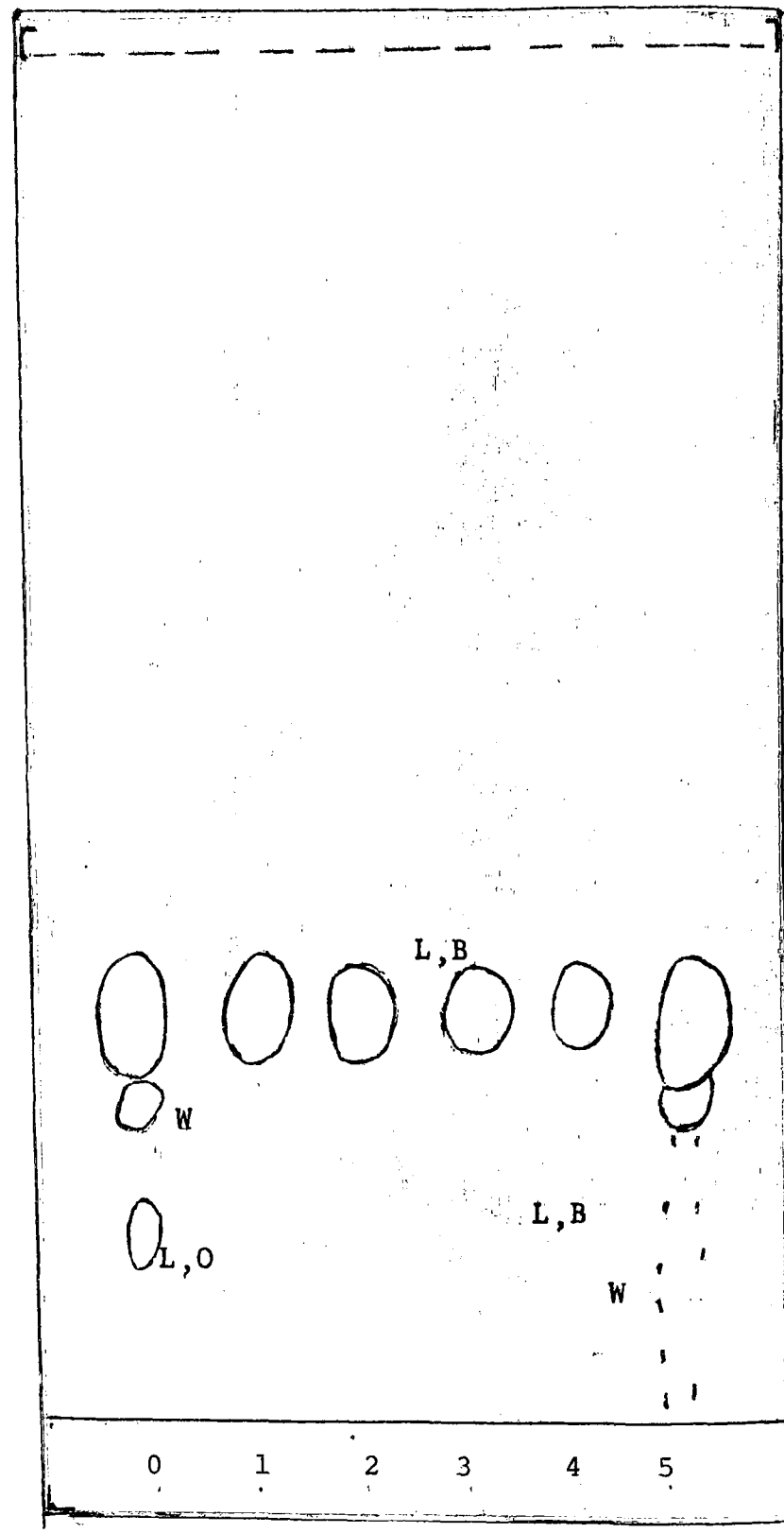
L,O - Light Orange

Dotted lines indicate tailing



Chromatogram XX

Purified Benzo[b]fluoranthene - Large Column



Solvent System:

Toluene

Adsorbent:

Alumina
Brinkmann

Detection:

U.V. (360,254 mμ)
Iodine Vapor

Quantity:

4γ per spot as 0.4%
Solution
Methylene Chloride

Color:

L,B - Light Blue

W - White

L,O - Light Orange

Dotted lines indicate tailing

Chromatogram XXI

Zone Refined Benzo[b]fluoranthene

Solvent Front

Solvent System:

Toluene, Ethanol, Water (4:17:4)

Adsorbent:

X

Polyamide 6.6 Acetylated

Y

Polyamide II Acetylated

Brinkmann

Detection:

U.V. (360,254 mμ)

Iodine Vapor

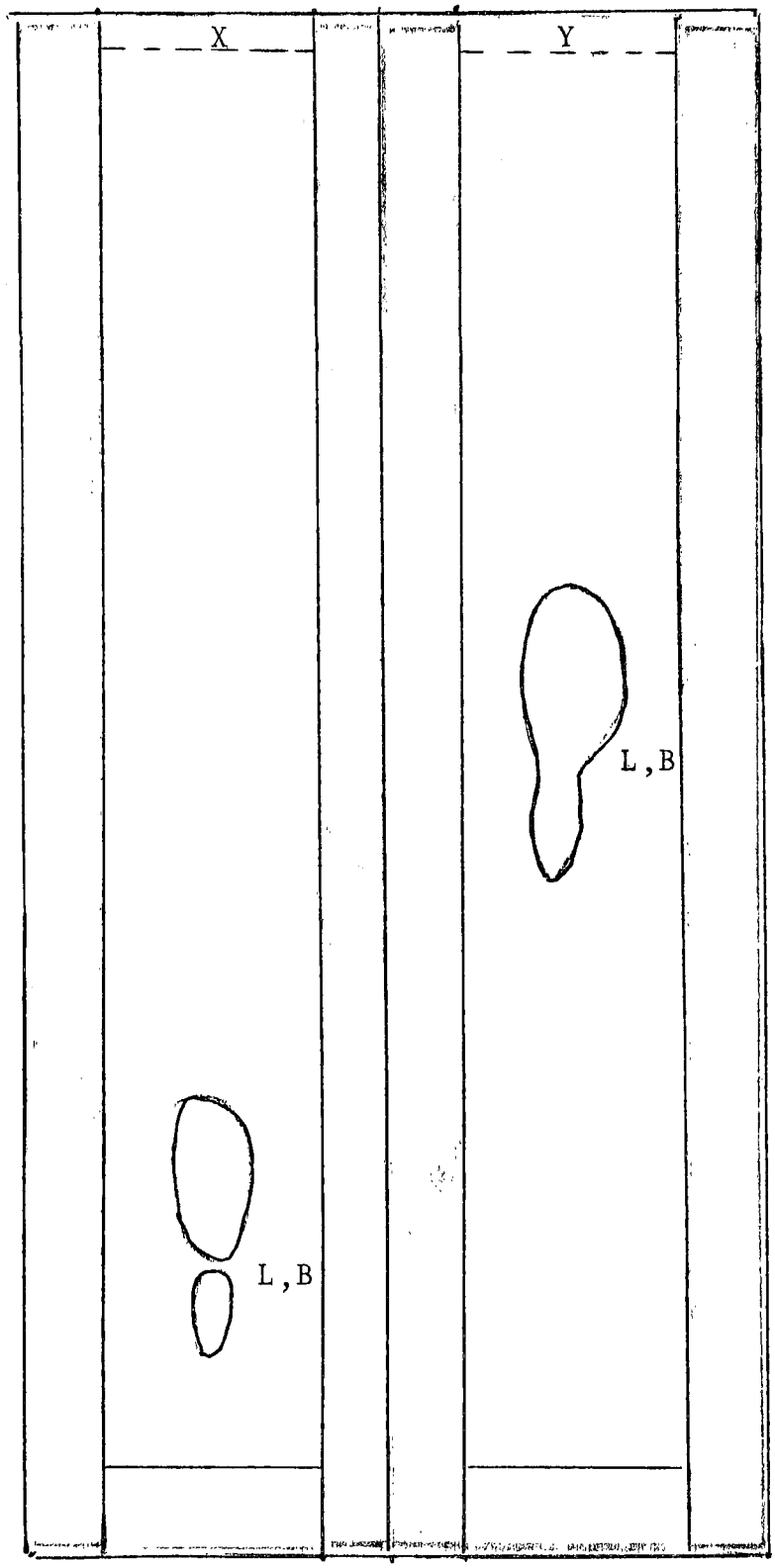
Quantity:

4γ per spot as 0.4% solution

Methylene Chloride

Color:

L,B - Light Blue



Starting Spot

Chromatogram XXII

Zone Refined Benzo[b]fluoranthene

Solvent System:

Benzene
Heptane
(1:1)

Adsorbent:

Charge Transfer
0.3% Caffeine Coated
on Silica Gel.

Brinkmann

Detection:

U.V. (360,254 mμ)
Iodine Vapor

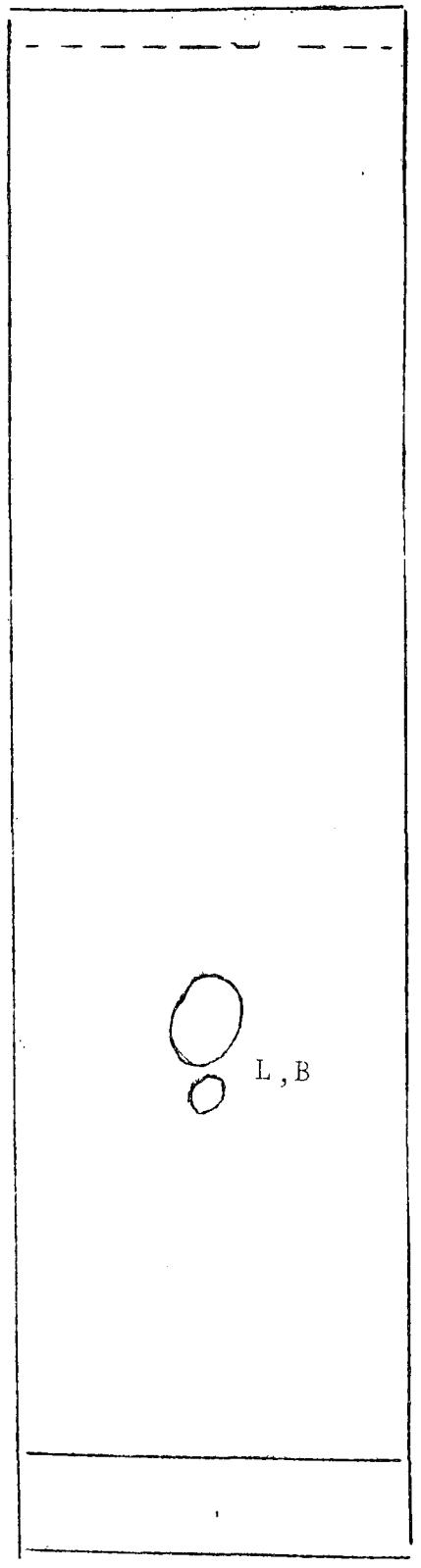
Quantity:

4γ per spot as 0.4% Solution
Methylene Chloride

Color:

L,B - Light Blue

On dark purple background



Chromatogram XXIII

Crude Benzo[k]fluoranthene

Solvent System:

Hexane, toluene
(3:1)

Adsorbent:

Silica Gel.
Brinkmann

Detection:

U.V. (360,254 mμ)

Quantity:

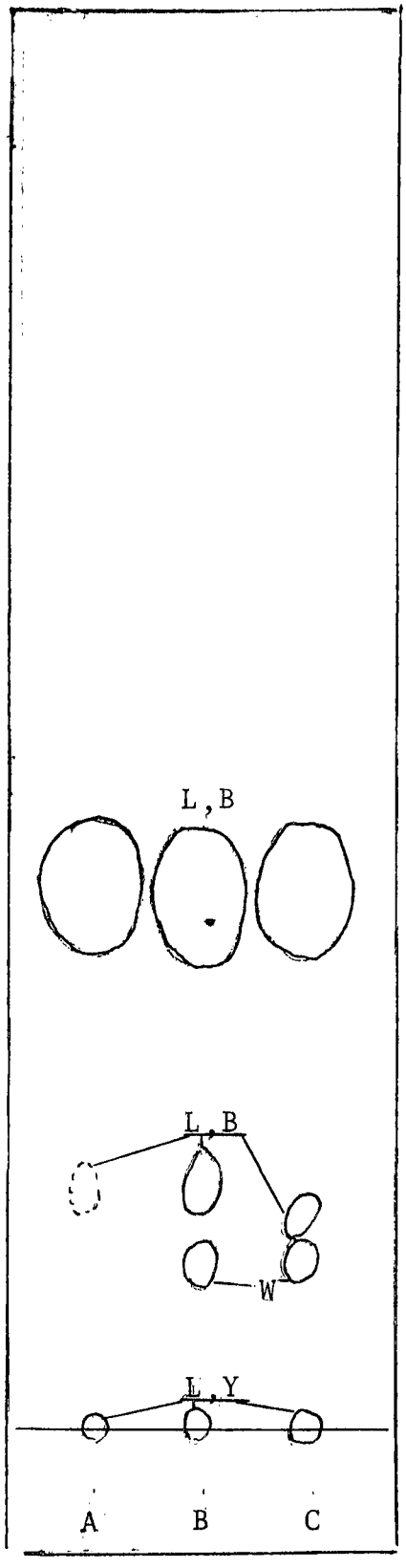
4γ as 0.4% solution
Methylene Chloride

Color:

L,B - Light Blue

W - White

L,Y - Light Yellow



Chromatogram XXIV

Pyrene

Solvent System:

Carbon Tetrachloride

Adsorbent:

Alumina
Brinkmann

Detection:

U.V. 254,360 mμ

Quantity:

10γ as 0.5% solution
Methylene Chloride

Code:

A - Crude

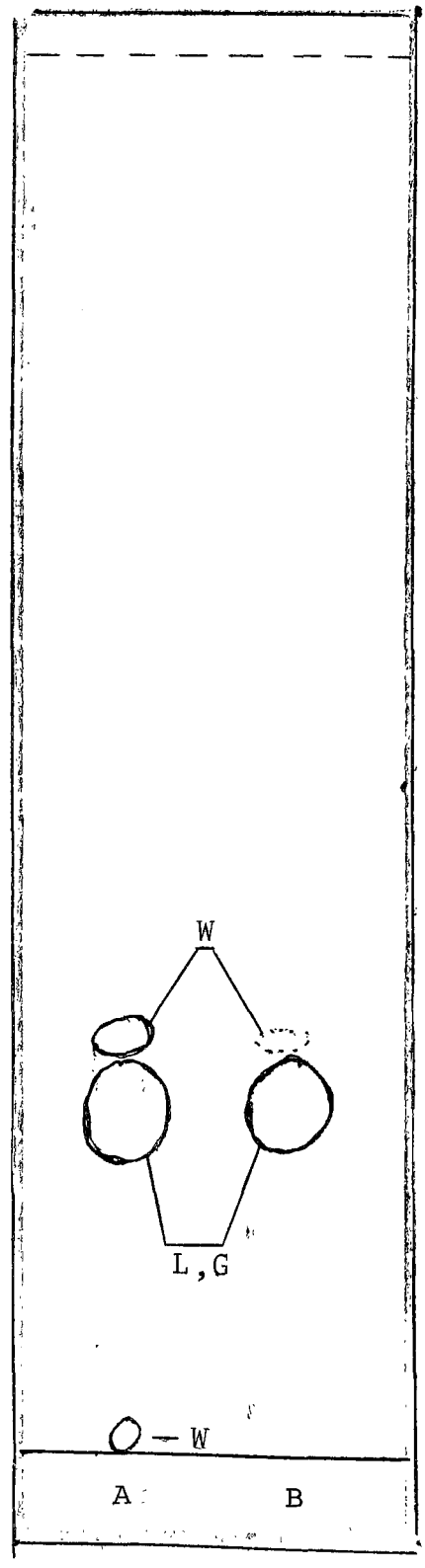
B - Purified

Dotted area indicates trace amount

Color:

L,G - Light Green

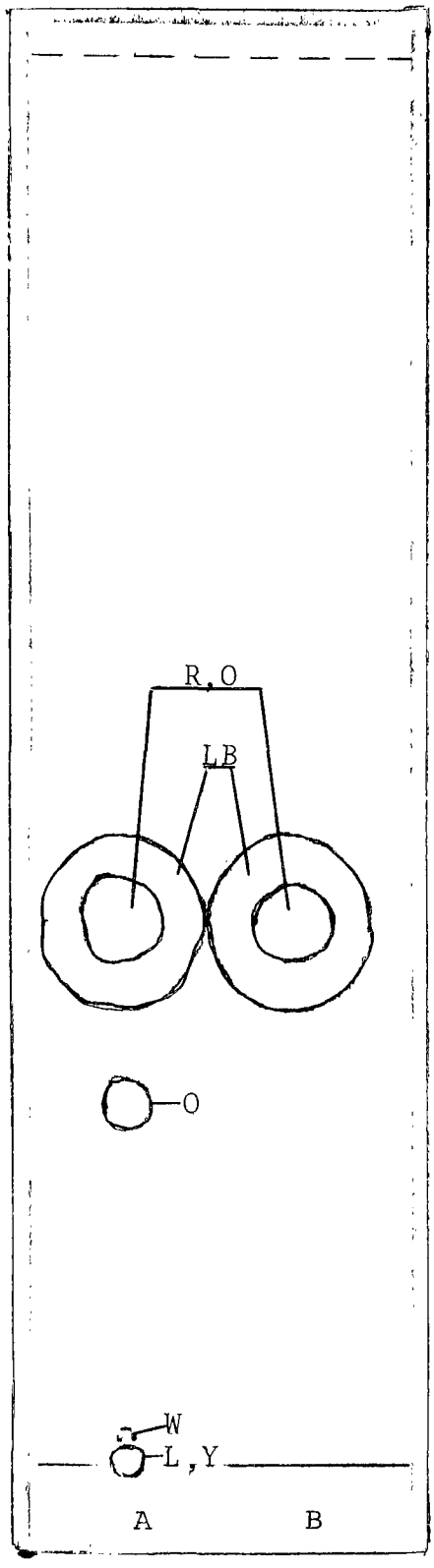
W - White



Chromatogram XXV

Pyrene-1-Carboxyaldehyde

Solvent front



Starting Spots

Solvent System:

Benzene
Heptane
Chloroform
(1:1:1)

Adsorbent:

Alumina
Brinkmann

Detection:

U.V. 360 mμ

Quantity:

10γ as 0.5% Solution
Methylene Chloride

Code:

A - Crude
B - Purified

Color:

R,O - Red Orange
L,B - Light Blue
O - Orange
W - White
L,Y - Light Yellow

Chromatogram XXVI

Hexahydropyrene

Solvent System:

Tetrahydrofuran
Diethyl Ether
Hexane
(10:35:20)

Adsorbent:

Polyamide 11
Brinkmann

Detection:

U.V 254 mμ

Quantity:

10γ as 1.0% solution
Methylene Chloride

Code:

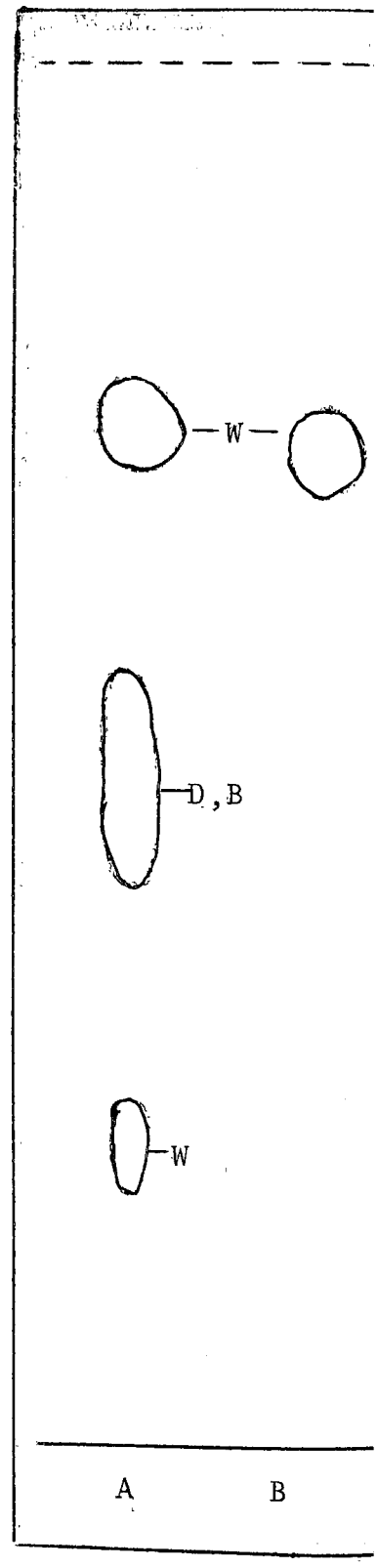
A - Crude

B - Purified

Color:

W - White

D,B - Dark Blue



Decahydrobenzo[e]pyrenone

Solvent System:

Benzene

Adsorbent:

Silica Gel
Eastmann

Detection:

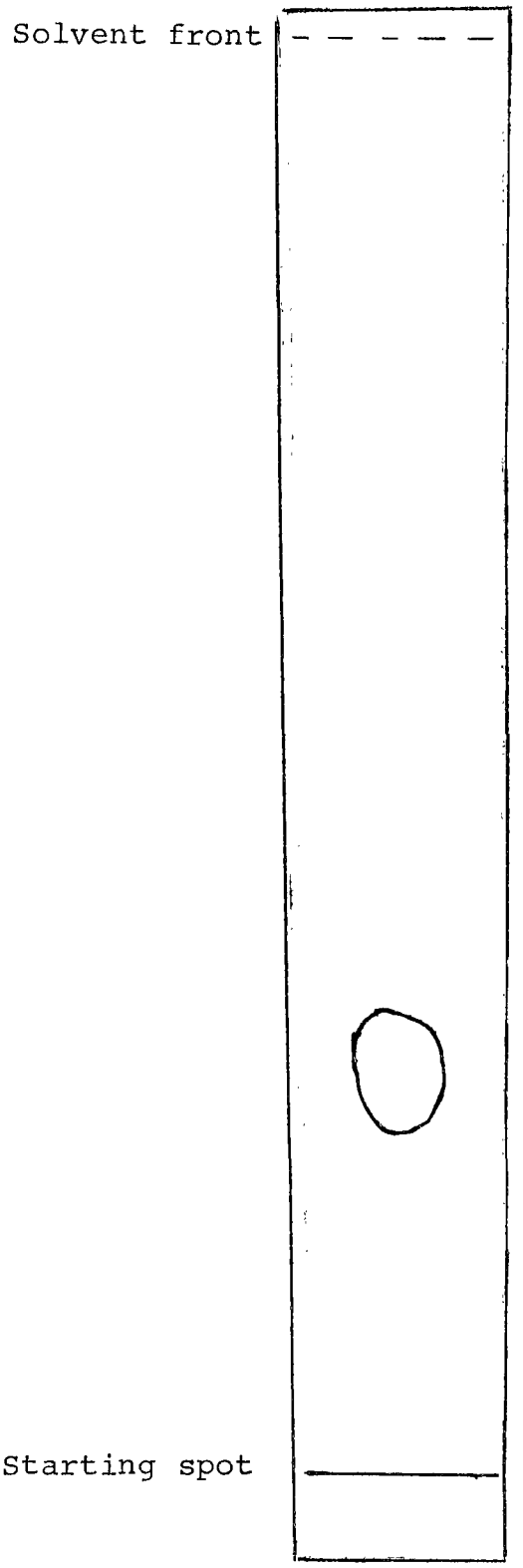
U.V. 254, 360 mμ

Color:

Yellow - Green

Quantity:

5γ as 0.1% solution
Methylene Chloride



Chromatogram XXVIII

Decahydrobenzo[e]pyrene

Solvent System:

Hexane
Toluene
(3:1)

Adsorbent:

Silica Gel
Eastmann

Detection:

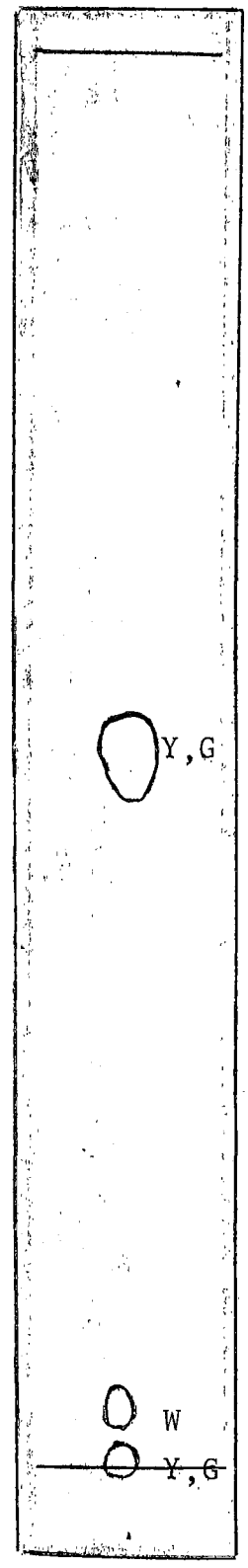
U.V. 254 mμ

Quantity:

10γ as 0.5% solution
Methylene Chloride

Color:

Y,G - Yellow-Green
W - White



Chromatogram XXIX

Acenaphthenequinone

Solvent System:

Methylene Chloride
Benzene (1:1)

Adsorbent:

Silica Gel.
Eastmann

Detection:

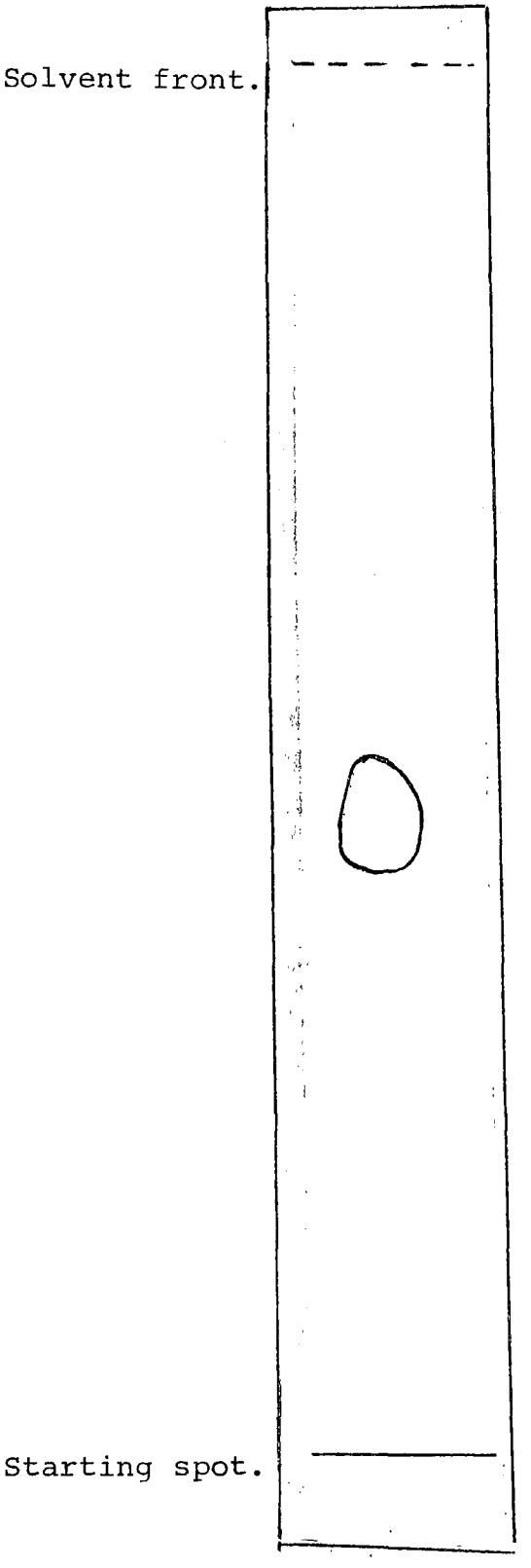
U.V. 254 mμ

Color:

Black

Quantity:

5γ as 0.1% solution



TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-650/2-74-040		

4. TITLE AND SUBTITLE	5. REPORT DATE
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	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Dr. Robert Fuhrmann, Allen Tunick and Louis Palmer	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Allied Chemical Corporation P. O. Box 1021R Morristown, New Jersey 07960	1AA010
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15. SUPPLEMENTARY NOTES

16. ABSTRACT

Experimental work was performed with the objective of preparing six condensed polynuclear hydrocarbons at a purity equal to or exceeding 99.9+%. The amounts to be prepared were 20 g. of benzo(a)pyrene, and 10 g.each of benz(a)anthracene, benzo(e)pyrene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

At the time the contract was terminated, chrysene was the only compound whose quantity and purity had been shown to meet the specifications. Four other compounds, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, and benzo(k)fluoranthene were in the process of purification and synthesis. No progress was obtained in the purification efforts on benz(a)anthracene.

Experimental details as well as analytical methods and safety procedures developed during the course of the work are described.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Aromatic Polycyclic Compounds Synthesis Crystallization Purification Gas Chromatography Zone melting Chromatographic analysis Primary Standards		

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