Table I. Bron	nate Remaining after Boilin Concentration, Millimole/Liter		
$\begin{array}{c} 2.0\\ 2.0^{a}\\ 3.0\\ 4.0\\ 4.0^{a} \end{array}$	0.10, 0.06, 0.14, 0.13, 0.15, 0.10,	0.05, 0.14, 0.15, 0.06, 0.12, 0.09,	0.06 0.02 0.16 0.07 0.13 0.08
• Phenol was added to thes	se solutions.		
Table II.	Ratios o	f Peak	Heights
Mass Numbers	Pure Eth; Bromi	ylene de	Gas from Trap

79/81 93/95 107/109 $1.0 \\ 1.28 \\ 1.06$ $\substack{1.0\\1.26\\1.06}$

a Consolidated Engineering Corp. Model 21-103 mass spectrometer.

A Beckman Model H pH meter was used for determination of pH. Polarograms were measured with a Sargent Model III polarograph.

DISCUSSION

At each pH used, the concentration of bromate remaining after boiling was estimated by comparison of the diffusion current with diffusion currents obtained with similar solutions containing added bromate. Results for cases in which bromine was added before acidification are given in Table I. In all cases where bromine was added after acidification no detectable difference

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was found between blank runs and those with bromine added. The half-wave potentials of the solutions to which bromine had been added were the same as for similar bromate solutions within 0.01 volt. These results indicate that bromate is formed in alkaline solution and is not completely removed by boiling. Evidence that the oxidizing agent is a bromine compound rather than iodate formed from iodide in the reagents is shown in Table II.

The material in the trap had the same mass spectrum as ethylene bromide and no indication of any iodine compound was found. Because of difficulties with absorption in the mass spectrometer inlet system, mass spectra were not used for quantitative measurements of bromine.

From the above it appears that oxidation of iodide to iodate by bromine must be carried out after acidification to avoid the formation of bromate which is difficult to remove and which would interfere with the titration of the resulting iodate.

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Separation of Fluoranthene and Chrysene by Molecular Distillation

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THE separation and purification of polynuclear hydrocarbons by crystallization are tedious and often unsuccessful because of the tendency of such compounds to form solid solutions. Separation by conventional fractional distillation at reduced pressure frequently leads to difficulties owing to the high melting points of many of these hydrocarbons, which solidify and clog condensers, stopcocks, and receivers. The successful isolation of coronene from coal-hydrogenation oil by a codistillation technique (9) in the molecular still prompted an investigation into the general applicability of the tool for separating mixtures of polynuclear hydrocarbons.

The method that may be used for separating closely related polynuclear hydrocarbons is a modification of the technique of molecular distillation devised by Hickman and called "analytical distillation" (θ , 10). In this procedure, the substance under investigation is dissolved in a solvent (carrier oil) and subjected to repeated distillations in a cyclic molecular still. Successive distillations are performed at progressively higher temperatures. The rate of elimination of solute is proportional to the product of its concentration and its distillability. The latter is a function of its vapor pressure and increases with temperature, but the concentration of solute decreases as the distillation proceeds. A plot of the concentration of solute in the distillate as a function of temperature has been proved experimentally (2) and theo-

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retically (θ) to resemble a probability distribution curve. This curve is called the "elimination curve" of the substance. Under strictly standardized conditions, the temperature at which the distillate contains the maximum concentration of solute (elimination temperature) is reproducible to within 1° or 2°. Thus, the technique may be used as an analytical tool for the identification of the solute (3, 5, 7).

The object of the present investigation was to determine the elimination curves of the two closely related polynuclear hydrocarbons fluoranthene and chrysene and to attempt their separation by molecular distillation. The difference between the elimination temperatures of two similar materials may conceivably be increased by:

Dilution of the mixture that is to be separated with a compounded carrier medium having the same distillability as the mixture. This technique, called "amplified distillation," has been successfully employed by Weitkamp (11) for the separation of methyl esters of fatty acids.

Use of an azeotrope-forming carrier which has a selective affinity for one of the components or which forms azeotropes with both components, the difference in distillability of the azeotropes being greater than the difference in distillability of the two pure components. Azeotrope formation at very low pressures has yet to be definitely demonstrated.

Gradual reduction in cycle time as the distillation progresses. This device might shift the elimination temperature of the more volatile component to a lower value; once the distilland is freed of this component, the elimination temperature of the other component may be shifted to a higher value. This method has been studied by Embree (2).

Tab	le I. Mol	lecular Dist (Experii	illation of nent 1)	Fluorant	hene
			Grams		
Charge.	Polyethyler Polyethyler Polyethyler Tetraethyle Fluoranthe	ne glycol 200 ne glycol 300 ne glycol 400 ene glycol ne	$186.7 \\ 186.7 \\ 163.6 \\ 201.6 \\ 11.3 \\ \overline{749.9}$		
	Rotor		Fraction	Fluora	nthene
Fraction	° C.	Pressure, μHg	Weight, Grams	Concn., %	Weight, Grams
1 2 3 4 5 6 7 8 9 10 11 Residue Loss Total	80 90 100 120 130 140 150 160 170 180	37 29 38 38 34 89 35 34 32 34 32 34 34	$\begin{array}{c} 15.3\\ 30.2\\ 56.5\\ 111.6\\ 99.3\\ 42.2\\ 45.9\\ 31.2\\ 31.0\\ 50.8\\ 187.5\\ 12.6\\ 749.9 \end{array}$	$\begin{array}{c} 2.48\\ 2.96\\ 3.38\\ 3.31\\ 2.73\\ 1.95\\ 1.32\\ 0.99\\ 0.11\\ 0.07\\ 0.05 \end{array}$	$\begin{array}{c} 0.38\\ 0.89\\ 1.91\\ 3.69\\ 2.71\\ 0.82\\ 0.61\\ 0.31\\ 0.03\\ 0.03\\ 0.03\\ 11.41 \end{array}$

The most suitable carrier oils for the hydrocarbons appeared to be polyglycols, which are commercially available in a wide variety of molecular-weight ranges and are soluble in water, thereby facilitating the recovery of hydrocarbon material. Furthermore, hydrocarbons frequently form azeotropes with glycols

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and are appreciably soluble in glycols, even at room temperature.

Materials. A technical grade of fluoranthene manufactured Materials. A technical grade of intoranthene manuactured by the Reilly Tar and Chemical Corp. was used. Ultraviolet spectrophotometric analysis showed that it contained 94.21% of fluoranthene and 1.01% of chrysene; the balance of the material was not characterized because it did not interfere in any The technical grade chrysene manufactured by the Reilly way. Tar and Chemical Corp. contained 96.49% of chrysene and 3.51% of fluoranthene. Polyethylene glycols 200, 300, and 400, and tetraethylene glycol, manufactured by the Carbide and Carbon Chemical Co., were used; the numbers following the name of the glycol refer to the average molecular weights.

Apparatus and Procedure. Distillations were conducted in a Apparatus and Frocedure. Institutions were conducted in a centrifugal, cyclic, batch, molecular still, Type CMS-5, manufac-tured by Distillation Products, Inc. The polynuclear compounds were dissolved in glycol and sucked into the glass reservoir of the still. After degassing at a rotor temperature of 50° to 70° C. the pressure was decreased and the temperature of the rotor was fixed for the collection of the first fraction. (Pressures were determined by a MacLeod gage: the Pirani gage furnished with the molecular still performed unsatisfactorily.) When degassing When degassing was complete, internal recycling was stopped by closing the ball valve and opening the stopcock to the distillate receiver. This operation started a cycle which ended when all the liquid had passed over the rotor and the residue had been collected in the aluminum cup. The residue was allowed to drain back into the glass reservoir, and a second cycle was started. The second cycle was complete when all the liquid had again passed over the rotor. At this moment, internal recycling was resumed; the first dis-tillate fraction, collected during the two full cycles, was removed. A new distillate receiver was connected and evacuated by means of a side line. When the rotor reached the next predetermined temperature, internal recycling was stopped and collection of the second fraction was started. Distillation rate and cycle time were determined by means of a stopwatch.

All but the last fractions were collected in this way. The last fractions, usually not more than three in each run and containing virtually no detectable amounts of polynuclear compounds, were collected by allowing uninterrupted recycling for a time approximately equal to that taken for collecting the previous fraction. The technique was changed because the time intervals gradually decreased as the amount of material in the still was reduced so that, while collection of the first fraction required about 30 minutes, the last fractions were collected in less than 5 minutes, and the first and second cycles could not be segregated.

Analytical Method. All fractions were analyzed with a Beckman ultraviolet spectrophotometer Model DU. Samples of about 1 gram of polyglycol containing a small quantity of poly-nuclear hydrocarbon were diluted with 95% ethyl alcohol (benzene-free), and each reading was corrected for absorbance by the glycols. This correction is significant for concentrated solutions.

The ultraviolet spectra of pure fluoranthene and pure chrysene were determined and found to be identical with those previously reported (4). Determination of the amount of hydrocarbon in a solution containing only one hydrocarbon requires one absorbance measurement; values at 360.0 m μ for fluoranthene and 267.3 m μ for chrysene were used. For determining the composition of a mixture of the two hydrocarbons, the concentration of each was



Figure 1. Elimination Curve of Fluoranthene

Table II. Molecular Distillation of Chrysene (Experiment 2)

Charge.	Polyethyle Polyethyle Polyethyle Chrysene	ne glycol 200 ne glycol 300 ne glycol 400	Grams 225.0 202.0 200.0 0.300 627.3		
	Rotor		Fraction	Chrysene	
Fraction	Temp., °C.	Pressure, μ Hg	Weight, Grams	Conen., %	Weight, Mg
1 2 3 4 5 6 7 8 9 10 11 12 13 14 17 16 17 18 Residue Loss Total	$\begin{array}{c} 80\\ 90\\ 100\\ 110\\ 120\\ 130\\ 140\\ 150\\ 160\\ 170\\ 180\\ 200\\ 210\\ 220\\ 230\\ 240\\ 250 \end{array}$	85 78 85 74 108 99 95 102 101 103 105 105 105 105 115 140	$\begin{array}{c} 3.0\\ 6.2\\ 12.7\\ 24.2\\ 45.4\\ 29.1\\ 36.1\\ 36.1\\ 42.0\\ 45.8\\ 42.0\\ 45.8\\ 23.1\\ 23.1\\ 23.1\\ 23.4\\ 627.3\\ \end{array}$	$\begin{array}{c} 0.0087\\ 0.0080\\ 0.0099\\ 0.0179\\ 0.0396\\ 0.0590\\ 0.0979\\ 0.1151\\ 0.1484\\ 0.0925\\ 0.0708\\ 0.0365\\ 0.0072\\ 0.0044\\ 0.0044\\ 0.0018\\ 0.0021 \end{array}$	$\begin{array}{c} 0.26\\ 0.50\\ 2.17\\ 4.33\\ 13.77\\ 25.02\\ 28.49\\ 35.79\\ 53.57\\ 58.74\\ 31.36\\ 24.99\\ 16.32\\ 3.02\\ 1.80\\ 2.10\\ 0.51\\ 0.49\\ 303 \end{array}$





calculated from the observed absorbances at 267.3 and 340.0 m_{μ} by means of the simultaneous equations:

 $A_{257,3} = 568.848 \ c + 45.300$ $A_{340,0} = 1.724 \ c + 38.300 \ f$

where c and f are the concentrations of chrysene and fluoranthene in grams per liter, and $A_{267,8}$ and $A_{840,0}$ are the observed absorbances of the mixture at the wave lengths noted. The measurements at both wave lengths must be made (or adjusted) to the same dilution. The coefficients of c and f are the four specific extinction coefficients (4) (absorbance in a 1-cm. cell per concentration in grams per liter) for the two pure hydrocarbons at the two chosen wave lengths. All measurements were made in a 1-cm. cell and concentrations were chosen to give absorbance values in the range 0.2 to 0.9. No normalizing factors were employed.

Experiments. The elimination curve at 30- to 35-micron pressure secured with 12 grams of fluoranthene in 750 grams of a mixture of glycols is plotted in Figure 1 from the data in Table I.

A solution of 0.3 gram of chrysene in 627 grams of mixed glycols was distilled at approximately 100-micron pressure with the results shown in Table II and Figure 2. Although the pressure in this experiment was higher than that in Experiment 1, the difference in elimination temperatures was great enough to assume that separation of the two hydrocarbons is possible at the lower pressures. Accordingly,

the following experiments were performed.

A mixture of 1.2 grams of fluoranthene and 0.3 gram of chrysene was diluted with 800 grams of a solvent mixture containing equal parts of tetraethylene glycol and polyethylene glycol 200, 300, and 400, and distilled at a pressure of 50 to 80 microns. The elimination temperature for fluoranthene was 110°C. and that of chrysene was 150°C. Seventy-six per cent of the fluoranthene was recovered with an average purity of 92%; 48% of the fluoranthene had an average purity of 95%.

A mixture of 1.1 grams of fluoranthene and 0.29 gram of chrysene was distilled from 793.8 grams of a solvent containing equal parts of tetraethylene glycol and a polyethylene glycol fraction boiling at 160° to 185° C. (1 to 10 microns). The first three fractions were collected at a constant rotor temperature of





100° C. according to the following technique. The condensed distillate was recycled to the reservoir, while the residue was collected in the cup until approximately half the material remained in the reservoir. At this point the recycling of distillate was discontinued and the fraction was collected until the reservoir was exhausted. The contents of the residue cup were then returned to the reservoir and the process was repeated at same rotor temperature the for the next fraction. This procedure served to concen-trate the fluoranthene before the product was collected. Unfortunately, chrysene was also concentrated at this rotor temperature. The remaining fractions were collected in the usual way. The results are given in Table III and Figure 3.

Fractions 7 through 14 from experiment 4 (from $140 \degree C$.) were diluted with an equal volume of polyethylene glycol 200 and distilled in the usual fashion. The results are shown in Table IV and Figure 3. Of the chrysene (21% pure, solvent-free basis) originally charged to the still in experiment 4, 5.5% was recovered with an average purity of 90% and 25% with an average purity of 82%. Chrysene was recovered from the fraction collected at its elimination temperature by precipitation with water, extraction with benzene, evaporation of the benzene, solution with alcohol, and precipitation with water. The crude product was filtered, washed with ethyl alcohol, dried, and sublimed. Its melting point was 253° to 255° C. [literature 254.1° to 254.4° (1)].

DISCUSSION

The results demonstrate that it is possible to separate fluoranthene and chrysene by dissolving the mixture in a suitable polyglycol mixture and subjecting the solution to molecular distillation in a cyclic still. The very low pressure possibly has the effect of increasing the relative volatility of the mixture of hydrocarbons. No attempt was made to determine whether true azeotrope formation occurred or whether there was only codistillation of solute and solvent. The major component of the mixture (fluoranthene) was recovered in good yield and was fairly pure. Repeated distillation was necessary to secure relatively pure chrysene. The rate of product removal in experiment 4 was excessively rapid for the first fractions; about 200 drops were collected per minute, which is four times as much as recommended for good results. Hickman and Trevoy (8) have recently pointed out that very small rates (1 to 10 drops per minute) are sometimes conducive to high relative volatilities ("superalphas"). By changing the molecular weight distribution of the glycols one should be able to avoid the excessive rates of distillation experienced here.

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Analytical Applications of the Cyanohydrin Reaction

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R ECENT work (1) on the kinetics of cyanohydrin formation has shown that in buffered acetate media both propionaldehyde and acetaldehyde react quantitatively with hydrogen cyanide. These rate studies suggested that certain analytical applications could be devised—namely, the quantitative analysis for halide ions in the presence of cyanide and the quantitative determination of acetaldehyde and propionaldehyde.

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At the pH of sodium cyanide solutions, the reaction is almost instantaneous. However, at this pH the equilibrium would be shifted and the reaction might not be quantitative. In order to obtain information about the completeness of reaction, the following procedure was used.

Twenty-five milliliters of 0.12N aldehyde solution (an excess) were added to 10 ml. of a 0.2N solution of sodium cyanide. The solution was acidified with 6 ml. of 6N nitric acid. On the addition of 0.1N silver nitrate, a precipitate was formed in the case of the acetaldehyde and propionaldehyde solutions but not in the case of formaldehyde solutions, indicating that the reaction was complete only in the latter case.

The procedure was modified for propional dehyde and acetal dehyde solutions as follows: six drops of bromocresol purple indicator (pH range 5.2 to 6.8) were added to a solution containing an aldehyde and sodium cyanide. The solution was slowly titrated with 0.1N nitric acid over a 10 to 15-minute interval to

Table IV.Molecular Distillation of Mixture of Fluoranthene and Chrysene
(Experiment 5)

$\begin{array}{c} \text{iment 4} & 344.7 \\ & \underline{345.2} \\ \hline 689.9 \\ \text{action} & \underline{Fluo} \\ \hline Concn \end{array}$	containing 58.95 and 94.21 mg. ranthene	o mg. of fluoran of chrysene) Chrys	thene	
etion Fluo	ranthene	Chrvs		
eight Concn		011130	Chrysene	
rams $\times 10^3 \%$	Weight, mg.	Concn., X 10 ³ %	Weight, mg.	(Glycol-Free Basis), %
$\begin{array}{ccccccc} 47.3 & 12.34 \\ 51.0 & 18.57 \\ 52.4 & 22.27 \\ 46.3 & 23.68 \\ 42.6 & 15.33 \\ 39.3 & 8.40 \\ 34.6 & 4.76 \\ 36.9 & 3.66 \\ 44.8 & 2.79 \\ 91.3 & 4.73 \\ 58.2 & 1.74 \\ 52.1 & 1.77 \\ 36.3 & 3.23 \\ 20.8 \\ 26.0 \\ 39.9 \\ 91.3 \\ 20.8 \\ 26.9 \\ 39.9 \\ 91.4 \\ 26.2 \\ 39.9 \\ 91.4 \\ 30.4 $	5.84 11.33 11.67 10.96 6.53 3.30 1.65 1.35 1.25 4.73 1.01 0.92 1.17 61.71 terfering absorbs	2.29 5.58 12.30 24.64 45.59 52.15 38.93 17.52 5.68 1.18 0.74 0.43 0.58	$\begin{array}{c} 1.08\\ 3.40\\ 6.45\\ 11.41\\ 19.42\\ 20.50\\ 13.47\\ 2.54\\ 1.08\\ 0.43\\ 0.22\\ 0.21\\ \end{array}$	$\begin{array}{c} 15.61\\ 23.08\\ 35.60\\ 51.01\\ 74.84\\ 86.13\\ 89.09\\ 82.74\\ 67.02^a\end{array}$
	$\begin{array}{rrrr} \begin{array}{c} \text{sight,} & \text{Conen.,} \\ \text{rams} & \times 10^{3} \ \% \\ 17.3 & 12.34 \\ 31.0 & 18.57 \\ 52.4 & 22.27 \\ 45.3 & 23.68 \\ 42.6 & 15.33 \\ 39.3 & 8.40 \\ 34.6 & 4.76 \\ 36.9 & 3.66 \\ 44.8 & 2.79 \\ 31.3 & 4.73 \\ 55.2 & 1.74 \\ 52.1 & 1.77 \\ 52.1 & 1.77 \\ 52.1 & 1.77 \\ 52.1 & 1.77 \\ 52.3 & 23.23 \\ 20.8 \\ 26.0 \\ 89.9 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c cl(10) cl($