

The analysis of straight-chain aliphatics by urea partition chromatography and gas-solid chromatography

C_{15} through C_{36} *n*-paraffins and α -olefins from a low-temperature coal tar have been analyzed by a combination of urea adduction in a highly efficient liquid-liquid partition chromatography process followed by gas-solid chromatography on alumina-coated capillary columns operated up to 400° .

In previous work *n*-paraffins and α -olefins in the range C_{10} through C_{16} were successfully analyzed by gas-liquid chromatography on a polyphenyl ether column¹. However, this column could not be used for the characterization of pitch oils because the maximum operating temperature was 220° and even at this temperature there was some bleeding. In the present work it has been found that gas-solid chromatography with alumina-coated columns can be used at least as high as 400° for the analysis of aliphatic hydrocarbons at least through C_{36} . Standard urea adduction procedures failed to work on complex, high-boiling pitch oils, but it was found that a modification of a columnar process described in a patent² gave complete recovery of the straight-chain material.

A mixture of 40 parts by weight of urea and 60 parts of 20-100 mesh silica gel was packed dry in a 19 mm internal diameter, 23-in. length glass column. About 20 ml of a urea-saturated solution, in 90 volume % methanol and 10 volume % water, was passed through the column, and the excess was allowed to drain through. About 1 g of

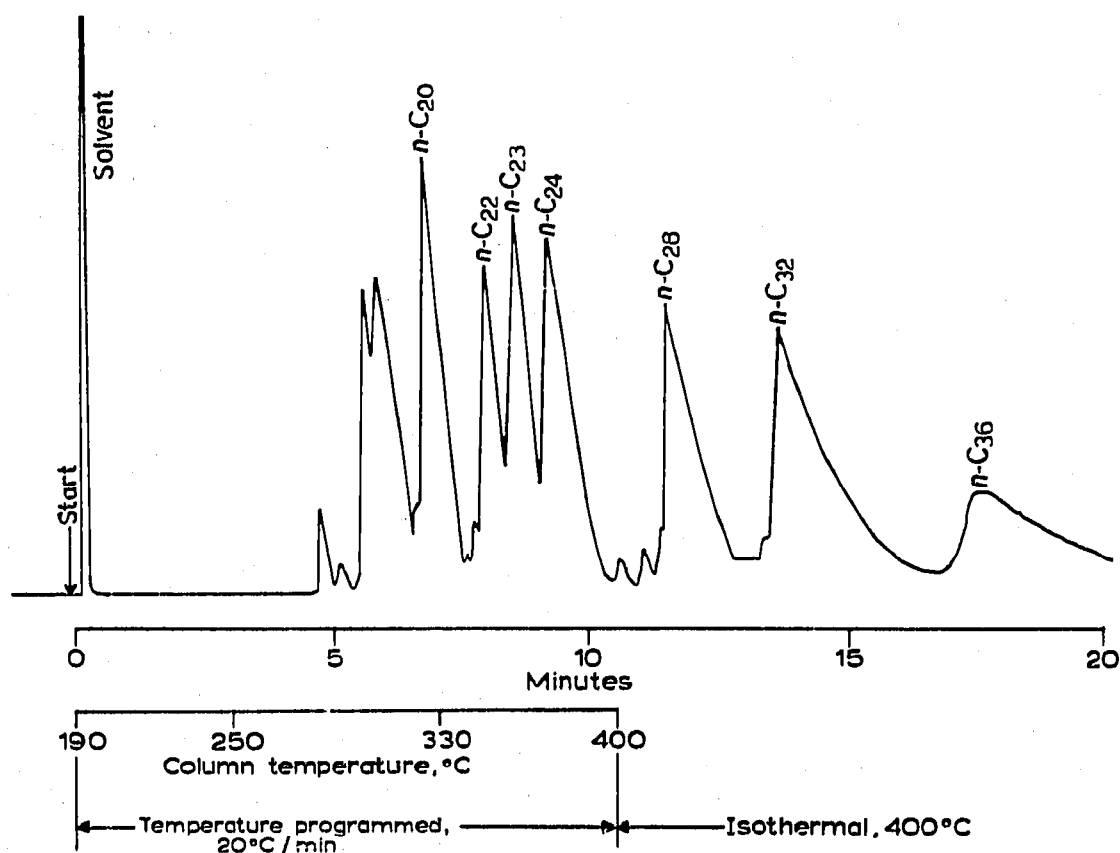


Fig. 1. Gas-solid chromatography of C_{20} through C_{36} *n*-paraffins on an alumina-coated column.

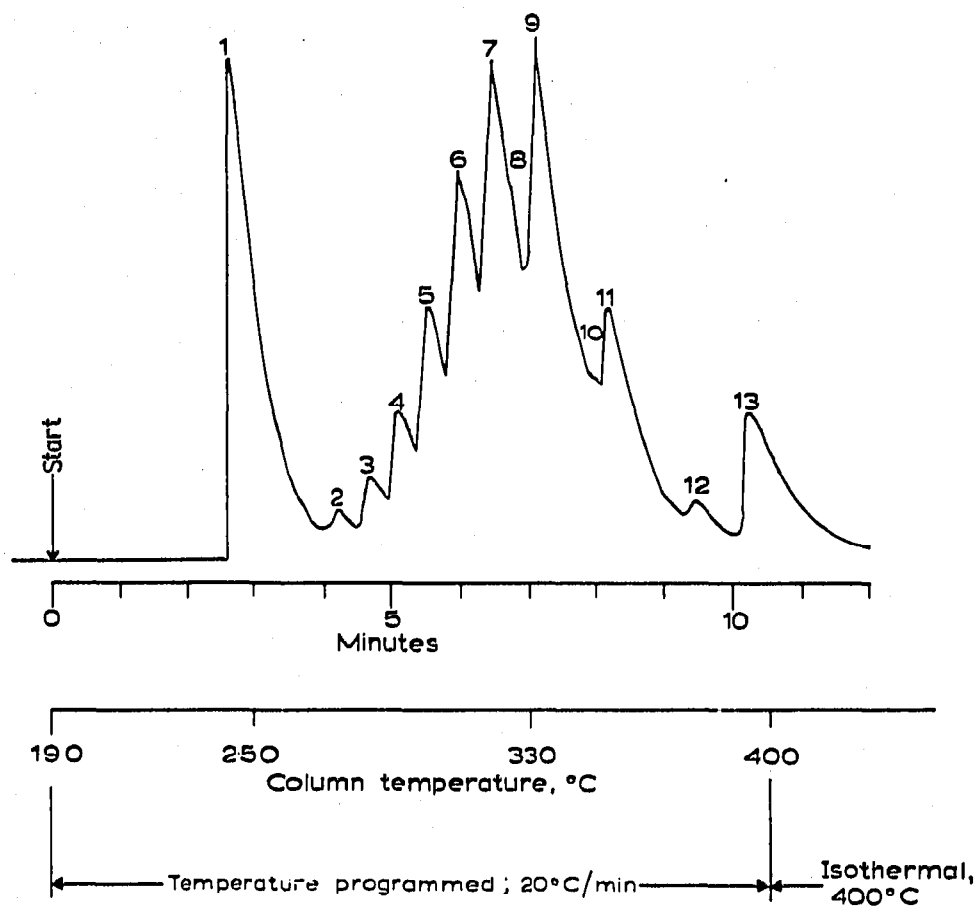


Fig. 2. Gas-solid chromatography of straight-chain aliphatic pitch oil fraction 1 (C_{15} - C_{21}).

the aliphatic pitch oil fraction was charged. If the sample was not entirely liquid, a little *n*-pentane was added to it. These fractions, containing the highest carbon number *n*-paraffins and α -olefins, had been obtained from the pitch of a low-temperature West Virginia bituminous coal tar. The uncomplexed, branched material was eluted from the column with about 20 ml *n*-pentane. About 40 ml water was passed through the column to destroy the complex. This was followed by about 20 ml *n*-pentane to dissolve out the released straight-chain material. The *n*-pentane solutions were each washed with equal volumes of water in a separatory funnel, and the *n*-pentane was removed with dry nitrogen. The yields of straight-chain material ranged from 41 to 61 weight %, and the yields of branched-chain material ranged from 39 to 59 weight % for these various fractions. Infrared analysis³ of the pitch oil fractions was in agreement with the results of the urea fractionations, and synthetic test mixtures yielded pure compounds as shown by subsequent gas chromatography. Infrared analysis³ of the urea adducted material indicated that it was free of branched paraffins and olefins. A small amount of *trans*-olefins was present but not sufficient to affect the quantitative analysis of the α -olefins.

A matched pair of 50 ft. by 0.02 in. internal diameter γ -alumina-coated aluminum capillary columns was used with a dual flame detector; temperature programming was 190° to 400° at 20° per min. The results with a synthetic mixture containing C_{20} , C_{22} , C_{23} , C_{24} , C_{28} , C_{32} , and C_{36} *n*-paraffins are shown in Fig. 1. Of

interest are the six or more unlabelled peaks in this chromatogram due to impurities present in some of these high carbon number samples. The straight-chain pitch oil fractions were analyzed in this manner, using a charge of from 0.4 to 1.6 microliters and an injection chamber temperature of 400°. The results for the lowest carbon number fraction, C₁₅ to C₂₁, are shown in Fig. 2. This fraction had been obtained from the pitch oil by a spinning band distillation at 0.02 mm Hg. These results are of interest because they demonstrate the presence of rather low carbon number aliphatics in the pitch and also show the carbon number distribution in this distillate fraction, with a maximum at C₁₇ to C₁₈. Peaks 1 and 13 are due to the internal standards *n*-tridecane

TABLE I

GAS-SOLID CHROMATOGRAPHIC ANALYSIS OF STRAIGHT-CHAIN ALIPHATICS FROM PITCH OIL FRACTION 1

Peak No.	Compound	Relative retention to <i>n</i> -C ₁₃	Weight %
1	<i>n</i> -Tridecane	1.00	(internal standard)
2	<i>n</i> -Pentadecane	1.61	0.5
3	1-Pentadecene	1.79	1.3
4	<i>n</i> -Hexadecane	1.96	2.1
5	1-Hexadecene	2.11	3.9
6	<i>n</i> -Heptadecane	2.27	7.6
7	1-Heptadecene	2.46	8.4
8	<i>n</i> -Octadecane	2.58	4.1
9	1-Octadecene	2.73	16.0
10	1-Nonadecene	3.06	1.2
11	<i>n</i> -Eicosane	3.15	6.9
12	1-Heneicosene	3.63	1.1
13	<i>n</i> -Tetracosane	3.94	(internal standard)

TABLE II

GAS-SOLID CHROMATOGRAPHIC ANALYSIS OF STRAIGHT-CHAIN ALIPHATICS FROM PITCH OIL FRACTION 4

Peak No.	Compound	Relative retention to <i>n</i> -C ₂₀	Weight %
1	<i>n</i> -Eicosane	1.00	(internal standard)
2	<i>n</i> -Pentacosane	1.46	0.1
3	1-Pentacosene	1.50	0.8
4	<i>n</i> -Hexacosane	1.56	1.4
5	1-Hexacosene	1.61	1.5
6	<i>n</i> -Heptacosane	1.64	4.2
7	<i>n</i> -Octacosane	1.70	8.9
8	1-Octacosene	1.78	2.2
9	<i>n</i> -Nonacosane	1.80	6.8
10	1-Nonacosene	1.89	2.0
11	<i>n</i> -Triacotane	1.91	4.2
12	1-Hentriacontene	2.02	1.7
13	<i>n</i> -Dotriacontane	2.07	3.2
14	<i>n</i> -Tritriacontane	2.20	1.1
15	1-Tritriacontene	2.28	1.7
16	1-Pentatriacontene	2.56	1.4

and *n*-tetracosane, respectively. The complete results for this fraction, and the highest carbon number fraction, are summarized in Tables I and II, respectively.

The individual *n*-paraffins and α -olefins were identified by means of relative retentions of pure compounds and correlation charts. It was found that the relative retentions of all α -olefins were equal to the relative retention of the *n*-paraffin of the same carbon number plus $5/8$ of the difference between the relative retention of that *n*-paraffin and the next higher *n*-paraffin. The resolution was not sufficient to obtain separate peaks for trace constituents so that an occasional carbon number in a series appeared to be missing. Studies with synthetic mixtures showed that if a significant quantity of a straight-chain compound was present a distinct peak was always obtained.

A variety of pitch oil fractions was analyzed by these procedures; *n*-paraffins in the range C_{15} through C_{33} and straight-chain olefins in the range C_{15} through C_{35} were identified and their amounts were determined. The results of the gas-solid chromatographic analysis of straight-chain pitch oil fractions on alumina-coated columns has demonstrated that the method will work on this high-boiling material, not more than 20 minutes being required per run. This particular use of these columns has apparently never been described.

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Zur Radiogaschromatographie von weissem Phosphor und Phosphorverbindungen

Weisser Phosphor und korrodierende Phosphorverbindungen wie PCl_3 , $POCl_3$ und Alkyl-Phosphorhalogenide lassen sich gaschromatographisch bestimmen, wenn die Teile des Gaschromatographen aus V2A-Stahl gefertigt sind. Bei Verwendung von Säulen aus 10 % Emulphor (Badische Anilin- und Sodafabrik AG) oder 10 % Silikonelastomer (Wacker Chemie GmbH) auf Kieselgur und Wasserstoff als Trägergas werden symmetrische Banden erhalten. Bei einer Säulenlänge von 2 m betrug die Zahl der theoretischen Böden *ca.* 3000.

Die in Fig. 1 gezeigte Messanordnung hat sich zur Radiogaschromatographie ^{32}P -markierter Verbindungen sehr bewährt. Mit Hilfe dieser Vorrichtung, die sich unmittelbar hinter der Wärmeleitfähigkeitszelle (Hersteller Fa. GowMac) befindet, wird die β -Aktivität des ^{32}P enthaltenden Gasstroms kontinuierlich mit Hilfe eines Zählrohrs gemessen. Das Zählrohr befindet sich hierbei auf Zimmertemperatur und

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