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Note

Rapid analysis of light hydrocarbons in stabilized crude oils by gas chromatography

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The direct analysis of crude oil in order to determine the constituents up to C_7^+ is a significant test for reservoir and production studies, and may reflect some of the characteristics of crude oil from the evaluation point of view. Gas chromatography provides excellent separations of very complex hydrocarbon mixtures in terms of accuracy, rapidity and simplicity.

Martin and Winters¹ were the first to attempt to determine the composition of crude oil up to C_7 by direct analysis in two stages. The volatile components were first separated from the crude oil by a precolumn and then passed into three chromatographic columns. All the columns were operated at room temperature and employed two internal standards, *cis*-2-pentene and ethyl acetate, and the time of analysis was *ca.* 3 h. Although this work was useful, the use of multiple columns to analyse complex samples boiling over a wide range is complicated and time consuming.

The Institute of Petroleum published a standard method² for the analysis of crude oils for C_2 – C_6 hydrocarbons by using Porapak Q precolumn and analytical columns and 2,2-dimethylbutane as an internal standard. However, this method was originally developed³ for North Sea crude oil, in which 2,2-dimethylbutane is not normally present. When the method is applied to other crudes, which may well contain 2,2-dimethylbutane, the latter is unsuitable as an internal standard.

British Petroleum⁴ developed another method, using a long capillary column attached to a precolumn and a backflushing technique, which is capable of determining individual hydrocarbons up to *n*-heptane, benzene and toluene and the carbon number distribution to C_9 . An indirect method for analysing crude oils has also been attempted⁵ in which distillation and gas chromatography using a capillary column and 1-pentene as an internal standard with temperature programming from 10 to 300°C are used to determine C_2 – C_{20} hydrocarbons. This type of procedure may result in inaccurate data, as losses of light hydrocarbons during the distillation are inevitable; in addition, the method is lengthy and requires considerable amounts of sample.

However, the analysis of crude oils for compounds above C_7 is not essential from the petroleum engineering point of view, where reporting of C_6 and C_7 as groups is the final goal and moving to a higher range will lead to erroneous results owing to the presence of sulphur, nitrogen and oxygen compounds in addition to the difficulty of providing high resolution for all hydrocarbons⁶. This paper described a rapid and

simple method for the analysis of crude oil employing a single conventional column with a precolumn containing a powerful adsorbent to eliminate sulphur-, nitrogen- and oxygen-containing compounds⁷ in addition to asphaltenic materials in order to obtain "genuine" hydrocarbons. For quantitative analysis, a non-hydrocarbon internal standard was added to the crude oil that would elute without interfering with the hydrocarbons of interest and that would meet the usual conditions for an internal standard.

EXPERIMENTAL

A Varian 3700 gas chromatograph equipped with a flame ionization detector (thermal conductivity detector is an alternative) and a Spectra-Physics 4270 computing integrator was used. Helium (purity 99.995%) was employed as the carrier gas and maintained at flow-rate of 25 ml/min in all experiments. A stainless-steel analytical column (4.5 m × 2.3 mm I.D.) packed with 10% (w/w) of Apiezon L on Chromosorb P AW (80–100 mesh) was used in conjunction with a stainless-steel precolumn (50 mm × 2.3 mm I.D.) packed with a 50:50 (w/w) mechanical mixture of molecular sieve type 5A and Fuller's earth (both 80–100 mesh). The operating conditions were as follows: column temperature, programmed from 60 to 180°C at 7°C/min; injection temperature, 150°C; detector temperature, 200°C; chart speed, 0.5 cm/min; sample size, 2 µl; and attenuation, 32.

High-purity chloroform was found to be a suitable internal standard, with good linearity over wide-range. Optimization was carried out, which indicated that addition of 4–5% (w/w) of chloroform to a known amount of stabilized crude oil was adequate. A sample of this mixture was shaken vigorously and introduced immediately by syringe into the gas chromatograph. To measure relative response factors, chloroform was mixed with known concentrations of high-purity hydrocarbons.

The crude oil sample was stored in a refrigerator before analysis. The addition of the internal standard may be done at ambient temperature and care was taken to minimize losses of light ends, and hence to improve the accuracy. Replacement of the precolumn packing after 25 injections is recommended in order to prevent contamination of the analytical column.

RESULTS AND DISCUSSION

Chromatographic analysis of hydrocarbons is normally effected with a non-polar liquid stationary, and in this work thermally stable Apiezon L on Chromosorb P was selected. The precolumn packing of a molecular sieve and Fuller's earth mixture was chosen on account of these adsorbents' ability to retain strongly sulphur-, nitrogen- and oxygen- containing compounds and asphaltenic materials; in addition, this packing provided the possibility to elute chloroform cleanly in the middle of chromatogram without interfering with hydrocarbons.

To confirm the accuracy of the results, standard mixtures of high-purity hydrocarbons and chloroform were prepared at different concentrations as indicated in Table I; the relative standard deviation did not exceed 0.55% in any instance.

Typical chromatogram of crude oil analysis is shown in Fig. 1, which illustrates a rapid separation in less than 10 min, including hexane components (the residue is

TABLE I
HYDROCARBON CONCENTRATIONS (% w/w) IN STANDARD MIXTURES DETERMINED BY GAS CHROMATOGRAPHY (GC) WITH A FIXED AMOUNT OF CHLOROFORM

Component	Sample 1		Sample 2		Sample 3	
	Actual concentration	GC measured ^a	Actual concentration	GC measured ^a	Actual concentration	GC measured ^a
<i>n</i> -Pentane	33.37	33.20	20.66	20.43	12.52	12.48
2,2-Dimethylbutane	2.93	2.96	1.50	1.49	0.74	0.73
<i>n</i> -Hexane	17.13	17.16	30.49	30.50	22.94	22.88
Benzene	5.73	5.55	7.57	7.62	9.36	9.28
<i>n</i> -Heptane	14.44	14.56	23.72	23.88	18.06	18.11
<i>n</i> -Octane	14.28	14.29	8.93	8.99	13.90	13.92
<i>n</i> -Nonane	8.61	8.57	2.58	2.64	16.69	16.65
<i>n</i> -Decane	3.51	3.71	4.55	4.45	5.79	5.95

^a Average of five runs.

considered to be C₇⁺). Fig. 2 shows an analysis in the presence of the internal standard, chloroform.

To obtain reliable results, relative response factors of hydrocarbons were

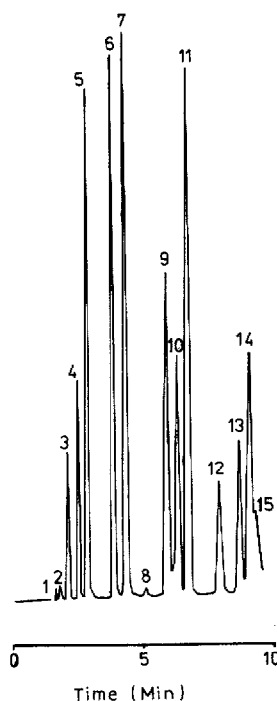


Fig. 1. Chromatogram of C₁-C₆ hydrocarbons in stabilized crude oil eluted from Apiezon L column by direct injection under conditions specified under Experimental. Peaks: 1 = C₁; 2 = C₂; 3 = C₃; 4 = iso-C₄; 5 = *n*-C₄; 6 = iso-C₅; 7 = *n*-C₅; 8-15 = C₆ components.

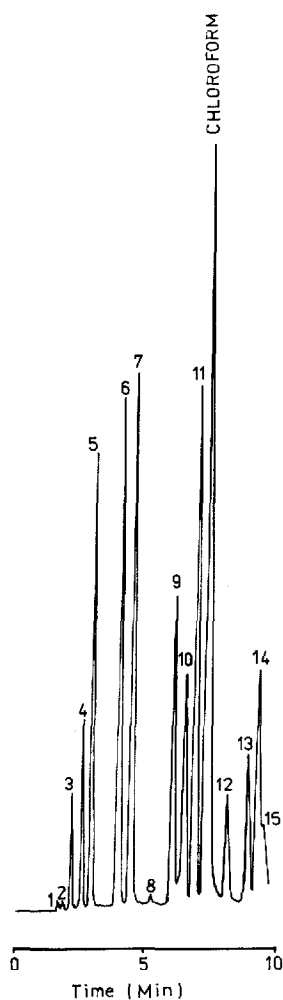


Fig. 2. Chromatogram of stabilized crude oil with chloroform as internal standard. Conditions and peaks as in Fig. 1.

calculated, and subsequently the concentrations of the hydrocarbons of interest were calculated by the equation

$$\text{Component (wt.\%)} = \left(\frac{TS}{GN} \right) \cdot 100 \cdot RRF$$

where T = peak area of component, G = peak area of chloroform, S = weight of chloroform, N = weight of crude oil and RRF = Relative response factor.

Table II gives results for the determination of light hydrocarbons in different types of stabilized crude oils yielded by a field separator (final stage of the production line). The determination of individual hydrocarbons up to C_5 in crude oils (produced

TABLE II

GAS CHROMATOGRAPHIC ANALYSIS OF DIFFERENT TYPE OF STABILIZED CRUDE OILS OBTAINED FROM A FIELD SEPARATOR

Results are expressed in % (w/w).

Component	Crude oil A (API = 40)	Crude oil B (API = 36)	Crude oil C (API = 27)
C ₁	0	0.03	0
C ₂	0.01	0.05	0.01
C ₃	0.12	0.25	0.27
iso-C ₄	0.15	0.42	0.20
n-C ₄	0.57	1.09	0.80
iso-C ₅	1.60	1.47	0.69
n-C ₅	3.55	1.59	0.99
C ₆ (group)	6.99	4.74	2.59
C ₇ ⁺	87.01	90.36	94.45
Total	100.00	100.00	100.00

under different conditions) is vital for selecting optimum conditions for field production, and Table III shows the analysis of a crude oil (API gravity 38) derived from a degassing operation by a laboratory separator at temperatures of 26, 50, 70 and 99°C, where the dramatic effect of temperature on the isolation of light hydrocarbons is observed.

A drawback of this method is the difficulty of injecting heavy crude oil (API gravity less than 20), which may be overcome by dilution with a suitable amount of an hydrocarbon heavier than C₇ (e.g., xylenes).

TABLE III

GAS CHROMATOGRAPHIC ANALYSIS OF CRUDE OIL (API GRAVITY 38) OBTAINED FROM A LABORATORY SEPARATOR AT DIFFERENT TEMPERATURES

Results are expressed in % (w/w).

Component	26°C	50°C	70°C	99°C
C ₁	Trace	0	0	0
C ₂	0.04	0.03	0.01	0
C ₃	0.31	0.25	0.19	0.05
iso-C ₄	0.33	0.22	0.12	0.05
n-C ₄	1.28	1.15	0.59	0.28
iso-C ₅	1.41	1.29	1.23	0.43
n-C ₅	2.06	1.95	1.25	0.79
C ₆ (group)	8.08	7.91	5.72	4.45
C ₇ ⁺	86.49	87.20	90.89	93.95
Total	100.00	100.00	100.00	100.00

CONCLUSION

The gas chromatographic determination of the light hydrocarbons composition up to C₇ in stabilized crude oils was accomplished in less than 10 min by a direct method using chloroform as a non-hydrocarbon internal standard. Genuine hydrocarbon peaks were obtained when a short precolumn packed with a molecular sieve and Fuller's earth mixture was incorporated to remove sulphur-, nitrogen- and oxygen-containing compounds.

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