Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Rapid Method of Identification and Assessment of Total Crude Oils and Crude Oil Fractions by Gel Permeation Chromatography

J. N. Done[a]; W. K. Reid[a]
[a] BP RESEARCH CENTRE THE BRITISH PETROLEUM COMPANY LIMITED SUNBURY-ON-THAMES, MIDDLESEX, ENGLAND

To cite this Article Done, J. N. and Reid, W. K.(1970) 'A Rapid Method of Identification and Assessment of Total Crude Oils and Crude Oil Fractions by Gel Permeation Chromatography', Separation Science and Technology, 5: 6, 825 — 842
To link to this Article: DOI: 10.1080/00372367008055543
URL: http://dx.doi.org/10.1080/00372367008055543

SEPARATION SCIENCE, 5(6), pp. 825–842, December, 1970

A Rapid Method of Identification and Assessment of Total Crude Oils and Crude Oil Fractions by Gel Permeation Chromatography*

J. N. DONE and W. K. REID
BP RESEARCH CENTRE
THE BRITISH PETROLEUM COMPANY LIMITED
SUNBURY-ON-THAMES, MIDDLESEX, ENGLAND

Summary

"Fingerprint" chromatograms of crude oils have been obtained using a simple gel permeation chromatographic system with a differential refractometer as detector and tetrahydrofuran as solvent. The elution time is less than 1 hr using a sample size of about 6 mg and the repeatability is good. When toluene is used as solvent, a different profile is obtained which is again unique for each crude oil.

The applications of this technique to crude oil assessment and composition of crude oil mixtures will be discussed since the "fingerprints" obtained have been shown to be unique for the 50 crude oils examined. Various crude oil fractions, e.g., gas oils and waxy distillates, have also been investigated. Chromatograms of oil pollution samples from the UK have indicated that certain types of pollution can be identified although present experience with a wide range of sample types is limited.

INTRODUCTION

The separation achieved by gel permeation chromatography (GPC), mainly based on molecular size, has given polymer and petroleum chemists a new method of attack on some of their more complex problems. Originally GPC using organic solvents was developed by Moore (*1*) who prepared cross-linked polystyrene gels of known pore

---

* Presented at the ACS Symposium on Gel Permeation Chromatography, sponsored by the Division of Petroleum Chemistry of the 159th National Meeting of the American Chemical Society, Houston, Texas, February, 1970.

size. The application of this technique to polymers (*2–4*) has been widespread using commercial apparatus (*5*) which produces molecular weight distribution analyses.

Although commercial instrumentation has been used almost exclusively in the polymer field, the petroleum chemist has been aware of the advantage of the gel permeation process. His usual approach, however, has been to conduct preparative scale separations and then characterize the fractions obtained by using such techniques as mass spectrometry, high temperature programmed gas liquid chromatography, NMR, etc. (*6–8*). Nevertheless, some molecular weight distributions of heavy petroleum materials have been reported using GPC (*9*). Bombaugh et al. have also shown (*10*) that it is possible to obtain chromatograms of total crude oils and have published the GPC chromatogram of a Kuwait crude oil before and after removal of the light ends by distillation. Other contributions have also been made by workers in the petroleum field to the fundamental studies of the GPC of both large and small molecules (*11, 12*).

This paper describes the use of a liquid chromatography detector (a Waters Associates R4 Differential Refractometer) in a simple GPC system to obtain chromatograms of total crude oils and crude oil fractions. By this method "fingerprint" chromatograms can be obtained in under 1 hr and the profiles have been shown to be unique for each of the crude oils examined.

The applications of the technique to crude oil identification, classification, and characterization and to crude oil fractions are discussed and so too is its application to the examination of oil pollution samples. Essentially the technique provides a simple, analytical scale separation procedure which produces results useful to the petroleum chemist.

EXPERIMENTAL

Columns of 60 Å Styragel (24 in. × 3/8 in. i.d.) were packed in both tetrahydrofuran (THF) and toluene using the high pressure packing apparatus previously described by Waters Associates (*13*). Both the solvents were redistilled before use and, during the chromatography, a nominal solvent flow of 70 ml/hr was maintained using a micropump (Type M, Distillers Company Limited) at a fixing setting. The efficiencies of the columns were estimated using samples of toluene and THF and the columns were found to have theoretical plate counts in excess of 2000/ft.

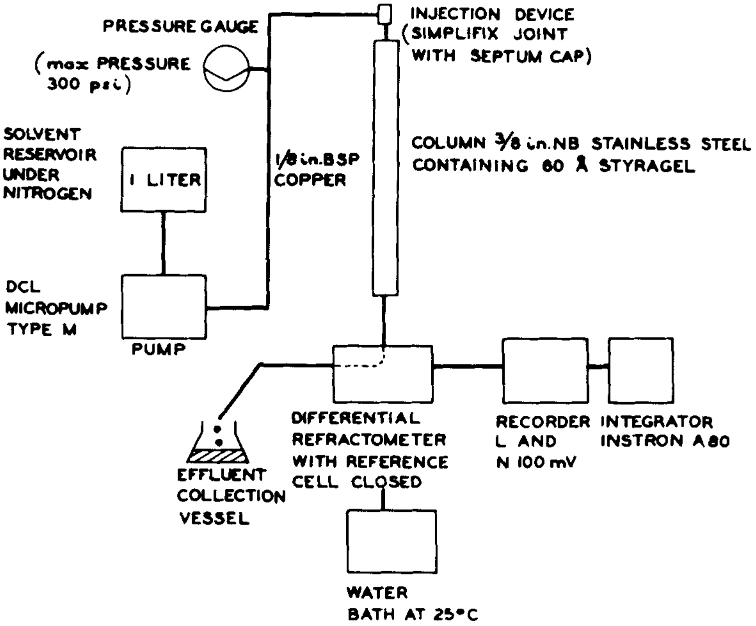

FIG. 1. Block diagram of system used to study crude oils and crude oil fractions by GPC.

The detector used in this work was a differential refractometer (Waters Associates), the inlet connections of which had been modified to reduce the dead volume. The reference cell, which was used with pure solvent trapped inside it, and the sample cell of the refractometer were kept at 25°C by a constant temperature water bath. A block diagram of the system is shown in Fig. 1.

The response of the detector will depend on the components being eluted and this complicates interpretation of the chromatograms. The use of the two separate solvents, THF and toluene, gives different chromatograms because the base refractive index (RI) is changed from 1.4040 to 1.4969. These effects will be discussed later in the paper.

Samples of crude oils, crude oil fractions, pollutants, and blends of crude oils and pure materials were run. The less viscous crude oil fractions and blends were injected without dilution but the other samples were first diluted in the ratio of 1:2 with solvent. The samples were injected with a microsyringe through a septum onto the column and each was run three times. The sample size chosen was between

TABLE 1

Typical Measurements of a Crude Oil Chromatogram to Give Figures for Profile Definition

	Distance of ordinate from exclusion peak (mm)																
	−8.5	−2	0	3	11	15.5	25	33	38	44.5	51	57	64	67.5	72	76	82
Height of ordinate (mm)																	
Run 1	3.5	166.1	226.1	155.7	94.2	93.0	83.8	74.2	64.3	50.3	40.6	30.5	20.3	22.1	15.2	6.1	0.5
Run 2	.3	162.3	231.9	158.8	92.2	90.9	82.0	72.6	63.5	49.8	39.4	32.0	21.1	22.1	14.7	5.1	0.8
Run 3	2.8	160.0	230.0	152.9	91.7	90.4	81.3	71.9	61.5	47.5	37.8	30.2	19.3	19.8	12.2	3.8	0.0
Average value	3.2	162.8	229.3	155.8	92.7	91.4	82.4	72.9	63.1	49.2	39.3	30.9	20.2	21.3	14.0	5.0	0.4

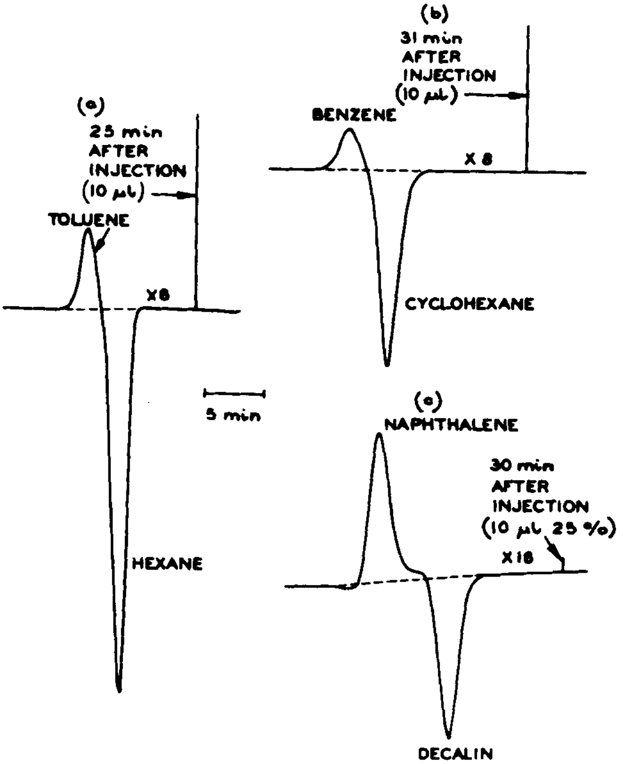

FIG. 2. GPC chromatograms of blends of pure hydrocarbons. Detector: Waters Differential Refractometer. Column: 2 ft × ⅜ in. NB stainless steel, 60 Å Styragel. Solvents: (a) tetrahydrofuran; (b) and (c) toluene. Temperature: 25°C.

10 and 30 µl depending on the response of the detector to the sample.

The chromatograms obtained using THF were treated in two ways. All of them were integrated to give the area of the exclusion peak and the total area using an Instron A80 integrator. Three chromatograms of each crude oil were run and the average values calculated. Using the average figures, the per cent area corresponding to the exclusion peak and the response of the sample, measured in counts per milligram, were calculated. The chromatograms obtained for 16 crudes were defined by measuring the height of the profile above the baseline at a number of fixed distances from the exclusion peak. The three repeat chromatograms produced for each of the crudes were treated in this way and the average values calculated. A typical set of figures for the Kuwait crude oil is shown in Table 1.

All the crude oil samples were also chromatographed using toluene as solvent. Kuwait crude oil fractions were run using both solvents while the blends of pure materials were run under the column conditions given in Fig. 2.

RESULTS AND DISCUSSION

The authors consider that this technique of examining crude oils by GPC is novel and that it may have a wide range of applications in petroleum and refining technology.

The chromatograms obtained in this work from crude oils and crude oil fractions are essentially plots of change of RI compared to a reference against molecular weight or, more correctly, molecular size. The two parameters of RI and molecular weight are important in petroleum technology and have been utilized previously, for example in the n-D-M method (*14*), for characterizing and analyzing petroleum materials. The peaks and valleys produced in the GPC "fingerprints" of crude oils and crude oil fractions are obviously related to types and amounts of hydrocarbons present, although the present work has not considered this in detail.

Important features of this work are the production of chromatograms in only 40 min and the requirement for less than 10 mg of crude oil. It is considered that the technique could easily be put on a routine basis and, furthermore, as the residence time of the components of the oil is between 20 and 40 min, samples can be injected about every 20 min without risk of overlap. Thus, in practice, 3 chromatograms can be produced in each hour. The cost of the equipment is approximately £1700 ($4000), including refractometer, recorder, integrator, and pump.

The use of efficient columns with different pore sizes from those considered here may well reveal more detail in the exclusion peak of the chromatogram. However, the aim of the present system has been to keep the technique as simple and as rapid as possible.

Pure Compound Blends

It is well known that adsorption effects in GPC cannot be ignored and some blends of pure hydrocarbons have been examined on the present GPC system to determine the magnitude of this effect in toluene and THF. The chromatograms obtained from blends of aromatic hydrocarbons with saturated hydrocarbons of approximately the same molecular weight (Fig. 2) show that adsorption of the aromatics occurs both in toluene and THF. This is evident from the increased elution time of the aromatics compared to saturate compounds of the same average molecular size. It can also be seen that this adsorption effect is more pronounced in toluene and that the use of toluene as solvent (and thus as reference) can indicate the aromatic or saturate nature of crude oils or crude oil fractions from the positive or negative peaks.

Crude Oil Fractions

Crude oil fractions from Kuwait crude oil, gasoline (C_5, 149°C), kerosene (149–232°C), light gas oil (232–343°C), heavy gas oil (343–371°C), waxy distillate (371–525°C), and residue (>525°C), have all

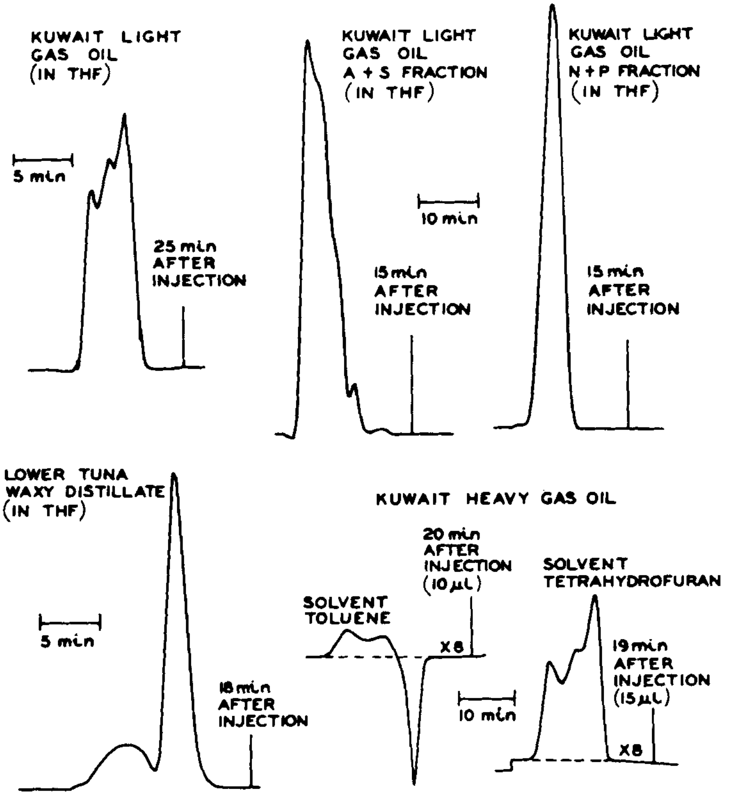

FIG. 3. GPC profiles of petroleum fractions.

<table>
<tr><th>Group</th><th>"Fingerprint"</th><th colspan="4">Approximate Grouping according to "Fingerprint" Type in THF</th></tr>
<tr><td>A</td><td></td><td colspan="4">Amna, Khafji, Kuwait, Ratawi, Arabian Heavy, Sarir, Tia Juana 102LP, Bachaquero (Venezuela), Trinidad Soldado, Marguerite Lake (Canada)</td></tr>
<tr><td>B</td><td></td><td colspan="4">Iranian Light, Arabian Light, IMEG "A", IMEG "B", Iranian Heavy Middle Ground Shoal, Soldatno Creek Swanson River (both Alaska) Fyzabad (Trinidad), Oficina (Venezuela), Kern River (USA)</td></tr>
<tr><td>C</td><td></td><td colspan="4">Arzew Blend, Zarzaitine (Algeria), ADLEG, Qatar, ADMEG (Umm Shaif), ADMEG (Zakum)</td></tr>
<tr><td>D</td><td></td><td colspan="4">Ebocha, Imo River, Nigerian Light, Obigbo North (all Nigeria)</td></tr>
<tr><td>E</td><td></td><td colspan="4">Flounder, Halibut, Kingfish, Lower Tuna (all Australia) Maui (New Zealand)</td></tr>
<tr><td rowspan="2">Profiles not occurring in the above groups</td><td>
Moonie (Australia)</td><td>
Cori (Libya)</td><td>
Minas (Sumatra)</td><td>
Puri (Papua)</td></tr>
<tr><td>
Barracouta (Australia)</td><td></td><td></td><td>
Kapuni (New Zealand)</td></tr>
</table>

FIG. 4.

been chromatographed using both THF and toluene as solvent. From these results it was shown that 60 Å Styragel excluded the residue from the pores and effected fractionation of the remainder. Adsorption of the aromatics in each fraction was evident with both solvents and confirmation of this was obtained by studying fractions obtained by silica gel chromatography of Kuwait light gas oil. The chromatograms in THF of the two main fractions (A + S and N + P) showed that the N + P fraction eluted first followed by the A + S fraction which gave a much broader peak. Work on the waxy distillates from two Australian crudes has shown that this separation by polarity is also occurring with these fractions. The chromatograms obtained in toluene all show more extensive adsorption than in THF. The appropriate chromatograms, not all on the same scale, are shown in Fig. 3.

The extension of this work to a wide variety of fractions, use of longer columns, and the use of different gels and solvents could, it is believed, lead to a much greater use of GPC in the study of petroleum

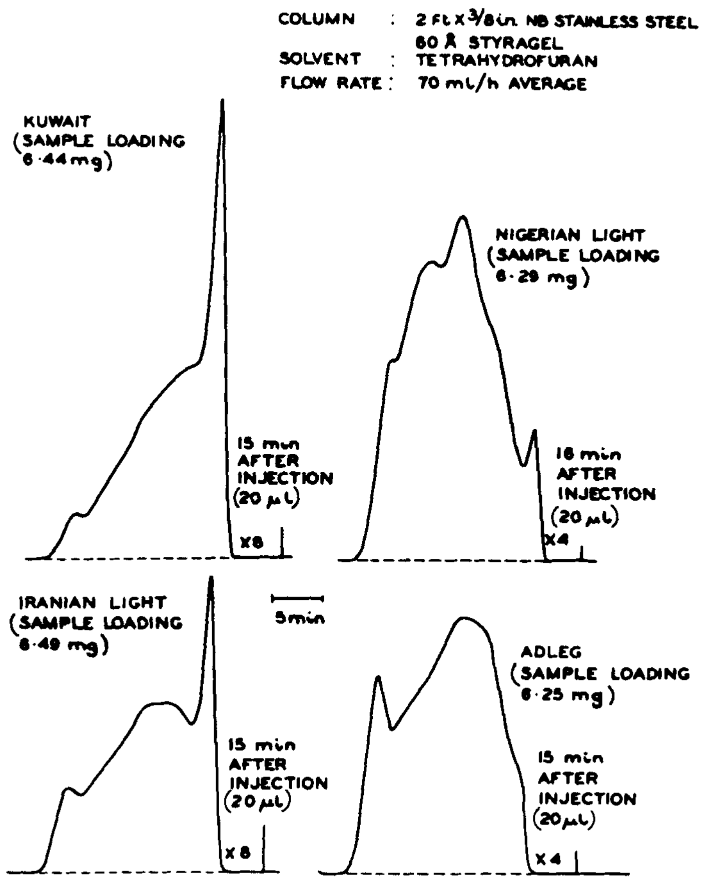

FIG. 5. Examples of GPC chromatograms of crude oils. Column: 2 ft × ⅜ in. NB stainless steel, 60 Å Styragel. Solvent: tetrahydrofuran. Flow rate: 70 ml/hr average.

fractions. The interpretation of these chromatograms would, however, not be straightforward as the response of the detector to different A + S fractions would not necessarily be the same due to compositional differences.

Crude Oils

By using the experimental conditions discussed above, over 40 crude oils listed in Fig. 4 have been chromatographed. Each chromatogram obtained has been shown to be unique and may be considered as a

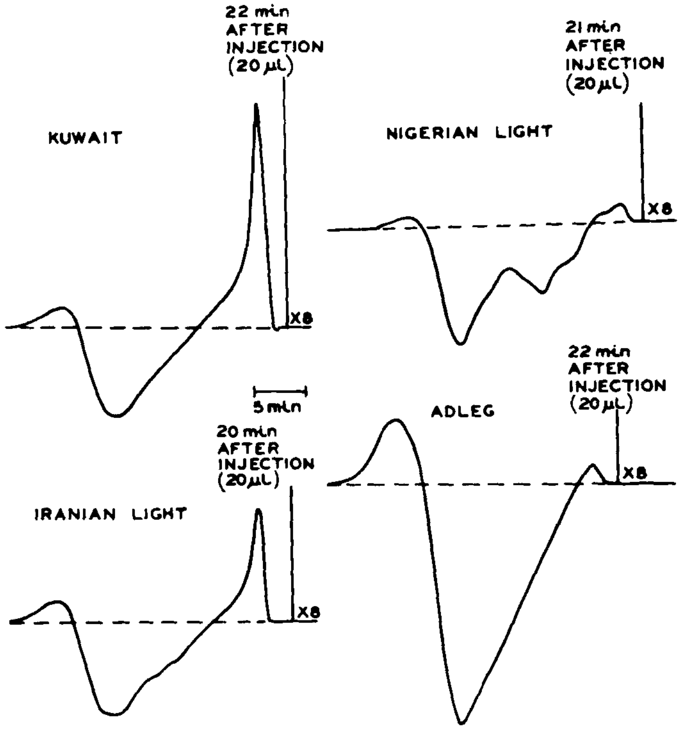

FIG. 6. GPC chromatograms of crude oils using toluene as solvent (compare Fig. 5). Column: 2 ft × $\frac{3}{8}$ in. NB stainless steel, 60 Å Styragel.

"fingerprint" of the crude oil. Four examples of such chromatograms are shown in Fig. 5 for Kuwait, Nigerian Light, Iranian Light, and ADLEG crude oils in THF. When the solvent is changed to toluene, different, but once again "fingerprint" chromatograms are obtained for these crudes as shown in Fig. 6.

Although unique, the crude oil chromatograms fall into definite classes depending mainly on the light or heavy nature of the crudes. The four Gippsland crudes, Kingfish, Flounder, Lower Tuna, and Halibut, give similar chromatograms in THF with little or no exclusion peak visible. However, each chromatogram has a characteristic pattern as is shown in Fig. 7. In addition, profiles in THF of two North American crudes, a South American crude, and one Russian crude are shown in Fig. 8.

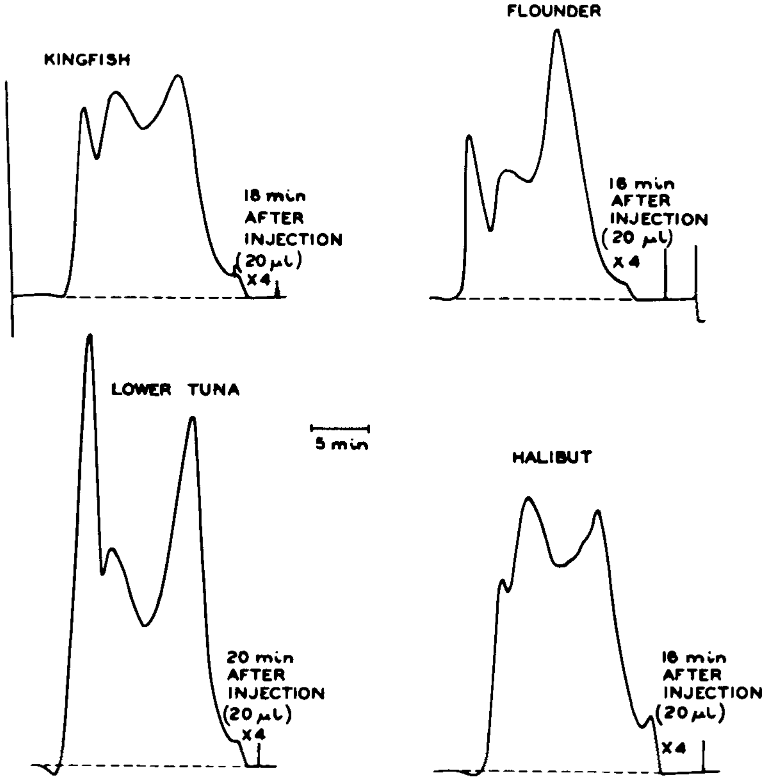

FIG. 7. GPC chromatograms of four Gippsland crudes using tetrahydrofuran as solvent.

The definition of a crude oil by a unique "fingerprint" is obviously valuable, and this technique may prove a quick method for examining a new crude or crude blend as information on the general character of the material can be established very quickly.

The fingerprints, although unique for each crude, appear to fall into definite groups as shown in Fig. 4. The significance of these similarities is, however, not yet understood. Obviously they do not correspond to the traditional methods of classification and, apart from the Nigerian and Australian crudes, there is no geographical or geological correlation.

Some of the crude profiles obtained do not fall into these groups and these are noted also in Fig. 4. These in general tend to be the profiles

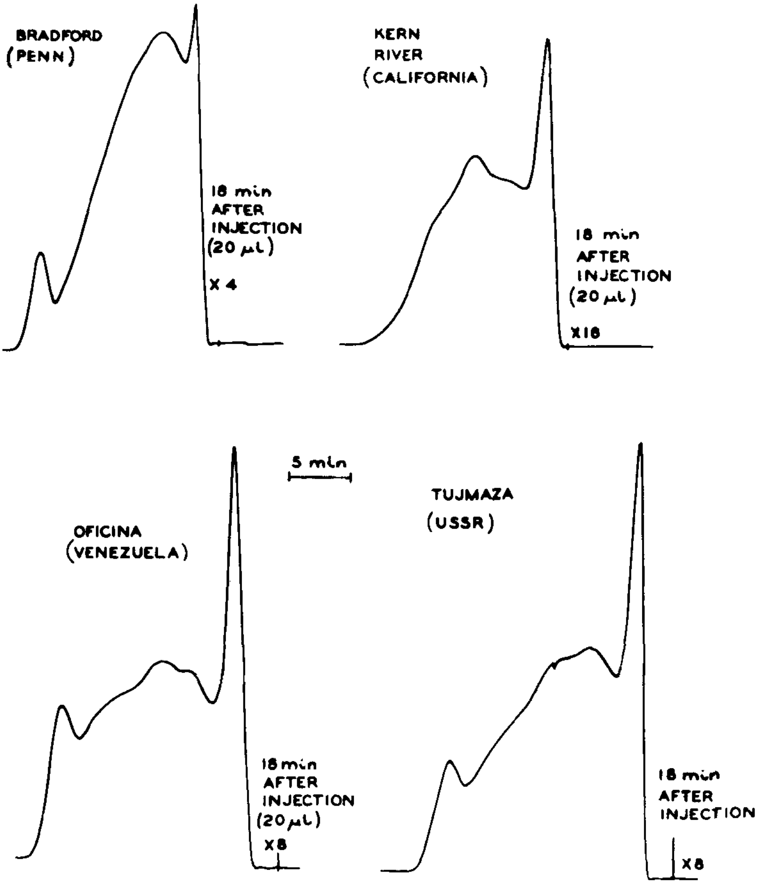

FIG. 8. Further examples of crude oil profiles on tetrahydrofuran.

from the lighter crudes. The "fingerprint" obtained from Barracouta crude is worthy of mention. From the chromatogram, which has a large negative peak in the low molecular region and a very small exclusion peak, it can be concluded that this is a light crude with a large amount of paraffinic material in the low molecular weight portion and having practically no residue above 525°C. This has been confirmed by GLC analysis and distillation.

Chromatograms in THF have been obtained from different wells in the same field. In the two fields examined, Imo River and Zakum, the different well samples give different profiles, although those from the Zakum wells were very similar to each other.

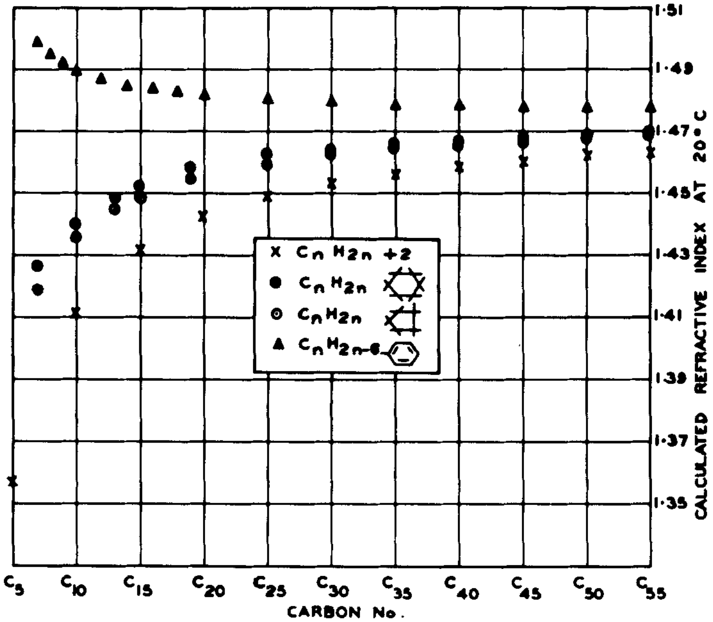

FIG. 9. Graph of refractive index vs. carbon number of four series of hydrocarbons.

Interpretation of Profiles

The interpretation of the profiles is dependent on knowledge of the refractive index of the components eluted. The calculated refractive indices (*15*) of four series of hydrocarbons are shown in Fig. 9. It can be seen that the values appear to approach a common figure as the molecular weight increases, and that in the low molecular weight region the differences in refractive index are greatest. This means that interpretation of the profile with respect to hydrocarbon type will have most meaning in the low molecular weight region of the profile. A qualitative estimate of the aromatic nature of the light end of the crude can thus be obtained by inspection of the final peak which is evident in many of the profiles. These estimates are, however, complicated by the fact that adsorption of polycyclic aromatics occurs and di- and tricyclic aromatics elute in the same region as monocyclic aromatics.

Another feature of this region of the profile is the accentuation of the final aromatic peak by the low molecular weight saturated and cyclic hydrocarbons. These compounds elute just before the aromatic peak and give a negative contribution to the response. Consequently the over-all effect observed in THF is a fairly sharp terminal peak. This effect is, however, most evident in the chromatograms using toluene when a large negative peak is nearly always present just before the final positive aromatic peak.

General interpretation is complicated by the overlap of aromatic hydrocarbons with nonaromatic hydrocarbons of lower molecular weight. The presence of polycyclic aromatics in certain crude oil fractions may also have considerable effect on the response since these compounds have appreciably higher refractive indices than nonaromatic and monocyclic aromatic hydrocarbons.

It can thus be seen that the interpretation of the profiles with respect to hydrocarbon composition of the crude is extremely difficult although it is possible to obtain some information of this nature from the profile.

Repeatability

In order for this technique to be useful in the applications discussed in this paper, the repeatability of the method must be good. It has been found that consecutive injections give good repeatability but poor injections or slight variations in flow rate do alter the peak height and the total peak width. However, with repeat injections of samples made up at different times, up to 2 weeks apart, slight differences have occurred in the low molecular weight region of the chromatogram. This could mean that the crude has lost some of the light ends or that water has been absorbed during storage. It is important therefore to ensure representative sampling of the crude and that water contamination be avoided if repeatable chromatograms are to be obtained. However, both short-term and long-term repeatability should be improved if the chromatographic conditions are carefully controlled.

Corrections can be applied to the chromatograms if the flow rate has differed from a standard value. Using the ratio of elution time of the whole profile to elution time of a standard chromatogram obtained at a fixed flow rate of 1.1 ml/min, the total area can be corrected to this standard elution time. The position of the ordinates used for the definition of the crude can also be corrected using this ratio.

Examples of the repeatability of consecutive runs of some of the crude oils are shown in Tables 1 and 2. The repeatability of the total

TABLE 2

Repeatability of Exclusion Peak Areas and Total Areas

Crude oil	Country of origin	Exclusion peak				Total			
		Run 1	Run 2	Run 3	Mean	Run 1	Run 2	Run 3	Mean
Kuwait Export	Kuwait	6516	6406	6220	6381	24143	23450	23455	23683
Amna	Libya	7380	7558	7648	7529	20127	19821	20635	20194
Khafji	Neutral Zone	6724	7110	7738	7191	17551	17902	17908	17787
Iranian Light	Iran	3802	3852	3814	3823	22271	21846	22482	22200
Arabian Light	Saudi Arabia	3734	3374	3668	3592	20966	20842	20575	20794
Ratawi	Neutral Zone	7305	6958	5978	6747	17638	17604	17415	17552
Sarir (Tobruk)	Libya	6186	5824	6254	6088	17575	17828	18086	17833
IMEG "A"	Iraq	5078	5228	5148	5151	26589	26666	26233	26495
IMEG "B"	Iraq	4418	4758	4650	4609	20989	21340	20788	21039
Tia Juana 102LP	Venezuela West	6176	6194	6340	6237	19792	20074	19929	19931
Arabian Heavy	Saudi Arabia	5126	6116	6440	5894	16220	16626	16517	16422
Nigerian Light	Nigeria	1376	1468	1488	1444	34670	34321	34090	34360
ADMEG (Zakum)	Abu Dhabi	3732	3718	3614	3688	40386	38922	38527	39193
Arzew Blend	Algeria	1614	1624		1619	26687	26358		26522
ADLEG	Abu Dhabi	2076	2112	2124	2106	30576	31354	31027	30986
Iranian Heavy	Iran	5856	5814	5716	5795	25182	24780	24262	24741

area is better than that of the exclusion peak. With some of the samples, such as Zakum crude, the exclusion peak measurement is difficult due to incomplete resolution.

Crude Oil Properties

Since the chromatographic profile of each crude oil examined to date appears to be unique, the possibility of determining crude oil properties by this method is being examined. Already it has been possible to estimate fraction yields from the chromatograms with reasonable accuracy.

For example, from investigations on Kuwait crude oil fractions it was shown that 60 Å Styragel excluded completely the crude residue (>525°C). Therefore the area of the exclusion peak should be related to actual per cent of residue and this has been shown to be reasonably correct.

The possibility of the method being used to estimate rapidly the amount of each crude in a crude oil blend has also been examined. Results to date are encouraging, although the accuracy of the estimates for a wide range of crudes and complexity of blends has not yet been established.

Oil Pollution

Work on oil pollution has so far been somewhat limited. However, whenever samples have been available they have been examined using the GPC system here described. The GPC chromatograms of two types of pollutants in the two solvents are shown in Fig. 10. Examples of the three main types of pollution, weathered crude oil, crude oil sludge, and fuel oil, have been examined and it is considered that with further experience, identification of the type of pollution will be possible.

As would be expected, the profile from the weathered crude (see Fig. 10) is similar to its parent crude (see Fig. 5) except that loss of light material is evident. Crude oil sludges, since they are crudes with extra waxy material, should give a profile similar to the weathered crude with an extra peak due to the wax just after the exclusion peak. This has been shown to be so for two crude oil sludge samples. Fuel oil pollution is the most difficult to deal with due to the wide variety of fuel oils used. It has been found, however, that the sharp cutoff in the chromatogram in the low molecular weight region is, so far, the best indication that the pollutant is a fuel oil.

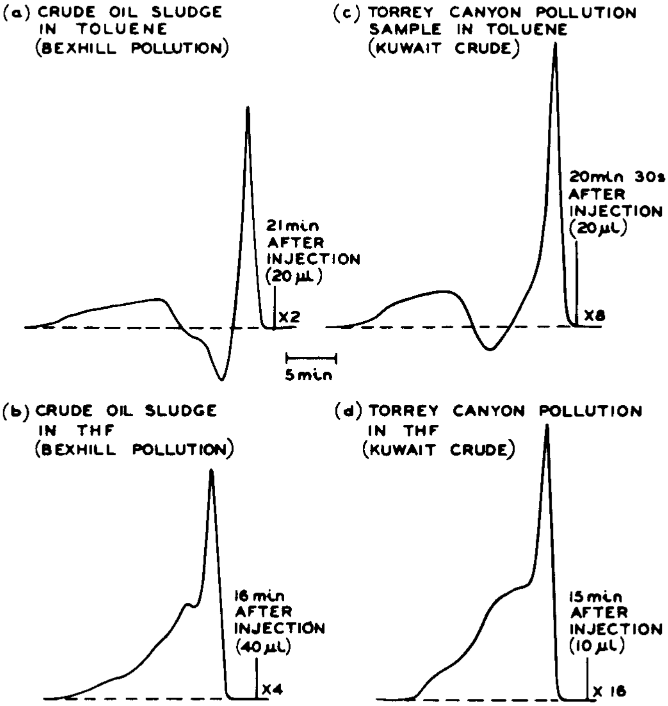

FIG. 10. GPC chromatograms of two pollution samples in toluene and tetrahydrofuran.

In the study of pollution, GPC has the distinct advantage that a profile of the *total* sample can be obtained rapidly. Present methods of pollution identification (*16*) are based on sulfur, vanadium, and nickel contents and GLC analysis, the latter being restricted by the relative involatility of the sample. GPC may well prove to be a valuable additional method for pollution analysis.

CONCLUSIONS

A rapid, relatively inexpensive method of producing GPC profiles of total crude oils has been developed. Each crude oil gives a unique chromatogram which, it is considered, opens up many possibilities for the application of the technique in the petroleum industry. The identification and partial characterization of crude oils and to a lesser extent crude oil fractions is considered to be possible, and further applications to crude oil blends and oil pollution problems have been indicated.

Further development of the technique, by using different size gels, different solvents, thermostatic control of columns, and possibly longer columns is obviously important in order to realize its full potential.

Acknowledgment

Permission to publish this paper has been given by The British Petroleum Company Limited.

REFERENCES

1. J. C. Moore, *J. Polym. Sci., Part A,* **2,** 835 (1964).
2. J. Cazes, *J. Chem. Educ.,* **43,** A567 (1966).
3. M. Determann, *Angew. Chem. Internat. Ed.,* **3,** 608 (1964).
4. R. L. Pecsok and D. Saunders, *Separ. Sci.,* **1**(5), 613 (1966).
5. J. Cazes, *J. Chem. Educ.,* **43,** A625 (1966).
6. K. H. Altgelt, American Chemical Society, Division of Petroleum Chemistry, Atlantic City Meeting, September, 1965.
7. K. H. Altgelt, *J. Appl. Polym. Sci.,* **9,** 3389 (1965).
8. H. J. Coleman, D. E. Hirsch, and J. E. Dooley, *Anal. Chem.,* **41,** 800 (1969).
9. W. B. Richman, *Molecular Weight Distribution of Asphalts,* Waters Associates, Framingham, Massachusetts.
10. K. J. Bombaugh, W. A. Dark, and R. F. Levangie, *Separ. Sci.,* **3,** 375 (1968).
11. P. C. Talarico, E. W. Albaugh, and R. E. Snyder, *Anal. Chem.,* **40,** 2192 (1968).
12. B. J. Mair, P. T. R. Hwang, and R. G. Ruberto, *Anal. Chem.,* **39,** 838 (1967).
13. Waters Associates Inc., *Polystyrene Gel Column Packing,* Framingham, Massachusetts.
14. K. Van Nes and H. A. van Westen, *Aspects of the Constitution of Mineral Oils,* Elsevier, Amsterdam, 1951.
15. Ref. *14,* p. 81.
16. J. V. Brunnock, D. F. Duckworth, and G. G. Stevens, *J. Inst. Petrol.,* **54,** 310 (1968).

Received by editor September 1, 1969