THERMOGRAVIMETRIC STUDIES ON SOME IRAQI CRUDE OILS

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A rapid method for the characterization of some Iraqi crude oils is described, based on thermogravimetric data obtained using a selected heating program.

The data relating to light, middle and heavy cuts of the crudes, together with their residues estimated from the thermal curves, correlated well with the API gravity as well as with the sulphur and metal contents.

With the above technique, these parameters were also shown to change with depth in a given well.

Crude oils are complex mixtures; they differ in the contents of metals and sulphur and the types of hydrocarbon etc. Analytical methods make use of these different parameters in characterization of the oils. Techniques such as combined gas chromatography–mass spectrometry [1], pyrolysis gas chromatography [2], capillary gas chromatography [3], infrared spectroscopy [4], atomic absorption spectrophotometry [5], and the joint ASTM–IP methods for distillation ratios [6, 7], ash content [8], carbon [9], density and API gravity [10], are normally applied in this context.

Thermoanalytical methods are gaining more applications in this field [11]. Bae [12] applied the high-pressure thermobalance and thermogravimetry (TG) to determine the fire flooding conditions characteristic of crude oils [13]. TG has been used to determine the heavy tar fraction [14]. Dyszel [15] modified a rapid temperature-programmed TG procedure to distinguish Alaskan crudes from imported ones. The program included heating steps at a constant rate of 160 deg/min and isothermal steps at 350°, 500° and 750° for predetermined time intervals. The final step was combustion of the residue in air atmosphere between 500° and 750°. The study [15] did not take the compositions of the crudes into consideration as a basis for the explanation of the results.

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The present investigation involves the application of programmed thermogravimetry to some Iraqi crude oils and correlation of the results with their API gravity, and heavy metal and sulphur contents.

Experimental

Samples: Nine export crude oils were used in this investigation. The relevant data on these crudes are presented in Table 1.

Apparatus: The thermobalance used was a Heraeus TA 500 System. Heavy metal analyses were carried out with a Pye–Unicam SP 9–800 atomic absorption spectrophotometer.

Program: The selected program involved heating the crude oils to 350°, holding the temperature isothermal for 2.5 minutes, followed by heating to 550° and maintaining the temperature for 2 minutes at this level. The heating rate used was 100 deg/min. (Fig. 1.) Samples of 5–10 mg crude oil were placed in platinum crucibles and heated in a nitrogen atmosphere flowing at 250 cm^3/min.

Table 1 Some characteristics of the studied crude oils

Oil field[a]	S, %[b]	V, ppm[c]	Ni, ppm[c]	API
1	0.9	11.0	9.7	42.0
2	0.62	14.4	7.9	40.0
3	1.67	25.0	21.0	38.5
4	1.75	55.0	13.1	36.6
5	1.97	65.0	31.0	36.0
6	2.74	67.0	33.0	33.0
7	1.9	31.0	18.0	32.3
8	2.82	217.0	19.7	30.8
9	2.62	66.0	16.0	29.9

[a] Crude oils 1 and 2 form group one, crudes 3–7 form group two, and crudes 8 and 9 form group three; [b] determined according to IP method; [c] measured using atomic absorption spectrophotometry.

Results and discussion

The approximate API gravity and the sulphur and metal contents of the crude oils studied, together with their location, are shown in Table 1. The main features of the TG curves of the crudes are shown in Figs 2–4, representing high, medium and low API gravity, respectively. Data extracted from these curves are given in Table 2.

The first group, 1 and 2, has API gravity 42–40 and were the lightest. The light and middle fractions, referred to as L and M (temperature range: ambient–350°), were

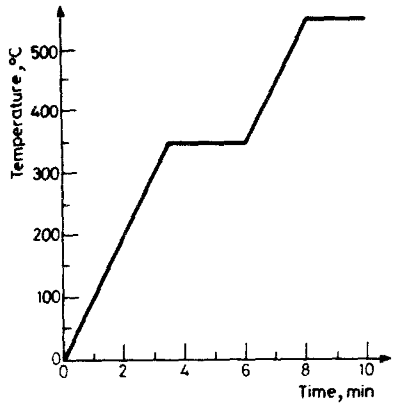

Fig. 1 Heating program

Table 2 Thermogravimetric data on the studied crude oils[a]

Field	(L + M),[b] %	*H*,[c] %	R, %	(L + M)/(H + R)
1	89.8	4.9	5.3	8.8
2	88.5	6.66	3.2	8.1
3	80.8	10.5	8.8	4.2
4	78.8	17.0	4.2	3.7
5	77.2	15.5	7.65	3.3
6	70.8	19.5	9.7	2.42
7	76.4	17.9	5.7	3.2
8	69.8	16.0	14.2	2.3
9	71.5	21.1	7.4	2.5

[a] Average of 3 determinations; [b] weight loss from start till end of 350 °C + hold; [c] weight loss from 350 °C + hold to end of 550 °C + hold.

Table 3 Thermogravimetric data on crude oil 4 taken from two different depths

Depth, m	(L + M), %	*H* frac., %	Residue, %	(L + M)/(H + R)
1040–1050	83.21	13.58	3.21	4.95
1067–1077	78.07	18.55	3.38	3.55

approximately 88–90%. They differ in their heavy cut fraction, referred to as H (temperature range: 350–550°), and the residues R. However, the (L + M)/(H + R) ratios were very similar (8.1–8.8) and were distinctly high compared to other studied crudes.

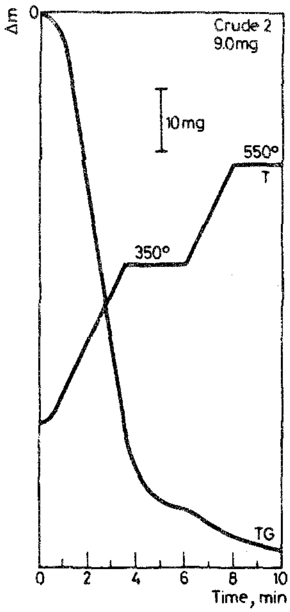

Fig. 2 TG curve of high API gravity crude (40.0)

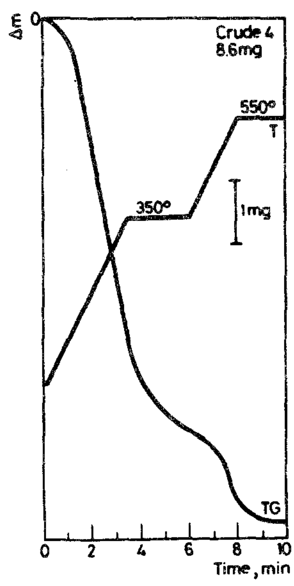

Fig. 3 TG curve of medium API gravity crude (36.6)

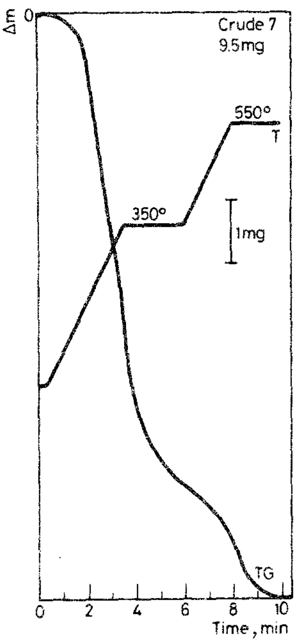

Fig. 4 TG curve of low API gravity crude (32.3)

The second group, 3–7, had API gravity 38.5–32.2, were characterized by an (L + M) fraction ranging from 71 to 80%, and differed in their heavy cut and residues. Their (L + M)/(H + R) ratios were a function of the API gravity and ranged from 4.2 to 3.2. Crude oil 6 was an exception: it had a higher (H + R) percentage and gave an (L + M)/(H + R) ratio of 2.4. Crude oils 4 and 5 were fairly similar, with ratios of 3.7 and 3.3, respectively.

The third group, 8 and 9, which were relatively heavy crude oils, gave (L + M)/(H + R) ratios of 2.3 and 2.5.

A plot of the (L + M)/(H + R) ratio versus API gravity is shown in Fig. 6; it seems to exhibit an exponential relation. It was interesting to observe that the release of some of the (L + M) fractions and also some of the heavy cuts was not uniform and complete in the heating-up periods of the heating program. In some instances, up to 20% was released in the hold-up periods, which indicated association behaviour and pyrolysis.

Correlation of the TG data with sulphur and metal contents: The percentages of the (L + M) fraction were plotted against the sulphur contents of the corresponding crude oils, as shown in Fig. 5. It seems that the sum of the light and middle cuts of the crudes is inversely proportional to the sulphur content. To extend this correlation, a sample of a condensate with a sulphur content of 0.13% was similarly analyzed, and

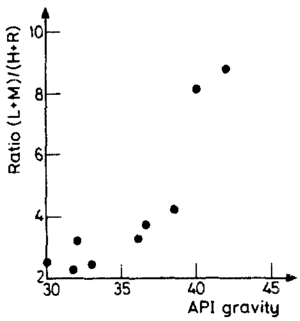

Fig. 5 Correlation between (L + M)/(H + R) ratio and API gravity

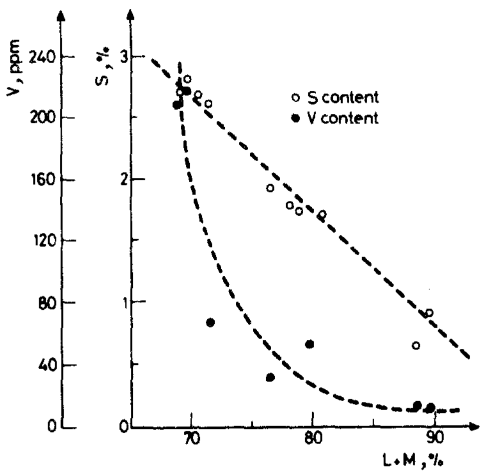

Fig. 6 Correlation between sulphur and vanadium contents and (L + M) percentages

complete volatilization was obtained up to 350°. The vanadium contents of the crudes were plotted against the (L + M) fraction, and can also be seen in Fig. 6.

Effect of depth: Table 3 illustrates data from the curves for crude oil 4 taken at two different depths, 1040–1050 m and 1067–1077 m. For a difference in depth of about 30 m, the (L + M) fraction decreased with increase in depth and heavier fraction increased significantly. There was a smaller change in the per cent residue, whilst the (L + M)/(H + R) ratio decreased significantly.

Finally, the TG technique could be introduced as a supplementary tool to characterize crude oils. It could be useful in obtaining approximate data for design purposes quickly. Factors weighing heavily in its favour are as follows:

1. The time factor, the run taking only 10 minutes.
2. No pretreatment is necessary.
3. The sample size, up to 10 mg being sufficient.

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Zusammenfassung — Es wird eine Schnellmethode zur Charakterisierung einiger irakischer Rohöle beschrieben, die auf mit ausgewählten Temperaturprogrammen erhaltenen thermogravimetrischen Daten beruht. Die sich auf die tief-, mittel- und hochsiedende Fraktion der Rohöle und deren Destillationsrückstände beziehenden, aus den thermischen Kurven erhaltenen Daten korrelieren gut mit der API-Dichte und dem Schwefel- und Metallgehalt. Es wird gezeigt, daß sich diese Parameter für Öl aus dem gleichen Bohrloch mit dessen Tiefe ändern.

Резюме — Описан быстрый метод охарактеризования некоторых сортов иракской сырой нефти, основанный на термогравиметрических данных, полученных при выбранной программе нагрева. Полученные на основе термических кривых данные, относящиеся к легким, средним и тяжелым сортам нефти, а также к их остаткам, хорошо коррелируются с их АПИ удельным весом с содержанием серы и металла. Этим методом было также показано, что найденные параметры изменяются с глубиной залегания нефтей.