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CHEMICAL EVALUATION OF CRUDE OILS BY PROGRAMMED THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

A method for the chemical evaluation of crude oils is described using a thermogravimetric analysis technique. In this method, a heating program is established including constant heating rate steps and two isothermal steps at 350 and 550 °C for two minutes each. Following this program, the thermogravimetric curves indicated two distinct weight loss steps. The first was between 25 and 350 °C, L + M, and the second was between 350 and 550 °C, H. The values of L + M, H and the residual material above 550 °C, R, were found to be independent of the heating rate and were characteristic of the crude oil analysed. The method was tested on seventeen crude oils with API gravity values of 42 down to 15.8. At a moderate heating rate (50 °C min^{-1}) a test run took only 15 min from which the above characteristic fractions could be estimated. These fractions, in addition to the ratio (L + M)/H + R) were correlated with the API gravity, and the vanadium and sulphur contents of the corresponding crude oils. Some useful relationships could be obtained.

INTRODUCTION

The importance of petroleum to various industries as a source of liquid fuels and basic raw materials accounts for the growing efforts directed towards its evaluation and characterization. In addition, oil spills in the marine environment necessitate the establishment of a rapid and reliable procedure for distinguishing crude oils of various origins. Many ASTM methods have been developed to this end and most of them are time-consuming and laborious. Meanwhile, thermoanalytical methods, thermogravimetry (TG), differential thermal analysis (DTA) and differential scan-

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ning calorimetry (DSC) were employed at a growing rate in the evaluation and characterization of crude oils and their products [1–11]. The potentials of TG enabled the differentiation [2] and characterization [10] of crude oils, and distillation curves of petroleum products were obtained using modified heating programs [7].

In the present work, a TG method is described for furnishing data from which the essential parameters of crude oils may be derived.

EXPERIMENTAL

The TG curves were obtained using a Heraeus TA 500 thermal analysis system and a Stanton–Redcroft TG 760 thermobalance under flowing N_2 atmosphere (25 ml min^{-1}). The heating program was a modified version of that proposed by Dyszel [2] and has been employed in previous works [5,10]. The samples (3–7 mg) were placed in platinum crucibles and heated in accordance to the program shown in Fig. 1 at heating rates of 10, 20, 50 and 100 °C min^{-1}. The vanadium (V) and nickel (Ni) contents of the crude oils were determined by flame atomic absorption spectrophotometry (AAS), following the recommended procedures [12], on a Pye–Unicam SP 9-800 AA

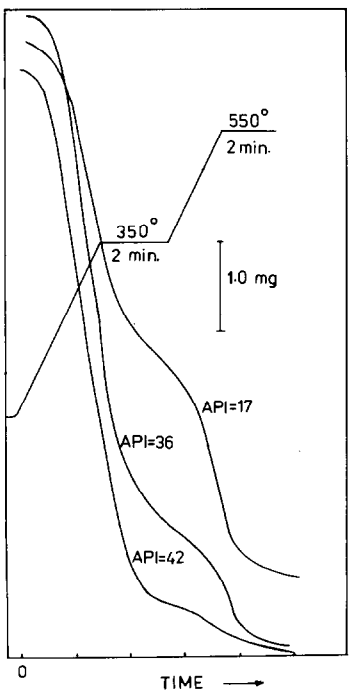

Fig. 1. The heating program used and the programmed TG signal of three crude oils.

spectrophotometer. The sulphur (S) content and API gravity were determined according to the standard procedures.

The evaluation of the mathematical equations was done on a Hewlett–Packard HP-9845 computer using a curve fitting and plotting program.

RESULTS AND DISCUSSION

The overall shape of the TG signals is shown in Fig. 1. In order to show the effect of heating rate on the extent of weight losses, several heating rates, 10, 20, 50 and 100 °C min^{-1}, were tested. The tests were carried out on three crude oils with a wide range of API gravity, 42, 36 and 17. Three characteristic fractions could be recognized for each crude oil (Fig. 1): the light and medium fraction (L + M), the weight loss up to 350 °C; the heavy fraction (H), the weight loss between 350 and 550 °C; and the residual material (R) at 550 °C. The programmed TG curves of the three crude oils were evaluated and the results are given in Tables 1–3.

Experimental results indicated that the characteristic fractions, L + M, H and R are only slightly affected by the heating rate. Thus, the proposed

TABLE 1

The characteristic fractions of crude oil (API gravity 42) at different heating rates

Heating rate (°C min^{-1})	L+M (%)	H (%)	R (%)	Sample size (mg)
10	92.0	6.15	1.85	6.4
20	92.0	6.2	1.8	7.4
50	92.0	5.0	2.9	6.3
100	91.5	6.3	2.2	7.2
Average	91.85	5.91	2.18	

TABLE 2

The characteristic fractions of crude oil (API gravity 36.2) at different heating rates

Heating rate (°C min^{-1})	L+M (%)	H (%)	R (%)	Sample size (mg)
10	80.5	12.5	7.0	6.4
20	81.2	11.4	7.4	5.4
50	80.5	12.0	7.5	7.0
100	81.5	12.3	6.2	6.6
Average	80.9	12.0	7.1	

TABLE 3

The characteristic fractions of crude oil (API gravity 17) at different heating rates

Heating rate (°C min^{-1})	L+M (%)	H (%)	R (%)	Sample size (mg)
10	52.4	30.2	17.4	7.45
20	54.0	28.0	18.0	7.0
50	50.2	32.8	17.0	7.8
100	50.2	31.3	18.5	6.4
Average	51.7	30.6	17.7	

weight loss and residue parameters can be regarded as criteria for the evaluation of crude oils.

The above-mentioned program was then applied to study the thermal behaviour of seventeen crude oil samples other than those already mentioned using a heating rate of 50 °C min^{-1}. The relevant data of these crude oils are given in Table 4. The programmed TG curves were evaluated and the characteristic fractions are listed in Table 5.

Preliminary correlations of L + M, H and R with the analytical data of the crudes were encouraging. The L + M fraction decreased exponentially with an increase in sulphur and vanadium contents (Figs. 2 and 3). However,

TABLE 4

Some properties of the crude oils

Crude oil	Sulphur content (%)	Vanadium content (ppm)	Nickel content (ppm)	API gravity
1	0.9	11	10	42.0
2	0.6	14	8	40.2
3	1.67	25	21	38.5
4	1.75	55	13	36.6
5	1.97	65	31	36.0
6	2.74	67	33	33.0
7	1.9	31	18	32.3
8	2.82	217	19	30.8
9	2.62	66	16	29.9
10	4.0	90	18	25.0
11	4.0	114	23	22.5
12	4.19	132	28	21.5
13	4.17	114	24	21.4
14	4.36	124	27	19.7
15	6.80	173	41	17.3
16	6.8	183	46	15.8
17	7.0	275	50	11.8

TABLE 5

The characteristic fractions of the crude oils

Crude oil	(L+M) 350 °C (%)	H 350–550 °C (%)	R 550 °C (%)	$\frac{(L+M)}{(H+R)}$
1	89.9	4.9	5.3	8.8
2	88.5	6.7	3.3	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	7.6	3.3
6	70.8	19.5	9.7	2.4
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
10	63.1	23.3	12.4	1.7
11	57.5	25.7	17.0	1.3
12	58.5	23.3	18.2	1.4
13	58.8	22.0	19.0	1.4
14	54.0	28.5	17.4	1.2
15	49.5	36.1	14.5	0.98
16	50.0	35.0	15.0	1.0
17	44.8	30.9	24.0	0.78

Fig. 2 indicated a possible linear dependence of the L + M fraction on the S content of the crude oil, provided that the latter does not exceed 5%, and can be expressed as follows

$$(L + M)\% = 100 - 10S \qquad (S \leqslant 5\%) \tag{1}$$

The H and R fractions were weakly correlated with the V and S contents (Figs. 4 and 5). The characteristic fractions were then correlated with the

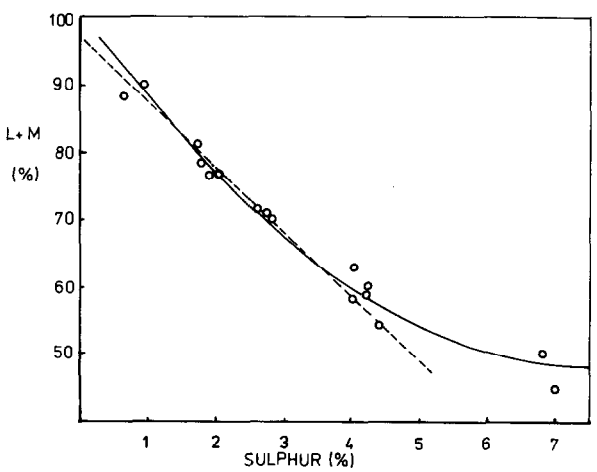

Fig. 2. The dependence of the L+M fraction on the sulphur content.

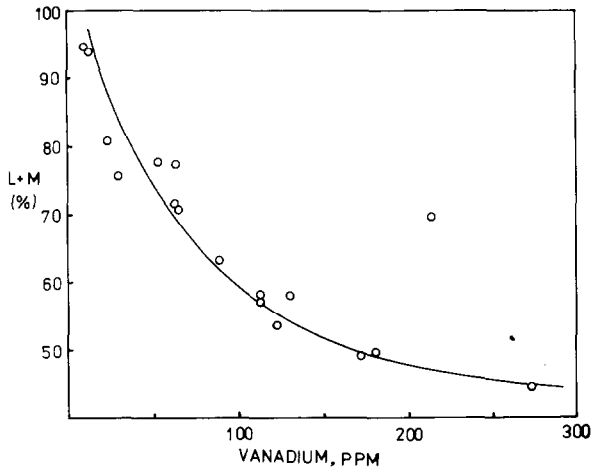

Fig. 3. The dependence of the L + M fraction on the vanadium content.

API gravity of the corresponding crude oils. A linear relationship could be obtained between the L + M fraction and the API gravity and can be described by the following equation

$$(L + M)\% = 26 + 1.5\ API \tag{2}$$

The relation is shown in Fig. 6. The H fraction could also be correlated with the API gravity and a straight line with a negative slope was found to describe this relationship as follows (Fig. 7)

$$(H)\% = 50 - API \tag{3}$$

By comparison, the correlation of the R fraction with the API gravity was weak and no reliable relationship could be derived (Fig. 8). Although the deviation of a natural system from linearity is to be expected, this could be attributed to the significant differences in the origin, age and composition of

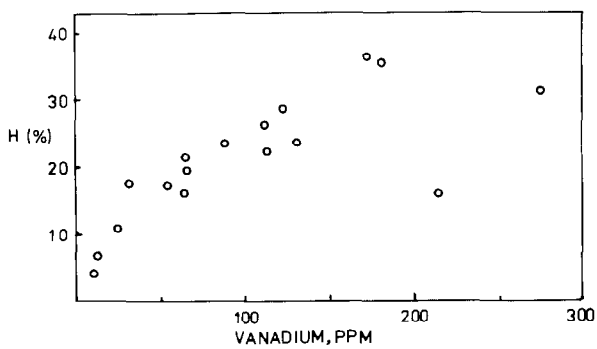

Fig. 4. The correlation of the heavy fraction H with the vanadium content.

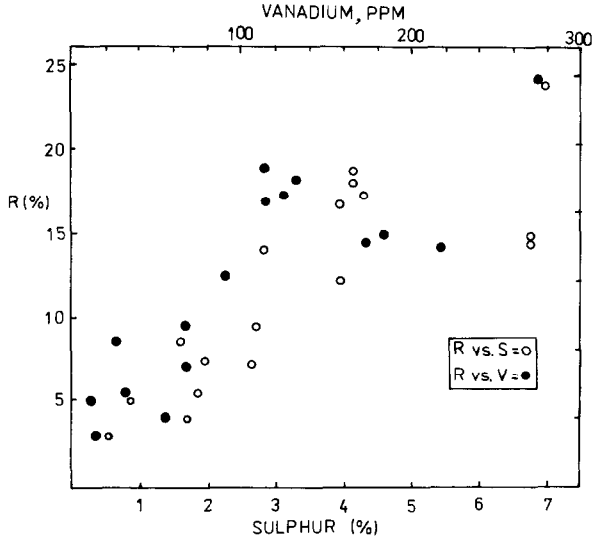

Fig. 5. The correlation of the residue R with the V and S contents.

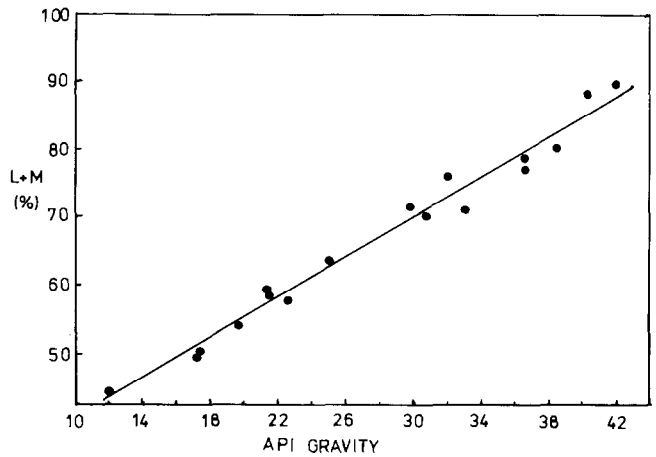

Fig. 6. The relation between the L + M fraction and API gravity.

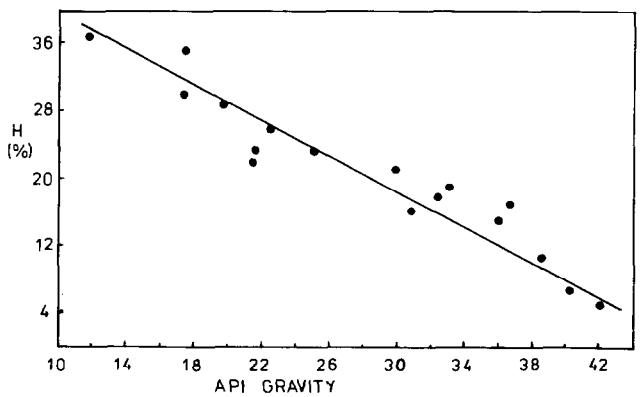

Fig. 7. The relation between the H fraction and the API gravity.

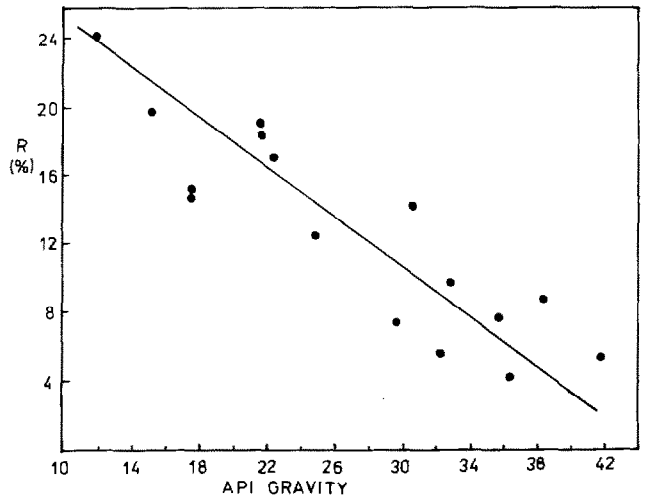

Fig 8. The relation between the residue R and the API gravity.

the crude oils and the characteristic parameters reflect the paraffinic or asphaltenic components.

In the search for characteristic parameters, the term $(L + M)/(H + R)$ was calculated from the available data (Table 5). When this ratio was

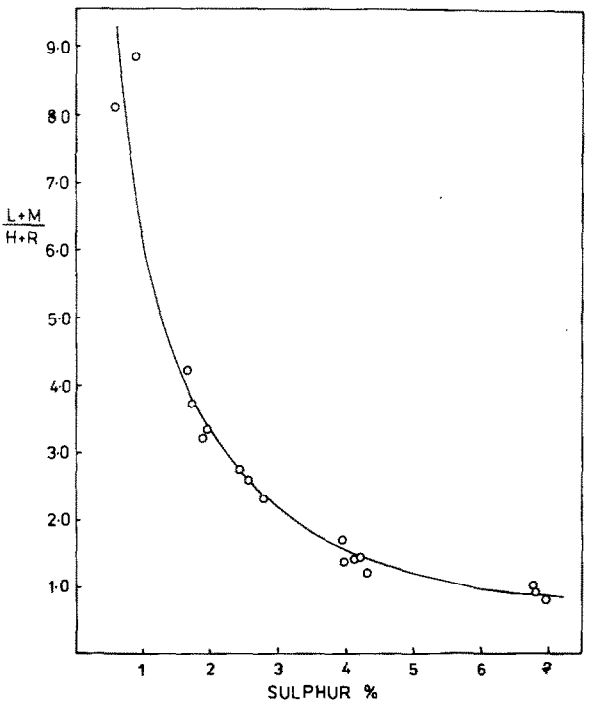

Fig. 9. The dependence of the ratio $(L+M)/(H+R)$ on the sulphur content.

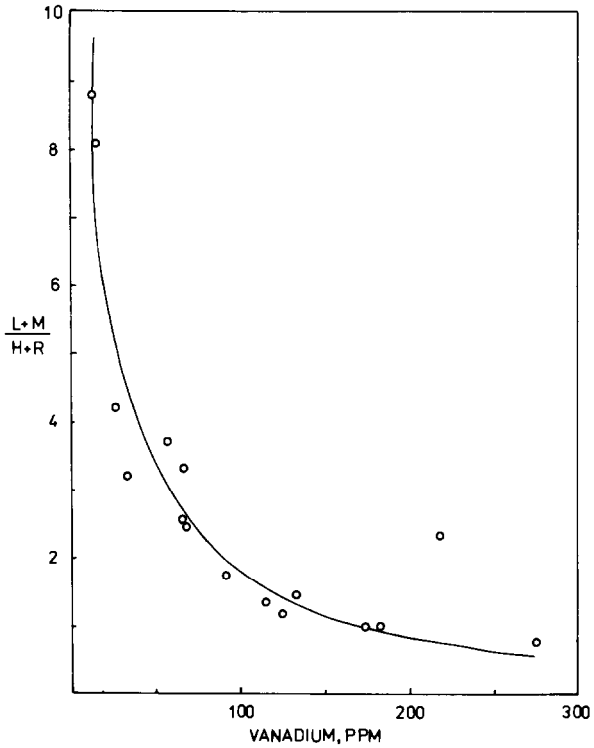

Fig. 10. The dependence of the ratio (L + M)/(H + R) on the vanadium content.

plotted against S and V contents, as well as the API gravity, interesting results were obtained (Figs. 9–11). The ratio (L + M)/(H + R) decreased in an exponential manner as the S and V contents of the crude oils increased, while the same ratio increased exponentially as the API gravity increased. The plots of Figs. 9–11 may be expressed mathematically as follows

$$\frac{L+M}{H+R} = 5.616\ e^{-0.3308\ X_1} \tag{4}$$

where $X_1 = S\% - 0.6$

$$\frac{L+M}{H+R} = 4.5405\ e^{-0.00776\ X_2} \tag{5}$$

where $X_2 = V_{ppm} - 10$

$$\frac{L+M}{H+R} = 0.27615\ e^{0.74435\ X_3} \tag{6}$$

where X_3 = API gravity.

The above data suggest that the plots of Fig. 9–11 can be directly employed by various laboratories to predict either the ratio (L + M)/(H + R) for any crude oil of known API gravity, S and/or V contents, or to predict the S and V contents and/or the API gravity for an unknown crude oil by

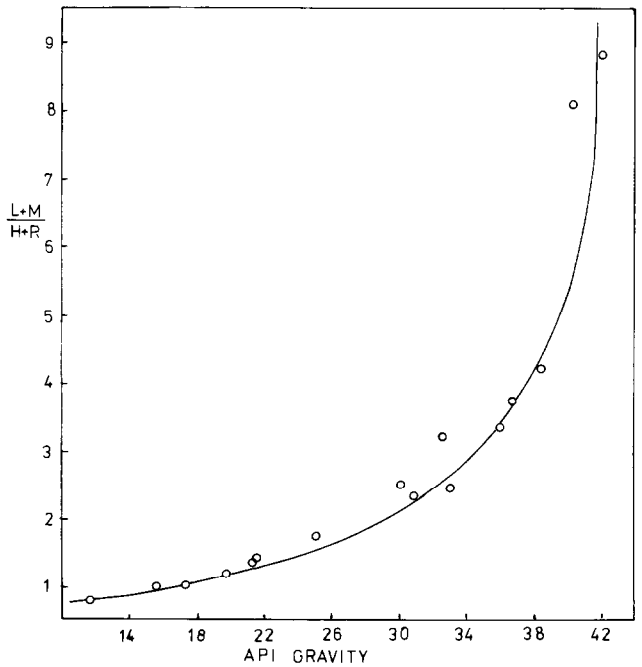

Fig. 11. The dependence of the ratio (L + M)/(H + R) on the API gravity.

carrying out a programmed TG experiment as shown above, which does not take more than 15 min, and estimating the ratio (L + M)/(H + R) to evaluate the corresponding V and S contents or API gravity by referring to the relevant plot.

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