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A THERMOGRAVIMETRIC METHOD FOR DISTINGUISHING ALASKAN CRUDE OIL FROM THAT OF OTHER WORLD SOURCES *

SUSAN M. DYSZEL

U.S. Customs Service, 1301 Constitution Ave. NW, Washington, DC 20229 (U.S.A.)

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ABSTRACT

A method for "fingerprinting" crude petroleum to determine the country of origin by thermogravimetry has been developed. Twenty-nine crude oil samples from various sources, both foreign and domestic, have been examined. Comparison of the thermogravimetric data, both graphically and numerically, yield a set of parameters which are useful in distinguishing between crude oil from the Alaskan Prudhoe Bay field and that of fields in other regions of the world.

INTRODUCTION

Crude oil is the lifeblood of the fuel and petrochemical industries in the United States. The U.S. Customs Service has a two-fold concern with crude oil shipments into U.S. ports; it is responsible for collecting import duties on foreign crude oils and, under the President's proposed energy package, enforcing the import quota on foreign crude oils. The situation is complicated by the fact that domestic crude oil from Alaska's Prudhoe Bay is also arriving by tankers at Eastern and Gulf ports and must be distinguished from imported crude oils. Fortunately, all crude oils are not identical. The diagenetic process of oil formation from organic-bearing sediments allows for variations in the relative proportions of hydrocarbons, sulfur, metals, and other trace substances. By looking at one or more of these quantities, a fingerprint might be made. A variety of analytical methods has been applied to crude oils and petroleum products [1]. A survey of the literature from 1963 to the present indicated that techniques such as simulated distillation by GC—MS [2], pyrolysis GC [3], capillary GC [4], infrared spectroscopy [5], and atomic absorption spectrometry [6] have been used along with the development of the ASTM—IP joint methods for distillation ratios [7,8], ash [9], carbon [10], density and API specific gravity [11].

Thermal analysis has also been employed to study the characteristics of petroleum and petroleum products. Bae published a design for a high pressure thermobalance [12] and demonstrated the application of thermogravimetry for determining fireflooding condition characteristics of crude oil

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[13]. Masek looked at heavy tar fractions by thermogravimetry [14], and also studied the effect of purge gas composition on the results of thermogravimetry of fuel oils [15]. Lubricating oils were the subject of Noel's investigation by thermal analysis [16] as it was for Novoded et al. [17]. Voelker and Fischer demonstrated the capability of thermogravimetry for microdistillation of petroleum and quantitation of asphaltic content [18]. The oxidation and vaporization characteristics of fuel oils were studied by Vaclav [19]. This current study has sought to develop an analytical method using commercially available equipment for the rapid differentiation of Alaskan crude oil from that of foreign sources by thermogravimetry.

EXPERIMENTAL

The instrumentation used in this study was the Perkin-Elmer TGS-2. During operation, the nitrogen purge gas entered the balance chamber, swept past the sample and exited at the bottom of the furnace tube. The sidearm inlet furnace tube allowed the addition of air to the gas stream. The nitrogen and air were controlled by standard tank regulators and in-line restricters. The flow was measured with a bubble flowmeter at the exit port on the furnace tube. The sample was contained in a small platinum sample pan (6 mm diameter by 2 mm high), suspended from the balance and surrounded by the microfurnace. The sample temperature was monitored by a thermocouple near the sample pan. The temperature of the furnace was calibrated using the Curie point method for nickel (magnetic transition temperature 354° C).

The crude oil samples were delivered in containers ranging in size from pint bottles to gallon cans. Immediately prior to sampling, each container was shaken vigorously to mix its contents. Individual samples were taken using a disposable glass pipet as a dip tube. A drop of the crude oil usually filled the sample pan. The one exception to this sampling procedure involved the Sumatran Crude from Indonesia (77-1415); in this case, a small spatula was used to transfer the crude oil, a soft solid, to the sample pan.

After loading the sample pan onto the balance, the furnace tube was closed and the system was purged with nitrogen for 2 min at 40° C to remove residual air. The samples were weighed during this purge sequence. Sample size was approximately 10 mg. At the end of the 2 min, the temperature program was started. The balance output was selected to display 100% sample weight full scale on the recorder. All weight losses were recorded in percent weight lost. The recorder chart speed was set for 0.5 in. min^{-1}. The timing was conducted using a combination of the furnace temperature controller for the heating segments and a stopwatch for the equilibration periods.

The analytical method involved temperature programming of the microfurnace and purge gas composition changes. The rapid heating capability of the microfurnace employed permitted reproducible temperature jumps at the rate of 160° min^{-1}. In this procedure, three such jumps, each followed by a period for temperature equilibration, were used along with a timed

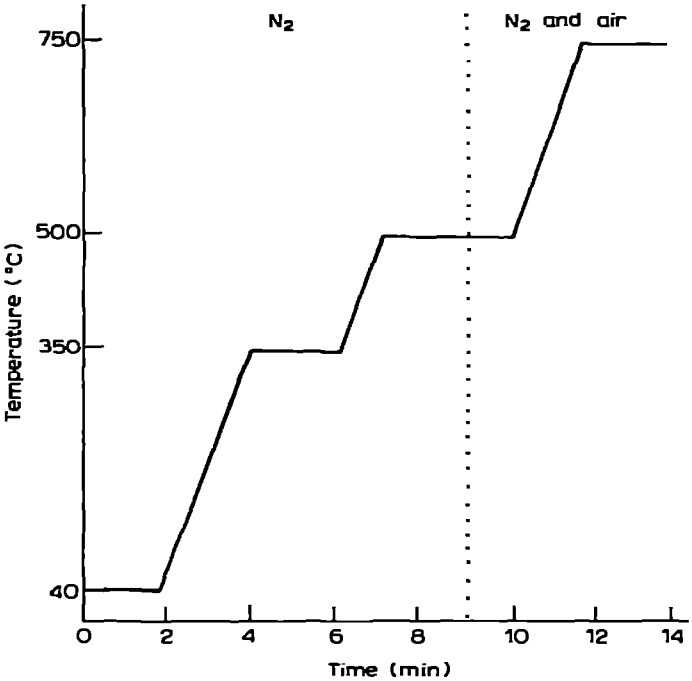

Fig. 1. Thermogravimetric temperature and purge gas program. Purge gas composition: N_2 flow rate, 40 ml min^{-1} (pyrolysis); air and N_2 flow rate, 44 ml min^{-1} (combustion). Temperature program: N_2 purge at 40°C for 2 min; heat 40 to 350°C at 160° min^{-1}; hold for 2 min; heat 350 to 500°C at 160° min^{-1}; hold for 2 min; admit air to purge stream; hold 1 min; heat 500 to 750°C at 160° min^{-1}; hold for 2 min. Total run time 14 min.

TABLE 1

Samples used in the study

Sample no.	Country	Field	Gravity (API°)
77013	UAE Sharjah	Mubarek	36.4
77012	UK North Sea	Hutton	36.6
77011	Indonesia offshore	Udang, East	39.6
77008	UK North Sea	Murchison	39.0
75047	Iran offshore	Rostam	36.8
75046	Norway North Sea	Ekofisk	32.3
74023	Iran offshore	Sassan	30.8
70025	Venezuela	Bachaquero	15.1
75048	Alaska	Kuparuk	28.2
71011	Alaska	Prudhoe	27.0
77-1420	Indonesia	Bekapai	40.4
77-1409	Indonesia	Walio	36.3
77-1313	Nigeria	Brass River	42.3
77-1572	Abu Dhabi	Murban	40.2
77-2654	Angola	Cabinda	32.7
77-1306	Malaysia	Miri Light	36.8
77-1413	Equador	Oriante	30.0
77-1341	UAE	Dubai	31.8
77-2565	Nigeria	Bonny	24.9
77-1415	Indonesia	Sumatran	34.8
78-751	Alaska	"Washington Trader", BP Oil, Inc.	26.3
78-750	Alaska	"Overseas Alaska", BP Oil, Inc.	25.0
78-749	Alaska	"Overseas Anchorage", BP Oil, Inc.	26.4
77-4720	Alaska	"Overseas Valdez"	26.4
77-4721	Alaska	"Gulf Prince"	26.5
70926-1, 2, 3	Alaska	Prudhoe Bay "New Orleans" Exxon	
78-02	Alaska	Sohio	

switch from nitrogen to a nitrogen—air mixture to change the purge gas atmosphere from one conducive to pyrolysis to that for combustion. A graphic illustration of the temperature and gas program is shown as Fig. 1. The percent weight lost for each sample at the end of the 350°, 500° and 750° equilibration periods were tabulated and the thermogravimetric curves were overlayed on a light box for graphic comparisons.

Samples having known country of origin and in some cases, oil field designations, were used to build the data base against which an incoming crude could be compared. Table 1 gives a listing of the crudes used in this study, along with the API Gravity where available. One of the Alaska crude samples was from the Kuparuk field, adjacent to the Prudhoe Bay Field, but from a different geologic reservoir. The other Alaskan crude oils were commercial samples, nominally from the Prudhoe Bay field, which traveled through the Trans Alaskan Pipeline System and were sampled either at Valdez or at their port of entry.

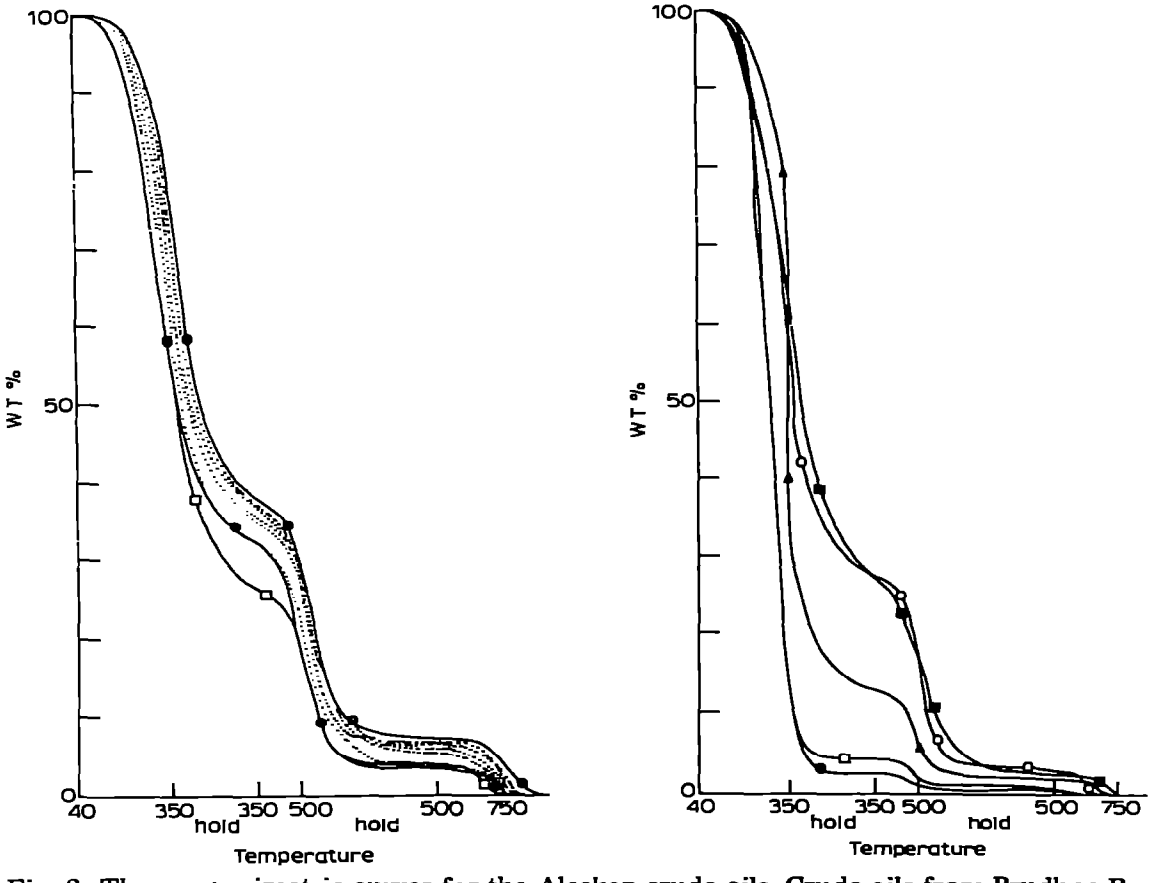

Fig. 2. Thermogravimetric curves for the Alaskan crude oils. Crude oils from Prudhoe Bay are within band designated by the closed circles. Crude oil from the Kuparuk field is designated by the open squares.

Fig. 3. Thermogravimetric curves for the Far East crude oils. □ Indonesia, Bekapai, 77-1420; ■ Indonesia, East Udang, 77011; ○ Indonesia, Sumatran, 77-1415; ▲ Indonesia, Walio, 77-1409; ● Malaysia, Miri Light, 77-1306.

RESULTS

Figure 2 illustrates the family of thermogravimetric curves generated by the Alaskan crudes under the described analytical program. There appears to be only one curve which is significantly different, particularly in the temperature region of the 350° hold to the 500° hold. This is the Alaskan crude from the Kuparuk field (75048).

Figure 3 displays the TG curves obtained from the five Far Eastern crude oils. Two of the oils from Indonesia (77011 and 77-1415) are similar to each other. There is insufficient information available to be able to determine whether the field named East Udang is near that of the Sumatran. Another Indonesian crude (77-1420) and the Malaysian crude (77-1306) are shown to have unusually high amounts of volatile components.

The thermogravimetric curves of the South American and European crude

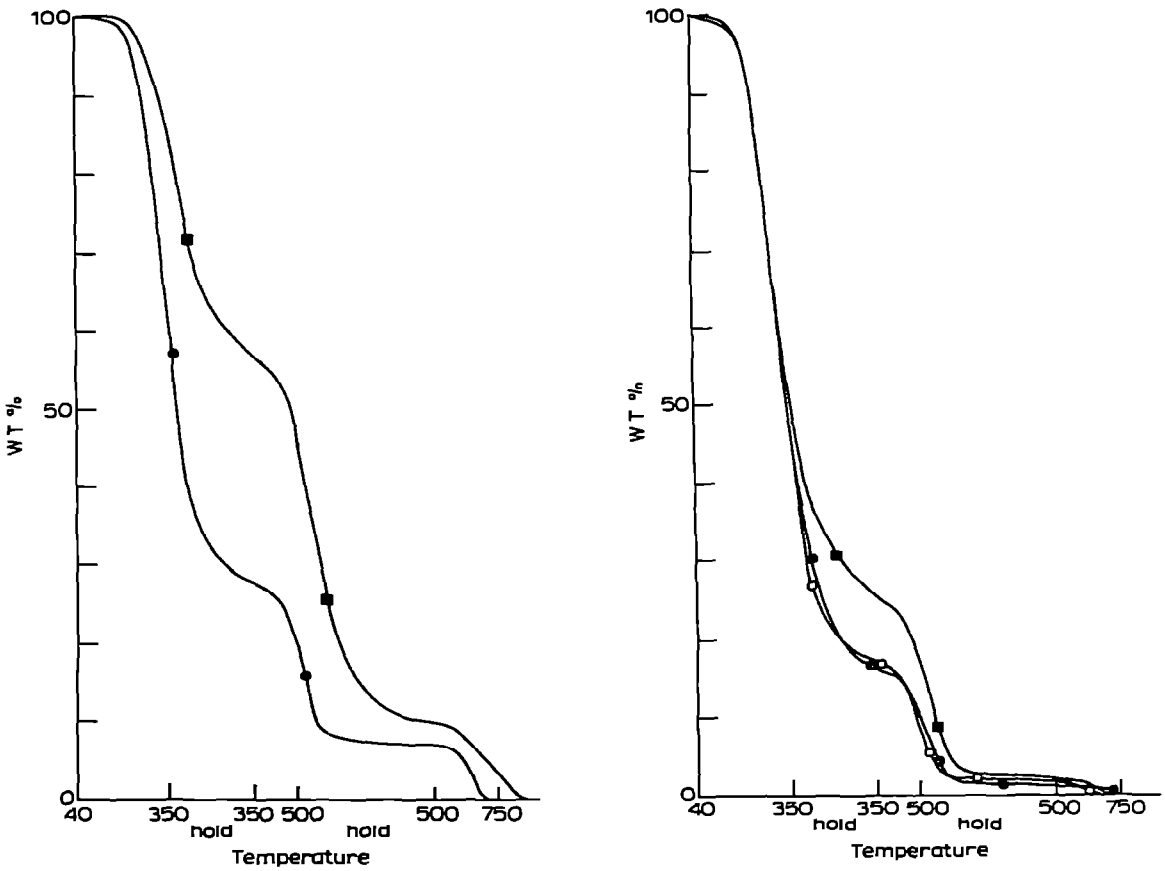

Fig. 4. Thermogravimetric curves for the South American crude oils. ● Equador, Oriante, 77-1413; ■ Venezuela, Bachaquero, 70025.

Fig. 5. Thermogravimetric curves for the European crude oils. ■ Norway, Ekofisk, 75046; ○ UK, Hutton, 77012; ● UK, Murchison, 77008.

oil samples are shown in Figs. 4 and 5, respectively. The two crudes from the United Kingdom's North Sea Fields of Hutton (77012) and Murchison (77008) are quite similar in the curves they generated. The Venezuelan sample of Bachaquero crude (70025) appears to be very different from any of the crude oils tested. This difference is also apparent in the low API Gravity of 15.1 for this crude.

In Fig. 6, the thermogravimetric curves obtained from two Iranian crudes (74023 and 75047), two UAE crudes (77-1341 and 77013) and one Abu Dhabi crude (77-1572) are displayed. The African crudes are shown in Fig. 7. The Nigerian Brass River crude (77-1313) is outstanding for its very large proportion of light hydrocarbons. In this case, the API Gravity was 42.3, indicative of a very light oil.

Graphical comparison of the thermogravimetric curves from the foreign crude oils with those from the Alaskan crudes yielded the following observations. The Far Eastern crude oils all had a greater proportion of light, volatile

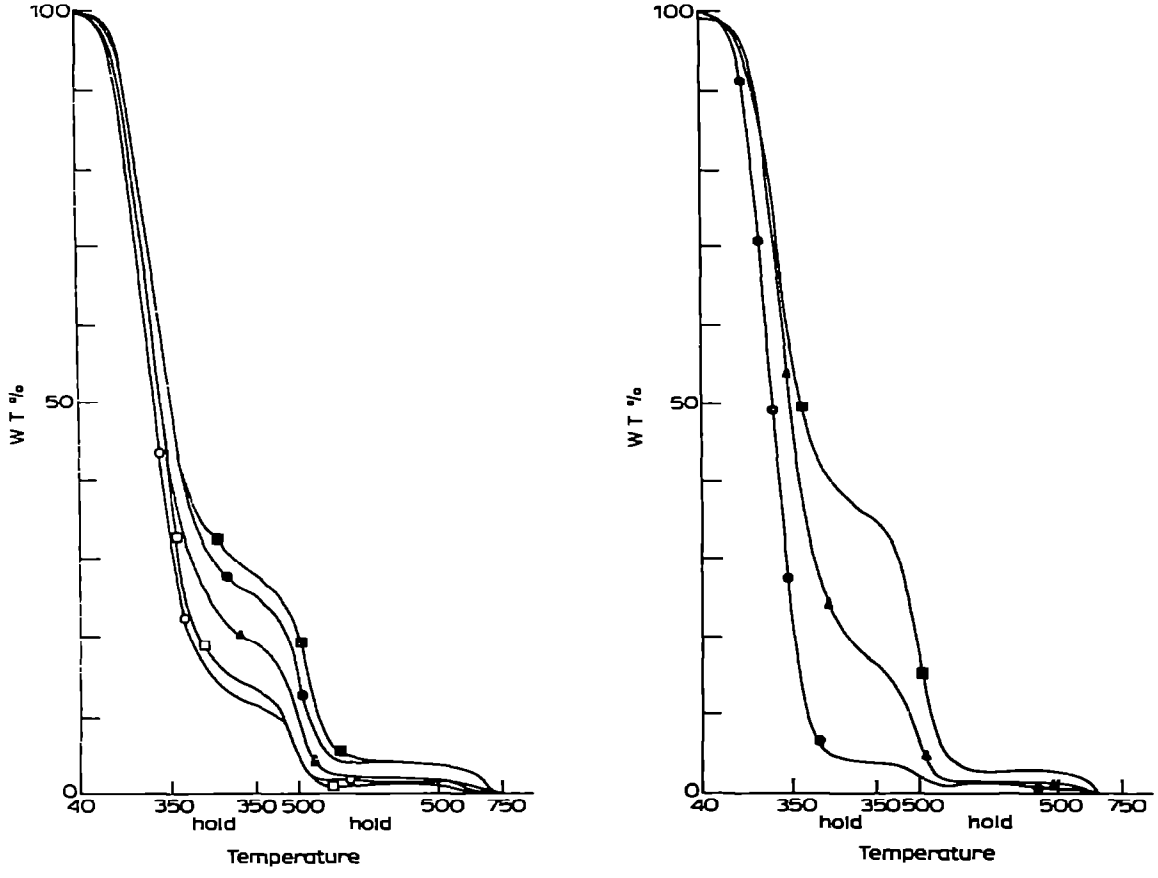

Fig. 6. Thermogravimetric curves for the Middle East crude oils. □ Abu Dhabi, Murban, 77-1572; ▲ Iran, Rostam, 75047; ■ Iran, Sassan, 74023; ● UAE, Dubai, 77-1341; ○ UAE, Mubarek, 77013.

Fig. 7. Thermogravimetric curves for the African crude oils. ■ Angola, Cabinda, 77-2654; ● Nigeria, Brass River, 77-1313; ▲ Nigeria, Bonny, 77-2565.

hydrocarbons than the Alaskan crudes as evidenced by the greater percent weight loss at the 350° hold point. No graphic overlap occurred when the South American and European crudes were compared with the Alaskan crudes. With the exception of the Venezuelan crude (70025), all the South American and European crude oil samples contained a greater proportion of light volatiles than the Alaskan. The Middle Eastern crude oils had one overlapping crude (74023) from Iran, which was sufficiently similar to the Kuparuk crude to rate as a possible match. The other Mid-Eastern crudes were demonstrated to be higher in light volatile content than the Alaskan. Of the African crude oils, the Angolan crude (77-2654) matched the Alaskan profile. Nigerian crudes contained more light volatiles than the Angolan or Alaskan.

Tables 2 and 3 detail the numerical data obtained from the thermogravimetric curves in terms of percent weight lost for the foreign and Alaskan crudes, respectively. The points were taken at the end of each equilibration step as defined by the heating program. These values were based on duplicate analyses for all samples and multiple analyses for the Alaskan crudes. In addition, the means, standard deviation and range are tabulated for the Alaskan crudes. In Table 4, the repeatability of the technique is demonstrated for multiple runs on the same bulk Alaskan crude oil sample (78-02).

TABLE 2

TG weight loss data for the foreign crudes

Sample no.	Country, field	Volatiles * (% wt.)	Non-volatiles ** (% wt.)	Residual carbon and ash *** (% wt.)
77-1420	Indonesia, Bekapai	96.0	4.0	
77-1409	Indonesia, Walio	87.3	10.9	1.8
77-1313	Nigeria, Brass River	96.0	3.5	0.5
77-1572	Abu Dhabi, Murban	87.0	11.7	1.3
77-2654	Angola, Cabinda	66.7	30.6	2.7
77-1306	Malaysia, Miri Light	98.0	1.7	0.3
77-1413	Equador, Oriante	73.0	20.0	7.0
77-1341	UAE, Dubai	74.5	21.5	4.0
77-2565	Nigeria, Bonny	83.8	15.2	1.0
77-1415	Indonesia, Sumatran	66.0	31.0	3.0
70025	Venezuela, Bachaquero	46.0	44.0	10.5
74023	Iran, Sassan	75.0	21.5	3.5
75047	Iran, Rostam	81.5	16.5	2.0
77008	UK, Murchison	84.0	14.5	1.5
77011	Indonesia, Udang, E.	71.5	26.0	2.5
77012	UK, Hutton	83.5	14.5	2.0
77013	UAE, Mubarek	87.5	11.5	1.0
75046	Norway, Ekofisk	74.5	23.1	2.5

* Weight loss at 350°C hold.
** Weight loss at 500°C hold.
*** Weight loss at 750°C hold.

TABLE 3

TG weight loss for the Alaskan crudes

Sample no.	Field	Volatiles * (% wt.)	Non-volatiles ** (% wt.)	Residual carbon and ash *** (% wt.)
70926-1	Exxon Prudhoe	65.0	31.5	3.5
70926-2	Exxon Prudhoe	67.0	29.5	3.5
70926-3	Exxon Prudhoe	62.5	33.5	4.0
71011	DOE Prudhoe	67.0	30.0	3.0
75048	DOE Kuparuk	71.5	24.5	4.0
78-749	BP Prudhoe	65.0	29.5	5.5
78-750	BP Prudhoe	62.5	31.5	6.0
78-751	BP Prudhoe	63.5	30.5	6.0
77-4720	Prudhoe	65.5	28.5	6.0
77-4721	Prudhoe	68.0	25.0	7.0
78-02	Sohio	61.2	31.6	7.2
	Mean	65.3 ± 2.9	29.6 ± 2.7	5.0 ± 1.5
	Range	61.2—71.5	24.4—33.5	3.0—7.2
Means, excluding 75048		64.7 ± 2.2	30.1 ± 2.3	5.2 ± 1.5

* Weight loss at 350°C hold.
** Weight loss at 500°C hold.
*** Weight loss at 750°C hold.

TABLE 4

Repeatability of method

Sample: 78-02 Sohio, Alaskan crude

Run no.	Volatiles * (% wt.)	Non-volatiles ** (% wt.)	Residual carbon and ash *** (% wt.)
1	64.0	29.5	6.5
2	65.0	28.0	7.0
3	67.0	22.5	10.5
4	66.5	24.0	9.5
5	59.0	33.0	8.0
6	63.0	29.0	8.0
7	62.0	31.0	7.0
8	62.5	30.0	7.5
9	63.0	30.0	7.0
10	62.0	31.3	6.7
11	63.0	29.5	7.5
12	61.0	31.5	7.5
13	58.5	34.5	7.0
14	59.0	34.0	7.0
15	58.5	35.0	6.5
16	61.0	32.5	6.5
17	61.5	31.0	7.5
18	61.5	31.5	7.0
19	59.0	34.0	7.0
Mean	61.9 ± 2.5	30.6 ± 3.3	7.4 ± 1.0
Range	58.5—67.0	22.5—35.0	6.5—10.5

* Weight loss at 350°C hold.
** Weight loss at 500°C hold.
*** Weight loss at 750°C hold.

TABLE 5

Three criteria for comparison

Country	Sample no.	Volatiles / carbon and ash	Non-volatiles (% wt.)	Graphic overlay
Alaskan Prudhoe	78-750	10.4	31.5	
	78-749	11.8	29.5	
	78-751	10.6	30.5	
	78-02	8.4	30.6	
	70926	17.0	31.5	
	71011	21.7	29.6	
	77-4720	9.8	24.4	
	77-7421	10.9	28.5	
Alaskan Kuparuk	75048	19.2	23.5	
Iran	74023	21.4	21.5	x
UAE	75047	40.8	16.5	
Abu Dhabi	77-1341	18.6	21.5	
Indonesia	77013	87.5	11.5	
	77-1572	66.9	11.7	
	77011	28.6	26.0	
	77-1415	22.0	31.0	
	77-1409	48.5	10.9	
	77-1420	2000.0	4.0	
Malaysia	77-1306	326.0	11.7	
Nigeria	77-1313	192.0	3.5	
	77-2565	83.8	15.2	
Angola	77-2654	24.7	30.6	x
Equador	77-1413	10.4	20.0	
United Kingdom	77008	56.0	14.5	
	77012	41.8	14.5	
Norway	75046	29.8	23.0	
Venezuela	70025	4.6	44.0	

TABLE 6

Crude oils which matched the Alaskan TG pattern

Graphic overlay of TG curves			
Mid East	74023	Iran	Overlays Kuparuk Crude
Africa	77-2654	Angola	Overlays Prudhoe Crude
Ratio of volatiles/residual carbon and ash (Alaskan range less than 22)			
Mid East	74023	Iran	21.4
	77-1341	UAE	18.6
South America	70025	Venezuela	4.6
	77-1413	Equador	10.4
Weight percent of non-volatiles (Alaskan range 23.5—31.5)			
Far East	77011	Indonesia	26.0
	77-1415	Indonesia	31.0
Africa	77-2654	Angola	30.6
Europe	75046	Norway	23.0

It was noted that the standard deviation for the multiple runs of one sample was quite similar to those obtained for all of the Alaskan samples.

The numeric data obtained were transformed into a set of values which ratioed the percent weight lost as light volatiles (350° point), *L*, to the percent weight attributed to the carbon and ash (750° point), *CA*. Table 5 lists the tabulations of *L/CA*, the percent weight lost as heavy non-volatiles, and the indication of a graphic match for each of the crude oils. Figure 8 illustrates the four crude oils which had a *L/CA* ratio of less than 22. The Alaskan crude oil illustrated in that figure is one run which matched the mean Alaskan crude thermal distribution and serves as a point of reference. Table 6 selects those crudes which have matches in any of the categories shown in Table 5. This tabulation indicates that none of the foreign crude oils tested had the matches in all three criteria necessary for classification as an Alaskan Crude.

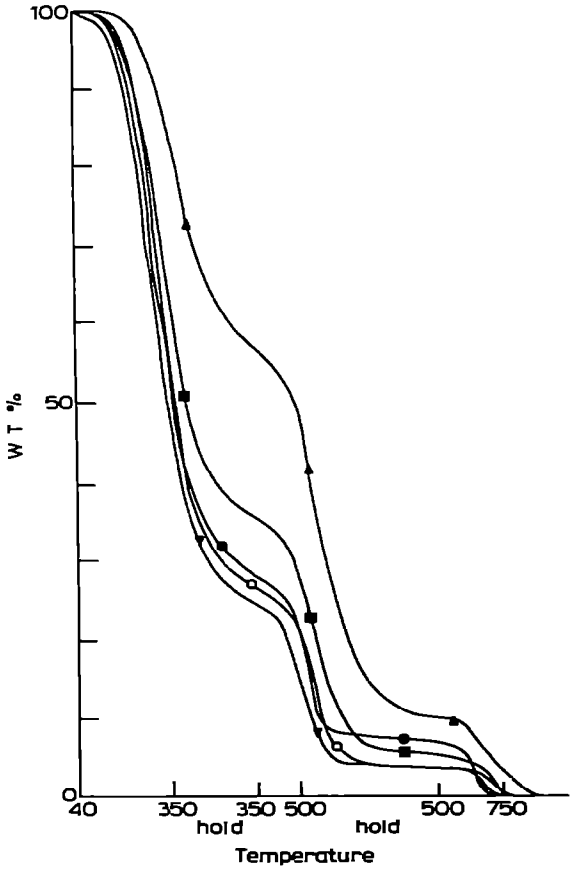

Fig. 8. Thermogravimetric curves of those crude oils having a light hydrocarbon/carbon-ash ratio of less than 22. ■ Alaska, Prudhoe, 78-02; ● Equador, Oriante, 77-1413; Iran, Sassan, 74023; ○ UAE, Dubai, 77-1341; ▲ Venezuela, Bachaquero, 70025.

DISCUSSION

The analysis of crude oil samples by thermogravimetry has been developed to provide a rapid method of distinguishing Alaskan Crude oil from that of foreign sources. The thermogravimetric curves, which resulted from the programmed application of heat to the crude oil sample, reflected their characteristic distribution of light volatiles, heavy non-volatiles and the residual carbon and ash content. The ability to quantitate the three portions of this distribution, along with the qualitative properties of the thermogravimetric curves has lead to the designation of three significant criteria for similitude: the graphic overlapping of TG curves with the Alaskan Crude, the L/CA ratio of less than 22, and the % wt. of heavy non-volatiles within the range of 23.5—31.5%. All of this information can be obtained from one thermogravimetric run using the temperature program described.

The method tested was rapid, the total elapsed time being 14 min per run. There was no sample preparation other than agitation of the bulk sample and no extensive clean-up afterwards, as the entire analytical sample is virtually consumed in the thermogravimetric process. The small sample size did not require large bulk samples and the thermogravimetric method eliminated most of the potential environmental pollution associated with other methods of analysis, such as fumes from ashing or solvents for cleaning IR cells. Nothing was added or removed from the sample prior to analysis. Thermogravimetry has, therefore, been shown to be a valuable technique for the characterization and fingerprinting of crude oils for the purpose of distinguishing between foreign and domestic origins.

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