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THE USE OF THERMOGRAVIMETRY AND NMR SPECTROSCOPY IN THE ATTEMPTED IDENTIFICATION OF THE SOURCE OF BABYLONIAN BUILDING ASPHALT

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ABSTRACT

This paper discusses the attempted identification of the source of asphalt (whether it was from the Qayarah or Heet locations), which was used in the building of the old city of Babylon. Thermogravimetry, differential thermogravimetry, ^{13}C and proton nuclear magnetic resonance spectroscopy were employed as the main analytical tools in this investigation, in addition to some standard methods of analysis. Results obtained indicated that the most probable source of Babylonian building asphalt was from Heet.

INTRODUCTION

The ruins of Babylon, the fabulous old city of culture and prosperity which existed 20 centuries B.C., stands some 95 km to the south of the modern city of Baghdad, the capital of Iraq.

Babylon is referred to in several holy texts and it was mentioned extensively by pioneering travellers. It was the most spectacular city of ancient times, with its hanging gardens, mighty fortifications and city gates, magnificent palaces, religious rites and ceremonies, and all the other trappings of power [1].

Various modifications of asphalts were used in the building of the old city walls, fortifications, construction of its irrigation networks, supply canals and the embellishment of palaces and streets. The origin of asphalt used, whether it came from the Qayarah or Heet locations lying some 400 km north of Baghdad and about 200 km north-east of Baghdad, respectively, has long been disputed, although some of the references refer to Heet as the

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most probable source, basing their conclusions mainly on geographical factors, i.e. Heet and Babylon lying on the same river, the Euphrates, which could have been used as a route for transportation of the asphalt [2].

Recently [3–6], thermoanalytical and nuclear magnetic resonance (NMR) techniques have been used extensively in the study and identification of many heavy petroleum fractions and products such as residues, asphalts and bitumens.

In this investigation, we report the attempted identification of the origin of the source of asphalt used in the buildings of Babylon, employing several advanced analytical techniques, mainly thermogravimetry, differential thermogravimetry, ^{13}C and proton nuclear magnetic (NMR) spectroscopy, in addition to some standard methods of analysis, such as adsorption chromatography and atomic absorption spectrophotometry.

The results obtained indicated that the most probable source of the asphalt used was from Heet.

EXPERIMENTAL

Samples

The two asphalts from Qayarah and Heet occur naturally and were obtained from their local sources. Babylonian asphalt was taken from the southern palace of the Babylonian ruins and cleaned thoroughly from any mud and soil prior to analysis.

Apparatus

Thermogravimetric (TG) and differential thermogravimetric (DTG) measurements were carried out in a Heraeus TA 500 thermal analyser. ^{13}C and proton NMR measurements were performed in a Bruker WH 300 FT super-conducting spectrometer equipped with Aspect 2000, a 128K computer operating at 300.3 MHz.

Adsorption chromatography was performed in a column of 1.4 cm i.d. and 120 cm in length packed with silica gel of mesh size 40. Metal analyses were carried out in a Pye Unicam SP-9-800 atomic absorption spectrophotometer. Sulfur-content determination was performed in a Telsec 100 P X-ray analyser.

Experimental procedure

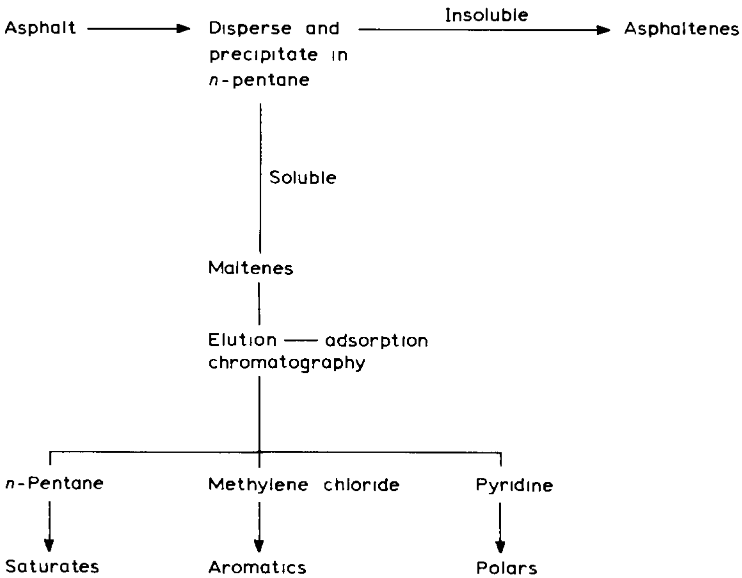
TG and DTG curves were recorded simultaneously by placing a sample of the asphalt weighing 5–10 mg in a platinum crucible and heating at a rate of

20 °C min^{-1} in an atmosphere of nitrogen or oxygen gas flowing at a rate of 100 cm^3 min^{-1}.

In the NMR measurements the asphalt sample (0.8 g) was dissolved in $CDCl_3$ (2 cm^3). A few drops of the internal reference, TMS, was added, this was followed by addition of dioxane (0.1 cm^3) as the integration standard. Quantitative ^{13}C NMR spectra were measured in a 10 mm o.d. Willmad tube using 1.5 cm^3 of the prepared solution. Chromium acetylacetonate (19 mg) was added as the relaxation agent in order to remove the difference in carbon relaxation time. Proton NMR spectra were measured in a 5 mm o.d. Willmad tube using 0.5 cm^3 of the same prepared solution.

For adsorption chromatography, the asphalt sample was agitated with *n*-pentane in a round-bottomed flask for 2 h, followed by reflux. The soluble matter was separated from the precipitated asphaltene by decantation and filtration. This was followed by washing with *n*-pentane to remove any adsorbed compounds, then drying and weighing the asphaltene fraction. The pentane solution containing the maltene was then introduced into the column. The ratio of sample to adsorbent was 1 : 40. The pentane elutant received contained the saturates. Elution with methylene chloride released the aromatic hydrocarbons. The final elution was made with pyridine in order to release the polar compounds (see Scheme 1).

All results are the average of three determinations.



Scheme 1. Separation of asphalts into four generic components by adsorption chromatography.

RESULTS AND DISCUSSION

The main features of the TG and DTG curves of the asphalts studied in an atmosphere of nitrogen or oxygen gas between room temperature and 800 ° C are displayed in Figs. 1–3 and represent Babylon, Heet and Qayarah, respectively.

It is clear from these figures that, under the inert atmosphere of nitrogen gas, the asphalts underwent volatilization which proceeded with a well-defined, single, broad transition, indicating a slow weight loss below 400 ° C and very rapid weight loss between 400 and 500 ° C. However, in the oxygen atmosphere, the thermogravimetric curves were of a rather complex nature, indicating the presence of multiplet transitions occurring over a wide temperature range and are related to exothermal oxidation reactions which increased in intensity with increasing temperature. A rapid weight loss was again recorded in the 400–500 ° C region.

The data extracted from the TG and DTG curves in nitrogen and oxygen atmospheres are displayed in Tables 1 and 2, respectively, indicating the percentage weight loss at 100 ° C intervals. The results presented confirmed the fact that the maximum weight loss was in the 400–500 ° C temperature region. It is also worth noting that a much higher percentage of residual matter remained at the end of the temperature program for the three

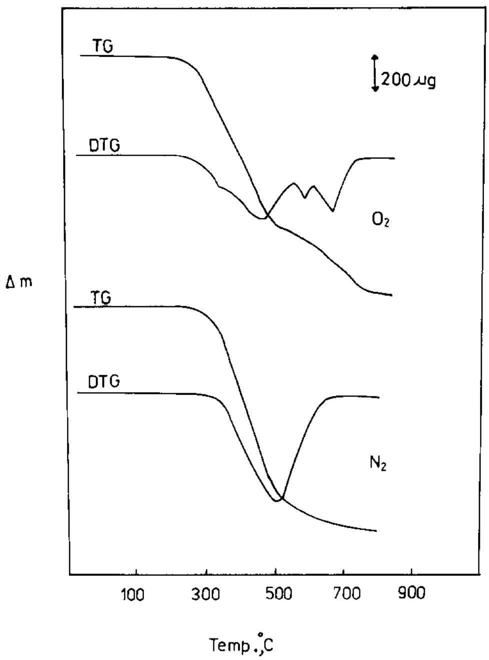


Fig. 1. TG and DTG traces of Babylonian asphalt in oxygen and nitrogen gases.

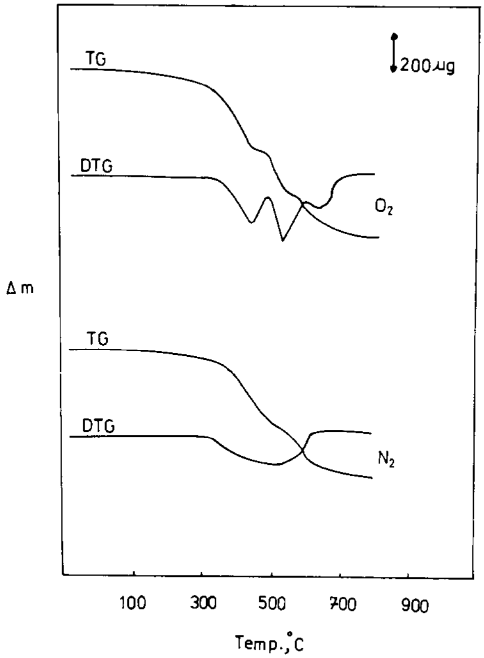


Fig. 2. TG and DTG traces of Heet asphalt in oxygen and nitrogen gases.

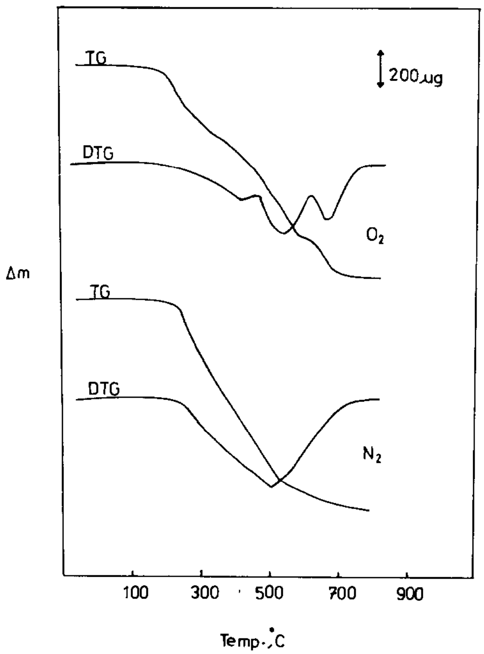


Fig. 3. TG and DTG traces of Qayarah asphalt in oxygen and nitrogen gases.

TABLE 1

Thermogravimetric data on asphalts studied in N_2 gas (from TG curves)

Temperature range (°C)	Weight loss (%)		
	Babylon	Heet	Qayarah
0–100	0	0	0
100–200	0	0	0
200–300	0.8	1.95	9.1
300–400	12.2	11.5	17.5
400–500	50.0	48.55	40.5
500–600	16.5	14.0	8.0
600–700	9.0	10.2	7.9
700–800	2.5	3.2	5.0
Residue	9.0	10.6	12.0

asphalts studied, when the determinations were performed in the inert atmosphere of nitrogen gas, compared to the residual matter that remained at the end of the temperature program when the determinations were performed in the oxidizing conditions of oxygen gas.

The combination of ^{13}C and proton NMR spectroscopy were used in the study of the average structural parameters (ASP) for Babylonian building asphalt (BAB), Heet (HE) and Qayarah (QA) asphalts. The ASPs were derived for the aromatic, asphaltene and polar fractions using the method described by Gillet et al. [3,4].

ASP results on the three studied asphalts, i.e. BAB, HE and QA, are shown in Table 3.

After inspection and examination of the thermal and NMR data presented in Tables 1–3, and from consideration of differences in values relative to Babylon, the results obtained indicate that there is a closer

TABLE 2

Thermogravimetric data on asphalts studied in O_2 gas (from TG curves)

Temperature range (°C)	Weight loss (%)		
	Babylon	Heet	Qayarah
0–100	0	0	0
100–200	0	0	0
200–300	11.0	10.5	16.0
300–400	14.8	15.5	16.0
400–500	28.2	25.0	30.3
500–600	22.0	22.7	17.0
600–700	19.3	20.0	18.5
700–800	2.0	4.3	2.2
Residue	2.7	2.0	0

TABLE 3

^{13}C and ^{1}H quantitative NMR spectra of aromatics, asphaltenes and polar fractions of asphalts studied

C [a] (%)	Aromatics			Asphaltenes			Polars		
	BAB	HE	QA	BAB	HE	QA	BAB	HE	QA
C_{ar}	30.94	28.33	34.12	48.98	50.82	50.62	50.62	52.54	53.25
C_{ar+ali}	11.51	11.95	13.94	16.33	15.25	14.46	22.2	23.73	23.38
C_{ar}, $H+CH_{3+n}+I$	19.42	19.17	18.8	32.65	30.95	36.14	27.16	28.8	29.87
C_{sat}	69.06	71.67	67.88	51.02	49.8	49.4	49.38	47.46	46.75
H (%)	BAB	HE	QA	BAB	HE	QA	BAB	HE	QA
H_{ar}	6.28	6.48	5.65	8.22	7.39	7.28	9.22	11.17	20.48
H_{sat}	93.72	93.52	94.35	91.78	92.61	92.72	90.78	88.83	78.31
$H_{\alpha sat}$	19.03	18.52	19.27	23.1	22.42	21.2	24.11	21.26	25.3
$H_{\beta sat.}$	51.38	49.63	55.15	49.2	49.1	49.05	45.39	48.16	42.17
$H_{\gamma sat}$	23.31	28.3	17.93	19.1	22.54	22.47	21.28	18.99	10.84

[a] Key: ar., aromatic; sat., saturated; ali., aliphatic.

TABLE 4

The composition of the asphalts studied

Composition	Babylon	Heet	Qayarah
Asphaltenes (wt.%)	88.24	50.15	26.56
Saturates (wt.%)	1.82	0.35	8.23
Aromatics (wt.%)	6.98	41.54	55.79
Polars (wt.%)	3.49	7.63	9.91
V (p.p.m.)	334.75	248	172.7
Ni (p.p.m.)	69.28	53.22	56.65
S (wt.%)	8.34	7.49	7.4

correlation between Babylonian and Heet asphalts when compared to that of Babylonian and Qayarah asphalts.

Adsorption chromatography was also employed, after deasphalting the samples using selective solvents, in order to obtain the compositional picture of the three asphalts studied, which is shown in Table 4. The table shows a high asphaltene content in the Babylonian sample, which can be attributed to the condensation of polar compounds due to aging and weathering: no significant correlation could be found in the results of the sulfur and nickel contents of the three asphalts studied. However, the value of the vanadium content of Heet asphalt was closer to that of Babylon when compared to the value of vanadium in Qayarah asphalt (Table 4).

It is possible to conclude, from the results obtained, that the most probable source of the asphalt used in the building of the old city of Babylon is Heet.

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