



## NRC Publications Archive Archives des publications du CNRC

### **Comparative study of organic matter derived from Utah and Athabasca oil sands**

Kotlyar, Luba S.; Ripmeester, John A.; Sparks, B. D.; Woods, J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /  
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

#### **Publisher's version / Version de l'éditeur:**

*Fuel*, 67, 11, pp. 1529-1535, 1988

#### **NRC Publications Record / Notice d'Archives des publications de CNRC:**

<https://nrc-publications.canada.ca/eng/view/object/?id=b4f75573-5aa3-40d4-8589-607e579bbbca>  
<https://publications-cnrc.canada.ca/fra/voir/objet/?id=b4f75573-5aa3-40d4-8589-607e579bbbca>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



National Research  
Council Canada

Conseil national de  
recherches Canada

Canada

# Comparative study of organic matter derived from Utah and Athabasca oil sands

L. S. Kotlyar, J. A. Ripmeester, B. D. Sparks and J. Woods

National Research Council of Canada, Division of Chemistry, M-12, Montreal Road, Ottawa, Ontario, Canada K1A 0R9

(Received 19 August 1987; revised 22 March 1988)

Asphaltenes derived from Athabasca and Utah oil sands have been characterized using different techniques. Several factors were found to differentiate these asphaltenes. Number average molecular weight of Utah asphaltene was significantly higher, which correlated with its higher light absorbing capacity, compared with that for Athabasca asphaltene. In Athabasca asphaltene, V and Ni were higher and Al, Mn, Mg, Ca, Ti, Fe were lower than those in Utah asphaltene. Structural models for these asphaltenes, as determined using a combination of  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectroscopy, were different with higher aromaticity and degree of condensation of aromatic rings for Athabasca asphaltene.  $^{13}\text{C}$  structural parameters for humic acids extracted from demineralized fines separated from Utah oil sands were compared with Athabasca oil sand humic acid. As in the Athabasca sample, aromatic carbon in Utah humic acid was shown to be the predominant type of carbon.

(Keywords: oil sand; asphaltene; humic acids)

Oil sands deposits are found throughout the world. The major deposits occur in Canada and contain 900 billion barrels of in place bitumen<sup>1</sup>. The Utah bituminous sand deposits (27 billion barrels of bitumen in place) are considered to be a significant resource<sup>2</sup>, although small compared with the total oil sand deposits of Alberta. Interest in oil sands as an additional source of energy has increased in recent years and it is realized that characterization of oil sands is an important step, which is useful in the context of recovery and upgrading of bitumens. Oil sand is a complex mixture of organic and inorganic mineral substances. The organic matter present in oil sand can be divided into two main categories:

1. Bitumen: soluble in organic solvents such as toluene. It can be considered to be a physical mixture of maltenes, resins and asphaltenes. It is known<sup>3</sup> that the asphaltene fraction present in bitumen introduces serious problems during bitumen recovery and upgrading. Therefore to improve bitumen separation and refining a better understanding of the chemistry of different asphaltenes is needed.
2. Humic matter: fulvic acids are soluble at both high and low pH, humic acids are soluble only at high pH, while humins are completely insoluble. Although humic matter occurs in oil sand in only small amounts, its characterization is of a great importance because it is believed<sup>4-6</sup> that the presence of humic matter renders the surfaces of some inorganic matter in oil sands hydrophobic thus influencing the recovery of bitumen.

Athabasca asphaltene and humic acid have been studied by several authors<sup>3-5,7-15</sup> whereas information concerning the corresponding fractions derived from Utah oil sand is virtually absent. The purpose of this work was to characterize the Utah asphaltene and humic acid in comparison with those separated from Athabasca oil sand.

## EXPERIMENTAL

The Athabasca and Utah oil sands samples used in this work were obtained from the Syncrude and the Sunnyside deposits, respectively. Before use, samples were delumped in a Comomil (Quadro Engineering Inc., Waterloo, Ontario, Canada), carefully homogenized and stored in sealed containers.

Bitumen separation and analysis of the oil sands was performed using the Soxhlet extraction-Dean and Stark method<sup>16</sup>, with toluene as solvent. The excess toluene was removed at 90°C in a Brinkmann rotary evaporator under reduced pressure. Samples were then dried to constant weight in a Brinkman SC/24R sample concentrator at 80°C under nitrogen.

Asphaltenes were separated from the bitumens by a standardized procedure that involved dissolution of the bitumen in an equal volume of benzene and subsequent dilution of the solution with  $\approx 40$  volumes of *n*-pentane<sup>17</sup>. To reduce the ash level, asphaltenes were dissolved in dichloromethane and centrifuged for an hour at 428 g in an IEC Model CRU-5000 centrifuge.

The elemental analysis (C,H,N) was performed using a Perkin-Elmer model 240 CHN analyser. The insoluble organic carbon content (IOCC) of all solid fractions was obtained by subtracting carbonate carbon from the total carbon. Carbonate carbon was analysed titrimetrically after acid digestion using a Carbon Dioxide Coulometer Model 5010 (Ref. 18). Sulphur was analysed by a titrimetric oxygen flask combustion method, using a Schöniger type combustion apparatus<sup>19</sup>. Metals were analysed semiquantitatively by d.c. arc emission spectrometry.

The molecular weights of the asphaltenes were determined by vapour pressure osmometry (v.p.o.) using a Westcan Model 232A instrument. The determinations were carried out in benzene at three concentrations and

extrapolated by computer to infinite dilution. Separation of bitumen free oil sands solids into fines (<38  $\mu\text{m}$  fraction) and coarser particles was performed using wet sieving. To concentrate the humic matter, fines were leached with acids using a procedure described elsewhere<sup>20</sup>. For humic and fulvic acids extraction, samples of demineralized fines were digested with 2% aqueous NaOH at 70°C for a week in accordance with the procedure outlined previously<sup>4</sup>. Fulvic acids content was insufficient for any analysis to be performed. The humic acids suspensions were initially freeze-dried, with final moisture removal being carried out at room temperature in a vacuum desiccator over  $\text{P}_2\text{O}_5$ .

Proton n.m.r. measurements were performed on a Bruker MSL300 spectrometer. Spectra were recorded in a  $\text{CDCl}_3$  solution.  $^{13}\text{C}$  n.m.r. spectra were run using the same instrument. A paramagnetic relaxation agent, chromium (III) acetylacetonate was added to the solutions of asphaltenes in  $\text{CDCl}_3$  to allow for a short delay time between pulses in the carbon-13 channel. Data was collected at a sweepwidth setting of 50 kHz, with inverse gated proton decoupling to suppress nuclear Overhauser enhancement (nOe). A pulse flip angle of 45° was used with a pulse repetition time of 2 s. Between 10 000 and 20 000 transients were collected to obtain an adequate signal to noise ratio.

$^{13}\text{C}$  n.m.r. spectra of humic acids dissolved in 0.5N NaOD at a concentration of 50–100 mg ml<sup>-1</sup> were also obtained on a Bruker MSL-300 spectrometer. As there were no sharp features in the spectra, the free induction decays (FIDs) were truncated at 0.5 K before zerofilling to 4 K. Between 20 000 and 50 000 transients were collected to obtain an adequate signal to noise ratio.

## RESULTS AND DISCUSSION

The compositions and the fines content of the oil sand samples studied are shown in Table 1. With respect to bitumen concentration both Athabasca and Utah oil sands represent low grade material (<7% bitumen). Although amounts of bitumen present in these oil sands are similar, it is apparent that the fines and water content of Utah oil sand is significantly lower than those of the Athabasca. These data are in accord with results reported elsewhere<sup>2</sup>. It can be also seen from Table 1 that both oil

sands have approximately the same amount of toluene insoluble organic matter, which is evident from the similar insoluble organic carbon content (IOCC) of the bitumen free solids.

### Elemental analysis, molecular weight and metal content

Bitumens extracted from Athabasca and Utah oil sands were subjected to precipitation of asphaltenes by using *n*-pentane. Results showing yield of asphaltenes are given in Table 2 together with their elemental composition, the H/C atomic ratios and number average molecular weights (MW). It can be seen that the asphaltene content of Athabasca bitumen is slightly lower than that of Utah bitumen. Elemental analysis data for both asphaltenes are similar, but the H/C ratio for asphaltene derived from Utah oil sand is higher than that for Athabasca asphaltene, suggesting a lower degree of aromatic ring condensation in the former case. As can be seen from Table 2 the most significant difference between these two asphaltenes is their number average molecular weights (MW) as determined by v.p.o.

There are also apparent differences between these asphaltenes in terms of their metals content as shown in Table 3. First, the concentration of nickel and especially vanadium is higher in Athabasca than in Utah asphaltene, which could be due to the differences in their source materials. The forms in which Ni and V occur in Athabasca bitumens have been discussed in numerous papers<sup>21–25</sup>. It is accepted that these heavy metals occur as vanadium and nickel porphyrins or chelated compounds associated with asphaltene. In the case of Utah oil sand, V has been found to be present in the organic fraction in the V<sup>4+</sup> state (Circle Cliffs and Boscan formation) as well as inorganically bound in the clay fraction (P. R. Spring formation)<sup>26</sup>.

Second, the concentrations of Mn, Fe, Mg, Ca, Al, Ti are greater in Utah asphaltene. The presence of Al, Mg, Mn, Ca, Ti is believed<sup>23,26</sup> to be due to entrained mineral matter, which is extremely difficult to separate from the asphaltenes<sup>7</sup>. The fact that Utah asphaltene has a higher concentration of these elements agrees with the previously reported observation<sup>7</sup> that higher molecular weight asphaltene fractions have a greater tendency to trap inorganic matter. Iron could occur in asphaltenes as part of the inorganic matrix, as low molecular weight, highly polar compounds or high molecular weight metal complexes<sup>23,26</sup>.

### Characterization of asphaltenes by absorption spectrometry in the visible region

The absorption spectra of bitumens in solution follow the Lambert–Beer law:

$$A = \log P_0/P$$

$$A = \epsilon Cd$$

where A, adsorption; d, length of light path in the cell

**Table 1** Composition and fines content of Athabasca and Utah oil sands

Oil sand	Composition (wt%)			IOCC <sup>a</sup> (%)	Fines <sup>b</sup> content (%)
	Bitumen	Solids	Water		
Athabasca	6.9	86.6	6.5	0.89	32.0
Utah	6.5	93.0	0.5	0.98	10.5

<sup>a</sup> Insoluble organic carbon content of bitumen free dry solids

<sup>b</sup> Based on bitumen free dry oil sand solids

**Table 2** Elemental composition and molecular weight of Athabasca and Utah asphaltenes

Asphaltene	Yield <sup>a</sup> of asphaltene (%)	Elemental composition (wt%)						MW	Average molecular formulae
		C	H	N	O (diff.)	S	H/C		
Athabasca	16.5	79.01	8.07	1.02	3.73	8.17	1.23	2618	$\text{C}_{172.4}\text{H}_{211.3}\text{N}_{1.91}\text{S}_{6.68}\text{O}_{6.10}$
Utah	17.8	80.48	8.67	1.48	1.27	8.10	1.29	6042	$\text{C}_{405.2}\text{H}_{523.8}\text{N}_{6.39}\text{S}_{15.29}\text{O}_{4.80}$

<sup>a</sup> % of bitumen

**Table 3** Metals analysis of Athabasca and Utah asphaltenes

Asphaltene	Metals content (ppm)							
	Mn	Fe	Mg	Ti	Ca	Al	Ni	V
Athabasca	2.3	260	41	34	120	150	240	640
Utah	330	4820	1060	240	1540	1140	170	21

**Table 4** K/C ratios and number average molecular weights for different asphaltenes

Asphaltene	K/C ratio	MW
Athabasca	25.27	2530
	26.77	2648 <sup>a</sup>
	25.83	2700
	26.07	2718
Utah	41.34	6042 <sup>a</sup>

<sup>a</sup> Elemental compositions for these asphaltenes are given in Table 2

(cm);  $C$ , concentration ( $\text{mg } 100 \text{ ml}^{-1}$ );  $e$ , molar extinction coefficient (molar absorptivity) specific for the substance under investigation. If  $d$  is equal to 1 cm,

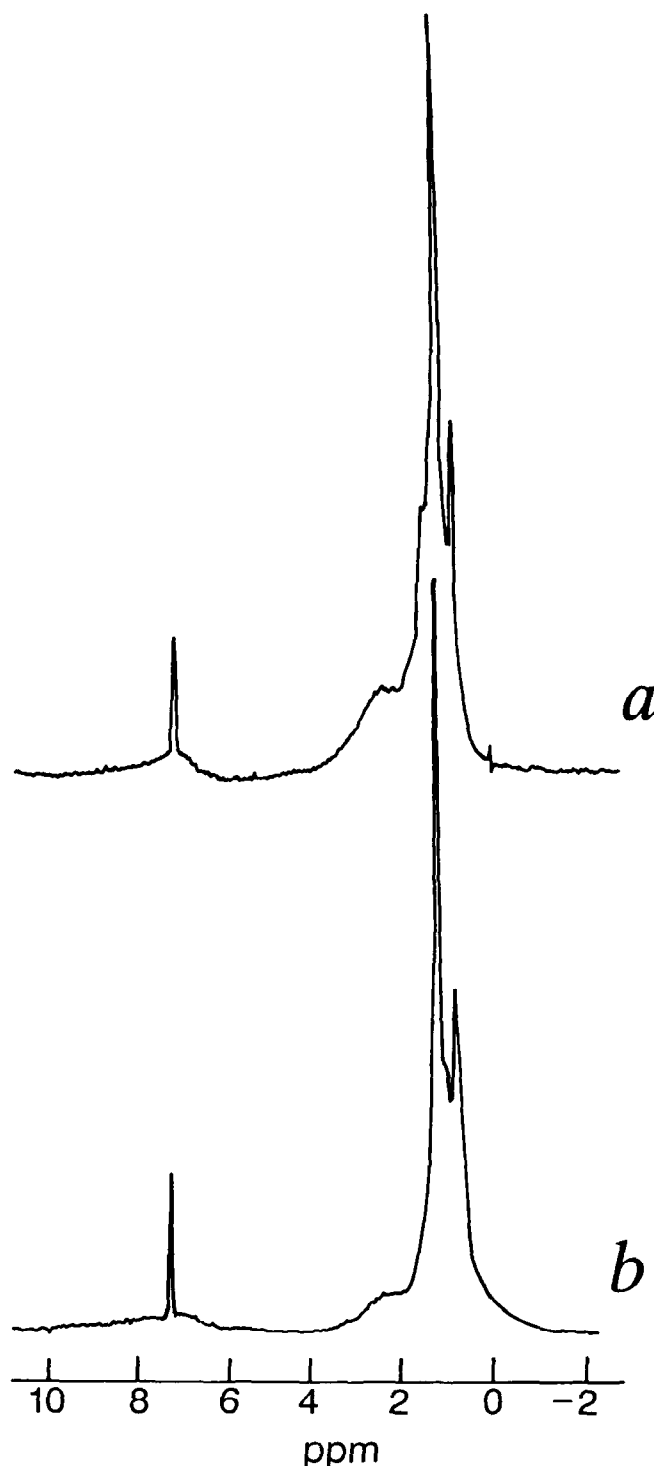
$$A = k = eC$$

where  $k$  is the extinction coefficient. In accordance with the Lambert–Beer law<sup>27</sup>  $\log k$  plotted against wavelength at various concentrations gives parallel curves indicating that the slope of the curves is independent of concentration, and depends only on molar absorptivity of the substance. Thus, the colour of the bitumens can be characterized by determination of the slope of the absorption curve. Another way to present the absorbance data is to plot the ratios of extinction coefficient ( $k$ ) to concentration ( $C$ ) versus concentration at any wavelength. This gives a family of straight lines parallel to the  $x$  axis. Consequently, not only the slope of the absorption curve but also the  $k/C$  ratio at any concentration and wavelength can be used for the characterization of bitumens and their fractions such as maltenes and asphaltenes.

It is noteworthy that, in accordance with Lambert–Beer law,  $k/C$  ratios determined for the whole bitumens (both Athabasca and Utah) at any wavelength are equal to the weighted sum of the  $k/C$  ratios for the corresponding asphaltenes and maltenes, indicating that there is no chemical interaction between these components. Previously<sup>28</sup> a direct proportionality has been found between  $k/C$ , determined at 530 nm, for number of Athabasca bitumens and the concentration of asphaltenes in these bitumens. This allowed approximate estimation of asphaltene content in Athabasca bitumens without actual precipitation. A wavelength of 530 nm was selected because it is commonly used for analysis of bitumen by the colourimetric method. In this work the  $k/C$  ratios for a number of Athabasca asphaltenes were examined and compared with those determined for Utah asphaltene at 530 nm. It was noted (Table 4) that  $k/C$  values for asphaltenes, separated from Athabasca bitumens, were in the narrow range from 25.3 to 26.8 whereas the  $k/C$  ratio of 41 determined for Utah asphaltene was significantly higher.

Similarly, number average molecular weights (Table 4) for Athabasca asphaltenes were in a relatively narrow

range from 2530 to 2718. The molecular weight of Utah asphaltene was 6042, which is much higher than that of Athabasca asphaltene. Although interpretation of light absorption data in terms of the structure and nature of absorbing substances is practically impossible, the results shown in Table 4 suggest a possible correlation between molecular (particle) weights of asphaltene chromophores and their light absorbing capacities. This suggestion is in agreement with a recent finding that the number of absorbing chromophores present in g.p.c. separated Athabasca asphaltene fractions increases with increasing molecular weight<sup>15</sup>.

**Figure 1** Proton n.m.r. spectra of asphaltenes: a, Athabasca; b, Utah

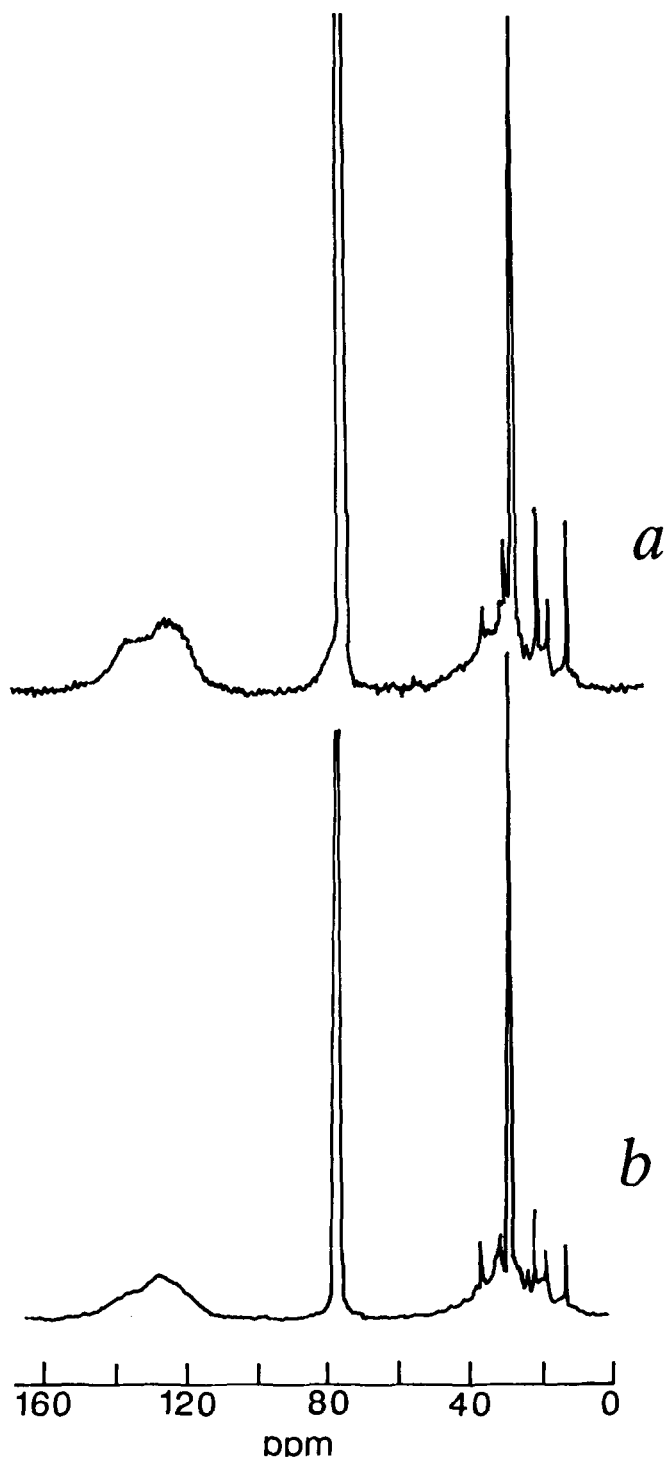


Figure 2 Solution  $^{13}\text{C}$  n.m.r. spectra of asphaltenes a, Athabasca; b, Utah. The signal at  $\approx 77$  ppm is due to  $\text{CDCl}_3$

#### $^1\text{H}$ and $^{13}\text{C}$ n.m.r. of Athabasca and Utah asphaltenes

Lately, a combination of  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectroscopy has been used extensively for structural characterization of petroleum, including Athabasca bitumens and asphaltenes<sup>10-12,29-31</sup>. In this work this method was used for determination of the average structural parameters for Utah asphaltene and to compare these parameters with those for asphaltene derived from Athabasca oil sand. Although there are certain limitations in application of this approach to characterization of high boiling and nondistillable

fractions with broad molecular weight distribution<sup>32</sup>, it is believed that comparison between average structural parameters of asphaltenes could reflect their gross structural differences.

Proton and  $^{13}\text{C}$  n.m.r. spectra of different asphaltenes are presented in Figures 1 and 2. Assignments for the chemical shifts observed are given in Table 5<sup>12,29,30</sup>. The relative proportions of different types of carbon and protons present in samples analysed were obtained by integration of the spectra and are given in Table 6. On the basis of the results presented in Table 6 the average structural parameters expressed as numbers of protons and carbon atoms in an average single molecule were calculated using the method described previously<sup>10</sup>. Notations for these parameters and equations used for calculations are listed in Table 7.

In addition to the relative proportions of different types of carbon and protons (Table 6), elemental compositions of asphaltenes and their number average molecular weights (Table 2) were used for calculation. Results showing average structural parameters for Utah and Athabasca asphaltenes are presented in Table 8. It can be seen that the aromaticity ( $C_{ar}$ ) of Utah asphaltene (34%) is apparently lower than that of Athabasca (46%). At the same time the  $H/C$  ratio (Table 2) for Utah asphaltene is higher than that for Athabasca asphaltene. These observations illustrate the inverse correlation between aromaticity and  $H/C$  ratio generally observed<sup>33</sup>.

For comparison purposes Table 8 also includes average

Table 5 Assignments for  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts

Chemical shift range (ppm)	Assignment	
$^1\text{H}$		
9.3–6.3	$\text{H}_{\text{ar}}$	Aromatic protons
4.5–1.9	$\text{H}_{\alpha}$	Protons attached to a saturated $\alpha$ -carbon <sup>a</sup>
1.9–1.0	$\text{H}_{\beta}$	Protons attached to a saturated $\beta$ -carbon ( $\text{CH}_3$ ) or to a $\beta, \gamma, \delta$ (or more) carbon <sup>a</sup> ( $\text{CH}_2, \text{CH}$ )
1.0–0.5	$\text{H}_{\gamma}$	Methyl protons on a $\gamma, \delta$ (or more) carbon
$^{13}\text{C}$		
160–118	$\text{C}_{\text{ar}}$	Aromatic carbons
70–10	$\text{C}_{\text{al}}$	Aliphatic carbons

<sup>a</sup> With respect to an aromatic ring

Table 6 The relative proportions of different types of protons and carbons present in Athabasca and Utah asphaltenes

	Asphaltene	
	Athabasca	Utah
%H		
$H_{ar}$	6.9	6.4
$H_a$	18.3	21.0
$H_\beta$	50.4	56.4
$H_\gamma$	23.2	15.8
$H_{al}$	93.1	93.6
%C		
$C^a$	46.0	34.0
$C_{al}$	54.0	66.0
$C_{29.7}$	12.5	22.9

<sup>a</sup> Aromaticity

<sup>b</sup> Internal methylene groups in a long paraffinic chain<sup>29,30</sup>  
 $\text{CH}_3-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_n-\text{CH}_2-\text{CH}_2-$

**Table 7** Average structural parameters derived from  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra

Symbol	Average parameter	Equation
$C_{\text{ar}}^n$	Number of aromatic carbon atoms in an average single molecule	$C_{\text{ar}}^n = C^n \cdot C_{\text{ar}} / 100$
$H_{\text{ar}}^n$	Number of aromatic hydrogen atoms in an average single molecule	$H_{\text{ar}}^n = H^n \cdot H_{\text{ar}} / 100$
$C_{\text{al}}^n$	Number of aliphatic carbon atoms in an average single molecule	$C_{\text{al}}^n = C^n - C_{\text{ar}}^n$
$H_{\text{al}}^n$	Number of aliphatic hydrogen atoms in an average single molecule	$H_{\text{al}}^n = H^n - H_{\text{ar}}^n$
$C_c^n$	Number of carbon atoms in condensed points in aromatic ring systems in an average single molecule	$C_c^n = C_{\text{ar}}^n - H_{\text{ar}}^n - C_{\text{a}}^n - \text{O}^n$
$C_{\text{a}}^n$	Number of alkyl substituents on aromatic ring systems in an average single molecule	$C_{\text{a}}^n = H^n \times H_{\text{a}} / r_{\text{al}} \times 100$
$r_{\text{al}}$	Ratio of the aliphatic hydrogen to carbon	$H_{\text{al}}^n / C_{\text{al}}^n$
K	Degree of condensation of aromatic ring systems	$C_c^n / C_{\text{ar}}^n$

$C^n$ ,  $H^n$ ,  $\text{O}^n$ , the numbers of carbon, hydrogen, oxygen atoms in an average single molecule calculated from molecular weight and elemental analysis data (Table 2). Oxygen is assumed to exist in the form of phenolic OH or aromatic ethers<sup>10</sup>

**Table 8** Average structural parameters calculated from  $^1\text{H}$  and  $^{13}\text{C}$  spectra of Athabasca and Utah asphaltenes

Average structural parameters	Asphaltene	
	Athabasca	Utah
$C_{\text{ar}}$	46.00 (49.0) <sup>a</sup> [48] <sup>b</sup>	34.00 [35.0] <sup>b</sup>
$C_{\text{ar}}^n$	79.30 (88.5) [84.0]	137.80 [144]
$H_{\text{ar}}^n$	14.6 (22.0) [22.0]	33.50 [30.0]
$C_{\text{al}}^n$	93.10 (93.5) [92.0]	267.40 [264]
$H_{\text{al}}^n$	196.70 (202) [190]	490.30 [492]
$r_{\text{al}}$	2.11 (2.16) [2.06]	1.83 [1.86]
$C_{\text{a}}^n$	18.30 (21.7) [24]	60.10 [66.0]
$C_c^n$	40.30 (39.1) [36.0]	39.40 [48.0]
K	0.48 (0.44) [0.43]	0.29 [0.33]
$C_{29.7}^n$	12.50 (12.5) [12.0]	22.90 [24.0]

<sup>a</sup> From Ref. 10

<sup>b</sup> The structural parameters of the models (Figure 3) proposed for Athabasca<sup>10</sup> and Utah asphaltenes

structural parameters for Athabasca asphaltene reported elsewhere<sup>10</sup>. It can be seen that there is a similarity between the two sets of data. Therefore the average structural model proposed by Suzuki *et al.*<sup>10</sup> has been accepted without any changes. The main assumption for this structural model was that individual particles, micelles, of Athabasca asphaltene (MW = 2500) contain  $\approx 2$  monomer units each having a MW of  $\approx 1000$ . Assuming that a monomer unit of Utah asphaltene has the same MW as Athabasca, a structural model of Utah asphaltene containing six monomer units is proposed.

Figure 3 shows structural models for Utah compared with Athabasca asphaltene<sup>10</sup>. The structural parameters for the models are presented in Table 8. Reasonable agreement with the parameters obtained using n.m.r. can

be noted. As can be seen from Table 8 and Figure 3 the models for Utah and Athabasca asphaltenes are significantly different. For example, one unit of Athabasca asphaltene contains 42 aromatic carbons ( $C_{\text{ar}}^n$ ) as compared with only 24 aromatic carbons present in Utah asphaltene. The number of carbon atoms in condensed points ( $C_c^n$ ) is 18 for Athabasca and 8 for Utah. It is apparent that the degree of condensation (K) of the Utah asphaltene is lower than that of Athabasca.

The chain length of the average paraffinic straight-chain was calculated knowing the value of  $C_{29.7}$  and taking into account that the carbon resonance at 29.7 ppm appears with the internal methylene groups more than three carbon atoms away from a branching point and more than four from a terminal point<sup>10</sup>. In Table 8  $C_{29.7}$  is 12 for Athabasca asphaltene and there are two monomer units in the micelle, then chain length is 6 per unit plus the number of carbons that are 'forgotten' in  $C_{29.7}$ , i.e. 5. Thus calculated, the chain length for an Athabasca asphaltene monomer unit appeared to be 11 compared with 9 for Utah. The Utah asphaltene is more abundant in naphthenic carbon than Athabasca.

It is believed<sup>34</sup> that the main factors responsible for molecular association in petroleum asphaltenes are  $\pi$ - $\pi$  bonding and hydrogen bonding. The degree of aromatic ring condensation in Utah asphaltene is lower than in Athabasca but at the same time the degree of association of monomer units in micelle is higher (6 units instead of 2), thus  $\pi$ - $\pi$  interactions do not seem to be the predominant factor in the association of Utah asphaltene.

#### $^{13}\text{C}$ n.m.r. spectra of humic acid

As was mentioned earlier (Table 1) both Athabasca and Utah oil sands have approximately the same amount of toluene insoluble organic matter, as indicated by similar IOCC of the bitumen free solids. Previously<sup>14</sup>  $^{13}\text{C}$  n.m.r. was used for structural analysis of humic acid extracted from density separated oils and solids closely associated with bitumen in Athabasca oil sand. The object of this work was to determine structural parameters for humic acid isolated from Utah oil sand. This humic acid was extracted from the fines fraction of Utah oil sand solids, previously demineralized to concentrate humic matter.  $^{13}\text{C}$  n.m.r. spectra for Utah humic acid is given in Figure 4. For comparison purposes spectrum for Athabasca humic acid<sup>14</sup> is also included.

The spectra are similar and could be divided into three main sections of chemical shift: 0 to 50 ppm (region I),

**Table 9**  $^{13}\text{C}$  n.m.r. chemical shift regions for various types of carbons present in humic substances

Region I (0–50 ppm)	Region II (110–160 ppm)	Region III (160–190 ppm)
Paraffinic $\text{C}:\text{C}-\text{C}^*-\text{C}$	Olefinic-C	Carboxyl $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OH} \end{array}$
$\begin{array}{c} \text{C} \\   \\ \text{C}^*-\text{C} \\   \\ \text{C} \end{array}$	Aromatic-C	Ester $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OR} \end{array}$
$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}^*-\text{C} \\   \\ \text{C} \\   \\ \text{C}-\text{CH}_3 \end{array}$		Amide $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{N} \end{array}$

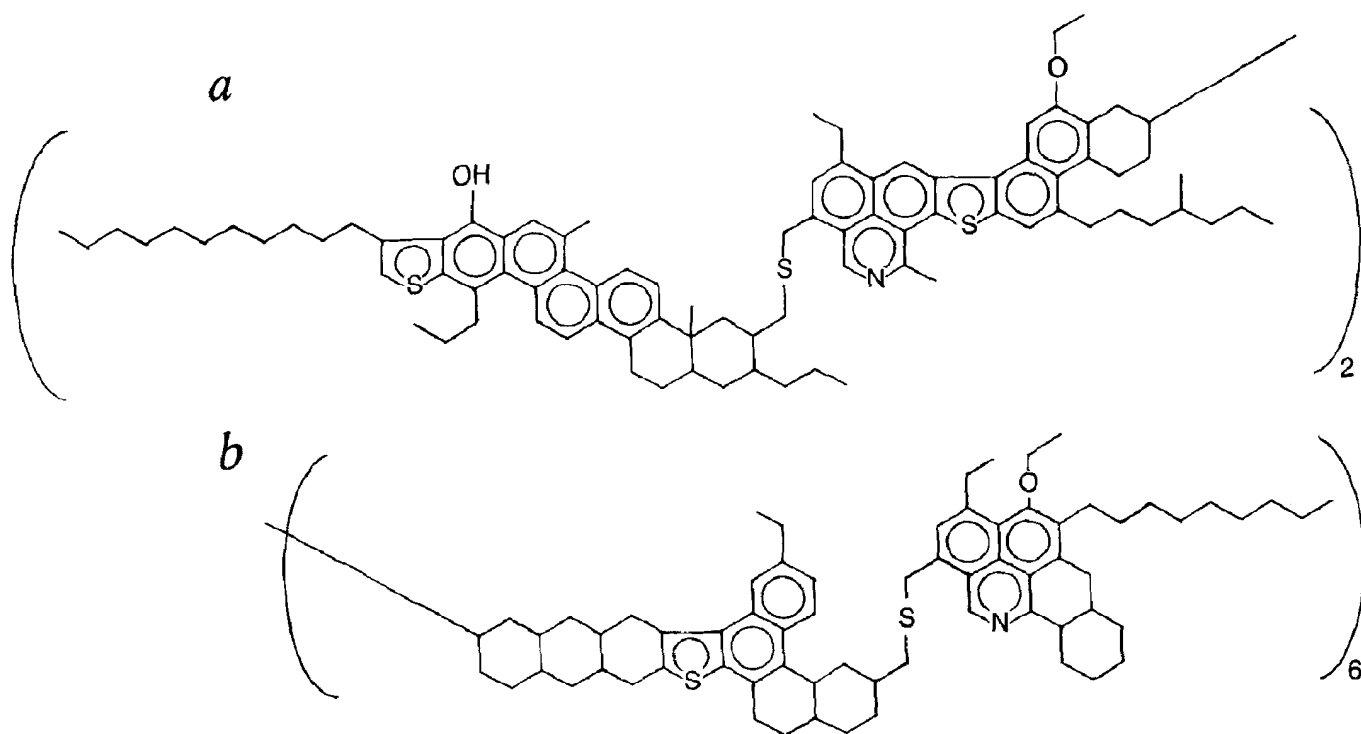


Figure 3 Average structural model of asphaltene: a, Athabasca; b, Utah. The structural parameters for these models are given in Table 8

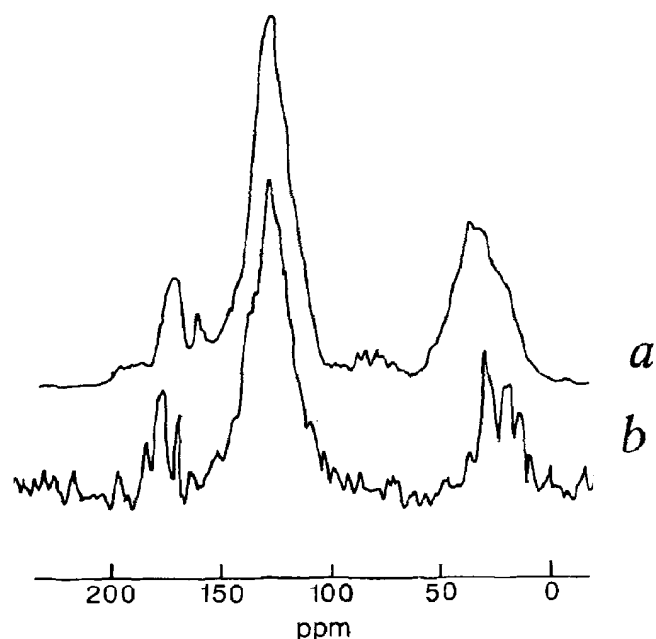


Figure 4 Solution  $^{13}\text{C}$  n.m.r. spectra of humic acid derived from oil sands: a, Athabasca; b, Utah

aliphatic; 110 to 160 ppm (region II), aromatic and olefinic carbon resonances. Olefinic carbon is not considered to be a major constituent of humic acids<sup>35</sup> and therefore aromatic carbons are expected to be predominant contributors to region II. This band can be subdivided into a band assigned to carbon bonded only to hydrogen or carbon (110–145 ppm) and a band assigned to O- and N-substituted carbon (145–160 ppm); 160 to 190 ppm (region III) carboxyl, amide carbonyl and ester carbonyl groups.

Assignments for chemical shifts in these regions<sup>35</sup> are given in Table 9. The dominant signal in region I is

observed at  $\approx 30$  ppm, which is assigned to carbon of polymethylene groups  $(\text{CH}_2)_n$ . The broad band of resonances present in the aliphatic region is an indication of a wide variety of carbon types (methyl, methylene and methine groups) being present. For Utah humic acid, signals in the aliphatic region are better resolved, indicating finer structure. Unfortunately, the low signal to noise ratio does not allow more information to be extracted from the spectra. In region II a strong broad peak is observed at 130 ppm and such resonances could be provided by unsubstituted and bridgehead aromatic carbons, or olefinic nuclei. Alkyl benzenes could also resonate in the 130 ppm region<sup>36</sup>. In region III, relatively strong signals are centred around 175 ppm, which is most likely that of carboxyl groups and amide carbon. In strongly alkaline solution phenolic carbon may also contribute to the spectral intensity in this region.

It is common to characterize humic acid by means of the aromaticity (per cent of carbon in 110–160 ppm region to total carbon), which is considered to give an indication of the relative contribution of terrestrial input into the sediment<sup>35–40</sup>. It has been observed, for example, that in the case of terrestrial humic acid derived from peats<sup>35</sup> and coals<sup>39,40</sup> aromatic structures are dominant and aromaticities are from 40 to 68%. Aromaticities of 53% and 48% determined for Utah and Athabasca<sup>14</sup> humic acid (Table 10) place these materials in the same range as those separated from coals and peat. Thus a comparison between the aromaticity data presented in Table 10 and those reported in the literature suggests that humic acid derived from Utah oil sand is largely terrestrial in origin as has been found for Athabasca humic acids.

## CONCLUSION

Asphaltenes derived from the Utah and Athabasca oil

**Table 10** Aromaticities of Utah and Athabasca humic acid

Humic acid	Aromaticity (%) <sup>a</sup>
Utah	53.1
Athabasca	48.1 <sup>b</sup>

<sup>a</sup>Per cent of carbon in 110–160 ppm region to total carbon<sup>b</sup>From Ref. 14

sands have been characterized using different techniques. Elemental compositions of the asphaltenes were similar but the H/C atomic ratio was higher for Utah asphaltene than for Athabasca. Number average molecular weights, light absorption in the visible region and metals content of these asphaltenes were significantly different. A combination of <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy was used for determination of structural parameters for the asphaltenes. The aromaticity of Athabasca asphaltene appeared to be higher. Structural models were different with a higher degree of condensation of aromatic rings for Athabasca asphaltene. <sup>13</sup>C n.m.r. spectra obtained for humic acid extracted from Utah and Athabasca oil sands solids were similar. On the basis of the aromaticity data it is suggested that humic acid derived from Utah oil sand has a significant terrestrial input as has been found for Athabasca oil sand.

## ACKNOWLEDGEMENT

The authors thank Dr A. Hardin for providing the Athabasca oil sand sample, and also acknowledge the help of M. R. Miedema (metal determination) and H. Séguin (elemental analysis).

## REFERENCES

- Berkowitz, N. and Speight, J. G. *Fuel* 1975, **54**, 138
- Miller, J. D. and Misra, M. *Fuel Proc. Technol.* 1982, **6**, 27
- Speight, J. G. in 'Characterization of heavy crude oils and petroleum residues', Symposium International, Lyon, France, 25–27 June 1984, p. 32
- Ignasiak, T. M., Zhang, Q., Kratochvil, B., Maitra, C., Montgomery, D. S. and Strausz, O. P. *AOSTRA J. Res.* 1985, **2**, 21
- Montgomery, D. S. in 'Characterization of heavy crude oils and petroleum residues', Symposium International, Lyon, France, 25–27 June 1984, p. 42
- Kotlyar, L. S., Sparks, B. D. and Kodama, H. *AOSTRA J. Res.* 1985, **2**, 104
- Ignasiak, T. M., Kotlyar, L., Samman, N., Montgomery, D. S. and Strausz, O. P. *Fuel* 1983, **62**, 363
- Speight, J. G. *Fuel* 1971, **50**, 102
- Selucky, M. L., Kim, S. S., Skinner, F. and Strausz, O. P. in 'The Chemistry of Asphaltenes' (Eds. J. W. Bunger and N. C. Li), Adv. in Chem. Series No. 195, Am. Chem. Soc., Washington DC, 1981, p. 83
- Suzuki, T., Iton, M., Takegami, Y. and Watanabe, Y. *Fuel* 1982, **61**, 402
- Cyr, N. and Selucky, M. L. *Liquid Fuels Technology* 1985, **3**, 377
- Cyr, N., McIntyre, D. D., Toth, G. and Strausz, O. P. *Fuel* 1987, **66**, 1709
- Majid, A. and Ripmeester, J. R. *Fuel* 1986, **65**, 1714
- Kotlyar, L. S., Ripmeester, J. A., Sparks, B. D. and Montgomery, D. S. *Fuel* 1988, **67**, 221
- Yokota, T., Scriven, F., Montgomery, D. S. and Strausz, O. P. *Fuel* 1986, **65**, 1142
- Blumer, J. T. and Starr, J. (Eds.) 'Syncrude Analytical Methods for Oil Sand and Bitumen Processing', Syncrude Canada Ltd, Edmonton, Alberta, Canada, August 1979, p. 58
- Mitchell, D. L. and Speight, J. G. *Fuel* 1973, **53**, 149
- Huffman, E. W. D., Jr. *Microchem. J.* 1977, **22**, 567
- Schöniger, W. in 'Proceedings of the International Symposium on Microchemistry, 1958', Pergamon, New York, 1960, p. 93
- Durand, B. (Ed.) 'Kerogen', Technip-Paris, 1980, p. 36
- Yen, T. F. in 'The role of trace metals in petroleum', Ann Arbor Science Publishers, Inc., Michigan, USA, 1975, 1–30
- Baker, E. W. in 'Organic geochemistry' (Eds. G. Eglinton and M. T. J. Murphy), Springer-Verlag, New York, 1969, 464–497
- Jacobs, F. S., Bashelor, F. W. and Filby, R. H. in 'Characterization of heavy crude oils and petroleum residues', Symposium International, Lyon, France, 25–27 June 1984, p. 173
- Kukes, S. G. Proc. 34th Canadian Chem. Eng. Conf., Quebec, September–October 1984
- Jacobs, F. S. and Filby, R. H. *Anal. Chem.* 1983, **55**, 74
- Graham, W. R. M. *Am. Chem. Soc. Div. Pet. Chem., Prepr.* 1986, **31**, 608
- Wright, W. D. 'The measurement of colour', A. Hilger Ltd, London, 1969, pp. 1–29
- Kotlyar, L. S., Sparks, B. D. and Woods, J., unpublished data
- Gillet, S., Rubini, P., Delpuech, J.-J., Escalier, J.-C. and Valentin, P. *Fuel* 1981, **60**, 220
- Gillet, S., Rubini, P., Delpuech, J.-J., Escalier, J.-C. and Valentin, P. *Fuel* 1981, **60**, 226
- Dickinson, E. M. *Fuel* 1980, **59**, 290
- Boduszynski, M. M. *Am. Chem. Soc. Div. Pet. Chem., Prepr.* 1983, **28**, 1376
- Huc, A. Y., Behar, F. and Roussel, J. C. in 'Characterization of heavy crude oils and petroleum residues', Symposium International, Lyon, France, 25–27 June 1984, p. 99
- Yen, T. F. *Energy sources* 1974, **1**, 447
- Hatcher, P. G., Breger, I. A., Dennis, L. W. and Maciel, G. E. in 'Aquatic and Terrestrial Humic Materials' (Eds. R. F. Christman and E. T. Gjessing), Ann Arbor Science Publishers, Michigan, 1983, p. 37
- Hatcher, P. G., Maciel, G. E. and Dennis, L. W. *Org. Geochem.* 1981, **3**, 43
- Calderoni, G. and Schnitzer, M. *Geochim. Cosmochim. Acta* 1984, **48**, 2045
- Hatcher, P. G., Schnitzer, M., Dennis, L. W. and Maciel, G. E. *Soil Sci. Soc. Am. J.* 1981, **45**, 1089
- Verheyen, T. V., Johns, R. B. and Blackburn, D. T. *Geochim. Cosmochim. Acta* 1982, **46**, 269
- Ibarra, J. V. and Juan, R. *Fuel* 1985, **64**, 650