Identification, Detection and Characterization of Individual Tar Sand Phases using Diffuse Reflectance Spectroscopy (0.35–2.6 μm)

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Abstract. The combined ultraviolet, visible, and near-infrared reflectance spectra of raw tar sands exhibit a number of resolvable absorption bands in the 0.35–2.6 μm wavelength region. These bands are related to the abundances and compositions of the various phases. Adsorbed, structural and free water absorption bands appear near 1.4, 1.9, 2.2, and 2.3 μm and are strongest in the lowest organic-highest clay sample spectra. The broadness and fine structure of these bands indicate that much of the water is present in a variety of complexed forms, and that the clays are somewhat structurally disordered. Absorption bands due to the bitumen fraction are found near 1.7 μm and between ~2.3 and 2.6 μm. They are primarily due to overtones and combinations involving the various C–H stretching fundamentals, and most are not overlapped by the absorption bands of the other phases present. An increase in the intensity of the bitumen absorption bands is accompanied by a decrease in the intensity of the various water and clay absorption bands, and vice versa. The various absorption bands are sufficiently resolvable to allow the development of correlations between spectral and material properties. Quartz shows no diagnostic absorption bands in this wavelength region, consequently its abundance cannot be determined directly by reflectance spectroscopy alone.

These results have implications for developing automated analytical systems capable of providing near real-time continuous assays of many physical and chemical properties of tar sand in industrial operations which utilize continuous feed processes, in remote sensing detection of hydrocarbons, and field analysis of samples using portable instrumentation.

Key words: Reflectance spectroscopy/tar sands/near-infrared/phase characterization

INTRODUCTION

The Athabasca tar sand deposit, located in northeastern Alberta, is one of the largest known petroleum deposits in the world. It consists of viscous organic matter embedded in clastic sediments of the Cretaceous McMurray and Clearwater formations. This material is a heterogeneous mixture of bitumen (with its myriad chemical and structural forms), water, quartz sand, clay minerals and a number of other minerals [7]. Knowledge of the physical and chemical properties of tar sand is essential for improving bitumen extraction efficiencies and understanding the processes of tar sand formation and emplacement. A large number of analytical methods are routinely employed to characterize various material properties [2,3]. Diffuse reflectance spectroscopy (DRS) is an analytical technique which has been very successful for
characterizing the physical and chemical properties of geological materials but has not yet been adequately assessed for its applicability to hydrocarbon analysis. The 0.35–2.6 μm diffuse reflectance spectra of a suite of tar sand samples from the Athabasca deposits were measured in order to determine whether characteristic absorption bands can be found which correlate with the various physical and chemical material properties. The results may also be applicable to the study of other tar sands and heavy oils.

**DRS VERSUS OTHER ANALYTICAL TECHNIQUES**

DRS in the ultraviolet (UV), visible (V), and near-infrared (NIR) spectral regions (~0.35–2.6 μm) has a number of advantages over other analytical methods. Spectral measurements are highly reproducible because little or no sample preparation is required to yield useable results. This is particularly significant for materials such as tar sands which may undergo chemical alteration in the course of sample preparation for transmission spectroscopy [4]. DRS is a mature, proven, non-destructive analytical technique with the potential to provide, continuous, real-time assays of raw tar sands and various separates. Measurements can be made in the field using portable instrumentation.

Ultraviolet-visible-near infrared (UV-V-NIR) spectral studies can provide information complementary to other analytical techniques and are suited to situations requiring rapid turnaround times and comparisons with field studies. Mid- and far-infrared spectroscopy are powerful tools for elucidating the types and configurations of atomic bonds in many organic materials including tar sands [4,7–9]. The types and intensities of fundamental vibrational and rotational modes are useful for understanding the atomic configurations which give rise to these features. The UV-V-NIR wavelength regions are useful for examining combinations and overtones of the fundamentals (near-infrared), crystal field transitions (visible), and charge-transfer effects (ultraviolet) [10–12]. Multiatomic relationships (combination and overtone bands), monatomic electronic processes (crystal field effects), and long-distance atomic interactions (charge-transfer effects) manifest themselves in these wavelength regions.

**EXPERIMENTAL PROCEDURE**

The tar sand samples used in this study have been obtained from the Alberta Oil Sands Technology and Research Authority (AOSTRA) Oil Sands Sample Bank and are from the Syncrude Canada Ltd. and Suncor Canada Ltd. leases near Fort McMurray, Alberta. The samples were characterized by AOSTRA for location, date collected, particle size distribution, bitumen, water, and solids abundances. The handling of the samples beyond collection date is unavailable. While in the possession of the author, the samples were kept in airtight containers.

The reflectance spectra have been measured at the U.S. Geological Survey spectrometer facility in Denver, Colorado. Details of the instrumentation and data acquisition procedures can be found in References 13 and 14. A circular area of 22-mm diameter was imaged, the largest sample holder available. The samples were gently flattened to provide a level surface for measurement in order to minimize phase angle effects [6]. The sample spectra were measured relative to halon, which is a near-perfect diffuse reflector in the 0.35–2.6 μm wavelength region [15].

Tar sand reflectance spectra are affected by a number of internal and external parameters. Even with the minimum sample handling associated with DRS, inadvertent enhancement or suppression of phases may occur. Of particular concern is the smearing of bitumen on the sample surface, which may occur in the course of preparing a flat surface for spectral measurements. Smearing may also occur during "chopping" and homogenization of the material for a representative sample. However, this does not appear to be a problem because duplicate samples, one intensively and one lightly homogenized, yield nearly identical spectra.

Other internal parameters may also affect the spectral signature of geological materials, the most significant being packing, particle size, viewing geometry, and instrumentation [5,6]. The first two parameters are strictly applicable only to dry, powdered samples, while the latter two are laboratory dependent, and hence controllable, and introduce no unanticipated difficulties.

DRS differs from other spectroscopic techniques in that the background continuum is retained because it often contains useful information concerning sample composition [12,16]. Continua are sometimes constructed over short wavelength segments in order to isolate specific features for more detailed examination. Here, the continua have been constructed as straight-line segments tangent to the reflectance spectra on either side of a particular absorption feature. Band depths or band intensities are useful parameters and are measured
relative to the continuum \[17\]. Here, band depth \((D_b)\) will be defined as:

\[
D_b = 1 - \left( \frac{R_b}{R_c} \right)
\]

where \(R_b\) is the reflectance at the band minimum and \(R_c\) is the reflectance of the continuum at the same wavelength as \(R_b\). The bitumen reflectance spectra show a decrease in reflectance beyond \(\sim 2.25 \text{ \mu m}\) due to numerous overlapping absorption bands. In this wavelength region the straight-line continuum is constructed as a horizontal line tangent to the spectrum at the reflectance maximum near \(2.25 \text{ \mu m}\). Band wavelength positions, band area, band widths, absolute reflectance at specific wavelengths, and various ratios of these parameters are also useful for correlating spectral properties with sample characteristics \[17\].

**THE UV-V-NIR SPECTRAL REGION**

The UV-V-NIR spectral reflectance properties of the various phases present in tar sands have been previously examined to various degrees and can be used to predict whether these phases possess diagnostic spectral features which may appear in the raw tar sand spectra. This study is the first to look at the UV-V-NIR spectra of the phases as they occur in tar sand.

The ultraviolet, visible, and near-infrared spectral regions are most useful for examining charge transfer, crystal field transitions, and combinations and overtones of fundamental vibration and rotational bands. The combination and overtone bands can provide information on bitumen structure at a larger scale than is possible from fundamental bands alone because they may involve two molecular species sharing a common atom. Simultaneous excitations of delocalized species are weak or nonexistent \[18\].

**Ultraviolet and visible spectral region.** The ultraviolet and visible spectral regions exhibit absorption features largely due to charge-transfer crystal field effects \[10,19\]. Electronic transitions due to excitations of the bonding electrons in organic compounds appear in the 0.1–0.35 \(\text{\mu m}\) region. The maximum absorption tends to move to longer wavelengths and individual absorption bands become less distinct as the compounds become increasingly complex. Resolvable absorption bands attributable to specific organic components are not expected in this wavelength region.

The overall reflectance of a tar sand spectrum is expected to increase gradually towards longer wavelengths as electronic transition effects in molecular orbitals and charge transfers become less pronounced at lower energies. This reflectance increase is attributed to C–C electronic charge transfers and varies with the degree of coalification, carbonization, degree and type of aromatization, and coal type, and is present in coal, charcoal, oil shale and tar sand spectra \[16,20–23\]. As fixed carbon content increases, the reflectance spectrum acquires an increasingly red slope due to a higher degree of semi-conductivity \[24\]. Various metal-ligand combinations such as Fe–O can give rise to similar absorptions \[25\]. Fe–O complexes in the clays and V- and Ni-ligand bonds in the porphyrins probably contribute to the downturn in reflectance towards shorter wavelengths as well.

**The NIR spectral region.** The NIR spectral region will be most affected by first-order overtones and combinations of the most intense fundamental bands. These potential absorption bands and their predicted positions are listed in Table 1. These positions are derived from infrared transmission spectra of a range of organic materials, including tar sands \[17,26–28\]. Only the most intense absorption bands will be detectable because of the low albedo of tar sand. The intensities of these bands can only be estimated because of the paucity of spectral data for tar sands in this wavelength region. The predictions are based on the strength of the fundamental absorptions and the likelihood of simultaneous excitations. The likeliest places to look for absorption bands are the 1.7 \(\text{\mu m}\) and 2.2–2.6 \(\text{\mu m}\) regions (Table 1) \[18,22,23\]. Second-order overtones and more complex combination bands are expected to be weak or absent.

The 1.7 \(\text{\mu m}\) region is dominated by combinations and overtones of the various C–H stretching bands. The 2.2–2.6 \(\text{\mu m}\) range is an area of numerous overlapping absorption bands. This is primarily due to the fact that bitumen transmission spectra show a region of moderately strong absorption between \(\sim 1750\) and \(900\) cm\(^{-1}\) \[17,26–29\]. The large number of possible combination bands involving this spectral region likely precludes the use of the 2.2–2.6 \(\text{\mu m}\) range for more than general molecular assignments unless very sophisticated curve-resolving techniques are employed. If any bands are to appear against this backdrop of intense absorption, they will likely be combinations of the most intense fundamental absorptions — the C–H stretching modes. Both coal \[16,23\] and bitumen spectra \[26,27\] show few resolvable absorption bands in this region.
Table 1. Positions of the major organic fundamental absorption bands (cm⁻¹) and the predicted most intense overtone and combination bands (in microns)

<table>
<thead>
<tr>
<th>Band</th>
<th>Fundamental frequency cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3030</td>
<td>alkene, aromatic C–H stretch</td>
</tr>
<tr>
<td>(b)</td>
<td>2950</td>
<td>asymmetric CH₃ stretch</td>
</tr>
<tr>
<td>(c)</td>
<td>2920</td>
<td>asymmetric CH₂ stretch</td>
</tr>
<tr>
<td>(d)</td>
<td>2875</td>
<td>symmetric CH₃ stretch</td>
</tr>
<tr>
<td>(e)</td>
<td>2850</td>
<td>symmetric CH₂ stretch</td>
</tr>
<tr>
<td>(f)</td>
<td>1700</td>
<td>carbonyl/carboxyl C–O stretch</td>
</tr>
<tr>
<td>(g)</td>
<td>1600</td>
<td>aromatic carbon stretch</td>
</tr>
<tr>
<td>(h)</td>
<td>1450</td>
<td>asymmetric CH₂, CH₃ bend</td>
</tr>
<tr>
<td>(i)</td>
<td>1375</td>
<td>symmetric CH₃ bend</td>
</tr>
</tbody>
</table>

Combination and overtone bands

<table>
<thead>
<tr>
<th>Combination/ overtone band</th>
<th>Wavelength µm</th>
<th>Combination/ overtone band</th>
<th>Wavelength µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(a)</td>
<td>1.650</td>
<td>(e + f)</td>
<td>2.198</td>
</tr>
<tr>
<td>(a + c)</td>
<td>1.681</td>
<td>(c + g)</td>
<td>2.212</td>
</tr>
<tr>
<td>2(b)</td>
<td>1.695</td>
<td>(e + g)</td>
<td>2.247</td>
</tr>
<tr>
<td>(a + e)</td>
<td>1.701</td>
<td>(b + h)</td>
<td>2.273</td>
</tr>
<tr>
<td>2(c)</td>
<td>1.712</td>
<td>(c + h)</td>
<td>2.288</td>
</tr>
<tr>
<td>(b + d)</td>
<td>1.717</td>
<td>(b + i, d + h)</td>
<td>2.312</td>
</tr>
<tr>
<td>(c + e)</td>
<td>1.733</td>
<td>(e + h)</td>
<td>2.326</td>
</tr>
<tr>
<td>2(d)</td>
<td>1.739</td>
<td>(d + i)</td>
<td>2.353</td>
</tr>
<tr>
<td>2(e)</td>
<td>1.754</td>
<td>(c + j)</td>
<td>2.532</td>
</tr>
</tbody>
</table>

Clay minerals and free water will display a number of absorption bands in the NIR spectral region. These bands are almost exclusively confined to regions near 1.4 and 1.9 µm while clay displays additional absorption bands between 2.2 and 2.45 µm. The positions, shapes, and intensities of these bands are excellent indicators of clay abundances and types, and free water abundance and degree of polymerization [12,30–34].

RESULTS

A suite of eight tar sand samples ranging from 3.2–15.1 weight % bitumen have been characterized spectrally. The samples have been divided into low, medium, and high bitumen content groups by dividing the range of probable bitumen content (~0–15 wt%) into three equal groups. This division is artificial because the groups merge into each other both spectrally and compositionally. For this initial survey of spectral types a representative sample of each group is presented, along with a discussion of the material properties which give rise to specific spectral features.

Low bitumen content spectra. The reflectance spectrum of a tar sand sample containing 3.2 wt% bitumen is shown in Figure 1. The overall low reflectance of the spectrum precludes the positive identification of many absorption bands because of the low signal-to-noise ratio. The least ambiguous bands along with the measured band depths are listed in Table 2.

The overall decrease in reflectance towards shorter wavelengths can be attributed to the various C–C and metal-ligand charge transfers. Superimposed on this dropoff is a slight additional decrease in reflectance at ~0.4 µm. This feature (if it is an actual absorption band) probably represents a Soret band. It is not prominent \((D_b \approx 6\%)\) because it occurs in an area of intense absorption (< 3% average reflectance) which masks all but the most intense absorption bands. The distinct change in slope and the apparent complexity of the spectrum near 0.87 µm cannot be unambiguously assigned, partly because it occurs in an area of poor
Figure 1. The UV-V-NIR reflectance spectrum (0.35–2.6 μm) of tar sand sample 82-15. This spectrum is representative of the low-bitumen content group.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>82-05</th>
<th>87-04</th>
<th>86-19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen (wt%)</td>
<td>3.2</td>
<td>8.1</td>
<td>13.2</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>8.1</td>
<td>6.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Solids (wt%)</td>
<td>88.7</td>
<td>83.3</td>
<td>83.9</td>
</tr>
<tr>
<td>&lt; 400 mesh (wt%)</td>
<td>32.1</td>
<td>29.3</td>
<td>6.0</td>
</tr>
<tr>
<td>&gt; 400 mesh (wt%)</td>
<td>67.9</td>
<td>70.7</td>
<td>94.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Band minimum (μm)</th>
<th>Db</th>
<th>Db</th>
<th>Db</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>7.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1.39–1.41</td>
<td>4.5</td>
<td>6.0</td>
<td>3.0</td>
</tr>
<tr>
<td>1.72–1.75</td>
<td>1.8</td>
<td>9.9</td>
<td>18.6</td>
</tr>
<tr>
<td>1.92–1.95</td>
<td>19.0</td>
<td>10.4</td>
<td>3.8</td>
</tr>
<tr>
<td>2.10</td>
<td>5.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2.15–2.18</td>
<td>4.1</td>
<td>9.6</td>
<td>11.4</td>
</tr>
<tr>
<td>2.21</td>
<td>6.5</td>
<td>15.5</td>
<td>14.3</td>
</tr>
<tr>
<td>2.31</td>
<td>14.8</td>
<td>40.2</td>
<td>54.3</td>
</tr>
<tr>
<td>2.35</td>
<td>13.9</td>
<td>38.9</td>
<td>55.0</td>
</tr>
<tr>
<td>2.45</td>
<td>16.9</td>
<td>35.6</td>
<td>47.9</td>
</tr>
<tr>
<td>2.55</td>
<td>22.1</td>
<td>33.9</td>
<td>38.6</td>
</tr>
</tbody>
</table>
detector response. It may represent iron charge transfer and crystal field bands and/or water absorption bands. The former explanation is favored because water is relatively transparent at these wavelengths.

The non-linear spectral slope between 0.87 and 1.4 μm and the absorption minimum at ~0.95 μm is characteristic of many ferrous iron-bearing silicate minerals [35]. The presence of this band in the tar sand spectrum may be an expression of the various iron phases which contaminate the clays [7]. The water overtone band at 0.98 μm is not a significant contributor to his feature because more intense water overtone bands near 1.20 μm are not apparent [33].

The high clay content (< 400 mesh = 32.1%) of this sample is manifested in the prominent bound and structural water absorption bands. The band depths of the 1.4, 1.9, and 2.2 μm bands are 4.5, 19.0, and 6.5%, respectively (Table 2). There is a contribution by free water to the 1.9 μm band, but no evidence for it at 1.45 μm. This suggests that most of the water in the sample is associated with the clays primarily as bound water. The Athabasca clays are highly absorbing and this may be related to the structural disorder in the finest clay fractions [1, 36]. The broadness of the 1.4 and 1.9 μm bands is evidence for disordered or structurally diverse clays [30, 31, 35].

Absorption bands which can be assigned to specific bitumen components should be present around 1.7 μm and longwards of ~2.2 μm. The 1.7-μm area is obscured by the noise in the data and the apparent absorption band (D_b < 2%) cannot be assigned to any particular organic overtone with any confidence. The weakness of this band is consistent with the low bitumen content of the sample. A number of weak absorption bands in the 2.05–2.25 μm region are best explained as overlapping structural OH bands due to the clays. The absorption band at 2.20 μm is probably an overlap of the structural water band and a CH_{2} + CH_{3} = CH_{3} combination band (c + g; Table 1), since no other strong organic band occurs in this region. A strong (D_b = 14.8%), well-defined absorption band is present at 2.3 μm. This band is also likely an overlap of a clay structural water band and an organic combination band. If only clay were present this band would be of lower intensity than the 2.2 μm band. From Table 1, the likeliest candidate organic bands are b + i, e + h, and d + h. The relative contribution of each band cannot be determined because of the limited spectral resolution. There is general decline in reflectance longwards of 2.3 μm which is probably a combination of dominant clay bands and subordinate organic bands. Once again, spectral resolution does not permit specific assignments of the bands to be made.

**Medium bitumen content spectra.** The reflectance spectrum of sample 87-04 (Figure 2) is representative of

![Figure 2](image_url)

*Figure 2.* The UV-V-NIR reflectance spectrum (0.35–2.6 μm) of tar sand sample 87-04. This spectrum is representative of the medium-bitumen content group.
medium bitumen content spectra. Interpretation of this spectrum is facilitated by the higher overall reflectance and decreased noise. There is no evidence for a porphyrin absorption feature at 0.4 μm, although it may be obscured by the low reflectance. The reflectance minimum occurs at ~0.42 μm, whereas in the low bitumen sample the minimum occurs shortwards of 0.35 μm. There are a number of weak and questionable absorption features superimposed on the reflectance increase towards longer wavelengths. Individual absorption bands are not expected to be seen at ultraviolet and visible wavelengths [37]. The shortest wavelength-resolvable absorption bands are found at 1.38–1.43 μm (D_b = 6.0%) and can be ascribed to bound and structural water in clays. The broadness and fine structure of the spectrum in this region indicates a number of structural sites and/or some disorder. Here are no possible combinations or low order overtones of bitumen-associated fundamentals of sufficient intensity in this wavelength region. The 1.9-μm bound water band, like the 1.4-μm band, is also broad and intense (D_b = 10.4%). Free water absorption bands are weak or absent with the exception of the 1.9 μm band where a shoulder appears on the long wavelength side of the band near the position expected for free water.

More intense combination and overtone bands of organic fundamentals reflect the higher bitumen content of this sample, with the 1.7-μm region being the most apparent affected. The complex shape of the 1.7-μm feature is due to the overlap of multiple bands. The strongest candidate bands are first-order overtones (2b, 2c, 2d, 2e) and combinations (a + e, b + d, c + e) of the CH_2 and CH_3 stretching modes. The maximum band depth is 9.9% at 1.72 μm. The 2.15–2.20 μm interval shows at least two bands and is probably due to contributions from both organic combination bands and clay–OH bands. The decreasing dominance of the clays can be seen from the change in the slope between 2.3 and 2.6 μm. It has a more positive slope than low-bitumen spectra, and is intermediate between low-bitumen and high-bitumen spectra. The sharp decline in reflectance at 2.3 μm is more pronounced in the more bitumen-rich spectra, as expected, and the 2.3–2.6 μm region also shows more detail. This is likely due to the decreasing influence of the poorly-defined clay bands and the short wavelength wing of the OH/H_2O fundamental. The absence of a reflectance decline from 2.3 to 2.6 μm, which is characteristic of clays, is further evidence for the increasing spectral dominance of bitumen.

In addition to the absorption band at 2.31 μm, a discrete band also appears at 2.35 μm. The best candidate for this band is a combination of a CH_3 stretch with a CH_3 bend (d + i, Table 1). Other absorptions in the 2.3–2.6 μm area are less well-defined but are primarily due to the combinations listed in Table 1. Small contributions are also made by numerous combination and overtone bands which have been ignored because of their perceived secondary importance [18,22,23].

**High bitumen content spectra.** Sample 86-19 (Figure 3) is representative of high bitumen content spectra (13.2 weight%) and is characterized by low overall reflectance (< 15%). In this respect it more closely resembles the low bitumen spectra.

The reflectance minimum of this sample occurs at ~0.47 μm. There is no evidence of a Soret band at 0.40 μm. Reflectance rises smoothly from the minimum towards higher wavelengths. As was the case for the low bitumen spectrum, absorption features may be present near 0.9 μm but the noise in the data prevents positive identification of discrete features. At ~1.4 μm there is a weak (D_b = 3%), poorly resolved absorption band due to structural and bound water. The bitumen-associated first-order overtone bands of CH_2 and CH_3 are very prominent near ~1.7 μm. Second-order overtones of these bands would be expected at 1.13–1.17 μm but are not evident. This supports the exclusion of all the higher-order overtones from consideration as significant contributors to the reflectance spectra. The expected OH and H_2O bands at 1.9 μm are weakest (D_b = 3.8%) in this spectrum, which is consistent with the low water (2.5%) and clay content (6%) of the sample.

At least two bands are present between 2.15 and 2.20 μm and they cannot be unambiguously assigned at present. The 2.30 and 2.35 μm bands are extremely intense (D_b = 54–55%), in keeping with the high bitumen content. The rise in reflectance from 2.3 to 2.6 μm is also more pronounced. The rise in reflectance is probably due to the 2.3 and 2.35 μm bands increasing in depth at a greater rate than the rest of this wavelength interval. Band depths were measured at 2.55 μm using the horizontal continuum as previously defined, and it was found that the band depth at 2.55 μm increases in the sequence 22%–34%–39% with increasing bitumen content. The depth of the 2.3-μm band increases more dramatically from 15% to 40% to 54%. On average the band depth between 2.3 and 2.6 μm increases with
increasing bitumen content although the spectral details change.

**DISCUSSION**

The spectra of low, medium, and high bitumen content tar sands show distinct spectral differences which are related to changes in phase composition and abundance. The small sample size precludes the development of rigorous quantitative calibrations at this stage. However, many encouraging spectral parameters have been identified for further investigation.

**Structural and bound water bands.** The most prominent water absorption bands are present near 1.9 μm and become more intense with increasing water content (Table 2). This wavelength region is also free of any interferences from detectable bitumen absorption bands. The broadness and complex shape of the 1.9-μm feature can be ascribed to the presence of water in multiple and/or poorly crystallized clay lattice sites, a factor confirmed by structural studies of the Athabasca clays [1,36]. There may be a spectral contribution due to free water at 1.95 μm but it cannot be unambiguously resolved. At the compositional extremes represented in this study, the 1.9-μm OH/H₂O bands either dominate the spectrum (Figure 1), or become so weak that they may be easily overlooked (Figure 3). The intensity of the 1.9-μm band can be related to the clay and water contents. For the samples studied, a minimum detection limit of 6% clay and 2.5% water is suggested, although once again, the relative contributions of the clay and water to this absorption band cannot be determined.

The absorption bands near 1.4 μm are more unambiguously assigned to structural and bound water in clays because the available data suggest that water in clays absorbs at different wavelengths than free water, even when polymerized (1.38–1.42 μm versus 1.45 μm). The broadness of the 1.4-μm band is characteristic of disordered clays and resembles the 1.9-μm band in this respect [38]. The fact that the three types of water absorb at different wavelengths and that this is expressed in the reflectance spectrum of raw tar sands makes this a fruitful area for further investigation.

The lattice-OH combination band expected at ~2.2 μm is actually weakest in the highest clay content sample (Table 2), suggesting that organic combination bands are also present in this region. Separation of the relative contributions from these two sources is not yet possible. The reflectance decrease from 2.2 to 2.6 μm
which appears in the low bitumen content spectrum (Figure 1) is characteristic of clays [39]. The spectral influence of the clays declines and absorption in this wavelength region becomes more intense as bitumen content increases.

**Porphyrin bands.** The intense Soret band is characteristic of porphyrins and should be present at \( \approx 0.4 \mu m \). It is only weakly indicated, if at all, in the lowest bitumen spectrum. All three tar sand spectra have roughly the same reflectance at 0.4 \( \mu m \) (2.3–2.5%) so that band suppression by opaque materials is not a viable explanation. The only difference in the three spectra is the slope of the reflectance at low wavelengths. The low bitumen spectrum has the steepest slope so that detection of an absorption band on a sloping continuum may be easier than on a more horizontal continuum. This is not a very satisfying explanation and a resolution of this issue cannot be made at this time.

**Bitumen bands.** The most intense overtone and combination bands of vibrational and rotational fundamentals of bitumen components fall broadly into two groups — near 1.7 \( \mu m \) and between 2.2 and 2.6 \( \mu m \) (Table 1). As expected, these bands are the most pronounced in the highest bitumen content spectra. The bands at 1.7 \( \mu m \) are virtually absent in the lowest bitumen spectra and the higher-wavelength bands are partially obscured by the clay-associated absorption bands. Up to six strong bands could be present near 1.7 \( \mu m \) (Table 1). The asymmetric appearance of the absorption feature in this region implies multiple overlapping absorption bands. The increase in band depth near 1.7 \( \mu m \) correlates with the rise in bitumen content. Sophisticated band deconvolution techniques will be required to sort out the relative contributions of each molecular component.

The absorption bands attributable to the bitumen component in the 2.2–2.6 \( \mu m \) region involve various combinations of vibrational fundamentals (Table 1). Individual bands are difficult to recognize because of the large number of possible fundamental combination bands. Resolvable bands are most evident in the highest bitumen spectra at 2.30 and 2.35 \( \mu m \) and are not significantly affected by clay–OH bands because the more intense \( \approx 2.2 \mu m \) clay band is only weakly indicated. The overall slope of the reflectance spectrum from 2.3 to 2.6 \( \mu m \) is also an indicator of bitumen content. The 2.3–2.6 \( \mu m \) slope changes from negative to positive with increasing bitumen content. The negative slope is characteristic of clay while the positive slope is characteristic of bitumen. All indications are that clay dominates the spectral signature of the lowest-bitumen samples. A positive slope results from the absorption at \( \approx 2.3 \mu m \) increasing at a faster rate than the absorption at longer wavelengths. The absorption bands at 2.15 and 2.2 \( \mu m \) do not show a simple relationship between bitumen or clay content and band depth, suggesting that both phases contribute to these features. This precludes the use of these bands for phase determinations, especially given the availability of more suitable absorption bands for clay and bitumen determinations. The rest of the 2.2–2.6 \( \mu m \) region is not resolvable into well-defined absorption bands, due to the large number of possible combination and overtone bands (Table 1).

Changing bitumen content also affects the ultraviolet and visible spectral regions. The point of minimum reflectance shifts to longer wavelengths as the bitumen content rises. Boyd and Montgomery [27] estimated that an average of five aromatic rings per molecule are present in the resin fraction of the Athabasca tar sands. Resin is the most abundant component in the bitumen fraction [1,27], therefore this number is probably a good estimate for the total sample. The wavelength position of the reflectance minimum of the bitumen-rich sample 86-19 (\( \approx 0.47 \mu m \)) suggests an average of six rings using the calibration of Badger [40]. This is in good agreement with conventional analytical results. The shift of the reflectance minimum to shorter wavelengths in lower bitumen samples is probably due to extremely intense mineral charge-transfer bands in the ultraviolet, suppressing the slight upturn in reflectance towards shorter wavelengths.

The overall appearance of the rise in reflectance from 0.5 to 1.5 \( \mu m \) changes between the difference groups. The bitumen-poor spectrum shows a linear increase in reflectance from 0.5 to 0.9 \( \mu m \) with a break in slope at this point and a more concave rise to 1.5 \( \mu m \). As the bitumen content increases the slope break disappears and the reflectance rise becomes increasingly concave. The decrease in reflectance towards shorter wavelengths is usually attributed to charge-transfer effects and there is no reason to question this assignment. The differences seen in these spectra probably reflect the relative contributions of the clay and bitumen to the spectral decline. The smooth slope of Figure 3 represents the continuum of charge-transfer energy levels expected in a material as complex as bitumen [37].
CONCLUSIONS

Raw tar sand spectra show diagnostic changes in spectral reflectance properties which are related to changes in phase abundances and compositions. The reflectance spectra of the samples representing the approximate extremes in common phase abundances tend to be dominated by that one phase. Prominent regions of absorptions are present in the spectra due to most of the major tar sand phases with the exception of quartz.

Absorption bands due to structural water in the clay fraction appear at ~1.4, 2.2, 2.3, and perhaps 2.15 μm. A decline in reflectance longwands of 2.3 μm is characteristic of clay-rich samples. Absorption bands due to adsorbed (bound) water are found near 1.4 and 1.9 μm. Prominent free water absorption bands are expected at 1.94 and 1.45 μm but are not evident. The intensities of the clay absorption bands correlate with the clay content. The 1.9-μm band dominates the spectrum of low-bitumen samples, while it is virtually absent in the high-bitumen spectra.

Absorption bands due to the bitumen fraction are present near 1.7 μm and 2.2–2.6 μm and all involve C–H stretching modes. The strengths of the 1.7-, 2.3-, and 2.35-μm bands all increase with increasing bitumen content. The 1.7-μm band is particularly useful because it is not interfered with by the absorption bands of other phases. A reflectance minimum present in the ultraviolet-visible region seems to give a good indication of the average number of aromatic rings per molecule for the bitumen-rich spectra.

The presence of distinct absorption features due to clay and bitumen provides an opportunity to develop spectral assaying as a means for characterizing tar sands. In addition, remote sensing detection and field assaying of samples may be feasible in light of these results. Further analysis of a larger suite of sample spectra is being undertaken on the basis of the results of this study. In addition, detailed chemical and spectral investigations of these samples are being performed in order to maximize the amount of information which can be derived from spectral reflectance studies of these materials.

ACKNOWLEDGEMENTS

This project and the author were supported by an Alberta Oil Sands Technology and Research Authority (AOSTRA) Postgraduate Scholarship and Research Allowance, and an American Association of Petroleum Geologists (AAPG) Grant-in-Aid #582-12-01. Thanks are also due to Dean Wallace and Deborah Henry of the AOSTRA Oil Sands Sample Bank for providing the raw tar sand samples and the available analyses, to Dr. R.N. Clark and Mr. G. Swayne of the U.S. Geological Survey in Denver for access to the spectrometer facility, and to Drs. D.G.W. Smith and R. St. J. Lambert for their support of this project.

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