Abstract. New experimental data as well as analysis of published databases show that the potential of UV-Visible absorption (UVVA) spectroscopy for characterization of asphaltenes may be strongly underestimated. Even the simplest single-parameter models for monotonous UVVA spectra of asphaltenes allow distinguishing various types of crude oils. The main practical problem is that generally crude oils and solutions of asphaltenes are opaque and have to be strongly diluted for UVVA analysis. Our experiments show that dilution may notably affect the measured UVVA spectra apparently due to de-aggregation of asphaltenes in a solution. In fact, previously reported UVVA spectra of asphaltenes/crude oils may have been strongly distorted by artifacts, affecting not only quantitative parameters (spectra’s slopes), but also qualitative features (a presence of strong “resonance” absorption peaks). In particular, the popular “Urbach tail” model implies that the slopes of UVVA spectra reflect population (molecular weight) distributions of asphaltenes. This interpretation is obviously incompatible with the newly observed concentration effects in toluene solutions. On the other hand, our experimental data as well as critical analysis of other publications on optical spectroscopy of asphaltenes, show that the mythical “resonance absorption” is merely a solvent-related artifact and should be disregarded as basically erroneous.

Further development of UVVA characterization techniques requires better understanding of the nature/composition of asphaltenes. A useful approach may be consideration of “molecular diversity” models, being developed for other systems with continuous UVVA spectra, in particular for humic acids and melanins.


Figure 3. a. - Conventional plot of the UVVA spectrum of diluted Tatarstan crude (1.2 10^{-4} v/v in toluene). The wavelengths indicated in the figure are those employed for evaluation of E4/E6 ratios. b. - A plot of the same spectrum, more appropriate for slope analysis. The indicated ranges of photon energies are those employed for evaluation of characteristic energies U1, U2 and U3
Table 1. Differentiation of oil types by non-coloration parameters of UVVA spectra

<table>
<thead>
<tr>
<th>Oil Type/Name</th>
<th>ρ (g/cm³)</th>
<th>S (wt.%)</th>
<th>ε₄₆₀ (1/μm)</th>
<th>U₃ (eV)</th>
<th>E₄/E₆</th>
<th>U₁/U₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sweet Light/Medium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ekofisk</td>
<td>0.829</td>
<td>0.17</td>
<td>0.030</td>
<td>0.37</td>
<td>4.29</td>
<td>1.56</td>
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<tr>
<td>Brent Blend</td>
<td>0.833</td>
<td>0.40</td>
<td>0.043</td>
<td>0.60</td>
<td>3.37</td>
<td>1.07</td>
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<tr>
<td>Oman</td>
<td>0.851</td>
<td>0.94</td>
<td>0.076</td>
<td>0.32</td>
<td>4.75</td>
<td>1.81</td>
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<tr>
<td>Ninian Blend</td>
<td>0.846</td>
<td>0.43</td>
<td>0.071</td>
<td>0.31</td>
<td>4.73</td>
<td>1.78</td>
</tr>
<tr>
<td><strong>Sour Heavy/Medium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Basra Medium</td>
<td>0.871</td>
<td>2.58</td>
<td>0.137</td>
<td>1.21</td>
<td>2.32</td>
<td>0.50</td>
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<tr>
<td>Romashkino(Urals)</td>
<td>0.857</td>
<td>1.80</td>
<td>0.224</td>
<td>1.05</td>
<td>2.49</td>
<td>0.61</td>
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<tr>
<td>Arabian Medium</td>
<td>0.883</td>
<td>2.85</td>
<td>0.238</td>
<td>0.97</td>
<td>2.53</td>
<td>0.70</td>
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<tr>
<td>Arabian Heavy</td>
<td>0.891</td>
<td>2.80</td>
<td>0.263</td>
<td>1.19</td>
<td>2.39</td>
<td>0.58</td>
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<td><strong>Our Crude</strong></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Concentr. Solution</td>
<td>-</td>
<td></td>
<td>-</td>
<td>0.44</td>
<td>5.15</td>
<td>1.41</td>
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<tr>
<td>Dilute Solution</td>
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<td></td>
<td>-</td>
<td>1.79</td>
<td>2.50</td>
<td>0.36</td>
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</tbody>
</table>

Figure 4. Effects of oil dilution by toluene on the shapes of UVVA spectra. Indicated in the figure are the net asphaltene concentrations in respective solutions.
Figure 5. Effects of oil dilution by toluene on UVVA characteristic energies U1 (circles), U2 (squares) and U3 (triangles)

Figure 6. Effects of oil dilution by toluene on UVVA parameter E4/E6

Figure 7. Temperature dependence of characteristic energy U1 in a toluene solution with ~ 150 mg/l asphaltenes
Figure 8. Difference spectra of oil samples with respect to solution with 40.7 mg/L asphaltenes. Indicated in the figure are net asphaltene concentrations in more dilute solutions.


**Figure 11.** Peak structures in UVVA spectra subjected to re-scaling via continuum removal by division. Vertical lines indicate absorption peaks of vanadyl petroporphyrins.


**Figure 13.** Representative examples of published “evidence” for resonance near-UV absorption of asphaltenes (cf. text).

Figure 15. Highly suspect coincidence of absorbance spectra for crude oils and asphaltenes of diverse origin from various publications (cf. text)


![Image](image1)


![Image](image2)


![UVVA spectra of small molecules of an organic acid](image1)

![UVVA spectra of oxidized small molecular precursors of melamins](image2)


![UVVA spectrum for an aqueous solution of melamins](image3)

![Molecular structures of melamin monomers](image4)


![Heteropolymeric “archipelago” model of melamins](image5)