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## **The Suggested “New Method for Determination of Dispersity in Petroleum Systems” is Based on Trivial Experimental Artifacts.**

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### **Abstract.**

A number of recent publications suggest a “new method for petroleum studies” based on circular dichroism (CD) spectra which presumably feature a “characteristic CD band near 300 nm”. The authors ascribe this band to “resonance absorption of pure asphaltene, measured by a number of authors”. In fact, neither of supporting references deals with optical absorption of asphaltenes. Moreover, 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. We conclude that the discussed “new method” is founded upon the same experimental artifacts and should be disregarded as basically erroneous.

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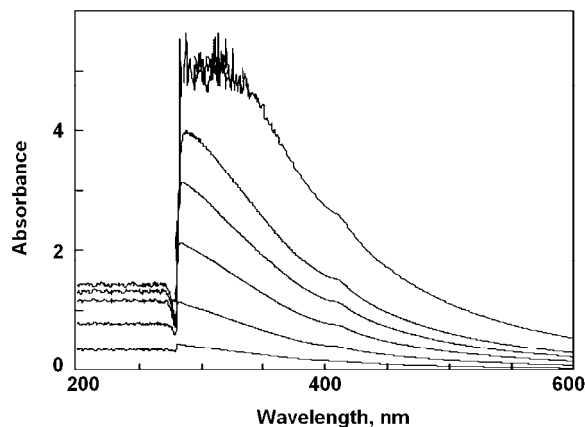
## Introduction

In spite of decades of extensive research by a variety of experimental techniques, the available information on the properties of high-MW crude oil constituents (in particular, of asphaltenes) still remains highly controversial.<sup>1</sup> Hence, some petroleum scientists in their understandable efforts to improve this situation try to suggest “new” methods/techniques for “interrogation” of crude oils. However, frequently they do not realize that the suggested methods either are not applicable to complex petroleum systems or are based on false information. A characteristic example is a series of recent publications,<sup>2-5</sup> advertising circular dichroism (CD) spectrometry as “the new method for determination of dispersity in petroleum systems”. The authors should have been warned by the fact that research groups, for years specializing both in petroleum studies and in applications of the CD technique,<sup>6</sup> never reported any noticeable CD activity in asphaltenes/crude oils. Moreover, as shown below, the major experimental evidence in support of the discussed “new method” most surely is just an experimental artifact, while “resonance absorption of asphaltenes”, quoted as an underlying mechanism, is non-existent.

## Discussion

**1. Some History of the “Resonance Absorption of Asphaltenes”.** Over past years, a number of publications have reported UV absorption spectra for dilute solutions of crude oils and of petroleum- and coal-derived asphaltenes (all in toluene) with prominent peaks at 288-310 nm (4.3 – 4.0 eV). As an example, Figure 1 shows representative data (re-plotted from Fig.1 of Ref.7) for solutions of Athabasca C7-asphaltenes with concentrations ranging (bottom to top) from 10 to 200 mg/L. The authors emphasize the presence of a common absorption maximum at 288 nm in most dilute solutions and recommend this wavelength as a standard one for calibration

of optical measurements. For further discussion it is important that they explain the apparent shift of this maximum to larger wavelengths (cf. the top curve in Figure 1) by that “the absorbance level exceeds the output range of the instrument” in more concentrated solutions.



**Figure 1.** “Prominent resonance peak” in dilute toluene solutions of asphaltenes (after Ref.7).

Another example is the study of the Furril and Hamaca asphaltenes.<sup>8</sup> The authors present absorption spectra for toluene solutions with concentrations of 50 mg/L, both of which exhibit a maximum of absorbance around 310 nm. On the basis that “the spectral location of the absorption maximum varies considerably and almost continuously for the different crude oils” they conclude that “the similarity of the absorption spectra of the asphaltenes studied evidence that the same type of chromophores is present in these fractions”. Yet another publication<sup>9</sup> reports absorption spectra for toluene solutions of asphaltenes with concentrations below 100 ppm, which exhibit a common absorbance maximum at 305 nm. The authors conclude that the value of this wavelength “hints to the possibility of observing two-photon absorption”.

Even more far-reaching conclusions were formulated in a publication on “pattern recognition method” for discriminating between crude oils belonging to different geographic origins.<sup>10</sup> Each oil is represented by a circular profile (“fingerprint”) that consists of parameter

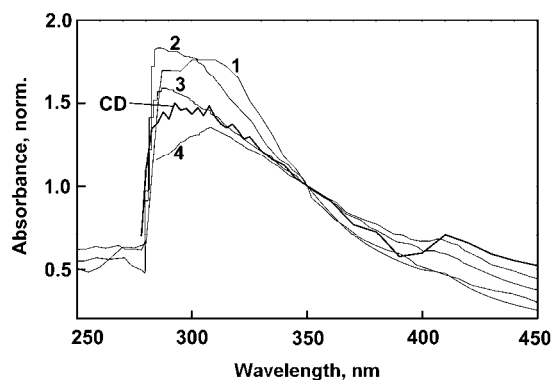
axes that radiate from the centre like spokes on a wheel. Two of the nine of these “individual” and “most representative” parameters are the intensity and the wavelength position of the discussed “characteristic absorbance maximum”.

Finally, a prominent absorbance maximum close to 300 nm has been reported for ppm (mg/L) solutions not only of crude oil asphaltenes, but also of asphaltenes, derived from coal.<sup>11</sup>

In our first publication of preliminary data on crude oil absorbance below 315 nm, we also reported “a strong resonance band, peaked at ~285 nm” and even attempted to ascribe this feature to specific “ $\pi$ - $\pi^*$  transitions in the conjugated aromatic chromophores of asphaltenes”.<sup>12</sup>

However, inter-comparison of “resonance UV peaks” revealed a striking and a highly suspect coincidence of experimental data reported by different research groups for asphaltenes/crude oils of diverse origin.<sup>13</sup> To emphasize coincidence, in Figure 2 the data from original publications are re-normalized to equal absorbances at 350 nm. The numbers denote optical absorbance spectra for the following toluene solutions: (1) of a Tatarstan crude with 26 mg/L asphaltenes;<sup>13</sup> (2) of coal asphaltenes, 34.8 mg/L;<sup>11</sup> (3) of asphaltenes from Athabasca bitumens, 100 mg/L;<sup>7</sup> (4) of asphaltenes from a Hamaca crude, 50 mg/L.<sup>8</sup> The thicker line represents the behavior of the “circular dichroism signal” for an oil solution with 11.2 mg/L asphaltenes,<sup>2-4</sup> discussed below (cf. Figure 5).

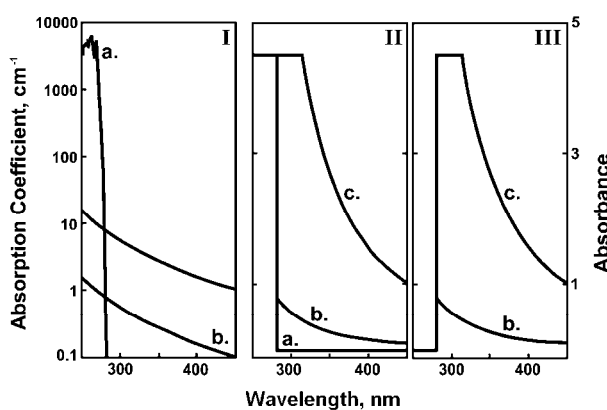
Further investigation of the data like those in Figure 2, definitely revealed that “near-300 nm resonance absorption” not only can not be regarded as a “fingerprint attribute” of crude oils/asphaltenes, but is non-existent, being merely a trivial experimental artifact near the absorption edge of the solvent (toluene).<sup>13,14</sup>



**Figure 2.** “Highly suspect coincidence” of absorbance spectra for crude oils and asphaltenes of diverse origin from various publications (lines 1-4). The thicker line “CD” shows re-plotted circular dichroism data from Refs.2-4.

**2. Apparent Origin of “Resonance Absorption” Artifacts.** The spectroscopy specialists may regard the following arguments as being obvious, however frequently we found it difficult to convey to petroleum scientists and practitioners the nature of the discussed solvent-related artifacts. A common reaction is: “can not be any solvent effects – these are accounted for in modern spectrometers”. A slightly more sophisticated response – “in spectrometers the solvent absorption is properly subtracted from the sample’s signal”. In our recent book<sup>14</sup> we classified such attitude as a “syndrome of expensive equipment” when one finds it difficult to believe that the newly-acquired expensive-modern-sophisticated-multifunctional-sensitive-automated-etc. spectrometer can provide questionable output. In fact it can – mainly for the reasons that nowadays the details of signal processing and solvent subtraction are buried somewhere deep in the circuits of electronic blocs. Artifacts due to subtraction rarely appear in conventional fairly concentrated solutions with comparable solvent and solute absorption coefficients. However, studies of crude oil or asphaltene solutions present a special case. Due to extremely high UV-Vis absorptivity of asphaltenes, acceptable absorbances ( $A < 2-3$ ) in conventional (cm-length) cuvettes

may be achieved only in highly diluted ppm (mg/L) solutions. In this case, as illustrated in Figure 3.I, the ratio of solvent/solute absorption coefficients increases catastrophically in the immediate vicinity of the solvent's absorption edge. For toluene (curve a.), non-zero absorption appears at wavelengths below 282 nm and 1M absorption coefficient sharply rises to  $6596\text{ cm}^{-1}$  at 261.75 nm.<sup>15,16</sup> Precise quantitative evaluation of molecular/molar absorptivities of asphaltenes is impossible owing to controversies regarding their molecular weights.<sup>1</sup> Hence, curves b. and c. in Figure 3.I show order-of-magnitude (but sufficient for further discussion) estimates for 1 ppm and 10 ppm concentrations in 1M toluene. In these estimates we employed experimental data for 315-750 nm asphaltene absorptivities<sup>17</sup> and extrapolated these to shorter wavelengths via a frequently-assumed exponential dependence of absorptivity on inverse wavelength.<sup>13,14</sup>



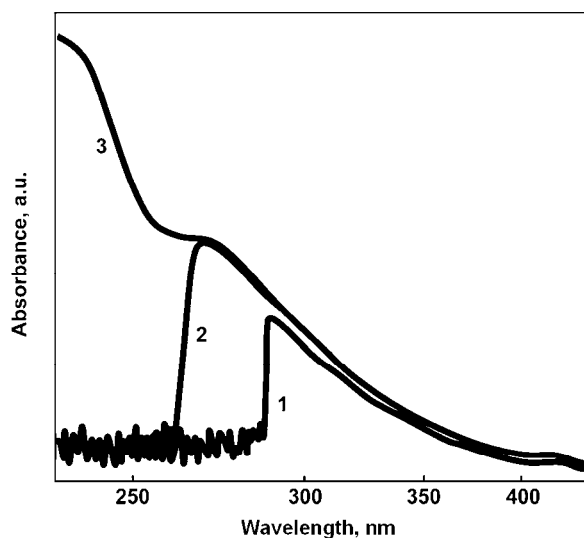
**Figure 3. I.** Absorption coefficients for: a. - 1M toluene; b.,c. - 1 ppm and 10 ppm of asphaltenes, respectively. **II.** Non-corrected absorbances for cm-length cuvettes with: a. - pure solvent (toluene); b.,c. - 1 ppm and 10 ppm solutions of asphaltenes in toluene. Note the instrumental cut-off at high absorbances. **III.** “Resonance absorption peak of asphaltenes” – an artifact of solvent subtraction procedure.

Figure 3.II shows estimated absorbances in cm-length cuvettes filled with pure toluene (curve a.), and with 1 ppm (curve b.) and 10 ppm (curve c.) asphaltene solutions in toluene. Of crucial significance is that calculations predict absorbance values rising above  $10^3$ , while any real spectrometer possesses certain threshold sensitivity to low relative intensities of the light, transmitted by a cuvette  $I_T/I_0$  (where  $I_0$  is incident intensity) and, hence threshold sensitivity to high absorbances  $A=-\log(I_T/I_0)$ . For many commercial spectrometers  $I_T/I_0$  thresholds are typically  $10^{-4} - 10^{-6}$  ( $A_{\max} \approx 4-6$ ). Any transmitted intensity below the threshold is fed into the processing electronic block as a common “noise” signal and, consequently, the respective processed absorbances are regarded as being “saturated” at a common maximum level. In Figure 3.II this “saturation” level corresponds to  $A=4.5$ .

In the final “solvent subtraction” operation in a spectrometer’s electronic block, processed absorbances of the solvent (curve a. in Figure 3.II) are numerically subtracted from absorbances of solutions (curves b. and c. in Figure 2.II). The result is provided as an output signal of a spectrometer which, in most situations, represents true absorption spectrum of the studied solute. However, in the vicinity of the solvent’s absorption edge, due to subtraction of equal (“saturated”) solution and solvent absorbances, the output signal sharply drops to (and remains at) close-to-zero level – an artifact absent in the properly measured absorption spectra. As illustrated in Figure 3.II, visually this artifact for toluene solutions may be classified as a sharp absorption maximum close to 300 nm and, evidently, is the persistent “resonance absorption peak of asphaltenes”, illustrated in Figures 1 and 2.

The direct experimental verification of the above conclusions was performed by studying absorption spectra of crude oil solutions in solvents with different absorption edges.<sup>13,14</sup> As shown in Figure 4 (spectra 1 and 2), the “UV artifact” does follow the changes in an absorption

edge of a solvent -  $\sim 282\text{-}285$  nm for toluene and  $\sim 265$  nm for carbon tetrachloride. The solvent-free absorbance spectrum of a neat crude oil (curve 3 in Figure 4) was obtained by a thin film technique.<sup>13,14</sup> This spectrum practically coincides with reliable parts of solution's spectra and does not exhibit any "resonance absorption".



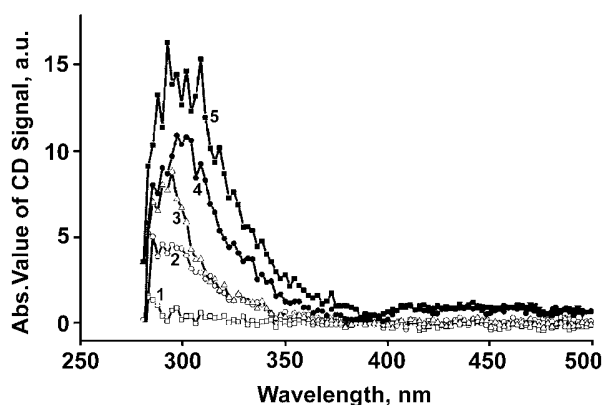
**Figure 4.** UV/vis absorption spectra of crude oil solutions in toluene (1), in  $\text{CCl}_4$  (2) and of a neat crude oil (3).

Summarizing, we conclude that many of previously reported UV/vis absorption properties of asphaltenes/crude oils may have been noticeably distorted by experimental artifacts. The most notorious artifact is "resonance absorption close to 300 nm".

**3. Relevance of Absorption Artifacts to the Suggested "New Method for Determination of Dispersity in Petroleum Systems".** The authors of the discussed "new method" (cf. Introduction) in all publications<sup>2-4</sup> present experimental circular dichroism (CD) spectra which exhibit "*the short-wave band with a maximum near 300 nm*". As their "CD signal"



is negative, for ease of comparison with the above results, in Figure 5 we show the discussed spectra in terms of respective absolute values.



**Figure 5.** Absolute value of “circular dichroism signal” in toluene solutions of a crude oil (1 cm cuvette) with asphaltene concentrations of: 1–0.3, 2–0.6, 3–3.7, 4–5.6, 5–11.2 mg/L. (After Refs. 2-4).

Immediately evident is close resemblance of CD data in Figure 5 to absorption data of Figures 1-4. Moreover, in discussion of their “300 nm CD maximum”, the authors directly state that<sup>2</sup> “*there is a correlation between the CD band position of crude oil toluene solutions and resonance absorption of pure asphaltene toluene solutions measured by a number of authors [10,14,15].*” Characteristically, non-existent “resonance absorption” they try to support by non-existent references. The first one is a publication on “The Critical Micelle Concentration of Asphaltenes As Measured by Calorimetry”,<sup>18</sup> while the second one is our paper on “Excess density in oilfield water - crude oil dispersions”.<sup>19</sup> Neither of publications provides any information on optical properties of asphaltenes/crude oils. The third publication is quoted as being in 2007 “in press”,<sup>20</sup> but it does not appear either in the 2007, or in the 2008 issues of the respective journal. Moreover, in an answer to our recent enquiry, an editor of this journal replied

that “we do not have a paper from this author in press; neither do we have a submission from him under consideration”.

It so happens, however, that disregarding wrong referencing, the coincidence with absorption artifacts is indeed strong enough to conclude that the “300 nm CD maximum” is an artifact of the same nature. To illustrate this coincidence, in Figure 2 we compare CD spectrum #5 from Figure 5 with the above discussed artifact “absorption peaks”. Furthermore, the obvious origin of CD artifacts is in instrumental “saturation” of processed absorbances, as discussed with respect to Figure 3. The only (non-principal) difference in CD measurements is that a spectrometer’s output is a difference of “saturation”-distorted signals not from non-polarized light passing through a solvent and a solution, but from left- and right-circularly polarized (CPL and CPR) light passing through the same solution. The inevitable result of measurements in the vicinity of the solvent (toluene) absorption edge is an artifact “maximum” of the type illustrated in Figure 3.III.

Suggestion of the discussed “new method” based on artifacts can not be excused by certain lack of previous information inherent to novel techniques. Strong solvent interference in CD measurements is well-known and has been discussed in multiple publications.<sup>21-23</sup> Moreover, in manuals for CD spectrometers it is emphasized<sup>23</sup> *“that whilst CD is a measure of the absorbance difference for CPL and CPR, the conventional absorbance of the sample must also be considered as it can severely impair the transmission of the probe beam, particularly in the far UV, to the point where no meaningful measurement can be made. This not only applies to the sample, but to the solvent as well, and oversights in this regard probably account for many unsuccessful or erroneous CD measurements.”* In the same manual it is specifically stated that for successful applications of CD technique *“an understanding of the limitations caused by sample and solvent absorption and some knowledge of the theory of CD measurement is*

*unavoidable.*” The above discussed artifacts in the suggested “New Method” clearly reveal the lack of expected understanding and knowledge.

### **Conclusions.**

Following the style of a recent critique of other methods for “optical interrogation” of petroleum,<sup>1</sup> we may conclude that frequent publications of such artifact as “resonance absorption band of asphaltenes” has caused a measure of confusion that hopefully now has been resolved and this episode in asphaltene studies has been closed for good.

Accordingly, we conclude that the suggested “New Method for Determination of Dispersity in Petroleum Systems”<sup>2-5</sup> also is founded upon the same trivial experimental artifacts and should be disregarded as basically erroneous.

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