Characterization of Asphaltenes and Crude Oils by Near-UV/Visible Absorption Spectroscopy

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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.
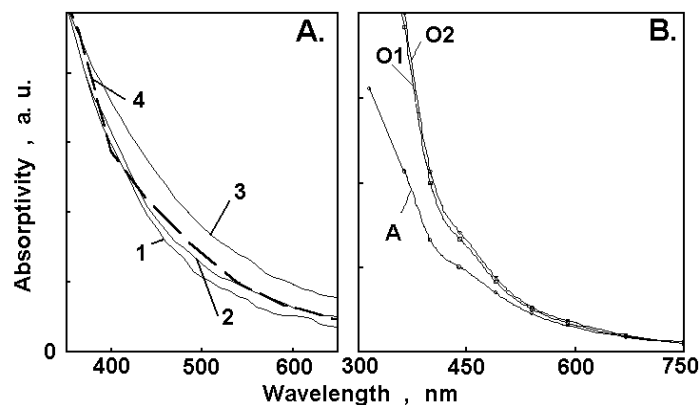

Figure 1. Continuous near-UV/visible absorption spectra for toluene solutions of: A - asphaltenes from various geographical/geological origins; B - as-recovered crude oils from Tatarstan [after: Evdokimov, I. N., Eliseev, N. Yu., and Akhmetov, B. R. (2003a). Assembly of asphaltene molecular aggregates as studied by near-UV/visible spectroscopy. I. Structure of the absorbance spectrum. *J. Petrol. Sci. Eng.* 37(3-4): 135-143.]
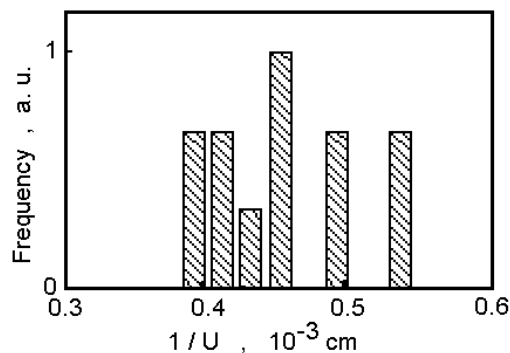

Figure 2. A distribution function for characteristic energies in UVVA spectra of native crude oils. [After: Mullins, O. C. (1993). *Method of Distinguishing between Crude Oils*. U. S. Patent 5,266,800]
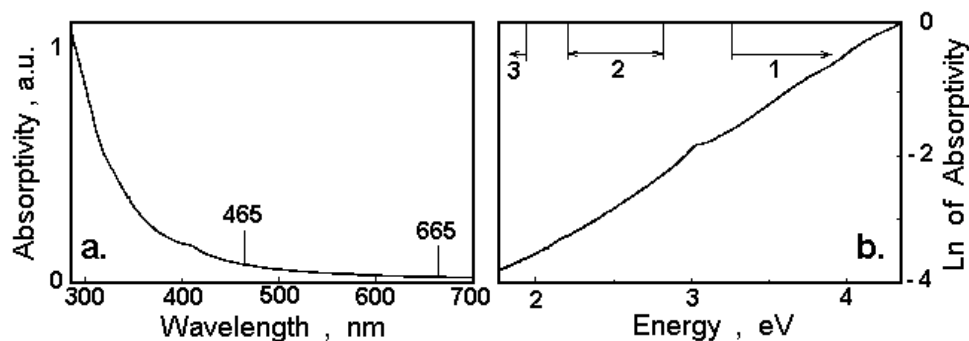

Figure 3. a. - Conventional plot of the UVVA spectrum of diluted Tatarstan crude (1.2 10^{-4} v/v in toluene). The wavelengths indicated in the figure are those employed for evaluation of E4/E6 ratios. b. - A plot of the same spectrum, more appropriate for slope analysis. The indicated ranges of photon 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

Oil Type/Name	ρ (g/cm^3)	S (wt.%)	ε_{460} (1/μm)	U3 (eV)	E4/E6	U1/U3
Sweet Light/Medium						
Ekofisk	0.829	0.17	0.030	0.37	4.29	1.56
Brent Blend	0.833	0.40	0.043	0.60	3.37	1.07
Oman	0.851	0.94	0.076	0.32	4.75	1.81
Ninian Blend	0.846	0.43	0.071	0.31	4.73	1.78
SourHeavy/Medium						
Basra Medium	0.871	2.58	0.137	1.21	2.32	0.50
Romashkino(Urals)	0.857	1.80	0.224	1.05	2.49	0.61
Arabian Medium	0.883	2.85	0.238	0.97	2.53	0.70
Arabian Heavy	0.891	2.80	0.263	1.19	2.39	0.58
Our Crude	0.876	1.80				
Concentr. Solution			-	0.44	5.15	1.41
Dilute Solution			-	1.79	2.50	0.36
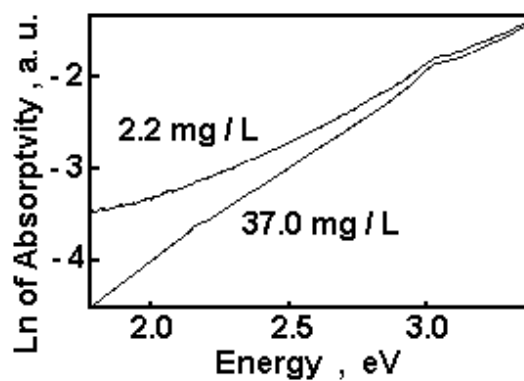
Figure 4. Effects of oil dilution by toluene on the shapes of UVVA spectra. Indicated in the figure are the net asphaltene concentrations in respective solutions
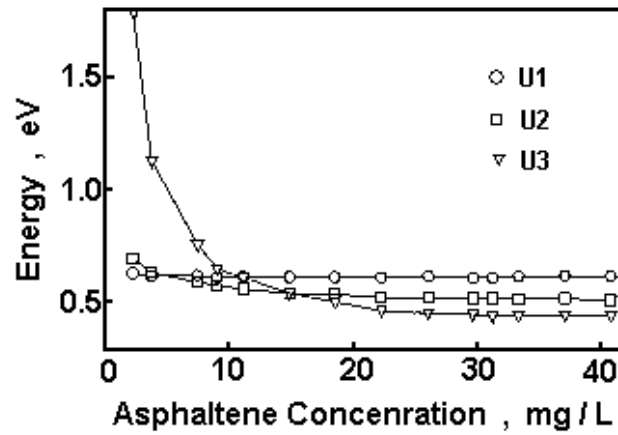
Figure 5. Effects of oil dilution by toluene on UVVA characteristic energies U1 (circles), U2 (squares) and U3 (triangles)
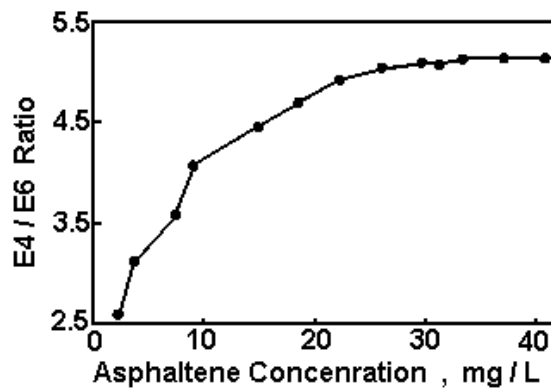

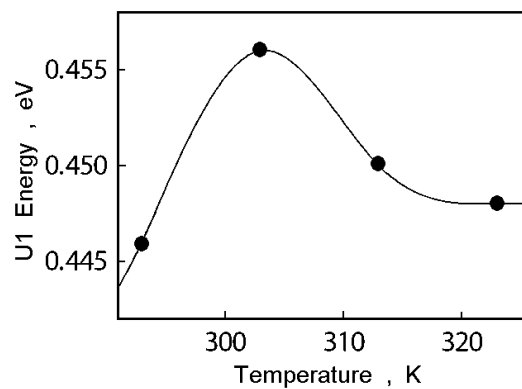**Figure 6.** Effects of oil dilution by toluene on UVVA parameter E4/E6

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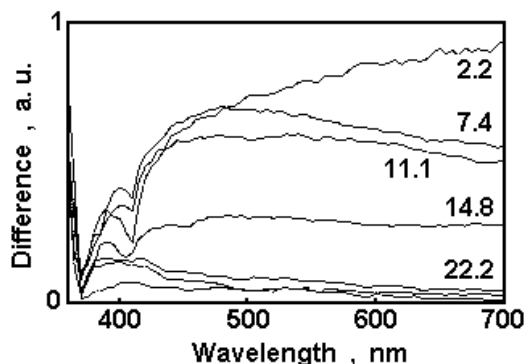
Figure 8. Difference spectra of oil samples with respect to solution with 40.7 mg/L asphaltenes. Indicated in the figure are net asphaltene concentrations in more dilute solutions
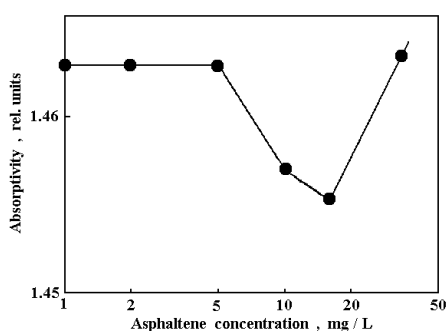

Figure 9. The earliest UVVA evidence of the onset of asphaltene aggregation at extremely low concentrations [after: Yokota, T., Scriven, F., Montgomery, D. S., and Strausz, O. P. (1986). Absorption and emission spectra of Athabasca asphaltene in the visible and near ultraviolet regions. *Fuel* 65(8): 1142-1149]
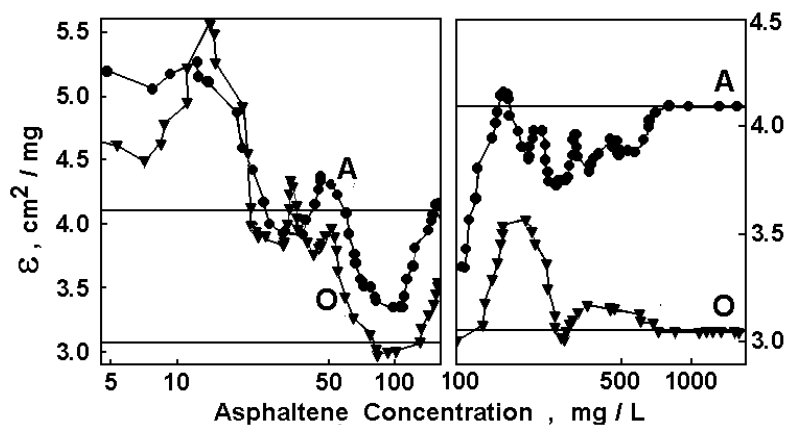

Figure 10. UVVA evidence of primary asphaltene aggregation, consecutive formation of various oligomers and precipitation of solid asphaltene nanocolloids in toluene solutions [Re-plotted from: Evdokimov, I. N., Eliseev, N. Yu., and Akhmetov, B. R. (2003b). Assembly of asphaltene molecular aggregates as studied by near-UV/visible spectroscopy. II. Concentration dependencies of absorptivities. *J. Petrol. Sci. Eng.* 37(3-4): 145-152]
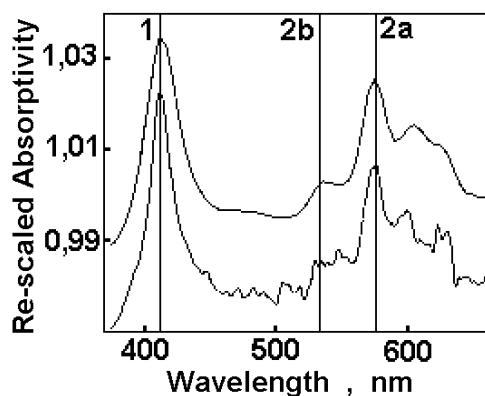
Figure 11. Peak structures in UVVA spectra subjected to re-scaling via continuum removal by division. Vertical lines indicate absorption peaks of vanadyl petroporphyrins
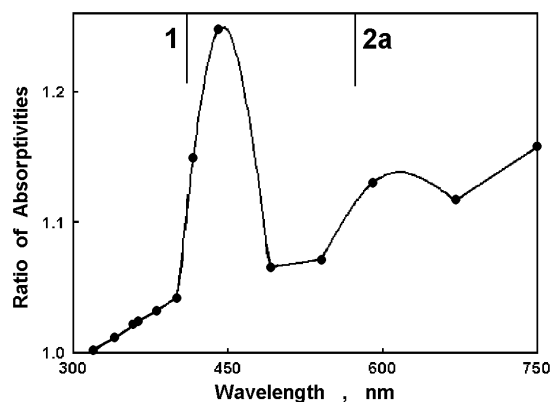

Figure 12. Strong porphyrin absorption bands of the asphaltene fraction stabilizing late droplet population in water/oil emulsion [After: Evdokimov, I. N., Efimov, Y. O., Losev, A. P., and Novikov, M. A. (2009). Morphological Transformations of Native Petroleum Emulsions. II. Studies of Sedimentation and Phase Separation. *Langmuir* (submitted)].
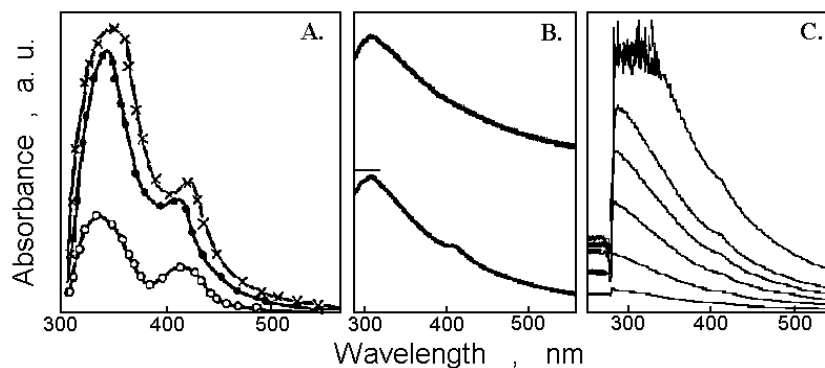

Figure 13. Representative examples of published "evidence" for resonance near-UV absorption of asphaltenes (cf. text)
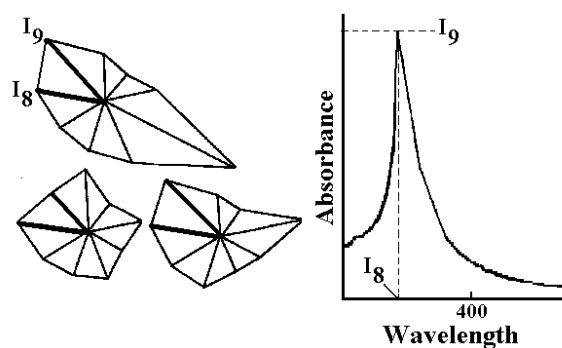
Figure 14. Employment of near-UV "characteristic absorbance maximum" for characterizing crude oils by "pattern recognition method". [After: Lai, E. P. C., Giroux, R. D., Chen, N., and Guo, R. (1993). Pattern recognition for screening of crude oils using multivariate circular profiles. *Can. J. Chem.* 73: 968-975.]
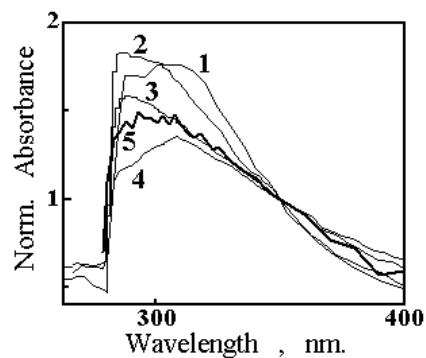

Figure 15. Highly suspect coincidence of absorbance spectra for crude oils and asphaltenes of diverse origin from various publications (cf. text)
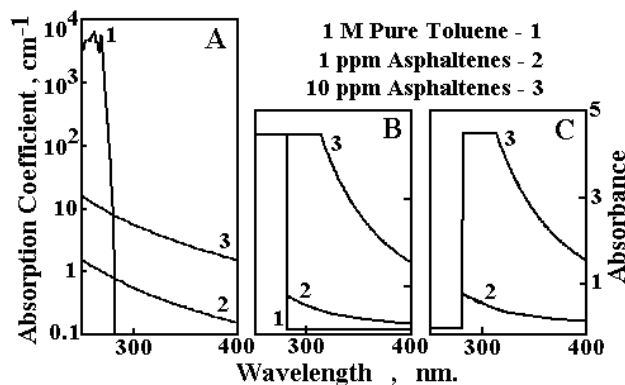

Figure 16. A - absorption coefficients for: (1) - 1M toluene; (2,3) – 1 ppm and 10 ppm of asphaltenes. B - non-corrected absorbances for cm-length cuvettes with: (1) – pure toluene; (2,3) - 1 ppm and 10 ppm solutions of asphaltenes in toluene. C. - "Resonance absorption peak of asphaltenes" – an artifact of solvent subtraction procedure [After: Evdokimov, I. N., and Losev, A. P. (2007b). *Potential of Optical Research Methods for Monitoring Oil Field Development.* Moscow: Neft I Gas, 228 p. (In Russian)]
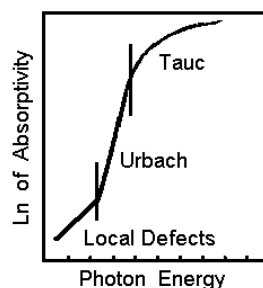
Figure 17. The main regions of continuous UVVA spectra in the "amorphous semiconductor" model [After: Adachi, S. (1999). *Optical Properties Of Crystalline And Amorphous Semiconductors: Materials And Fundamental Principles.* New York: Kluwer Academic Publishers. 280 pp.]
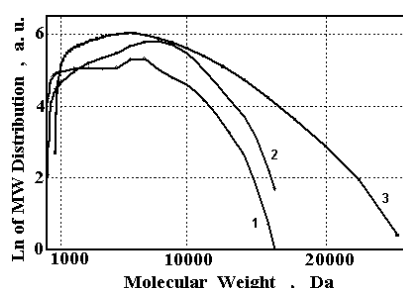

Figure 18. Logarithms of experimental MW distributions for asphaltenes of various crude oils precipitated with: (1) *n*-pentane and (2) *n*-nonane [after: Vazquez, D., and Mansoori, G. A. (2000). Identification and measurement of petroleum precipitates. . *J. Petrol. Sci. Eng* 26(1-4): 49-55]; and *n*-heptane [after: Gandhi, K. (2002). *Characterization of Crude Oils and Heavies.* Salt Lake City: University of Utah, Petroleum Research Center. - 37p; Leelavanichkul, P., and Hanson, F. V. (2002). *Crude Oil Characterization and Thermodynamic Modeling of Solid Precipitation in Crude Oils.* Salt Lake City: University of Utah, Petroleum Research Center. - 26p.]
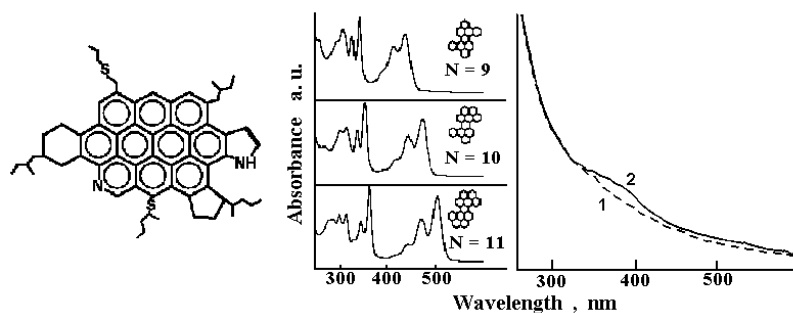

Figure 19. Left – a "continental" – type asphaltene molecule with a single large PAH chromophore [after: Rogel, E. (1995). Studies on asphaltene aggregation via computational chemistry. *Colloid. Surface. A.* 104: 85-93]. Centre - UVVA spectra of large PAH molecules [after: Fetzer, J. C. (2000). *The Chemistry and Analysis of the Large (C>=24C) Polycyclic Aromatic Hydrocarbons.* New York: Wiley-Interscience]. Right – continuous UVVA spectra for two fractions of molecular precursors of soot [after: Alfe, M., Apicella, B., Barbella, R., Tregrossi, A., and Ciajolo, A. (2007). Distribution of Soot Molecular Weight/Size along Premixed Flames as Inferred by Size Exclusion Chromatography. *Energy Fuels* 21(1): 136-140]
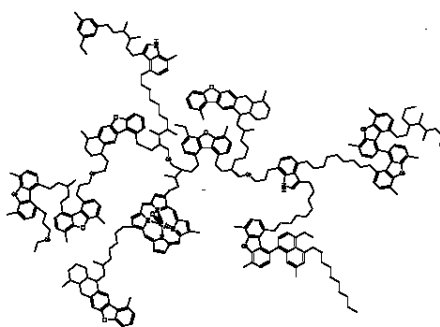
Figure 20. An "archipelago" – type asphaltene molecule with a structure typical for heteropolymers [after: Sheremata, J. M., Gray, M. R., Dettman, H. D., and McCaffrey, W.C. (2004). Quantitative molecular representation and sequential optimization of Athabasca asphaltenes. *Energy Fuels* 18(5): 1377-1384]
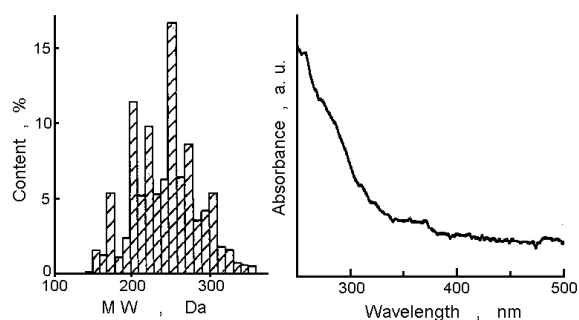

Figure 21. Left – a narrow MW distribution of 150-member molecular library from coal pitch. Right – a practically continuous UVVA spectrum of this small molecular library. [After: Ehrenfreund, P., d'Hendecourt, L., Joblin, C., and Leger, A. (1992). Visible absorption bands of coal pitch extract – implications for the diffuse interstellar bands. *Astron. Astrophys.* 266: 429-433]
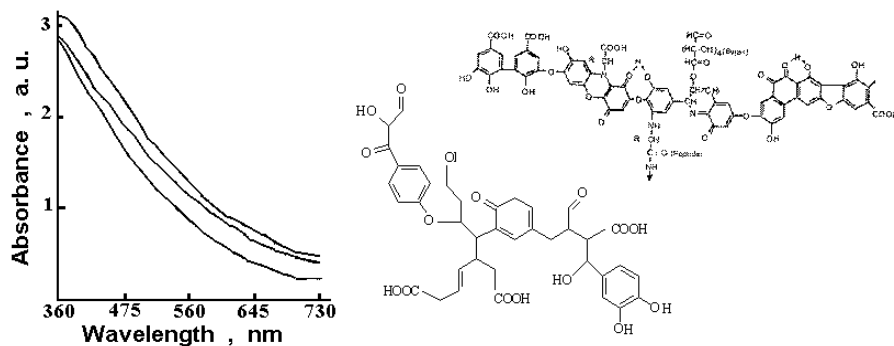

Figure 22. Left - continuous UUVA spectra for aqueous solutions of a humic acid and of its fractions [after: Mirave, J. P., and Orioli, G. A. (1987). Edaphic mobility of complete humic acid and fractions of high and medium molecular weight. *Plant Soil* 104(2): 169-174]. Right - structural models of humic acid heteropolymers [after: Stein, L. T., Kolla, S., Varnum, J. M., Davies, G., and Jansen S. A. (1997). Conformational modelling of a proposed building block of humic acid: Searching chirally undefined cinformational space. In: *The Role of Humic Substances in the Ecosystems and in Environmental protection, Drozd et al., Eds.* Wroclaw: PTSH–Polish Society of Humic Substances. pp 73-77]
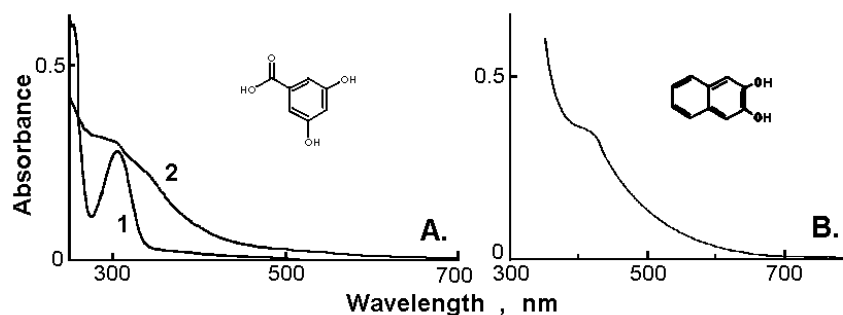
Figure 23. A. – UVVA spectra of small molecules of an organic acid before (1) and after (2) oxidation [after: Gelencsér, A., Hoffer, A., Kiss, G., Tombácz, E., Kurdi, R., and Bencze, L. (2003). In-situ Formation of Light-Absorbing Organic Matter in Cloud Water. *J. Atmosph. Chem.* 45(1): 25-33]. B. – UVVA spectra of oxidized small molecular precursors of melanins [after: Quattrone, A. J. (1977). Nonenzymic Spectrophotometric Determination of Potential Poison Ivy Cross-Reactors. *Clinic. Chem.* 23(3): 571-575]
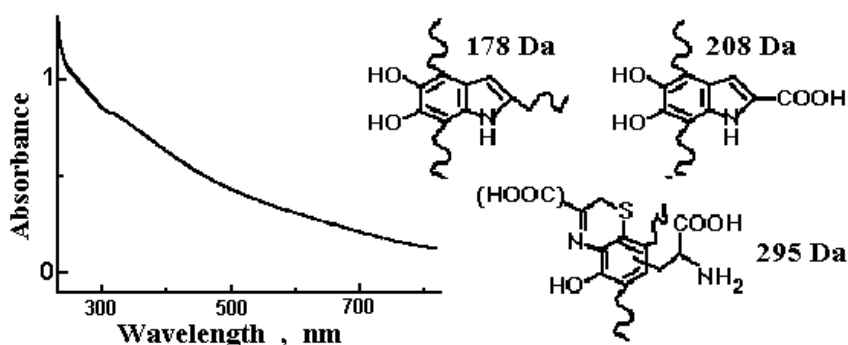

Figure 24. Left – a continuous UVVA spectrum for an aqueous solution of melanins [after Nofsinger and Simon, 2001]. Right – molecular structures of melanin monomers [after: Sarna, T., and Sealy, R. C. (1984). Photoinduced oxygen consumption in melanin systems. Action spectra and quantum yields for eumelanin and synthetic melanin. *Photochem. Photobiol.* 39(1): 69-74].
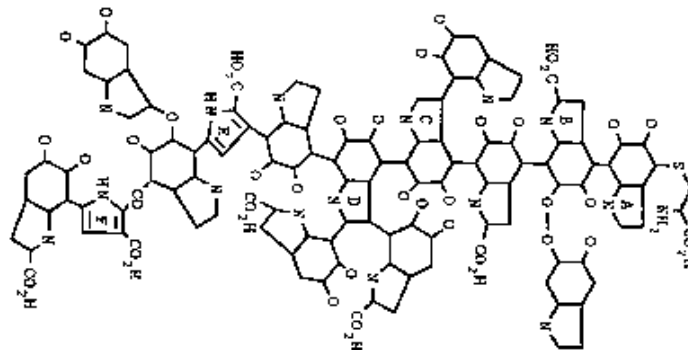

Figure 25. Heteropolymeric "archipelago" model of melanins [after: Prota, G. (1992). *Melanins and Melanogenesis*. New York: Academic Press. 290 p.]
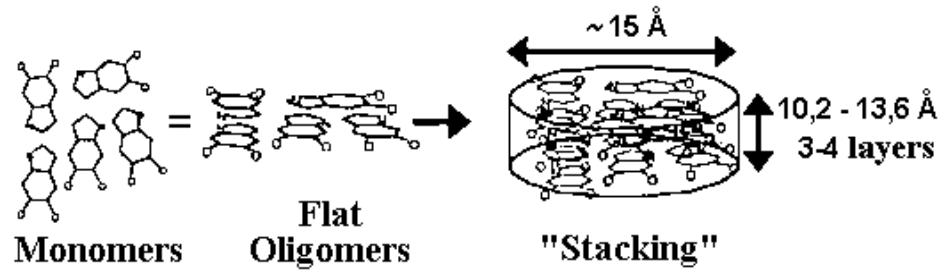
Figure 26. Multi-stage aggregation of melanins into diverse nanocolloids [after: Clancy, C. M. R., and Simon, J. D. (2001). Ultrastructural organization of eumelanin from *Sepia officinalis* measured by atomic force microscopy. *Biochemistry* 40(44): 13353-13360].