Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 512–514

UVC-induced photodegradation of *p*-arsanilic acid assisted by humic substances

Yuliya E. Tyutereva, Peter Sherin, Zizheng Liu, Victor F. Plyusnin and Ivan P. Pozdnyakov

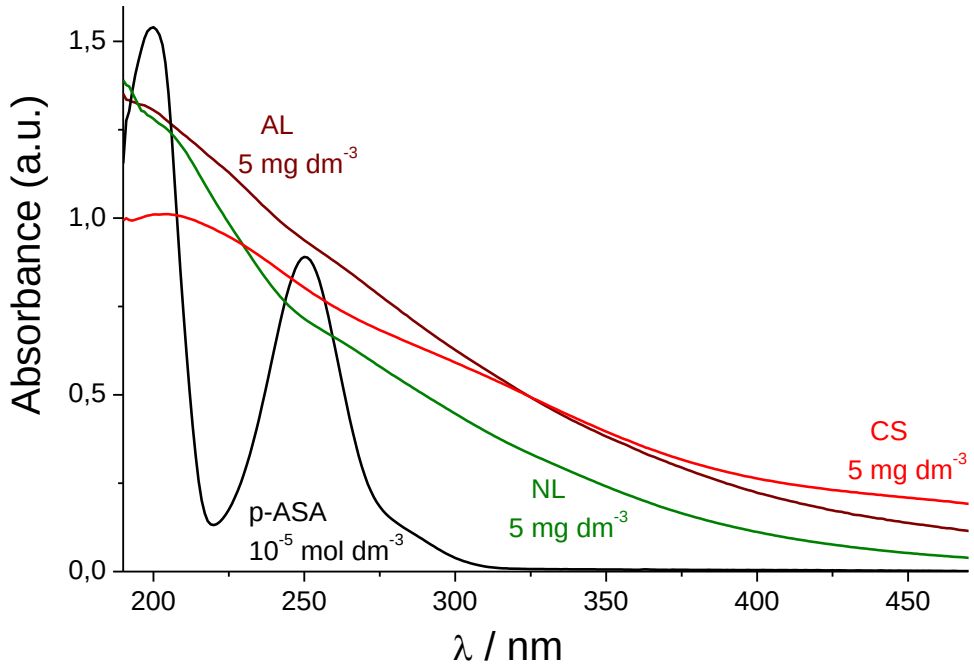

Figure S1 Absorption spectra of 10^{-5} mol dm^{-3} p-ASA and 5 mg dm^{-3} of CS, FA, and NL.

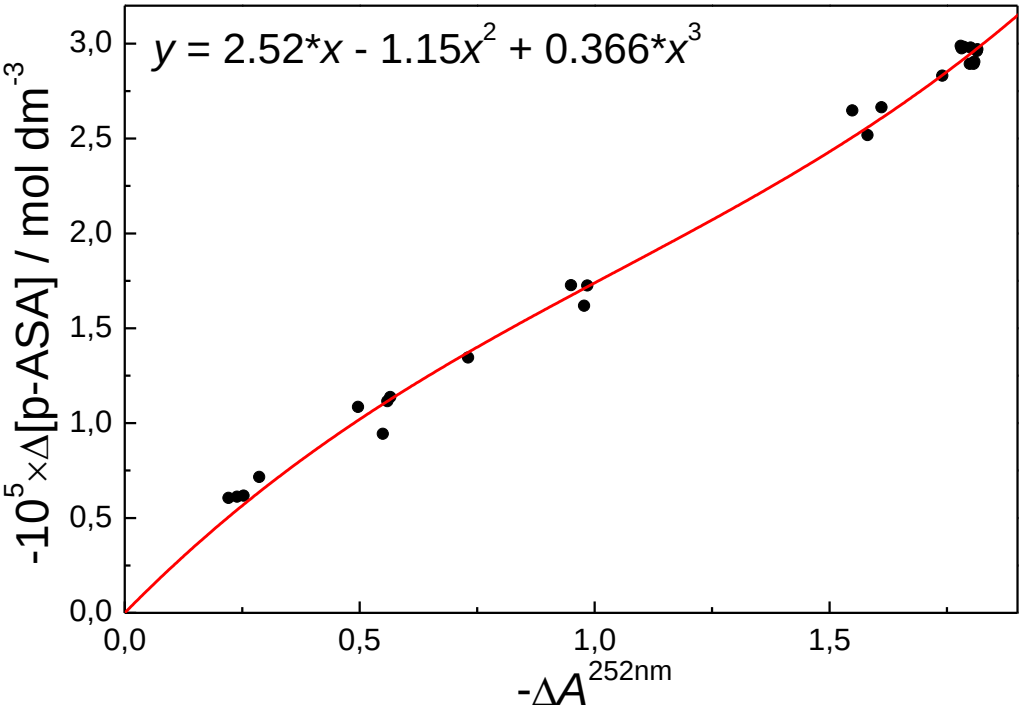

Figure S2 Dependence of concentration of photodegraded p-ASA (-Δ[p-ASA]) upon changes in the optical density at 252 nm ($-\Delta A^{252}$). Solid curve is the best fit, where the function is $y = 2.52x - 1.15x^2 + 0.366x^3$.

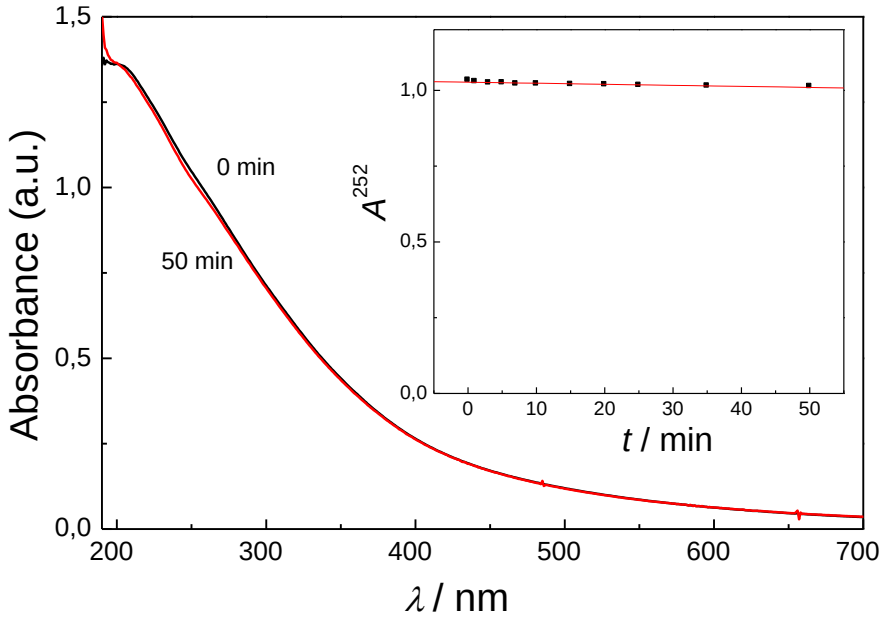

Figure S3 Absorption spectra of AL solution of fulvic acid (7 mg dm^{-3}) after 0 and 50 min of photolysis at 254 nm. The inset shows its absorption at 252 nm during UVC photolysis. Solid line in the insert is the best linear fit.

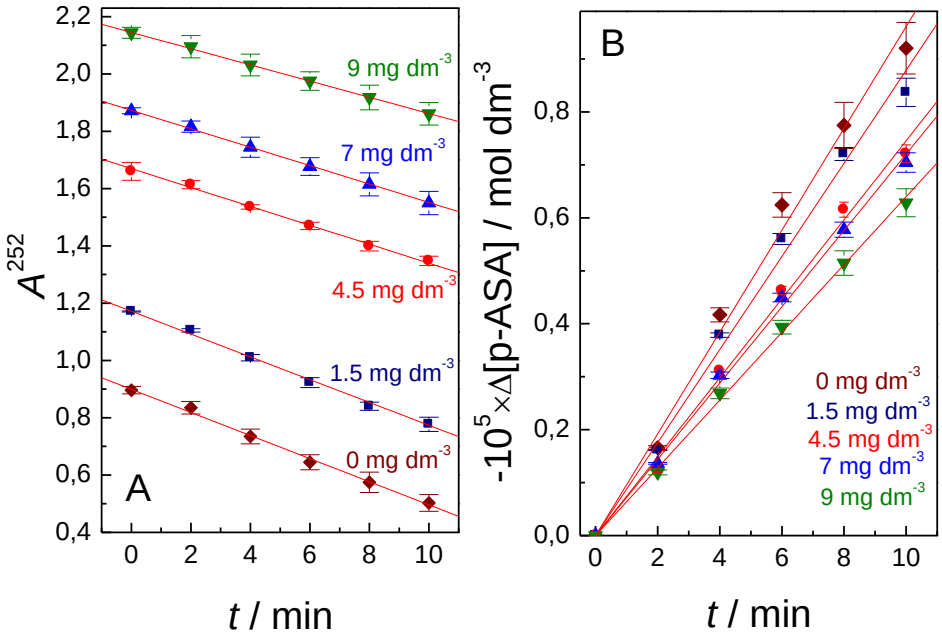

Figure S4 (*A*) Absorption of *p*-ASA (10^{-5} mol dm^{-3}) at 252 nm in the presence of AL at different concentrations during the steady-state (254 nm) photolysis. Solid lines are the best linear fits. (*B*) changes in the concentration of photodegraded *p*-ASA (-Δ[*p*-ASA]) calculated using the data shown in Figure S4 (*A*) and calibration curve in Figure S2. Solid lines are the best linear fits.

Derivation of equation (1)

The simplified scheme of *p*-ASA photolysis in the presence of HS could be presented as:

p-ASA —hν → products, φ_{ASA}

HS —hν → active species, φ_{HS}

Active species + p-ASA ⟶ products, γ_{ASA}

Wherein φ_{ASA} is the quantum yield of direct *p*-ASA photolysis, φ_{HS} is the quantum yield of active species generated by HSs photolysis, and γ_{ASA} is the probability of reaction of the active species with *p*-ASA. γ_{ASA} could generally depend on *p*-ASA concentration.

The initial rate of *p*-ASA photolysis in the absence of HS (r_0) could be expressed as:

$$r_0 = \varphi_{ASA} \times I_{abs}^{ASA} = \varphi_{ASA} \times I_0 \times \left(1 - 10^{-A_{ASA}}\right) \quad \text{(S1)},$$

wherein I_{abs}^{ASA} is the part of incident light absorbed by *p*-ASA, I_0 is the intensity of excitation source; and A_{ASA} is the absorbance of *p*-ASA solution at the excitation wavelength. In the presence of HS eq. (S1) has to be modified in order to take into account the absorbance of HS and a possibility of indirect *p*-ASA photodegradation caused by HS photolysis:

$$r = \phi_{ASA} \times I_{abs}^{ASA} + \gamma_{ASA} \phi_{HS} I_{abs}^{HS} \quad \text{(S2)},$$

wherein I_{abs}^{HS} is the part of excitation light absorbed by HS. Thus, the initial rate of *p*-ASA photodegradation in the presence of HS could be expressed using eq. (S3):

$$r = \frac{\phi_{ASA} \times A_{ASA} + \gamma_{ASA}\phi_{HS}A_{HS}}{A_{ASA} + A_{HS}} \times I_0 \times (1 - 10^{-(A_{ASA}+A_{HS})}) \qquad \text{(S3)},$$

wherein A_{HS} is the absorbance of HS at excitation wavelength. The ratio of the rate of *p*-ASA photolysis in the presence of HS (r) to the rate of *p*-ASA photolysis in the absence of HS (r_0) could be finally expressed as:

$$\frac{r}{r_0} = \frac{(A_{ASA} + \frac{\gamma_{ASA}\phi_{HS}}{\phi_{ASA}} A_{HS})}{A_{ASA} + A_{HS}} \times \frac{(1 - 10^{-(A_{ASA}+A_{HS})})}{1 - 10^{-A_{ASA}}} \qquad \text{(S4)},$$

It worth to note that during *p*-ASA photolysis both without and in the presence of HSs, the decrease of *p*-ASA absorption of about 25–30% was observed (Figure S3). It should lead to some underestimation of r values during the optical data processing. However, the ratio of r/r_0 should be the same as in the case of constant absorption of *p*-ASA, since both r and r_0 are decreasing in the same extent. So, no correction of r values is needed for the used experimental condition.