

## Photooxidation of arsenic(III) in the presence of fulvic acid

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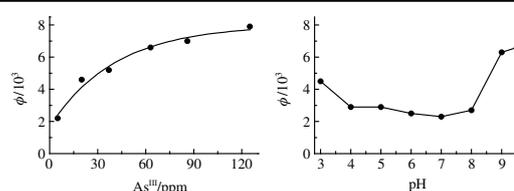
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The quantum yield of As<sup>III</sup> oxidation caused by the UV photolysis (282 nm) of fulvic acid H108498 in aqueous solution was measured and a qualitative model explaining its dependence upon pH and As<sup>III</sup> concentration was suggested.



Studies in the environmental chemistry of arsenic<sup>1–3</sup> are reasoned by its toxicity and carcinogenicity. In natural water, inorganic arsenic mainly occurs as arsenite (H<sub>3</sub>As<sup>III</sup>O<sub>3</sub>) and arsenate (H<sub>2</sub>As<sup>V</sup>O<sub>4</sub><sup>-</sup> or HAs<sup>V</sup>O<sub>4</sub><sup>2-</sup>),<sup>1</sup> and organic arsenic-containing compounds are monomethylarsonic (MeAsO<sub>3</sub><sup>-</sup>) and dimethylarsinic (Me<sub>2</sub>AsO<sub>2</sub>) acids. The maximum permissible concentration (MPC) of arsenic in drinking water is 10 μg dm<sup>-3</sup>, while its content in fresh water varies in a range of 0.1–75 μg dm<sup>-3</sup> (ref. 1) with an average value of about 1.4 μg dm<sup>-3</sup>. This level is exceeded in many regions of India, Argentina, Chile, Mexico, Bangladesh and Vietnam.<sup>4</sup> In the environment, the arsenite/arsenate ratio does not comply to thermodynamic equilibrium and about 20% of the element may exist as As<sup>III</sup>.<sup>5</sup> However, it is well known that As<sup>III</sup> is the most toxic arsenic species; therefore, the processes of its oxidative transformation into As<sup>V</sup> are of interest.

The photochemical oxidation of arsenite to arsenate plays an important role in the conversion of arsenic compounds in aqueous systems.<sup>6–8</sup> The process can be considerably accelerated by the addition of photooxidizers, e.g., the persulfate ion.<sup>9</sup> There are different strategies of As<sup>III</sup> photooxidation: direct photolysis<sup>10</sup> and photolysis in the presence of Fe<sup>III</sup> complexes<sup>11</sup> and iron-containing clays.<sup>12</sup>

Arsenic is partially complexed with humic and fulvic acids (HA and FA, respectively) under environmental conditions,<sup>13–15</sup> and this can be accompanied by As co-precipitation in the presence of iron oxides.<sup>16,17</sup> The formation of mixed As<sup>V</sup>–Fe<sup>III</sup>–FA or As<sup>V</sup>–Fe<sup>III</sup>–HA complexes leading to the change of mobility, bio-availability, solubility and photochemical properties of arsenic-containing compounds is also possible.<sup>18,19</sup>

It was reported<sup>20</sup> that the rate of As<sup>III</sup> photooxidation during irradiation with UV-A and visible light in the presence of HAS increased by a factor of 1.5–2, and the process was substantially dependent on initial As<sup>III</sup> concentration and pH. Nevertheless, there are no data on the mechanism of the process and the absolute values of the quantum yields of As<sup>III</sup> photooxidation in the presence of FA and HA.

The aim of this work was to obtain quantitative information regarding the influence of fulvic acid on the photooxidation of As<sup>III</sup> in aqueous solution.

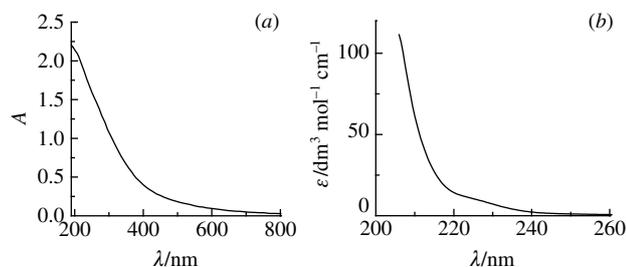
The technique of the study included UV irradiation of As<sup>III</sup> in aqueous solutions containing fulvic acid followed by arsenic species (As<sup>III</sup>, As<sup>V</sup>) and total arsenic determination.<sup>†</sup>

Figure 1 shows the absorption spectra of the aqueous solutions of As<sup>III</sup> and FA. The hydrolysis of sodium metaarsenite can be

<sup>†</sup> Sodium metaarsenite NaAsO<sub>2</sub> (97%, Xiya Reagent Center, China), sodium arsenate Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (99%, Alfa Aesar, A Johnson Matthey Co., China) served as As<sup>III</sup> and As<sup>V</sup> sources, respectively. Fulvic acid (Aladdin Industrial Corp.), H108498, CAS: 1415-93-6 [fulvic acid content, >90%; moisture, ≤ 2%; chloride (Cl), ≤ 0.05%; sulfate (SO<sub>4</sub>), ≤ 0.05%; ignition residue, ≤ 0.5%; C, 39.32%; H, 3.77%; N, 1.03%] was used without additional purification. Trace metal grade hydrochloric and nitric acids were obtained from ‘Reactiv’ (Novosibirsk, Russia). All other chemicals were of analytical grade or better. Deionized water was prepared using an Ultra Clear system (SG, Germany). FA concentration in working solutions was 50 mg dm<sup>-3</sup>, As<sup>III</sup> concentration was varied in a range of 5–125 mg dm<sup>-3</sup>. pH was controlled by an ANION-4100 ion meter (Infraspek-Analit, Russia) with an ESK-10614 combined electrode.

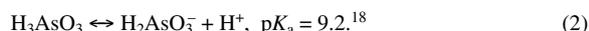
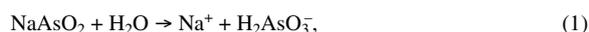
Photolysis was carried out in a quartz cell with an optical path of 1 cm at 298 K under atmospheric pressure. An Excimer XeBr lamp was used as a quasi-continuous source of UV irradiation at 282 nm (half width of light pulse was 5 nm, duration of pulses was 1 μs, frequency was 200 kHz, incident energy was 2×10<sup>16</sup> photon cm<sup>-2</sup> s<sup>-1</sup>).<sup>21</sup> Optical spectra were recorded using an Agilent 8453 spectrophotometer. For the calculation of As<sup>V</sup> quantum yields (mean errors, 10–20%), the lamp intensity was measured by a SOLO 2 power meter (Gentec EO).

Inductively coupled plasma atomic-emission spectrometry (ICP-AES) equipped with an Opal Mist nebulizer (iCap 6500 Duo, Thermo Scientific, USA) and a Hydride Generation additive (Thermo Scientific, USA) was applied to the determination of total arsenic and As<sup>III</sup> in solutions. The data processing was provided by the iTeva software. The concentration of As<sup>V</sup> was measured using a Metrohm 883 Basic IC Plus liquid chromatograph, IC (Metrohm, Switzerland) with a conductometric detector equipped with a 20 μl sample loop, a Metrosep A Supp 5 150/4.0 column and a suppressor module.



**Figure 1** Optical spectra of (a) FA (50 mg dm<sup>-3</sup>, pH 7.0) and (b) H<sub>3</sub>AsO<sub>3</sub> (pH 3) in aqueous solution.

described by equations (1) and (2). According to the value of  $pK_a$ , the neutral form H<sub>3</sub>AsO<sub>3</sub> absolutely dominates in solution at pH 3–8; at pH > 8, equilibrium (2) shifts towards the formation of ionic forms.

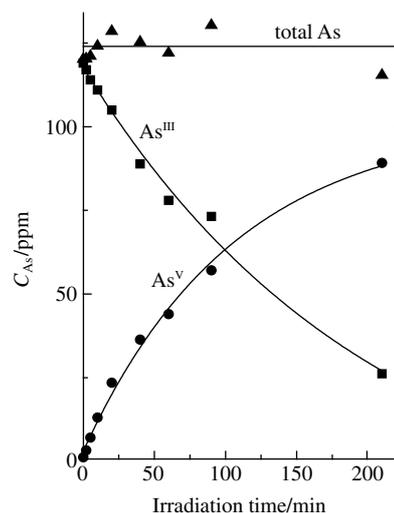


The irradiation (282 nm) of As<sup>III</sup> solutions in the presence of FA leads to photooxidation (Figure 2). In this experiment, the conversion of As<sup>III</sup> into As<sup>V</sup> was about 80% at an irradiation time of 210 min. The quantum yield of photooxidation was  $(8 \pm 1) \times 10^{-3}$ . This value is comparable with the quantum yield of photooxidation of As<sup>III</sup> initiated by colloidal Fe<sup>III</sup> hydroxide particles;<sup>11</sup> therefore, taking into consideration the commercial availability of FA, this way of photooxidation seems promising. Note that high (>1)<sup>10</sup> quantum yields of direct photooxidation of As<sup>III</sup> during irradiation at 254 nm cannot be of interest because of a very small absorption coefficient of H<sub>3</sub>AsO<sub>3</sub> in this region [ $\epsilon_{254 \text{ nm}} = 2.5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,<sup>10</sup> see also Figure 1(b)].

The mechanism of As<sup>III</sup> photooxidation initiated by FA is apparently connected with the formation of excited triplet states of FA (<sup>3</sup>FA) molecules. Triplets of humic substances were observed previously in laser flash photolysis experiments.<sup>24–28</sup> <sup>3</sup>FA can either react directly with arsenic-containing compound, or participate in generation of singlet oxygen,<sup>29</sup> which is able to oxidize As<sup>III</sup>. Indeed, it was found that the excitation of FA solutions

Kinetics of singlet oxygen luminescence was detected on a setup<sup>22</sup> based on a laser fluorimeter at the Institute of Physics, NASB. Excitation of samples was accomplished by Nd:YAG-laser (DTL-314QT, Russia) pulses (pulse duration, 10 ns; energy,  $\leq 1 \mu\text{J}$ ; and frequency, 2.5 kHz at  $\lambda = 532 \text{ nm}$ ). The band-pass interference filter (maximum at 1272 nm; halfwidth, 34 nm) was used for spectral selection. Quantum yields of singlet oxygen formation were determined using  $\phi(^1\text{O}_2, 532 \text{ nm})$  meso-tetra(*N*-methyl-4-pyridyl)porphyrin (TMpyP) tosylate as a standard  $\phi(^1\text{O}_2, 532 \text{ nm}) = 0.77$ .<sup>23</sup>

Total arsenic content was determined by ICP-AES using scandium as an internal standard at the following working parameters: power supply, 1150 W; argon flows, dm<sup>3</sup> min<sup>-1</sup>: 0.7 for the nebulizer, auxiliary – 0.5, cooling – 12. For the determination of As<sup>III</sup>, a hydride generation technique in combination with ICP-AES detection was used. A continuous flow hydride generation system consisted of a peristaltic pump for the reagents and sample introduction, a reaction chamber and a gas liquid separator. A 0.5% sodium borohydride stabilized by 0.05% sodium hydroxide was used as a reductant. The plasma parameters were optimized to get the best signal to noise ratio: power supply 1350 W; argon flows, dm<sup>3</sup> min<sup>-1</sup>: 0.5 for the nebulizer, auxiliary – 0.5, cooling – 12. The calibration was done at concentrations of 0.00001–1 mg dm<sup>-3</sup>. In all cases, the concentration of hydrochloric acid was 10%. To define As<sup>V</sup> in solution ion chromatography (IC) was applied using a mobile phase of  $3.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$  and  $10^{-3} \text{ mol dm}^{-3} \text{ NaHCO}_3$  at a flow rate of 0.7 dm<sup>3</sup> min<sup>-1</sup>. The calibration was done at 0.1–10 mg dm<sup>-3</sup> of As<sup>V</sup>. Both ICP-AES and IC methods exhibit precision about 5–10% in the region of test As<sup>III</sup> and As<sup>V</sup> concentrations.

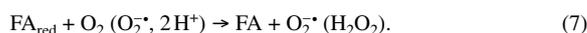


**Figure 2** Kinetic curves of changing As<sup>III</sup>, As<sup>V</sup> and total As concentrations during photolysis of air-equilibrated solution (pH 9.5) of 125 mg dm<sup>-3</sup> As<sup>III</sup> in the presence of 50 mg dm<sup>-3</sup> FA (points – experiment, curves – best monoexponential fit). Each point corresponds to the photolysis of 1 ml of fresh sample.

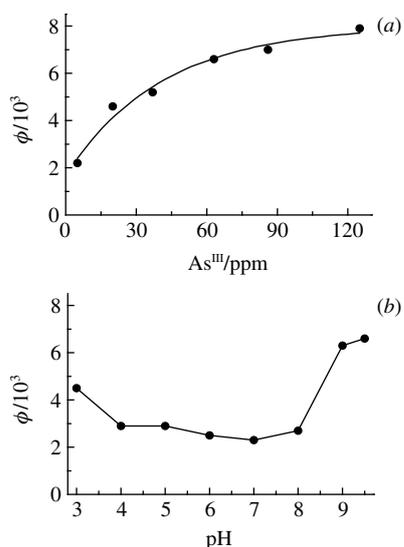
at 532 nm (pH 8) leads to singlet oxygen formation with the quantum yield  $\phi(^1\text{O}_2, 532 \text{ nm}) = 6 \times 10^{-4}$ . This value is typical of humic substances ( $10^{-4}$ – $10^{-2}$ ).<sup>29</sup> It should be expected that a shortening of the excitation wavelength would result in increasing the quantum yield of singlet oxygen.<sup>29</sup>

The quantum yield of As<sup>III</sup> photooxidation depends on the initial arsenic concentration and pH of solution (Figure 3). The dependence of quantum yield on As concentration reaches a plateau [Figure 3(a)] that indicates the complete capture of active intermediates (<sup>3</sup>FA or <sup>1</sup>O<sub>2</sub>) at high initial As<sup>III</sup> concentrations. The experimental data allow us to pose the following tentative kinetic scheme of As<sup>III</sup> photooxidation, which includes a competition of two mechanisms: M1, electron transfer from As<sup>III</sup> to <sup>3</sup>FA [equation (4a)]; M2, oxidation of As<sup>III</sup> by singlet oxygen [equation (4b)] formed at stage (3).

The assumed stages are then followed by As<sup>IV</sup> disproportionation and oxidation by dissolved oxygen [equations (5), (6)].<sup>30</sup> High photostability of FA solutions can be caused by reaction (7) implying reoxidation of reduced FA form by dissolved oxygen and a superoxide anion radical. The determination of the rate constants of reactions (3), (4a), and (4b) and the elucidation of the role of each assumed mechanism is beyond the scope of this communication.



The quantum yield of As<sup>III</sup> photooxidation does not depend on pH in a range of 4–8 [Figure 3(b)]; however, it increased by a factor of 2.5 with an increase in pH from 8 to 9.5. This fact correlates with a shift of equilibrium between As<sup>III</sup> forms [equation (2)] towards the formation of anionic form H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>, which can be more easily oxidized by <sup>1</sup>FA<sup>31</sup> or singlet oxygen. The marked increase in the quantum yield with decreasing pH from 4 to 3 can be caused by the protonation of FA (both in the



**Figure 3** Dependence of the quantum yield of  $\text{As}^{\text{III}}$  photooxidation in the presence of  $50 \text{ mg dm}^{-3}$  FA upon  $\text{As}^{\text{III}}$  concentration at (a) pH 9.5 (points – experiment, curves – best monoexponential fit) and (b) pH value of solution at a fixed  $\text{As}^{\text{III}}$  concentration of 100 ppm.

ground and in the triplet excited states), which provides stronger bonding with the  $\text{H}_3\text{AsO}_3$  molecule. Note that this explanation of dependences shown in Figure 3 does not suppose the active participation of singlet oxygen in the photooxidation process.

Thus, the quantum yields of  $\text{As}^{\text{III}}$  were measured under different conditions and a tentative model explaining the dependences of the quantum yield on arsenic concentration and pH was proposed.

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