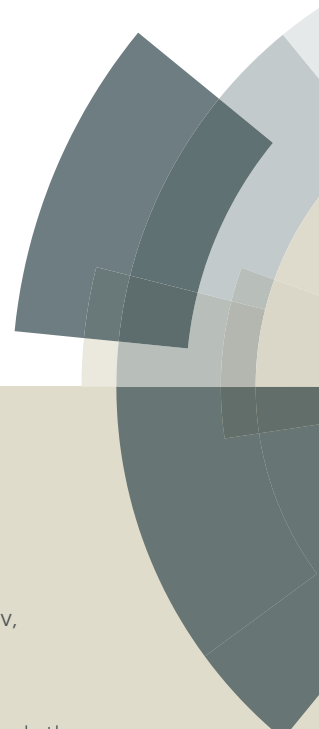


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Photochemical transformation of iron(III)–arsenite complex in acidic aqueous solution

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26 Abstract

27 Surface complexation between arsenious acid anions (As(III)) and ferric (hydr)oxides in water is important
28 for the transformation and transfer of inorganic arsenic species. The mechanisms of formation and the
29 photochemistry of dissolved Fe(III)–As(III) complexes in acidic aqueous solution are still unclear. Here, the
30 photooxidation of As(III) in the presence of Fe(III) ions in acidic media has been investigated by laser flash
31 and steady-state photolysis. At low arsenite concentration (< 1 mM), As(III) is oxidized by $\cdot\text{OH}$ radical
32 generated by photolysis of the FeOH^{2+} complex. At higher arsenite concentrations (>10 mM), photoactive
33 Fe(III)–As(III) complexes are formed ($\phi_{\text{Fe}}^{308} \approx 0.012$). At all arsenite concentrations, white FeAsO_4 colloid is
34 formed during As(III) photolysis in the presence of Fe(III) ions. Solid Fe(III)–As(III) complexes have been
35 prepared and characterized, and the photochemical transformation of As(III) to As(V) in solid Fe(III)–As(III)
36 complexes has been confirmed. These findings are important for a better understanding of the evolution of
37 As(III) species under environmental conditions and should provide guidance for detoxification of
38 As(III)-polluted water systems.

39 **Keywords:** Arsenite, arsenate, iron complexes; laser flash photolysis; $\cdot\text{OH}$ radical; photooxidation

40 Introduction

41 The problem of arsenic contamination requires urgent attention on a global scale because of its
42 carcinogenicity and toxicity. Thus, there has been great scientific interest in the chemistry and transformation
43 of arsenic species in the environment.^{1–3} In natural waters, arsenic exists in two main inorganic forms:
44 arsenite in the form of $\text{H}_3\text{As(III)O}_3$ and arsenate in the form of $\text{H}_2\text{As(V)O}_4^-$ and HAs(V)O_4^{2-} . In an
45 investigation of 65 well water samples in the United States, Sorg et al.⁴ found that arsenic existed mainly as
46 As(V) in 31 wells, mainly as As(III) in 29 wells, and as a mixture in the remaining 5 wells. The occurrence of

47 arsenic species is affected by environmental conditions. In particular, photochemical reactions under
48 ultraviolet (UV) and visible light may lead to the oxidation of arsenite to arsenate.⁵⁻⁷

49 In previous studies, the effects of dissolved ions and (hydr)oxides of transition metals (especially iron)
50 have been extensively examined. These species were found to play an important role in
51 co-precipitation/adsorption^{2,8,9} and in (photo)catalytic oxidation of As(III) to As(V) by dissolved oxygen and
52 hydrogen peroxide¹⁰⁻¹³. As(III) photooxidation on the surface of different kinds of (hydr)oxides
53 (ferrihydrite¹⁴, goethite^{15,16}, montmorillonite¹⁷, etc.) has raised concerns in this decade. However, previous
54 studies have been mainly concerned with the generation of reactive oxygen species (ROS); the relationship
55 between Fe and As, including photooxidation mechanisms of As(III), has usually been beyond the scope of
56 such studies. In recent years, the concept of complexation between arsenic and iron (hydr)oxides has been
57 proposed, and related works have been published in this area.^{14,16,18} Although such works have revealed the
58 ability of arsenic to complex with iron (hydr)oxides, the corresponding oxidation mechanisms were still
59 unclear until early 2014. Xu et al.¹⁹ proposed a novel pathway involving ligand-to-metal charge transfer
60 (LMCT) for arsenic oxidation in colloidal ferric hydroxide (CFH) systems. Their work confirmed the
61 complexation between As(III) and CFH and they elucidated the complex formation equilibrium constants at
62 near-neutral pH (6.0). However, in this study, the possibility of complexation between As(III) and free Fe(III)
63 ions in aqueous solution was not considered, and the photochemical reaction of the Fe(III)–As(III) complex
64 in aqueous solution remains unclear. To obtain a dissolved Fe(III)–As(III) complex in aqueous media, the
65 solution must be strongly acidic to prevent the formation of CFH.

66 The formation of As(IV) species as key intermediates is postulated in the ROS and LMCT mechanisms.
67 However, the conclusion of As(IV) formation has been based mainly on indirect results of the determination
68 of As(V) as the final oxidation product²⁰⁻²² or on the effect of different ROS scavengers on the As(III)

69 oxidation rate^{13,16,19}. Direct spectral or kinetic observations of As(IV) species formation during As(III)
70 photooxidation in the presence of iron complexes or (hydr)oxides are not yet available in the literature.

71 In the present work, optical spectroscopy, as well as steady-state (308 nm, XeCl excilamp) and
72 nanosecond laser flash photolysis (LFP; 266 nm, 6 ns, Nd:YAG laser) have been used to study complexation
73 and mechanistic aspects of the aqueous photochemistry of As(III) in the presence of Fe(III) in acidic media
74 (pH 3). Attention has been mainly paid to the determination of active intermediates, the rate constants of
75 elementary stages, as well as the construction of a detailed kinetic scheme for As(III) photooxidation in the
76 presence of iron species. This information should prove very useful in understanding the oxidation of As(III)
77 to As(V) in discharges of acid mine drainage (AMD), which contain high concentrations of both iron and
78 arsenite.²³ The As(III) concentration used in this work was higher than that usually found in AMD to obtain
79 good yields of Fe(III)–As(III) complexes, and experiments were conducted at low pH in order to prevent
80 Fe(III) precipitation. Preliminary preparation, characterization, and photolysis experiments on the solid
81 Fe(III)–As(III) complex were also conducted to demonstrate its photochemical activity in the solid state.

82 **Experimental**

83 **Chemicals**

84 All chemicals were of analytical grade and were used without further purification. As(V), As(III), and Fe(III)
85 solutions in deionized water were prepared from Na₂HAsO₄·7H₂O (Alfa Aesar, A Johnson Matthey Co.,
86 Tianjin, China), NaAsO₂ (Xiya Reagent Center, Sichuang, China), and Fe(ClO₄)₃ (Internet Aladdin Reagent
87 Database Inc., Shanghai, China), respectively. Ethanol was purchased from Tianjin Kermel Chemical
88 Reagent Co. Ltd. (Tianjin, China). Potassium borohydride (KBH₄), thiourea, ascorbic acid (VC), potassium
89 hydroxide (KOH), sodium hydroxide (NaOH), hydrochloric acid (HCl), ammonium fluoride (NH₄F), acetic

90 acid (CH_3COOH), and *o*-phenanthroline (phen) were purchased from Sinopharm Chemical Reagent Co. Ltd.
91 (Shanghai, China). Water of 18 M Ω cm resistivity was purified through a water purification system (Liyuan
92 Electric Instrument Co., Beijing, China) and was used for preparation of all samples.

93 **Preparation of solid Fe(III)–As(III) or Fe(III)–As(V) complex**

94 Experiments were conducted by using 100 mL aqueous suspensions or solutions of analytical grade
95 chemicals in a 250 mL beaker agitated mechanically by a magnetic stirrer. The reaction solution temperature
96 was kept at 0 °C by using a low-temperature cooling-liquid circulating pump.

97 Reaction solutions were prepared in aqueous HCl (pH 1) with fixed concentrations of As(III) (354 mM),
98 As(V) (118 mM), and Fe(III) (590 mM).

99 *Preparation of Fe(III)–As(III) complex:* 10 mL of Fe(III) reaction solution was added to 50 mL of As(III)
100 reaction solution (Fe(III)/As(III) molar ratio 1:3) at a rate of about 500 $\mu\text{L}/\text{min}$, and then the solution was
101 diluted to 100 mL and adjusted to pH 1. The solution was stirred for a further 2 h, whereupon 80–150 mL of
102 absolute ethanol was added. The excess of As(III) was precipitated as As_2O_3 and the residue was separated
103 from the supernatant by centrifugation at 10,000 rpm for 15 min. The Fe(III)–As(III) complex was collected
104 by vacuum freeze-drying and washed with pure ethanol, retaining the supernatant. It was subsequently
105 vacuum freeze-dried once more.

106 *Preparation of Fe(III)–As(V) complex:* 50 mL of As(V) reaction solution was added to 30 mL of Fe(III)
107 reaction solution (Fe(III)/As(V) molar ratio 3:1) at a rate of ca. 2.5 mL/min, and then the solution was diluted
108 to 100 mL and adjusted to pH 1. The solution was stirred for a further 2 h. The resulting suspension was
109 centrifuged at 10,000 rpm for 15 min, and the precipitate was washed three times with aqueous HCl (pH 1).
110 The product was dried at 60.0 °C for 6 h.

111 **Photolysis equipment and analysis**

112 The LFP setup in the time-resolved experiments was based on an LS-2137U Nd:YAG laser (Lotis III,
113 Belarus) with an excitation wavelength of 266 nm, a pulse duration of 5–6 ns, an illumination spot area of
114 0.03 cm^2 and an energy per pulse of up to 10 mJ. The device was similar to that described in a previous
115 work.²⁴ The time resolution of the setup was ca. 50 ns. Solutions in LFP experiments were refreshed after
116 each 100–150 pulses to avoid any possible influence of photogenerated FeAsO_4 flakes on the measurements.
117 For steady-state irradiation in aqueous solutions, XeCl excimer lamps (308 nm, produced by the Institute of
118 High Current Electronics, Tomsk, Russia) and the fourth harmonic of the Nd:YAG laser (266 nm) were used.
119 The lamp and laser intensities were determined by means of a ferrioxalate actinometer.²⁵

120 Unless otherwise specified, all photochemical experiments were performed in a 1 cm quartz cell in
121 air-equilibrated or argon-saturated solutions at an initial $\text{pH} \approx 3$, at 298 K, and under atmospheric pressure.
122 Argon-saturated solutions were obtained by constantly bubbling argon through the sample. UV spectra were
123 recorded on an Agilent 8453 spectrophotometer (Agilent Technologies). pH measurements were carried out
124 by using an ANION-4100 pH meter (Smolensk, Russia) with a combined electrode (ESK-10614).

125 Stability constants and absorption coefficients of the Fe(III)-As(III) complexes were estimated by
126 numerical fitting of the optical density change at 260 nm using a subprogram (script) generated in-house with
127 the commercially available Origin 8.0 software program and based on application of Newton's iterative
128 optimization method²⁶ (see ESI (E-Supporting Information) section "Determination of stability constants and
129 absorption coefficients of Fe(III)-As(III) complexes" for details).

130 The Fe(II) concentration after various photolysis times was measured by addition of the chelating agent
131 o-phenanthroline to the irradiated solution and then measuring the absorption of the $[\text{Fe(II)(phen)}_3]^{2+}$
132 complex at 510 nm (the molar absorption coefficient at 510 nm is $11000 \text{ M}^{-1} \text{ cm}^{-1}$).²⁵ To determine the total
133 iron concentration, VC was added to reduce Fe(III) to Fe(II) . The total iron concentration was then

134 determined in the same way as the Fe(II) concentration. The Fe(III) concentration was evaluated by a
135 subtraction method.

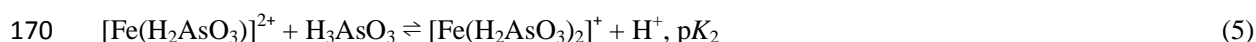
136 Arsenic speciation was analyzed by means of hydride generation–atomic fluorescence spectrometry
137 (HG–AFS; Titan Instruments Co. Ltd., Beijing, China). As(III) and total arsenic concentrations were
138 determined by controlling the concentrations of HCl and KBH_4 during hydride generation, as conducted in
139 our previous work.²⁷

140 X-ray diffractograms were recorded on an X'Pert Pro X-ray diffractometer (Cu- $\text{K}\alpha_1$ radiation, $\lambda = 1.54 \text{ \AA}$)
141 operated at 40 kV and 40 mA. Scans were performed from 10° to 80° at a step size of 0.026° . X-ray
142 photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250Xi spectrometer
143 using a monochromated Al- $\text{K}\alpha$ X-ray source. A pass energy of 20 eV with a 0.050 eV step size was used for
144 all samples. The XPS results were collected in binding energy form and were fitted by using a nonlinear
145 least-squares curve-fitting program (XPS Peak 4.1). The XPS spectra were analyzed after subtracting the
146 Shirley background applicable for transition metals. The percentage Lorentzian–Gaussian for fitting the data
147 was set at 20%.

148 To demonstrate the photoactivity of the Fe(III)–As(III) complex in the solid state, steady-state photolysis
149 of the solid product was performed. The solid Fe(III)–As(III) complex was the same batch as used in the XPS
150 and XRD measurements and had an Fe/As molar ratio of 1:0.92. The sample was placed on filter paper under
151 UV-C illumination (dominant wavelength 254 nm). The lamp (8 W, Cnlight Co., China) was fixed directly
152 above the sample at a distance of 50 mm. The UV irradiation intensity on the surface of the sample was
153 2.0 W/m^2 . The filter paper was divided equally into 16 parts. At each sampling time, the sample on one part
154 of the filter paper was dissolved in 50 mL of HClO_4 solution at pH 1 for further measurement of arsenic
155 species by HG–AFS.

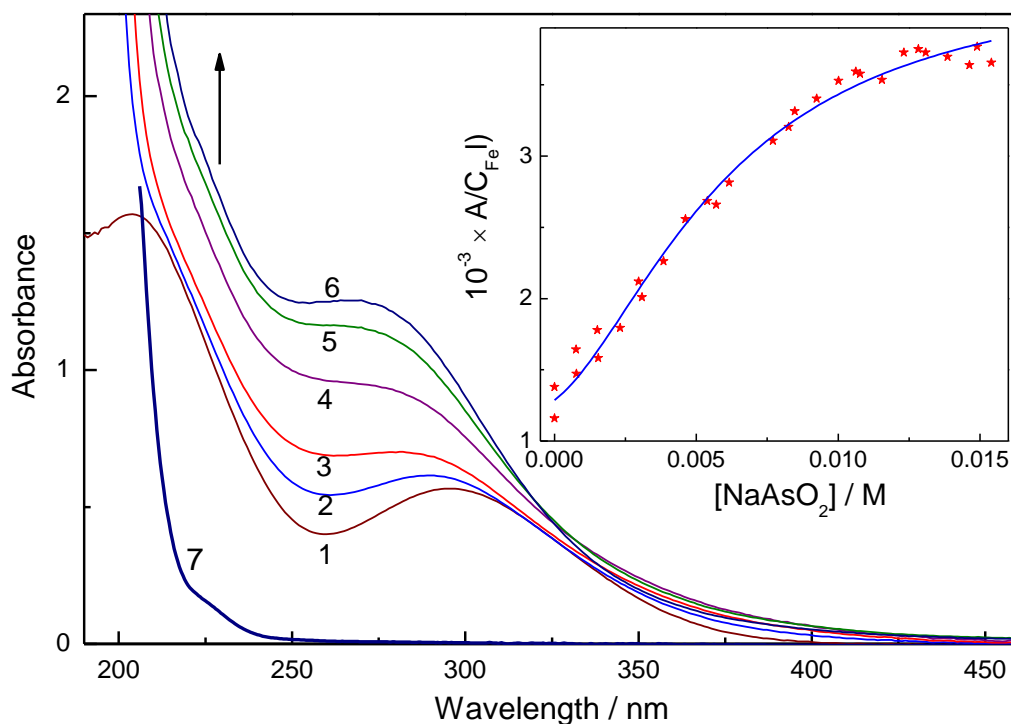
156 **Results and discussion**157 **Formation of the Fe(III)–As(III) complexes in aqueous solution**

158 The UV spectrum of the solution without As(III) was determined by the absorption of Fe^{3+} ($\lambda_{\text{max}} = 240 \text{ nm}$;
 159 $\varepsilon_{\text{max}} = 3800 \text{ M}^{-1} \text{ cm}^{-1}$) and the FeOH^{2+} complex ($\lambda_{\text{max}} = 300 \text{ nm}$, $\varepsilon_{\text{max}} = 1985 \text{ M}^{-1} \text{ cm}^{-1}$).²⁸ The addition of
 160 arsenite ions (1–15 mM) at pH 3 led to an increase in UV absorption with a gradual shift of the absorption
 161 maximum from 300 to around 270 nm without appearance of any isosbestic points. These observations
 162 indicated complexation between As(III) and Fe(III) and the formation of more than one complex in solution
 163 (Fig. 1). Information on complexation between As(III) and Fe(III) is absent in the literature, but it is known
 164 that Fe(III) forms both 1:1 and 1:2 complexes with H_3PO_4 ²⁹ and H_3PO_3 ³⁰ in acid media. Hence, the following
 165 main equilibria in a solution containing NaAsO_2 and $\text{Fe}(\text{ClO}_4)_3$ at pH 3 should be taken into account:



171 where K_{a} is the acid dissociation constant for H_3AsO_3 , K_{g} is the hydrolysis constant of Fe^{3+} , and K_1 and K_2 are
 172 the stability constants of 1:1 and 1:2 Fe(III)–As(III) complexes. Here, it is assumed that Fe(III) forms
 173 complexes with H_2AsO_3^- ion similarly to complexation with H_2PO_3^- .³⁰ The stability constants ($\text{p}K_1$, $\text{p}K_2$) and
 174 absorption coefficients (ε_1 , ε_2) of the 1:1 and 1:2 Fe(III)–As(III) complexes were estimated by numerical
 175 fitting of a curve of the optical density change at 260 nm using Newton's iterative optimization method²⁶ (see
 176 ESI section "Determination of stability constants and absorption coefficients of Fe(III)–As(III) complexes"
 177 for details). The best fit gave $\text{p}K_1 = 2.8$, $\text{p}K_2 = 2.5$, $\varepsilon_1 = 3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, $\varepsilon_2 = 4.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$

178 corresponding to the predominant formation of a 1:2 complex $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ (73% of total $[\text{Fe}(\text{III})]$) at an
 179 As(III) concentration of about 1.5×10^{-2} M. We assumed that at arsenite concentrations >10 mM, the main
 180 photoactive species in solution would be the $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ complex.

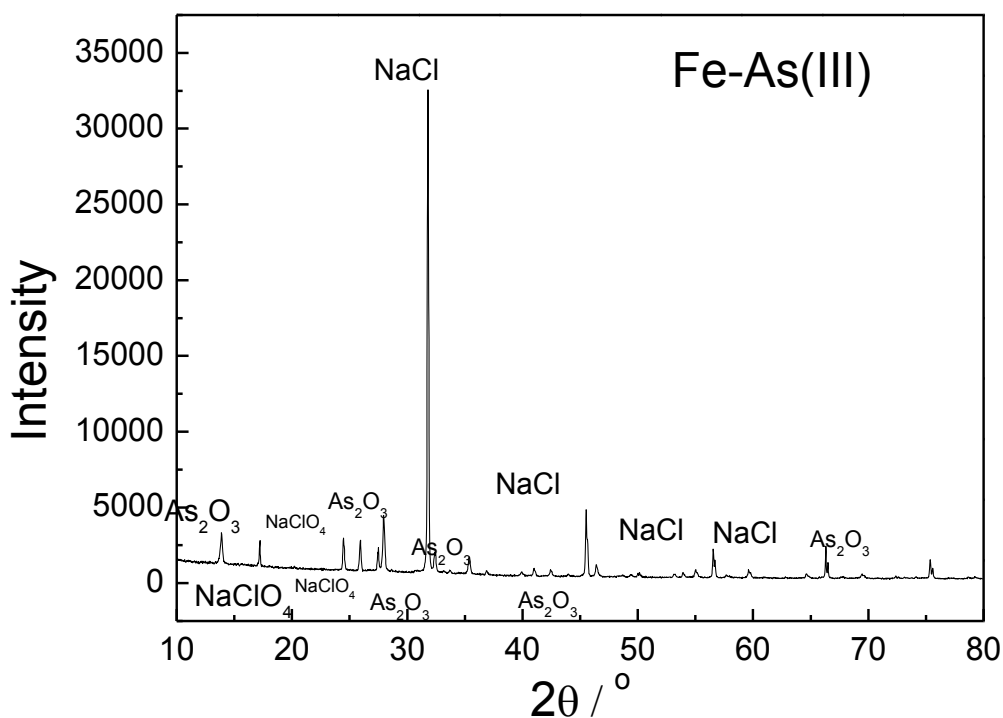


181
 182 **Fig. 1** Optical spectra of Fe(III) ions in the presence of 0 (1), 1.5 (2), 3.1 (3), 6.2 (4), 9.2 (5), and 15 mM (6)
 183 NaAsO₂. $[\text{Fe}(\text{III})(\text{ClO}_4)_3] = 0.34$ mM, pH 3. (7) Absorption spectrum of 15 mM NaAsO₂ alone. Inset:
 184 changes in optical density at 260 nm with the variation of $[\text{NaAsO}_2]$. The smooth curve is the best fit obtained
 185 by using Eq. (13) in the ESI.

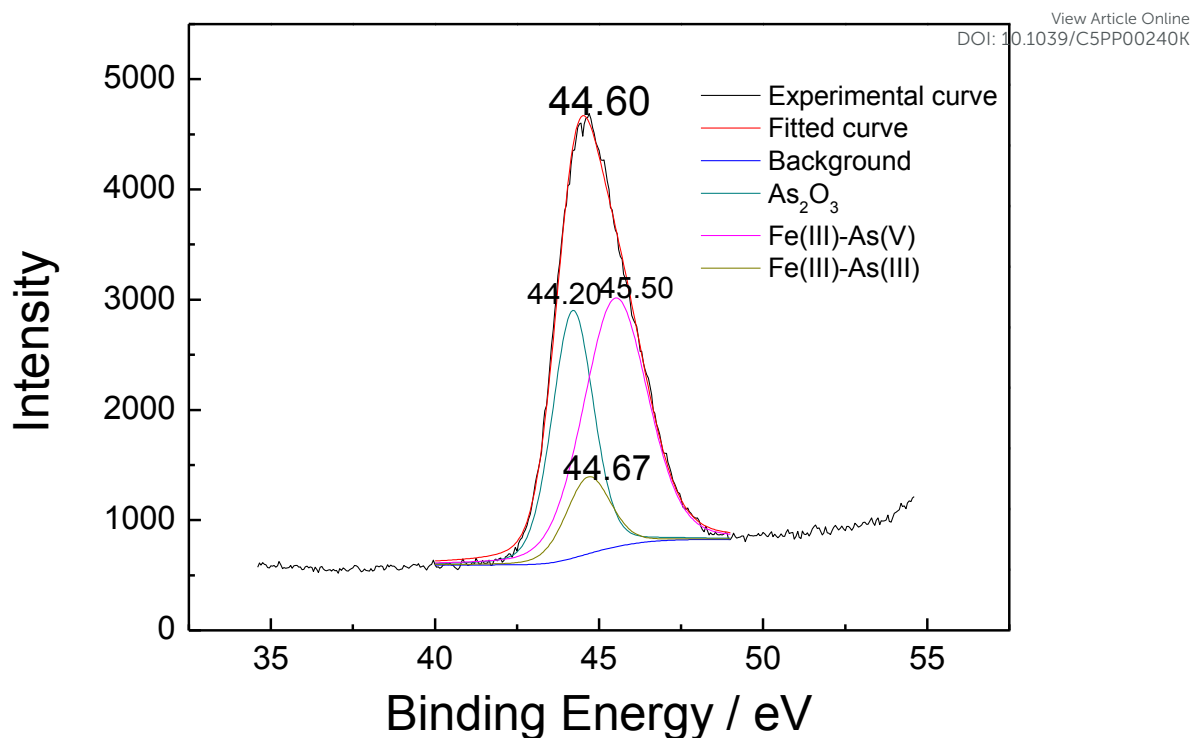
187 Formation of the Fe(III)–As(III) complexes in the solid state

188 A solid Fe(III)–As(III) product was also prepared and characterized. The solid Fe(III)–As(III) product
 189 obtained by the procedure described in the Experimental Section was dissolved in aqueous HClO₄ at pH 1.
 190 The As(III) and Fe(III) concentrations in solution were measured by HG–AFS and spectrophotometry,
 191 respectively. The results indicated that the solid Fe(III)–As(III) product consisted of 11.68% As(III) and

192 6.23% Fe(III). No As(V) was observed. Considering the characteristic XRD bands of ferric arsenate at $2\theta \approx$
193 28° and 58° ,³² the sample was analyzed by XRD to identify its phase (Fig. 2). As the characteristic peaks of
194 the Fe(III)–As(III) complex were not apparent, it was concluded that this product chiefly consisted of an
195 amorphous phase.



196
197 **Fig. 2** XRD pattern of solid Fe(III)–As(III) complex formed by direct mixing of Fe(III) and As(III) at pH 1
198 with ethanol. Experimental conditions: $[\text{Fe(III)(ClO}_4)_3] = 59 \text{ mM}$, $[\text{As(III)}] = 177 \text{ mM}$.

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199
200 **Fig. 3** As 3d XPS spectrum of solid Fe(III)–As(III) complex formed by direct mixing of Fe(III) and As(III) at
201 pH 1 with ethanol. Experimental conditions: [Fe(III)(ClO₄)₃] = 59 mM, [As(III)] = 177 mM.

202
203 To verify the presence of arsenic and to determine the oxidation of As(III) on the solid surface of the
204 Fe(III)–As(III) complex, the XPS spectrum of the solid Fe(III)–As(III) complex product was determined.
205 The results in Fig. 3 analyzed by XPS Peak 4.1 indicated that the As 3d spectrum could be fitted by three
206 species with binding energies at 44.20, 44.67, and 45.50 eV, respectively. The values of 44.20 and 45.50 eV
207 can be attributed to As₂O₃³³ and As(V)³⁴, respectively.

208 In order to determine the form of As(V) (45.50 eV) in Fig 3, the As 3d XPS spectrum of the precipitate of
209 the Fe(III)–As(V) complex formed by direct mixing of Fe(III) and As(V) at pH 1 was obtained (Fig. S1).
210 This solid Fe(III)–As(V) complex was further dissolved to determine the ratio of Fe(III)/As(V). In this way,
211 we confirmed that the Fe(III)–As(V) complex existed as FeAsO₄ with an approximately 1:1 Fe(III)/As(V)
212 ratio. The position of the peak in Fig. S1 is the same as that in Fig. 3, that is, located at 45.50 eV, higher than

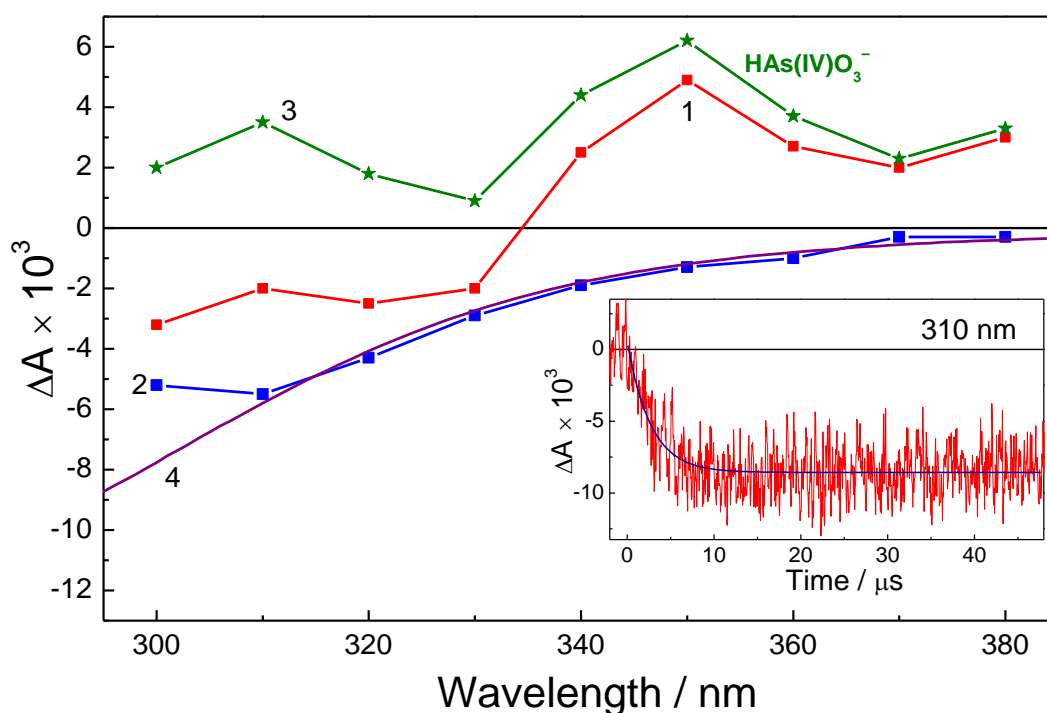
213 the binding energy of Na_3AsO_4 (44.9 eV).³⁵ Thus, the peak at 45.5 eV may be attributed to the higher binding
214 energy for As(V)–O coordination to an iron atom, i.e., As(V)–O–Fe(III).³⁶

215 However, the binding energy of As(III)–O is lower, at 44.6 ± 0.13 eV;³⁶ thus, the peak at 44.67 eV can be
216 assigned to As(III)–O–Fe(III). As shown in Fig. 3, As(III)–O–Fe(III) could be transformed to
217 As(V)–O–Fe(III) due to oxidation of As(III) by the high-energy X-rays deployed during the measurement.³⁷
218 The XPS spectra in Figs. S2 and S3 suggest that Fe(II)–As complexation took place and that
219 As(III)–O–Fe(III) was formed and underwent oxidation by X-ray energy. O_2 easily oxidized the generated
220 Fe(II) under acidic conditions, resulting in a low Fe(II) concentration. As shown in Table S1, considering the
221 data obtained from area estimation of the XPS spectra in Fig. 3 and the concentrations of arsenic species and
222 iron species measured by HG–AFS and spectrophotometry, the amount of arsenic coordinated to iron was
223 around 7.65%. Therefore, the Fe/As molar ratio of the solid complex was 1:0.92. However, the Fe/As ratio of
224 the solid Fe(III)–As(III) complex differed from that of the dissolved Fe(III)–As(III) (1:2) complex estimated
225 from UV spectrophotometric data (Fig. 1). Because the formation conditions of the complex were different,
226 the compositions of the complex in solution and in the solid state were also different.

227 **Photochemistry of the aqueous Fe(III)-As(III) system at high As(III) concentration: $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$**
228 **complex photolysis and As(IV) formation**

229 Steady-state (308 nm) photolysis of the $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ complex led to a disappearance of its absorption
230 bands and the appearance of Fe(II) with a quantum yield of 0.012 (Fig. S4). The formation of white flakes
231 was also observed during prolonged (ca. 60 min) steady-state irradiation at 308 nm at an incident light
232 intensity of 1.4×10^{16} quanta/s or 0.56 mM/min, which indicated the generation of colloidal ferric arsenate
233 (FeAsO_4) and occurrence of the reduction–oxidation reaction upon complex excitation. Similar results were
234 obtained during irradiation of the $[\text{Fe}(\text{III})(\text{H}_2\text{AsO}_3)_2]^+$ complex solution by pulses from an Nd:YAG laser at

235 266 nm. Decay of the complex absorption was observed with simultaneous Fe(II) photoproduction (the
 236 quantum yield of Fe(II) was estimated as 0.033). An increase in Fe(II) quantum yield with decreasing
 237 irradiation wavelength is a common feature of Fe(III) complex photochemistry.³⁸ The quantum yield of Fe(II)
 238 production from the $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ complex was lower than those for $\text{Fe}(\text{III})\text{OH}^{2+}$ or $\text{Fe}_{\text{aq}}^{3+}$ ($\phi_{280} = 0.31$ and
 239 0.05, respectively) and comparable with that for $\text{Fe}(\text{III})\text{SO}_4^+$ ($\phi_{280} = 0.008$).²⁸



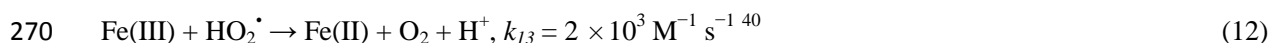
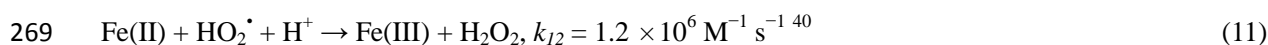
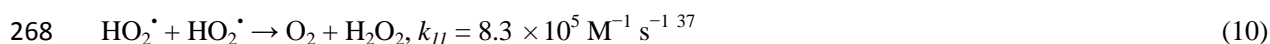
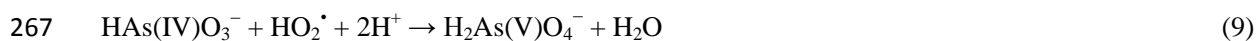
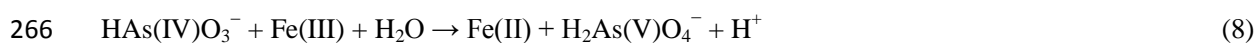
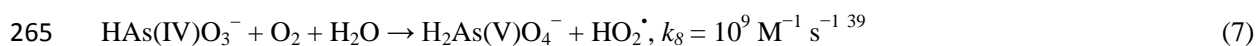
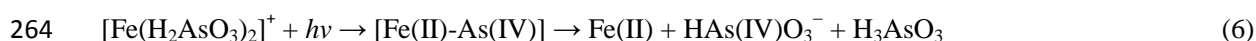
240
 241 **Fig. 4** Flash photolysis (266 nm) of the Fe(III)–As(III) system at pH 3. ΔA is the change in optical density.
 242 $[\text{Fe}(\text{III})(\text{ClO}_4)_3] = 0.34$ mM, $[\text{As}(\text{III})] = 17$ mM, excitation energy = 4.6 mJ/pulse. (1, 2) Transient spectra
 243 obtained at 0.05 and 48 μs after excitation, respectively. (3) Difference between spectra in (1) and (2)
 244 corresponding to the spectrum of $\text{HAs}(\text{IV})\text{O}_3^-$.³⁹ (4) Inverted absorption spectrum of the $[\text{Fe}(\text{III})(\text{H}_2\text{AsO}_3)_2]^+$
 245 complex. Inset: kinetic curve at 310 nm and the best monoexponential fit with a time constant of 3 μs .

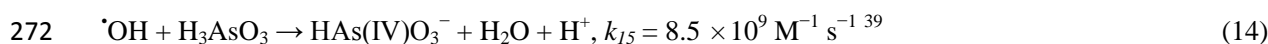
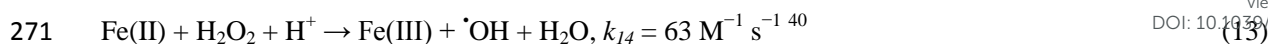
246
 247 Flash excitation of the Fe(III)–As(III) complex led to the appearance of a transient absorption with a
 248 maximum at 350 nm (Fig. 4). This transient signal is assumed to arise from $\text{HAs}(\text{IV})\text{O}_3^-$, formed by electron

249 transfer from the ligand to iron (reaction 6), based on a comparison with the known absorption spectrum of
 250 HAs(IV)O_3^- .³⁹ The lifetime of the latter species was about 3 μs under the experimental conditions used
 251 (Fig. 4).

252 After the disappearance of the initial transient signal, constant bleaching corresponding to decay of the
 253 initial complex was observed (Fig. 4, curve 2). The amplitude of bleaching at 310 nm measured at times <
 254 50 μs after excitation exhibited a linear dependence on the laser pulse intensity. This allowed us to estimate
 255 the quantum yield of $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ complex photolysis (0.023) by using a known value of the molar
 256 absorption coefficient ($2400 \text{ M}^{-1} \text{ cm}^{-1}$ at 310 nm). The absorption coefficient of the complex at 310 nm was
 257 obtained by the same procedure as for the absorption coefficient at 260 nm. The quantum yield of
 258 $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ complex photolysis was close to that of Fe(II) photoproduction at 266 nm. The difference
 259 between these values could be explained by reactions (11–13) occurring on timescales longer than 50 μs . The
 260 quantum yield of the $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ complex photolysis in acid aqueous solution was similar to that of the
 261 As(III)–CFH complex in the CFH system (ca. 0.01).¹⁹

262 On the basis of aforesaid findings, we propose the following general mechanism of $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$
 263 complex photolysis at pH 3:





274 where k_n are the rate constants of the reactions, with n being the number of the corresponding equation.

275 According to this mechanism, the first photochemical step is intersphere oxidation of the ligand, which leads

276 to the formation of an unstable $[\text{Fe(II)-As(IV)}]$ complex. This species dissociates at times shorter than 50 ns

277 with the formation of Fe(II) and As(IV) (reaction 6). This assumption is based on the detection of

278 non-coordinated HAs(IV)O_3^- immediately after excitation of $[\text{Fe}(\text{H}_2\text{AsO}_3)_2]^+$ and on the fact that elimination

279 of an $\cdot\text{OH}$ radical upon excitation of the FeOH^{2+} complex occurs in less than 50 ns.⁴¹ Initially formed As(IV)

280 is mainly oxidized by dissolved oxygen and Fe(III) ions to As(V) in reactions (8, 9), which determine the

281 lifetime of HAs(IV)O_3^- (ca. 3 μs). Additional oxidation of Fe(II) in Fenton-like reactions (11, 13) leads to the

282 generation of ROS, which can participate in further oxidation of As(III) and As(IV) (Eqs. (9) and (14)) on a

283 longer time scale.

284 In the final step, colloidal FeAsO_4 is formed (Eq. (15)). To test this hypothesis, colloids obtained after

285 photolysis and the product in solution obtained by preparation of the Fe(III)-As(V) complex were analyzed

286 for particle size and by UV/visible (UV/Vis) spectrophotometry. Fig. S5 shows photographs of the white

287 colloids that formed by direct mixing of Fe(III) and As(V) (A) and during photolysis of the Fe(III)-As(III)

288 complex (B) at pH 3. Both colloids were stable and did not precipitate. Fig. S6 shows the particle size

289 distributions of the colloids. The size of colloidal particles formed after photolysis was 5–54 μm , whereas the

290 particles of the Fe(III)-As(V) complex were of size 3–48 μm . We could not separate the colloidal particles

291 from the solution by filtration or centrifugation. However, the UV/Vis spectra of the colloids in Fig. S7

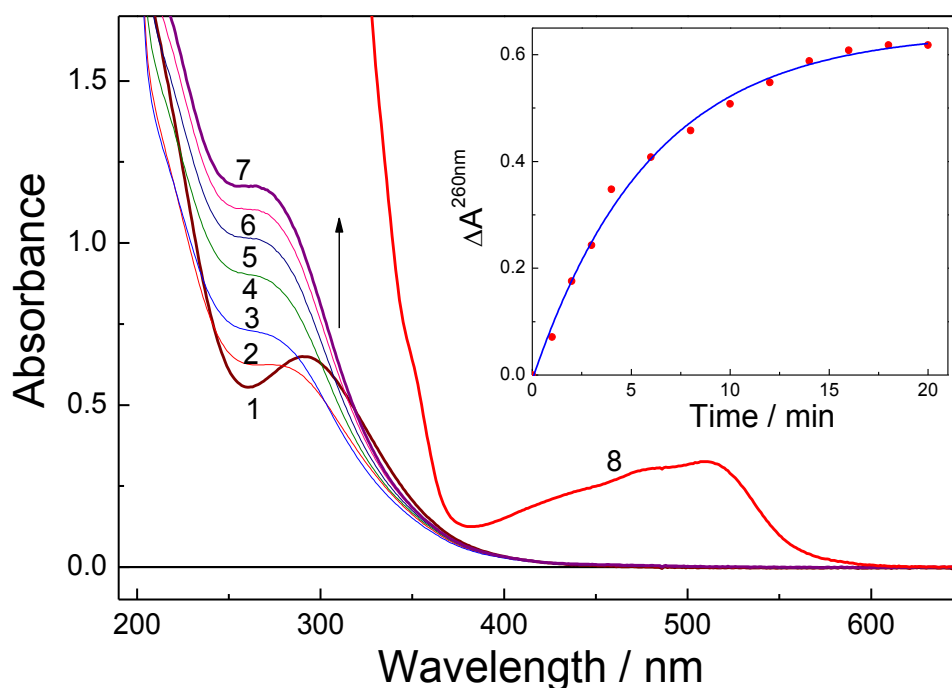
292 feature similar light absorption bands in the range 250–600 nm, confirming FeAsO_4 formation during

293 photolysis of the Fe(III)–As(III) complex.

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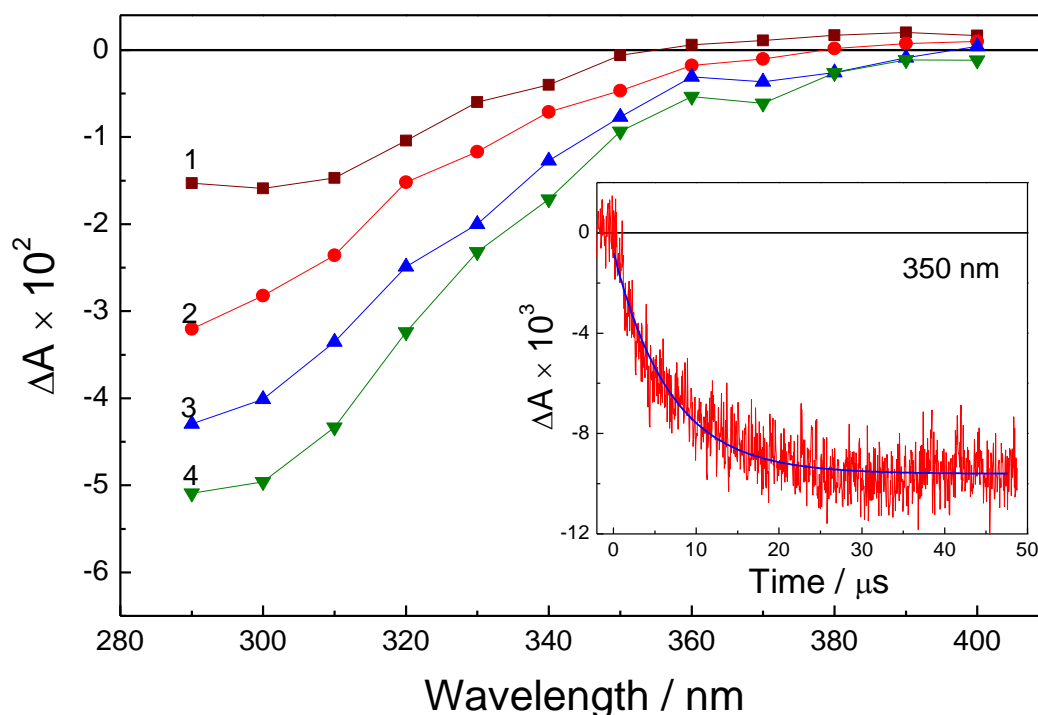
294 **Photochemistry of the aqueous Fe(III)-As(III) system at low As(III) concentration: Fe(III)OH²⁺**
295 **photolysis and mechanism of As(V) formation**

296 At low arsenite concentrations, the Fe(III)–As(III) system exhibits interesting photochemistry without
297 evident sedimentation and turbidity. At 1 mM As(III), 0.34 mM Fe(III), and pH 3, less than 10% of the Fe(III)
298 forms complexes with As(III) (Fig. 1). At pH 3, most Fe(III) (ca. 80%) exists as FeOH²⁺, which undergoes
299 photolysis to produce an $\cdot\text{OH}$ radical (Eq. (16)).⁴¹



301
302 **Fig. 5** Steady-state photolysis (308 nm) of the FeOH²⁺–As(III) system at pH 3. Experimental conditions:
303 [Fe(III)(ClO₄)₃] = 0.34 mM, [As(III)] = 1.1 mM, sample volume 2 mL, incident light intensity =
304 1.4×10^{16} quanta/s or 0.56 mM/min. (1–7) Spectra after 0 (1), 1 (2), 2 (3), 4 (4), 8 (5), 12 (6), and 20 min (7) of
305 irradiation. (8) Spectrum of the solution irradiated for 20 min after the addition of *o*-phenanthroline. Inset:
306 changes in optical density at 260 nm during irradiation.

307 During photolysis at 308 nm (Fig. 5) or 266 nm (Fig. S8), Fe(II) and an unknown photoproduct showing
 308 absorbance at 260 nm were formed. We assume the photoproduct to be an unidentified Fe(III) complex, since
 309 inorganic Fe(II) complexes exhibit low absorption in the UV region.^{25,42} Identification of the photoproduct
 310 will be the subject of further work.



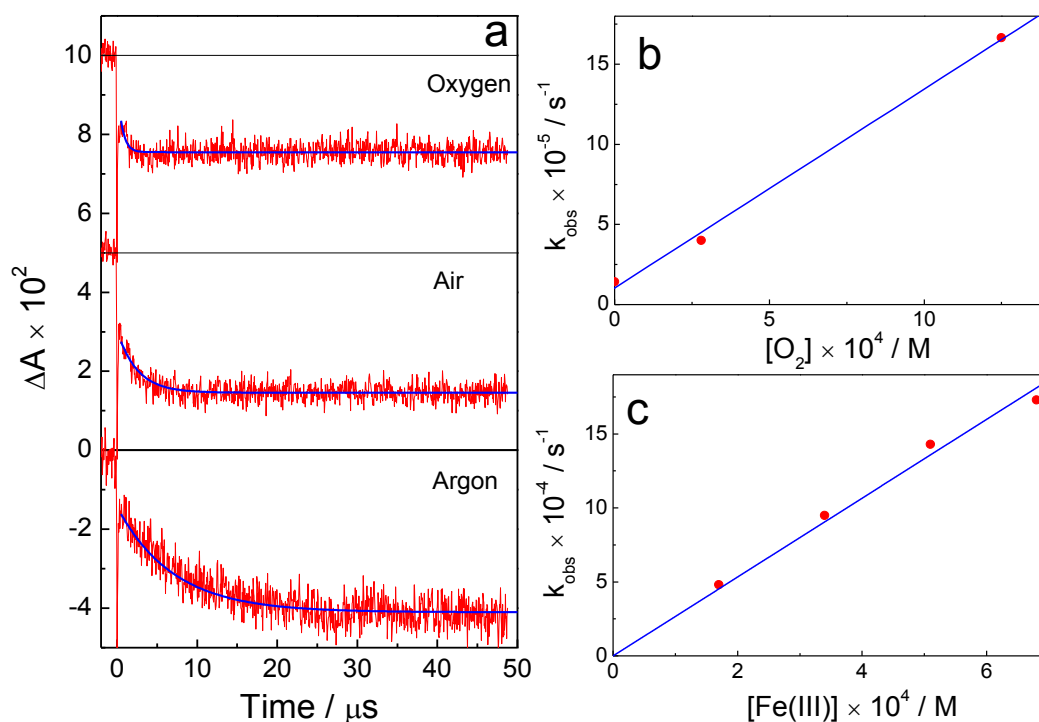
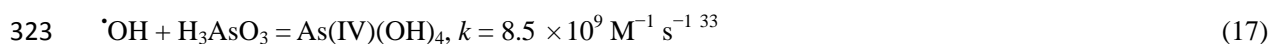
311
 312 **Fig. 6** Flash photolysis (266 nm) of the FeOH^{2+} -As(III) system at pH 3 in argon-saturated solution. ΔA is the
 313 change in optical density. Experimental conditions: $[\text{Fe(III)(ClO}_4)_3] = 0.34 \text{ mM}$, $[\text{As(III)}] = 0.5 \text{ mM}$. (1–4)
 314 Transient spectra at 0.2 (1), 2.8 (2), 10 (3), and 48 μs (4) after excitation. Inset: kinetic curve at 350 nm and
 315 the best monoexponential fit with a time constant of 7 μs .

316
 317 Excitation at 266 nm is favorable for the formation of Fe(II), whereas excitation at 308 nm leads to a
 318 greater photoproduct yield. We tentatively assume that the photoproduct is photoactive and that its excitation
 319 at 266 nm leads to the formation of additional Fe(II).

320 Flash excitation of FeOH^{2+} in the presence of As(III) led to the formation of a transient absorption signal

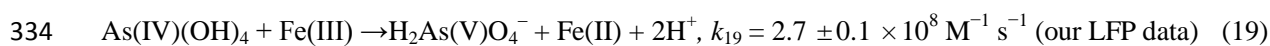
321 superimposed with bleaching because of the disappearance of the absorption of the complex (Fig. 6). This

322 signal can be assigned to As(IV)(OH)₄,³⁹ formed in a reaction with As(III) ions:



324
 325 **Fig. 7** Flash photolysis (266 nm) of the FeOH^{2+} -As(III) system at pH 3. ΔA is the change in optical density. (a)
 326 Kinetic curves at 310 nm in solutions with various oxygen concentrations. Smooth curves are the best
 327 monoexponential fits obtained by using Eq. (20). Experimental conditions: $[\text{Fe(III)(ClO}_4)_3] = 0.34 \text{ mM}$,
 328 As(III) = 0.5 mM. (b) Dependence of the observed rate constant (k_{obs}) on the concentration of dissolved
 329 oxygen. Experimental conditions: $[\text{Fe(III)(ClO}_4)_3] = 0.34 \text{ mM}$, As(III) = 0.5 mM. (c) Dependence of k_{obs} on
 330 the concentration of total Fe(III). Experimental conditions: argon-saturated solution, As(III) = 0.5 mM.

331
 332 As(IV)(OH)₄ decay depends on the oxygen and Fe(III) concentrations (Fig. 7a–c):



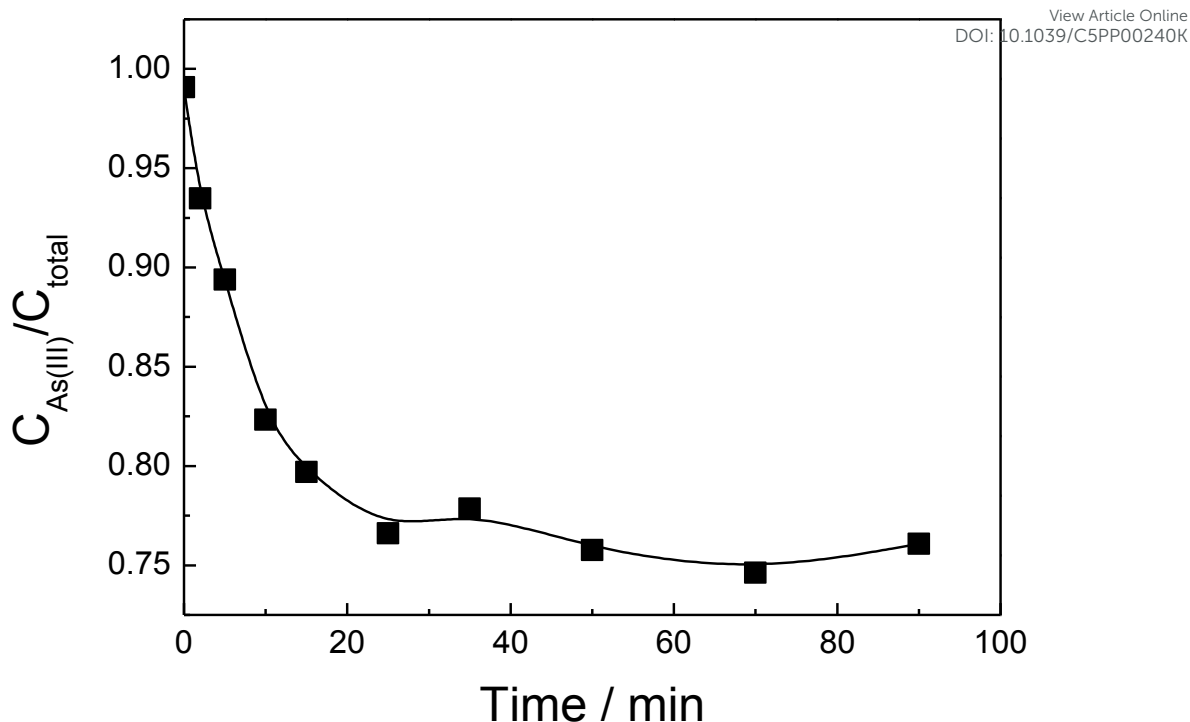
335 Reactions (18) and (19) compete with each other, as shown by the kinetic curves in Fig. 7a. An increase in
336 oxygen content in solution leads to a decrease in the lifetime of As(IV)(OH)₄ and to additional bleaching at
337 310 nm caused by reaction (19). Treatment of a set of kinetic curves at 310 nm obtained at different oxygen
338 and Fe(III) contents by Eq. (20) allowed us to determine the rate constants of reactions (18) and (19) from the
339 linear dependences of the observed rate constants (k_{obs}) on the oxygen and Fe(III) concentrations (Fig. 7b and
340 c):

$$341 \Delta A(t) = A_0 \exp(-k_{\text{obs}}t), k_{\text{obs}} = k_{18}[\text{O}_2] + k_{19}[\text{Fe(III)}] \quad (20)$$

342 where $\Delta A(t)$ is the change in optical density, and A_0 is the initial optical density. The value of k_{18} agrees well
343 with that obtained by Klaning et al. ($k = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).³⁹ Thus, the LFP experiments confirmed the
344 oxidation of As(III) by photogenerated $\cdot\text{OH}$ radicals with the formation of active As(IV) species. These
345 species in turn undergo oxidation to As(V) through reactions (18) and (19). The final reaction step should be
346 the same as for solutions with high As(III) concentration (reaction (15)).

347 **Photolysis of the solid product of the Fe(III)–As(III) complex**

348 As(III) photooxidation during photolysis of the solid product of the Fe(III)–As(III) complex was observed, as
349 shown in Fig. 8. After 50 min, the remaining As(III) in the sample had decreased to almost 75% of the initial
350 value. Because of light attenuation by the surface of the solid product, light cannot penetrate to the interior of
351 the product. The As(III) was not further oxidized after 50 min. The energy of UV-C irradiation in terms of
352 wavelength and intensity is much lower than that of the X-rays used for XPS analysis. The oxidation
353 efficiency of As(III) (25%) under UV-C irradiation was much lower than that associated with XPS analysis
354 (82.4%). This result implies that the Fe(III)–As(III) complex is sensitive to UV-C light and that As(III) is
355 prone to oxidation to As(V) through LMCT, even in the solid phase.



356

357 **Fig. 8** Steady-state photolysis of the solid Fe(III)–As(III) complex under UV-C irradiation (dominant
358 wavelength 254 nm). $C_{As(III)}/C_{total}$ is the proportion of As(III) in the total arsenic. The complex was the same
359 as that used in the XPS and XRD measurements; its Fe/As molar ratio was 1:0.92.

360

361 Conclusions

362 At high As(III)/Fe(III) ratio in solution at pH 3, an Fe(III)–As(III) complex forms as $[Fe(H_2AsO_3)_2]^+$. This
363 complex undergoes photolysis in acid solution with an Fe(II) production quantum yield of about 0.012.
364 Formation and photolysis of the Fe(III)–As(III) (Fe/As = 1:0.92) complex in the solid state were also
365 observed. As(III) in solution is oxidized to As(IV) through an LMCT mechanism and then to As(V) mainly
366 by the action of dissolved oxygen. At lower As(III)/Fe(III) ratio, As(III) photooxidation in acidic solution
367 occurs through indirect oxidation by the hydroxyl radical produced by photolysis of $Fe(OH)^{2+}$. These two
368 mechanisms of As(III) photooxidation in aqueous solutions could account for rapid oxidative transformation
369 of As(III) to As(V) in acid mine drainage exposed to sunlight. The relative contributions of these two

370 mechanisms depend on the As(III)/Fe(III) ratio. This work demonstrates that the complexation and
371 photooxidation process of Fe(III)-As(III) complexes should be taken into account when studying the fate of
372 arsenic in acidic water containing Fe(III).

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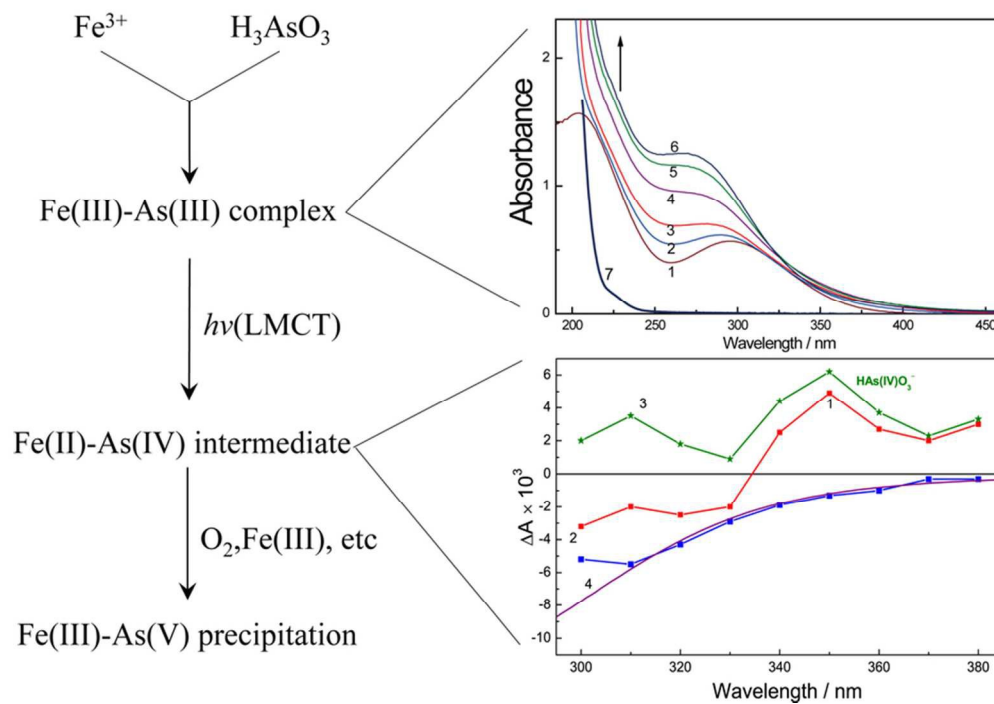
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Graphical Abstract

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Fe(III)–As(III) complex is characterized by UV/Vis spectra and its laser flash photolysis occurring via ligand-to-metal charge transfer results in the intermediate of Fe(II)–As(IV).



39x28mm (600 x 600 DPI)