X International Voevodsky Conference "Physics and Chemistry of elementary chemical processes"

THE USE OF IRON OXALATE COMPLEXES AND POTASSIUM PERSULFATE FOR PHOTODEGRADATION OF PARA-ARSANILIC ACID

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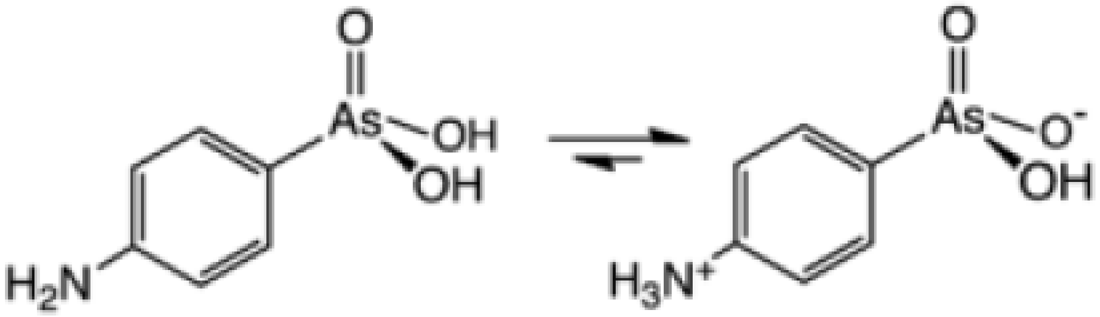
Introduction: problems and task statement



The use of arsenic-containing organic compounds:

- pesticides and herbicides
- food additives to overcome intestinal parasites and accelerated growth of livestock

Problem:

transformation of organic arsenic compounds with the formation of toxic inorganic forms of arsenic (arsenite and arsenate) and organic by-products under the influence of environmental factors.

It is relevant to study the mechanisms of photodegradation of p-arsanilic acid in natural waters and in the process of UV disinfection of wastewater

The natural content of the reagents used

ARSENIC

0.1 – 75 ppb in natural waters (1.4 ppb on average)

up to 0.2 ppm in polluted areas

Maximum permissible concentration in drinking water - 10 ppb

IRON

In the oceans: 0.1 – 1 ppb;

In the atmosphere: 5 – 500 ppb;

Swamps, rivers and lakes: 0.1 – 50 ppm

SULFATES

Rainfall: from 1 to 10 ppm;

Rivers and fresh lakes: from 5 to 60 ppm;

In groundwater, the content of sulfates can reach significantly higher values.

pH

Swamps, rainfall: 3.5 – 4.5

Rivers and lakes: 4 - 8

Oceans: 8 - 8.5

1 ppm = 1:10^6; 1 ppb = 1:10^9

1 ppm As(III) = 1.33×10^{-5} M

1 ppm Fe(III) = 1.79×10^{-5} M

Tasks:

- **Investigation of p-ASA photodegradation caused by photolysis of iron oxalate complexes in the presence of an additional oxidant - potassium persulfate (PS)**
  - Selection of conditions to achieve complete oxidation of p-ASA to inorganic forms of arsenic
  - Determination of yields and ratios of forms of inorganic arsenic

Methods:

- **optical spectroscopy**
- **stationary and nanosecond flash photolysis**
- **capillary electrophoresis (CZE) (NIIC SB RAS)**
- **Inductively coupled plasma mass spectrometry (ICP-AES) (NIIC SB RAS)**

The use of iron compounds in water treatment. Double effect: photochemistry and co-precipitation

Generation of oxidative radicals

$$FeOH^{2+} \xrightarrow{h\nu} Fe(II) + OH^{\bullet}$$

Generation of an active hydroxyl radical interacting with organic impurities, which leads to their degradation and mineralization.

$$Fe(II) + H_2O_2 = Fe(III) + {}^{\bullet}OH + OH^{-}$$

Co-precipitation

$Fe_n(AsO_4)_m(OH)_{3(n-m)}$ - А.Н. Белевцев, Л.В. Гандурина, П.А. Ивкин, А.В. Казаков, Вопросы защиты водных объектов от загрязнения соединениями мышьяка, 2010

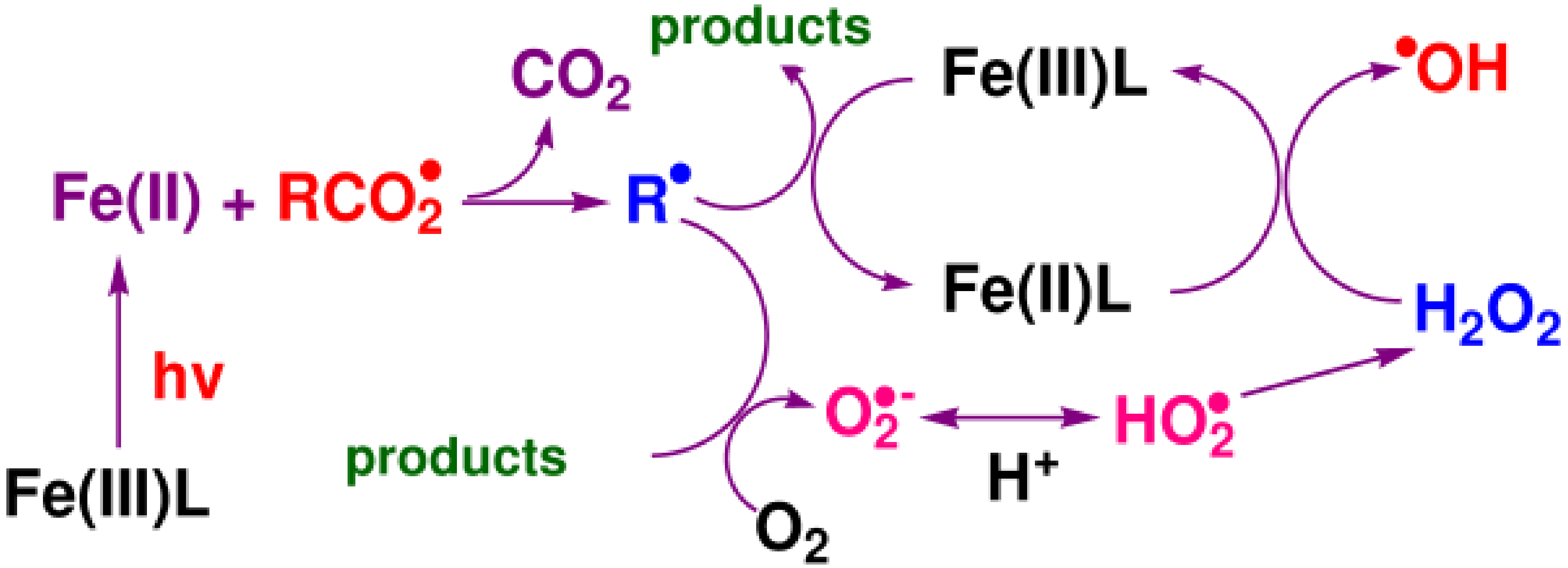
«Methods of wastewater treatment from arsenic by precipitation in the form of compounds with iron and calcium are cheap, effective and provide wastewater treatment up to sanitary standards.

At the same time, the use of iron (III) salts for arsenic deposition leads to a significant consumption of reagents and the formation of a large amount of difficult-to-filter precipitation…»

С.Ю. Владимиров, Н.В.Лебедева, А.В.Пронченко, К вопросу о способах извлечения мышьяка из мышьяксодержащих сточных вод, 2012

For the effective use of iron compounds in water treatment, it is necessary to understand the primary photochemical processes

Generation of oxidative radicals during photolysis of iron carboxylate complexes

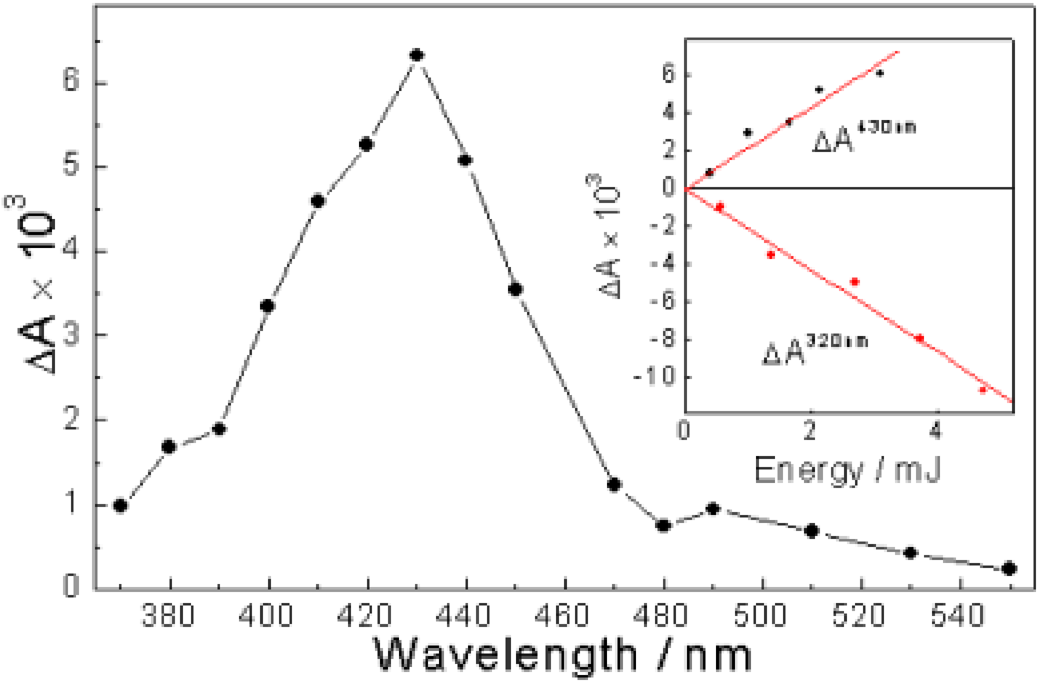


L – aliphatic carboxylic acid

Potassium persulfate

$$Fe(II) + S_2O_8^{2-} = Fe(III) + SO_4^{2-} + SO_4^{-\bullet}$$

Photooxidation of p-ASA by Fe(III) oxalate alone



Found $\varepsilon^{430} = 1600 \pm 300$ M^{-1} cm^{-1} for the adduct ($\mathrm{p}ASA - OH^{\bullet}$) and the reaction rate constant OH• with p-ASA: $k_2 = (8.6 \pm 0.5)\times10^9$ M^{-1}s^{-1}

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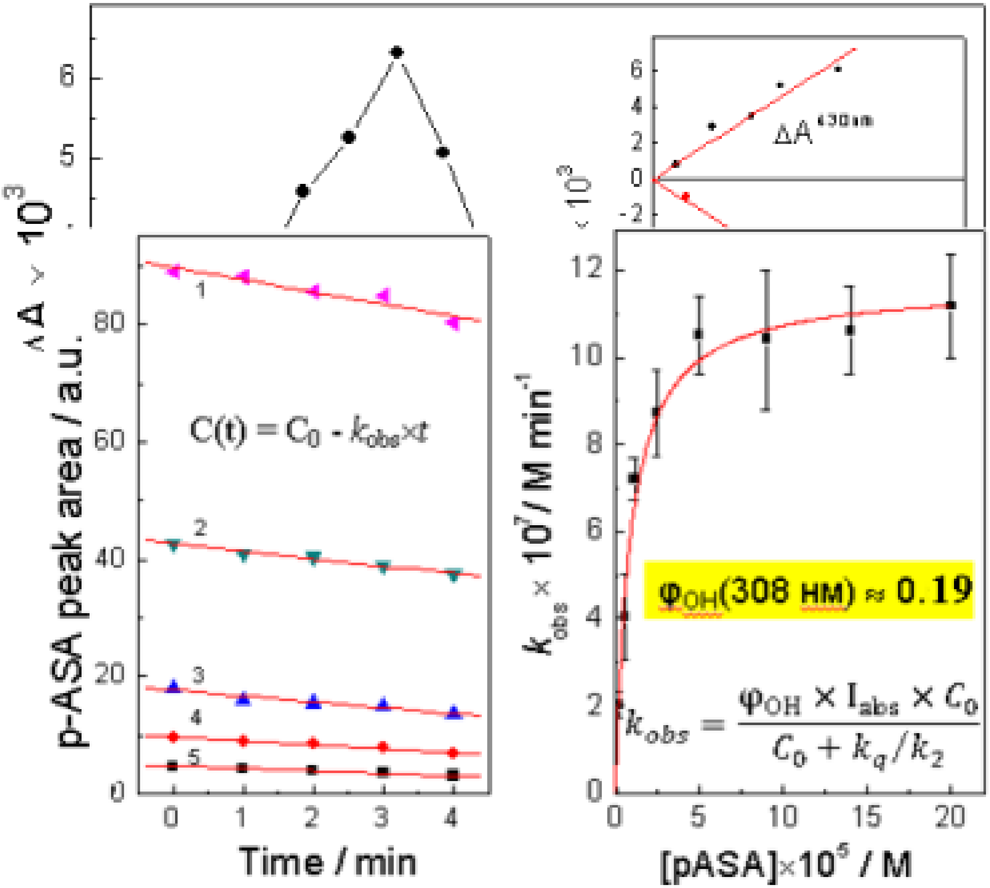

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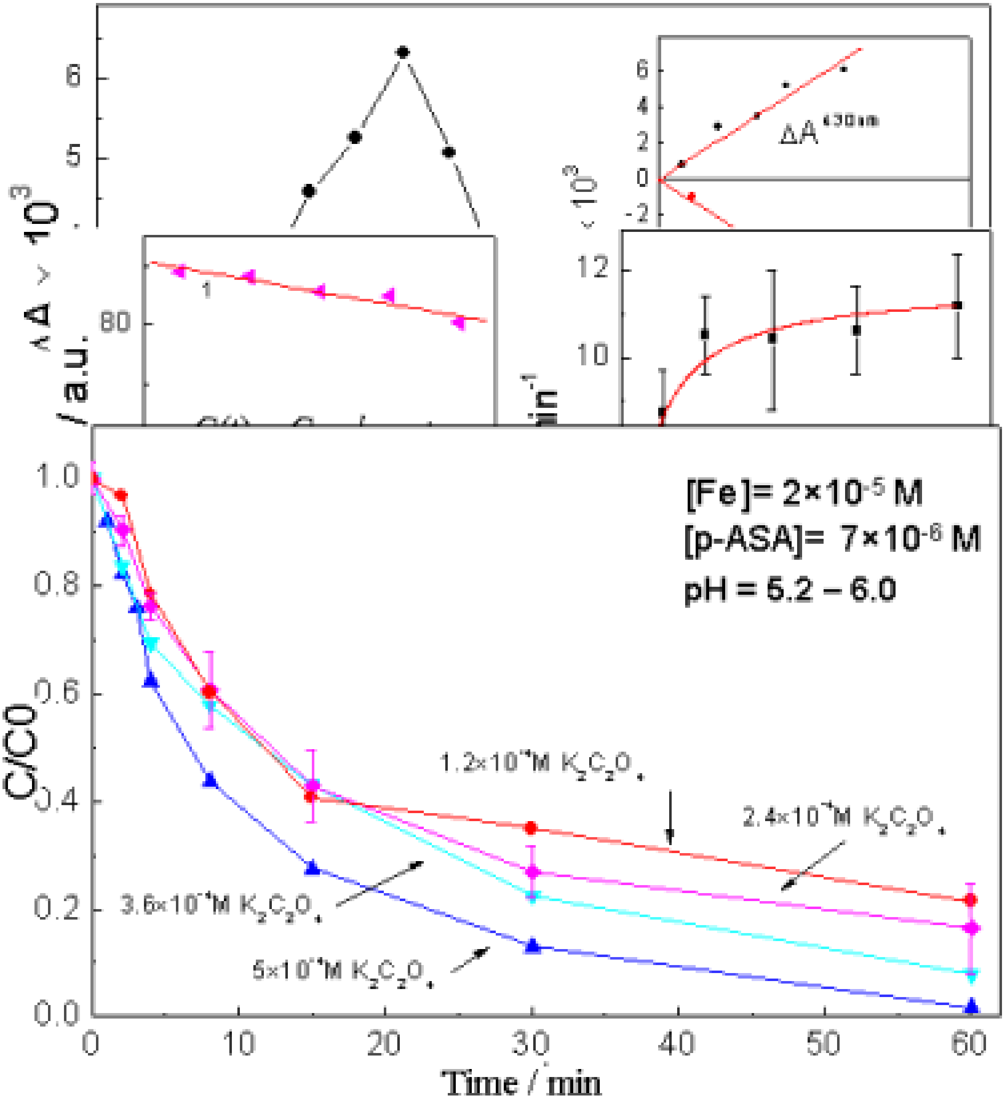
P-ASA photodegradation caused by photolysis of iron oxalate complexes is associated with the generation of OH radical, φ_{OH}(308 нм) ≈ 0.19

Photooxidation of p-ASA by Fe(III) oxalate alone



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A large amount of oxalate is needed for complete photooxidation of p-ASA.

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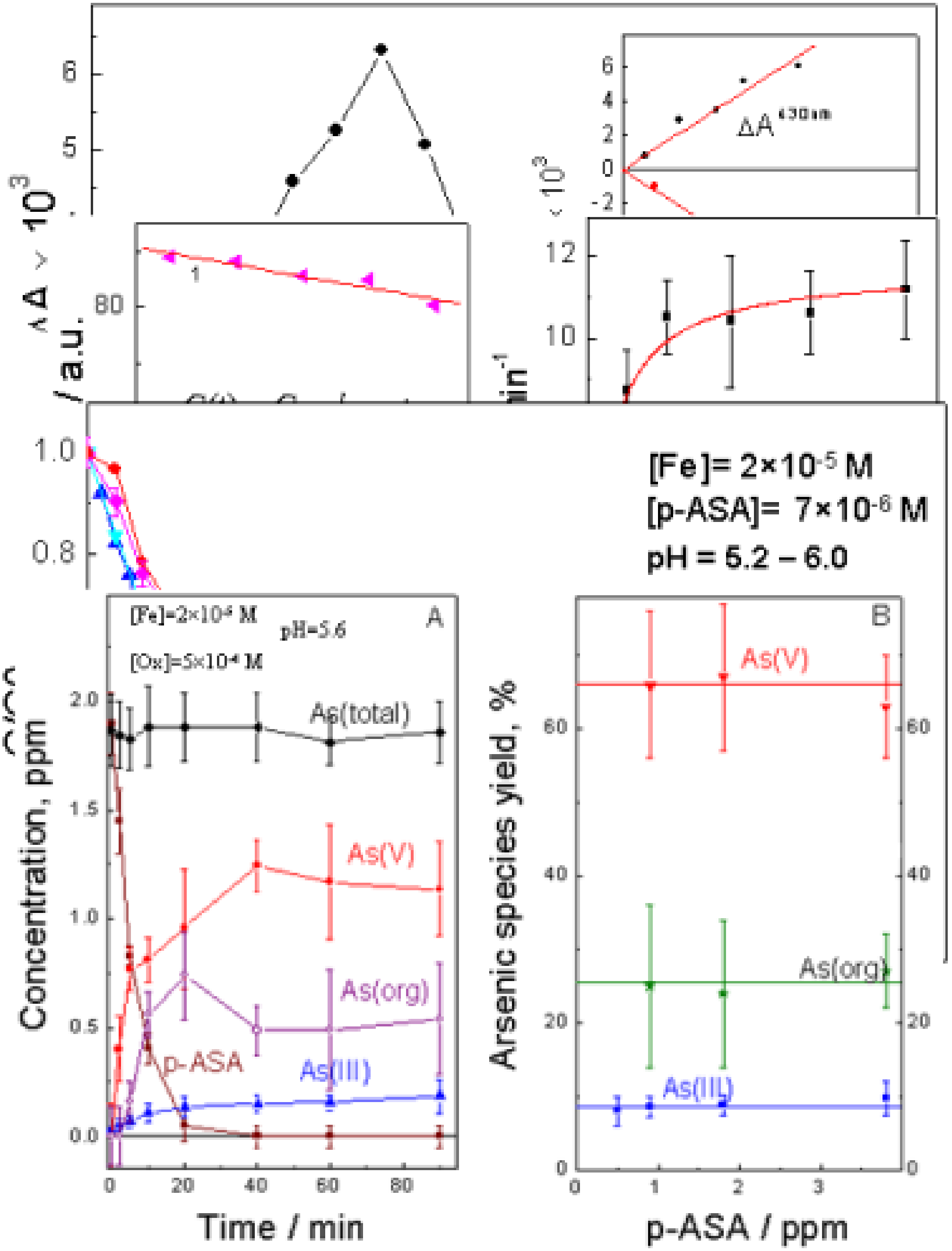

Found ε^{430} = 1600 ± 300 M^{-1} cm^{-1} for the adduct ($pASA - OH^{\bullet}$) and the reaction rate constant OH• with p-ASA: k_2 = (8.6 ± 0.5)×10^9 $M^{-1}s^{-1}$

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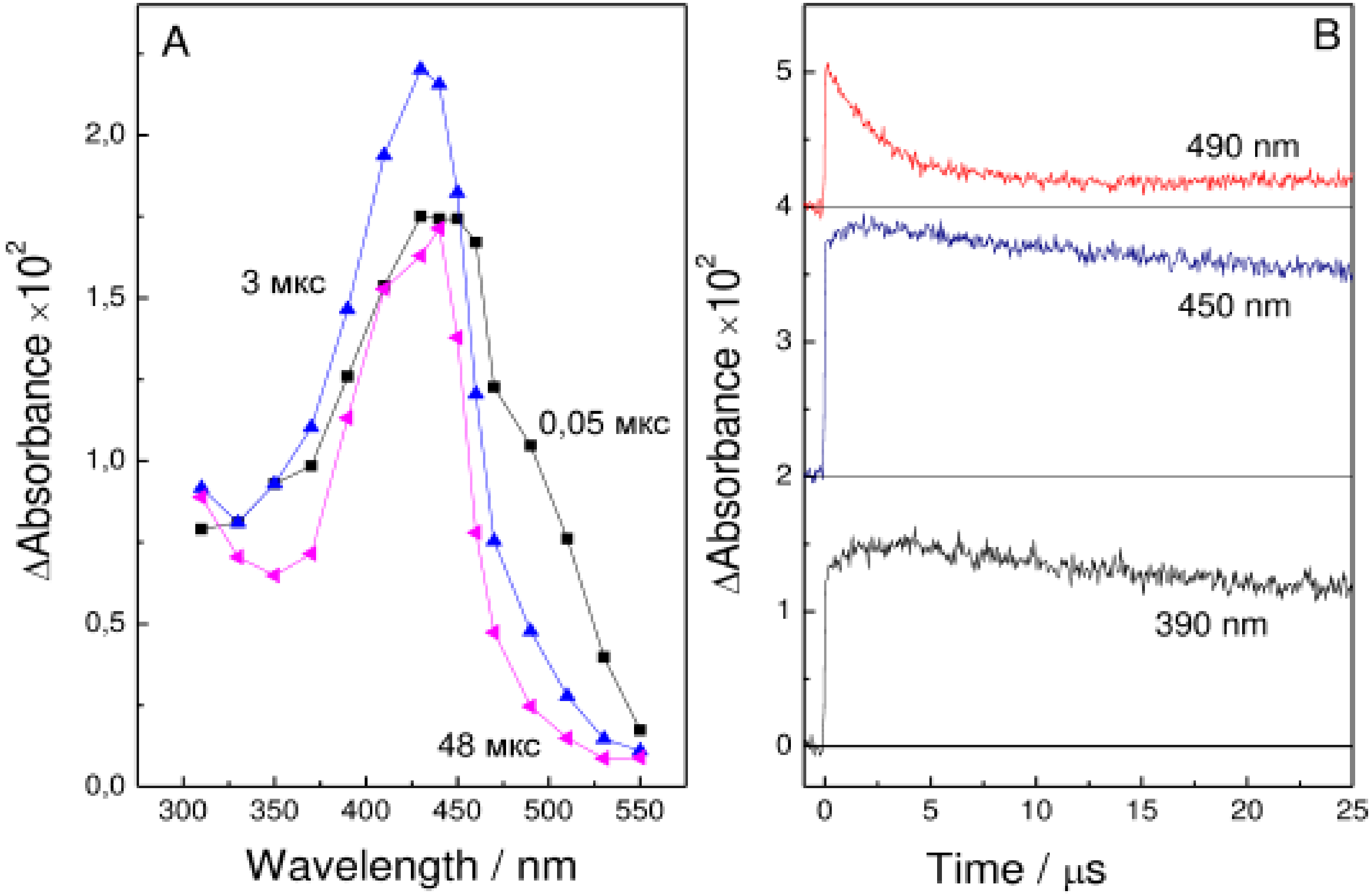
A large amount of oxalate is needed for complete photooxidation of p-ASA.

Complete photooxidation of p-ASA; formation of inorganic forms. The initial concentration of p-ASA does not affect the yield of arsenic forms.

Flash photolysis (266 nm) of PS in the presence of p-ASA

[PS]= 0,045 M, [p-ASA]: 1×10^{-4} M, pH = 7, 1,3 mJ / pulse

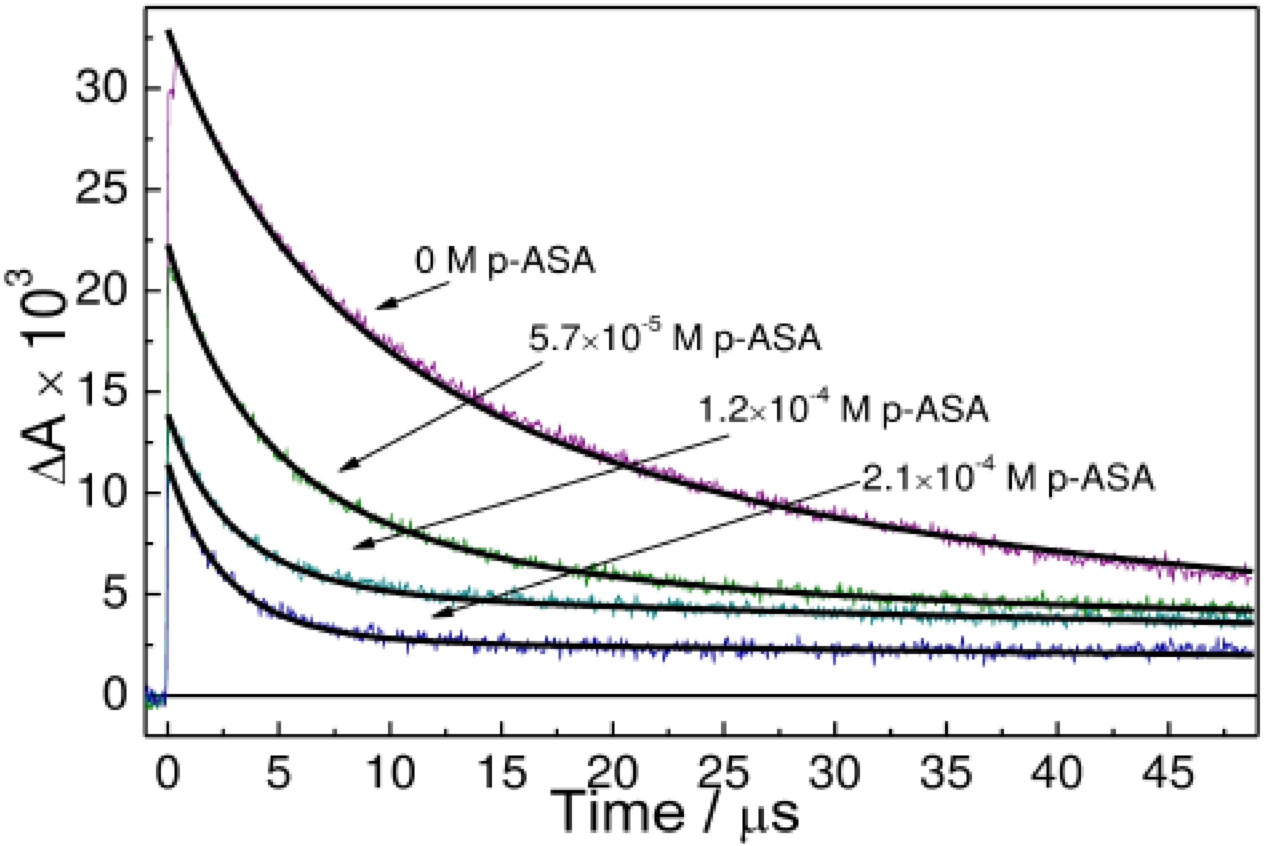


$S_2O_8^{2-} \xrightarrow{h\nu} SO_4^{-\circ} + SO_4^{-\circ}$ $\lambda_{\text{max}}(SO_4^{-\bullet}) = 450$ nm

$SO_4^{-\circ} + RNH_2 \xrightarrow{k_2} RNH_2^{+\circ} + SO_4^{2-}$ $\lambda_{\text{max}}(RNH_2^{+\bullet}) = 430$ nm

Flash photolysis (266 nm) of PS in the presence of p-ASA: numerical simulation

[PS]= 0,045 M; pH = 7; registration - 490 nm; 1,3 mJ / pulse



$$SO_4^{-\cdot} + SO_4^{-\cdot} \xrightarrow{k_1} S_2O_8^{2-} \quad (1)$$

$$SO_4^{-\cdot} + RNH_2 \xrightarrow{k_2} RNH_2^{+\bullet} + SO_4^{2-} \quad (2)$$

$$RNH_2^{+\bullet} \xrightarrow{k_3} P \quad (3)$$

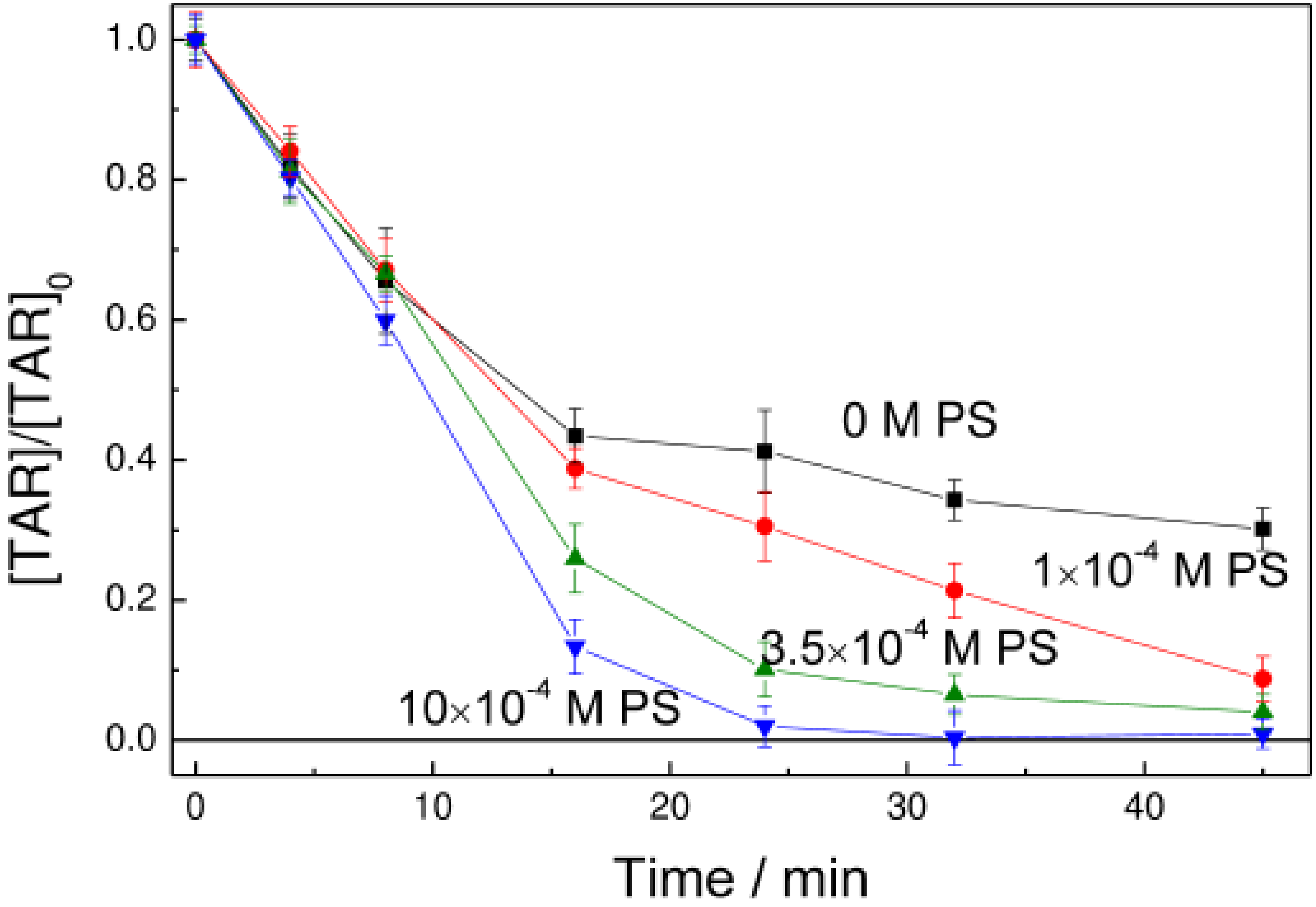
$2k_1 = 2.9\times10^9\ M^{-1}s^{-1}$ (literature)

$k_2 = (2.4 \pm 0.4)\times10^9\ M^{-1}s^{-1}$

$k_3 = (5.7 \pm 1.5)\times10^3\ M^{-1}s^{-1}$

$\varepsilon^{490nm}(RNH_2^{+\cdot}) = (3.4 \pm 0.5)\times10^2\ M^{-1}cm^{-1}$

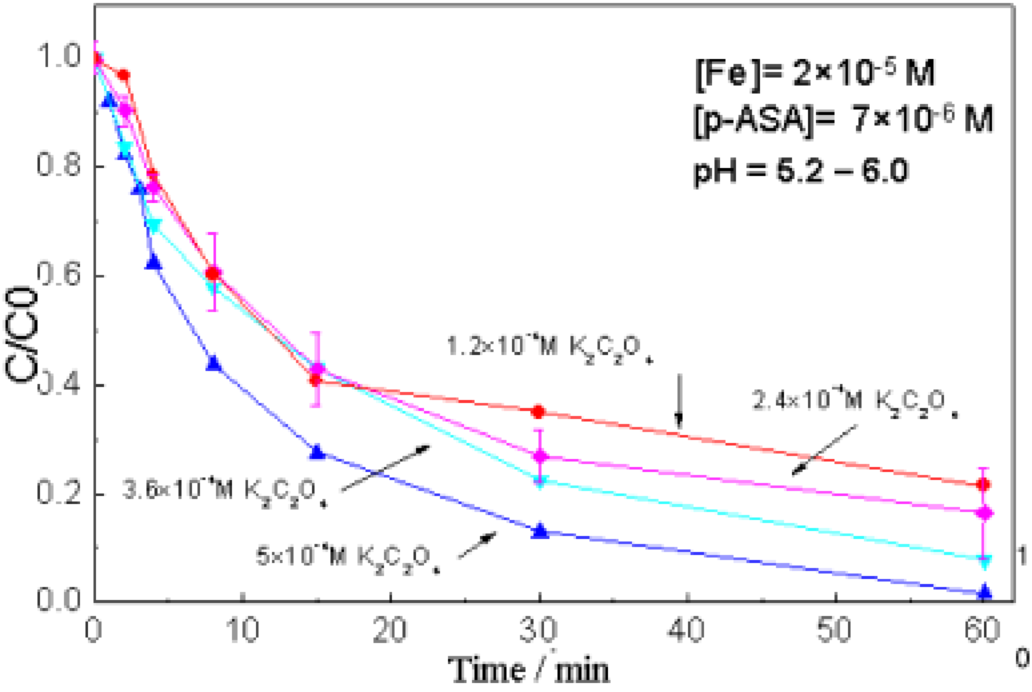
Stationary photolysis (308 nm) of p-ASA in the iron oxalate / PS system



[Fe(III)]= 2×10^{-5} M
[Ox]=1.2×10^{-4} M
pH = 6.7
[p-ASA]=7×10^{-6} M

The addition of 1 mM PS leads to complete oxidation not only of p-arsanilic acid, but also of organic aromatic products (TAR) at [p-ASA] < 0.5 ppm.

Stationary photolysis (308 nm) of pASA in the iron oxalate / PS system



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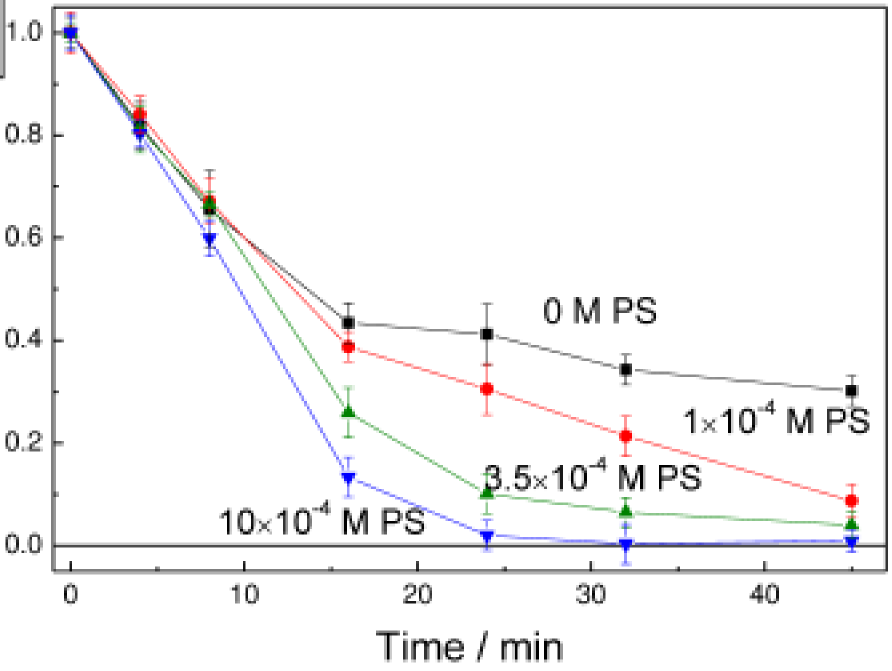
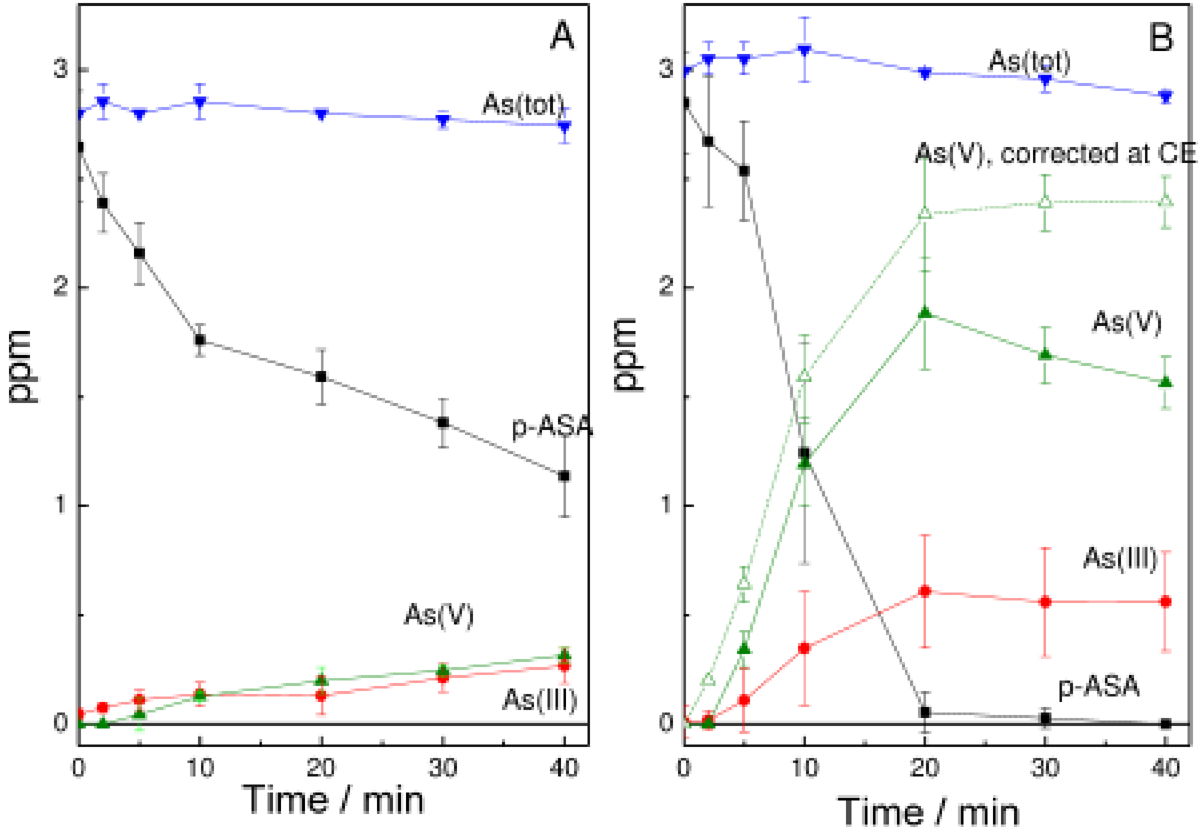


- PS accelerates the photodegradation process,
- The working concentration of oxalate decreases

Stationary photolysis (308 nm) of p-ASA in the iron oxalate / PS system

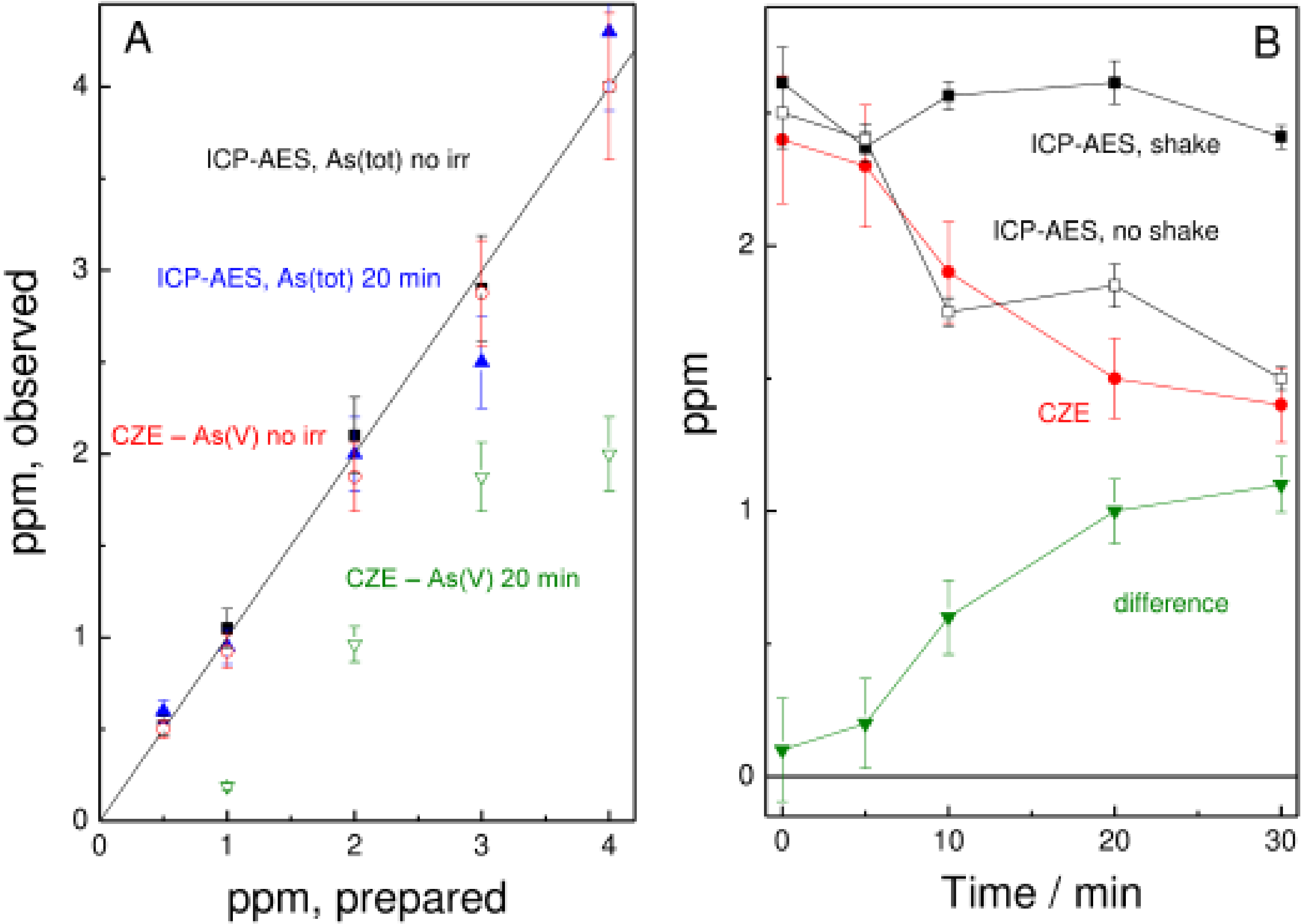
[Fe (III)] = 2×10^{-5} M, [Ox] = $1{,}2\times10^{-4}$ M, [PS] = 0 (A) и 10^{-3} M (B)



- Without PS (A) - only partial (about 50%) degradation of p-ASA and accumulation of a number of organic by-products is observed
- With PS (B) – complete oxidation of p-ASA and organic arsenic-containing products to inorganic forms, mainly As(V)
- $Fe(II) + S_2O_8^{2-} = Fe(III) + SO_4^{2-} + SO_4^{-\bullet}$

Stationary photolysis (308 nm) p-ASA in the iron oxalate / PS system: sorption of As(V)

[Fe (III)] = 2×10^{-5} M, [Ox] = 1,2×10^{-4} M, [PS] = 10^{-3} M



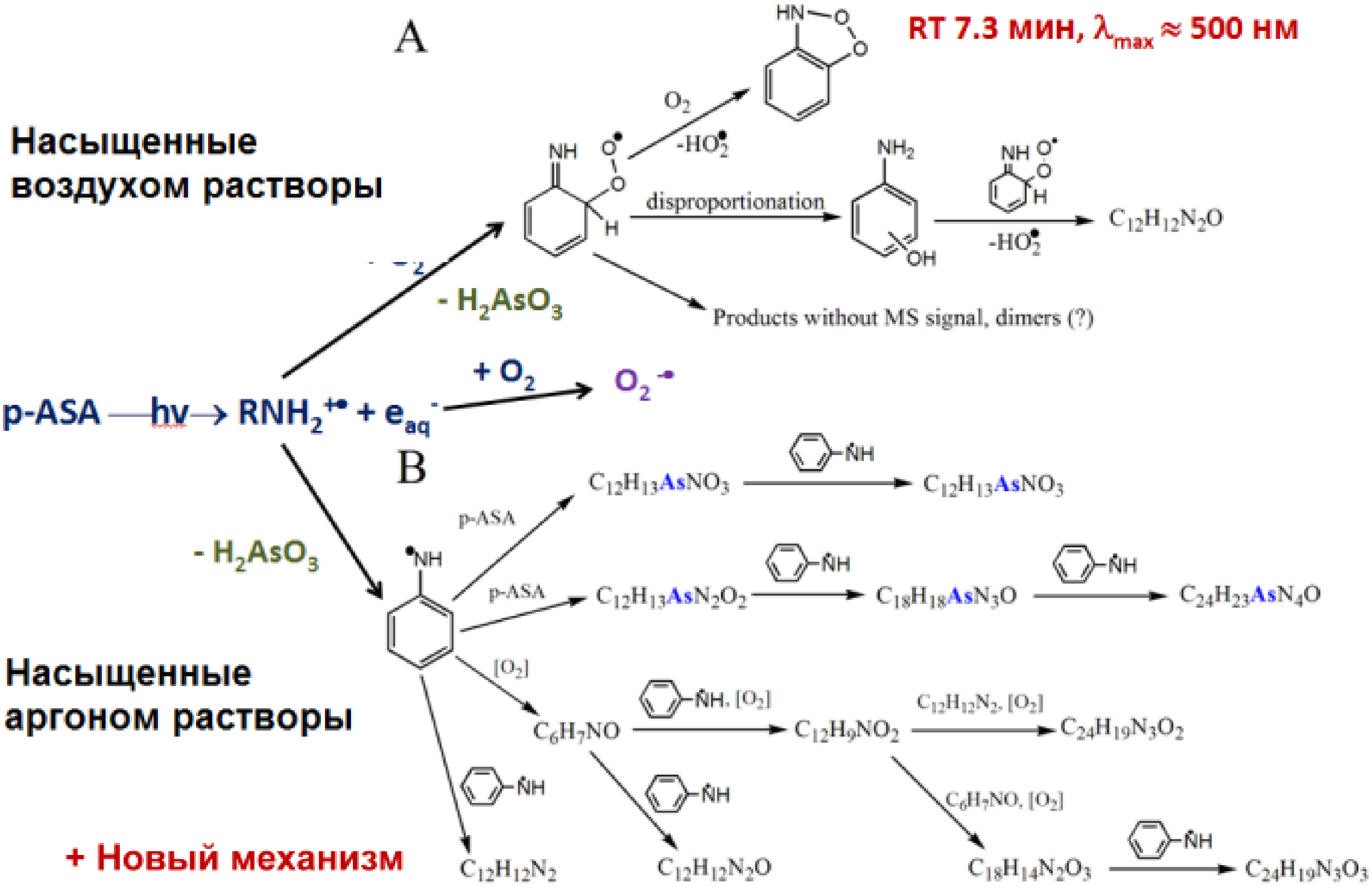
- As(V) partially binds to photo-generated colloids Fe(III).
- Colloidal particles settle, leading to a statistical underestimation of the concentration by the method CZE.

Main results:

- The rate constant of the $SO_4^{-\bullet}$ radical reaction with p-ASA monoanion is determined : $k = (2.4 \pm 0.4) \times 10^9\ M^{-1}s^{-1}$
- It is shown that the addition of persulfate accelerates the photodegradation of p-ASA due to the regeneration of the active form of Fe(III) and the appearance of an additional oxidative sulfate radical
- Conditions have been selected for the complete photooxidation of p-ASA and organic arsenic-containing products to inorganic forms of arsenic, mainly As(V)
- Partial sorption of arsenic (V) was detected, presumably on photogenerated Fe(III) colloids

Thanks for your attention!

Общая схема фотолиза p-ASA

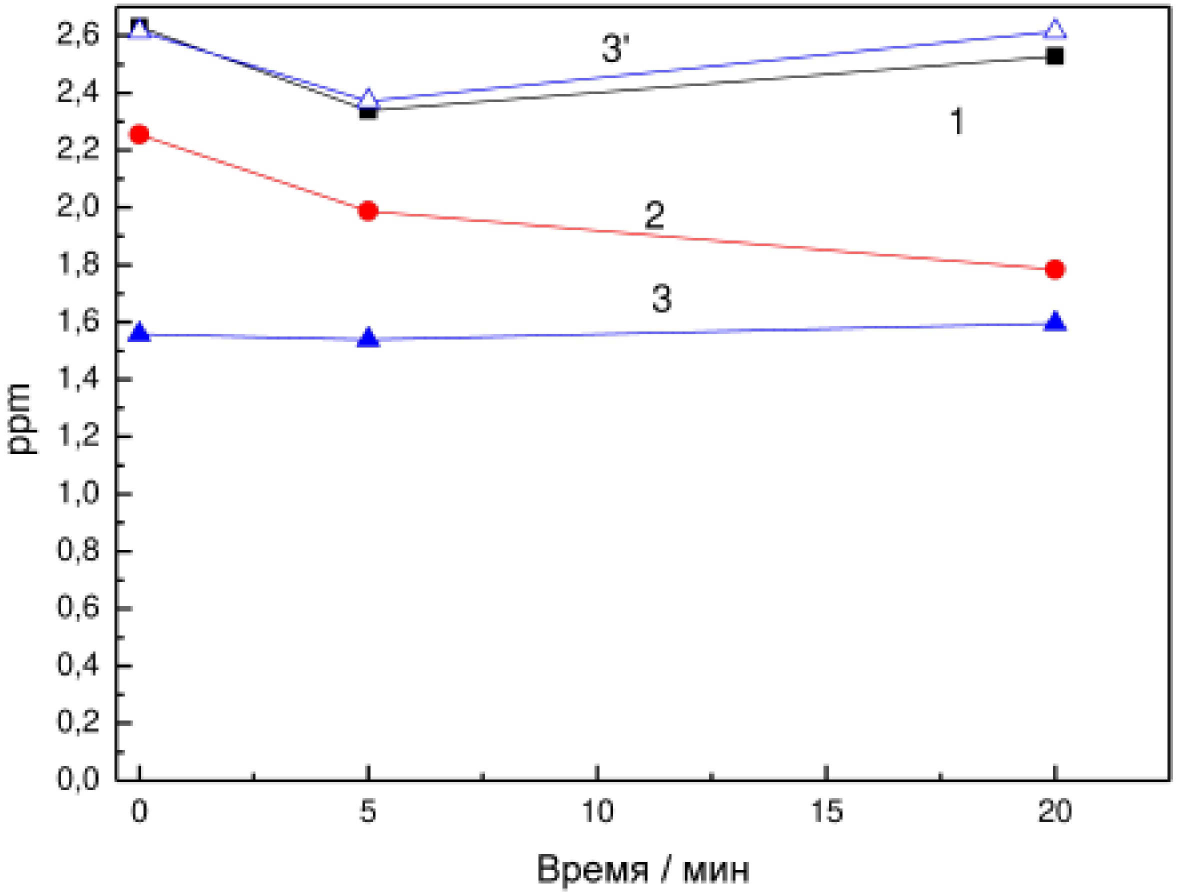


Насыщенные воздухом растворы

Насыщенные аргоном растворы

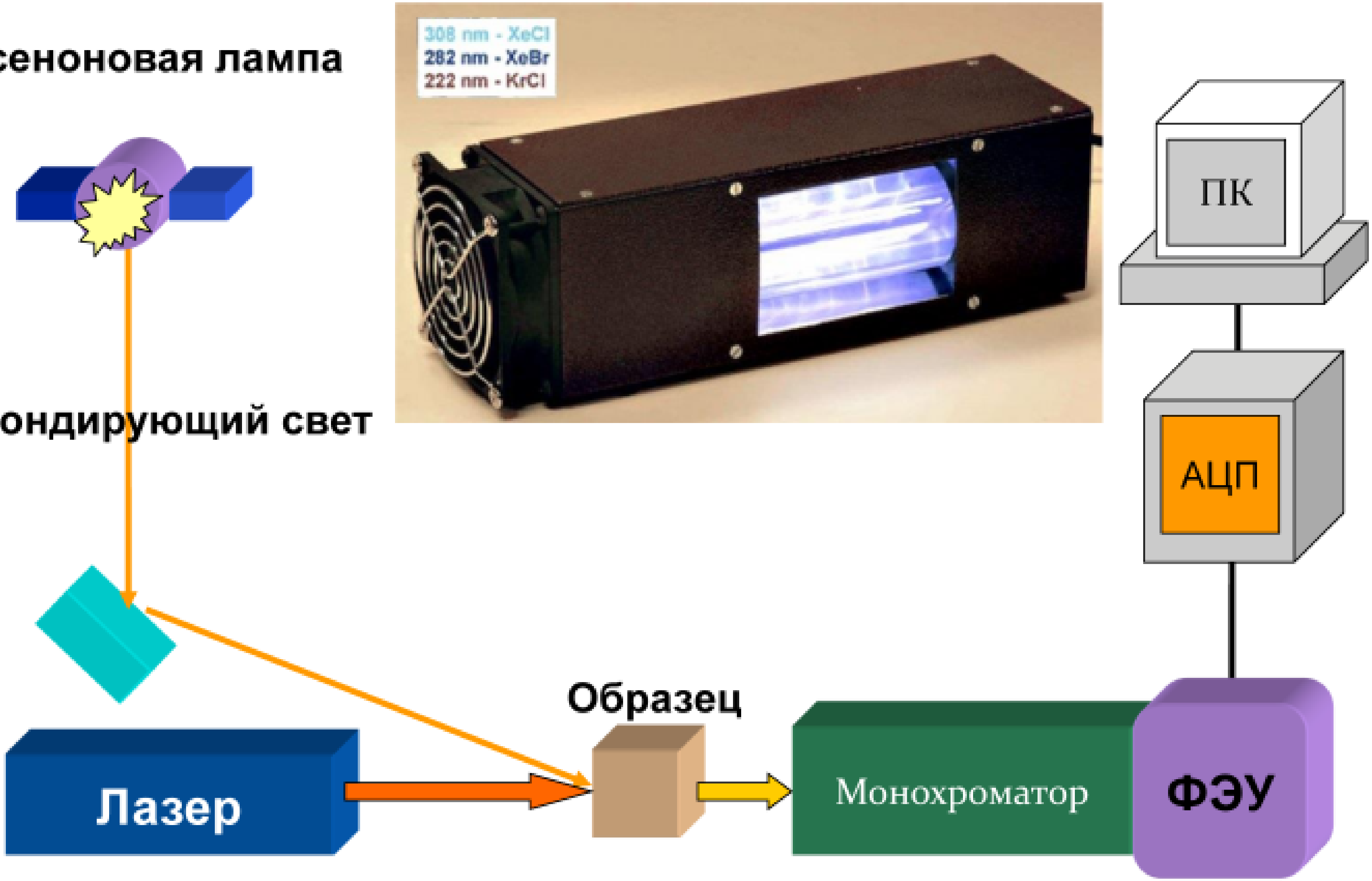
+ Новый механизм

Стационарный фотолиз (308 нм) p-ASA в системе оксалат железа / PS: сорбция As(V)



Измерение общей концентрации мышьяка в день облучения (1), через пять дней после облучения (2) и через восемь дней после облучения (3) без встряхивания. (3') - Измерение общей концентрации мышьяка через восемь дней после облучения со встряхиванием.

Стационарный и лазерный импульсный фотолиз



Ксеноновая лампа

ПК

АЦП

Зондирующий свет

Образец

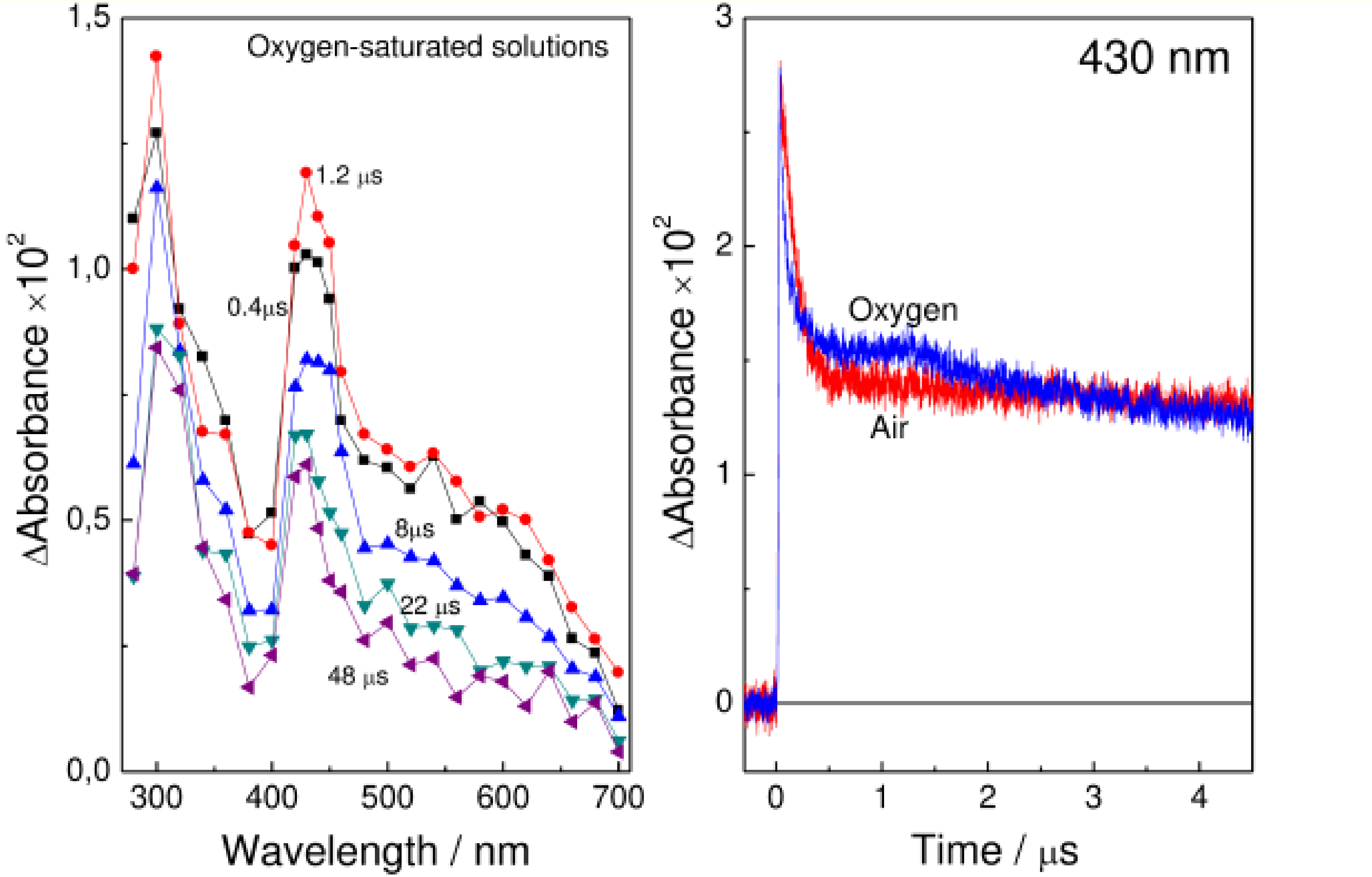
Лазер

Монохроматор

ФЭУ

Регистрируемый сигнал - изменение оптической плотности образца (*ΔA*)

Импульсный фотолиз (266 nm, воздух) p-ASA



- Наблюдается реакция первичного радикала с растворенным кислородом
- Нет указаний на образование триплетного состояния p-ASA (короткое время жизни и/или слабое поглощение?)

Реакция p-ASA с синглетным кислородом (SO)

SO фотосенсибилизатор:

meso-tetra-(N-methyl-4-pyridyl)porphyrin

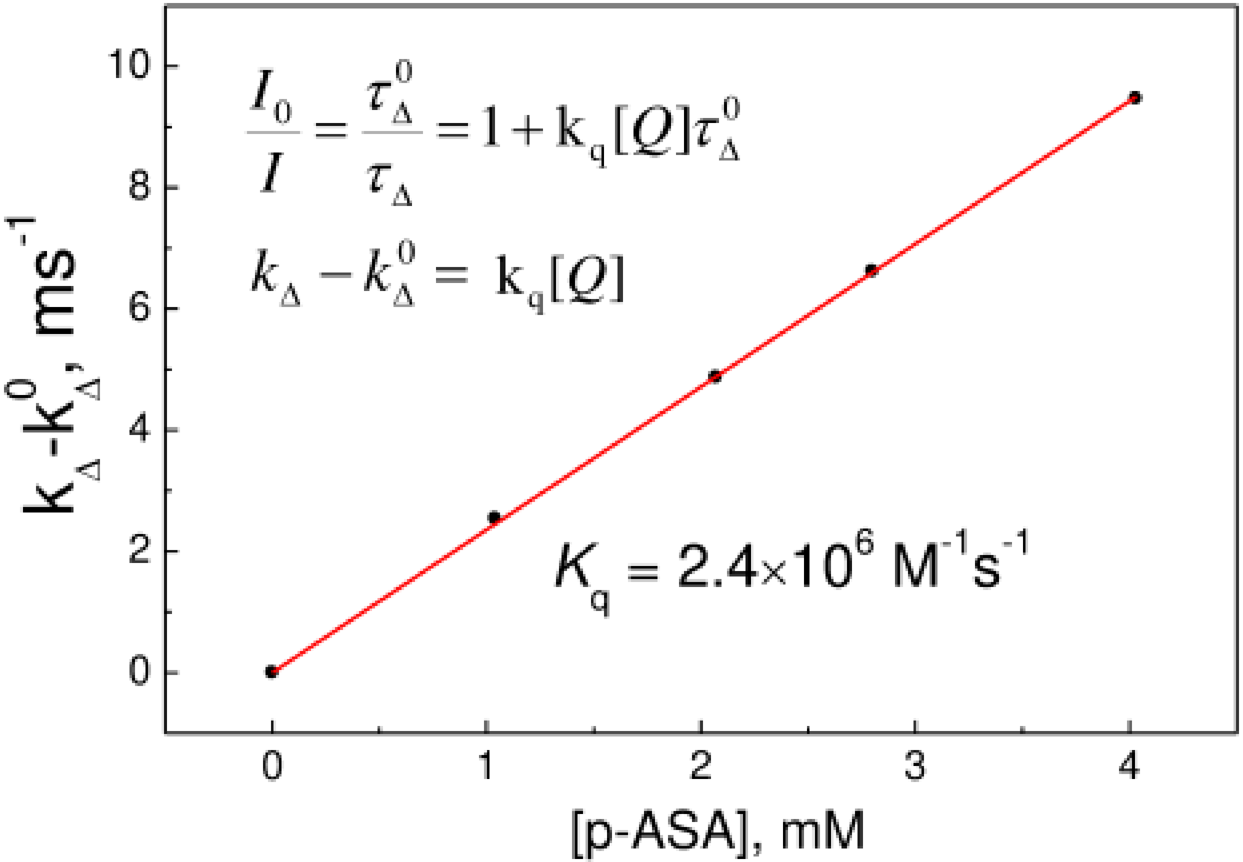
Tosylate (TMPyP), $\phi(^1O_2, 532\ \text{нм}) = 0.77$; D_2O

$$\text{TMPyP} \xrightarrow{h\nu} {}^3\text{TMPyP}$$

$$^3\text{TMPyP} + O_2 \longrightarrow \text{TMPyP} + {}^1O_2$$

$$^1O_2 \xrightarrow{k^0_\Delta} O_2$$

$$^1O_2 + \text{p-ASA} \xrightarrow{k_q} \text{quenching}$$



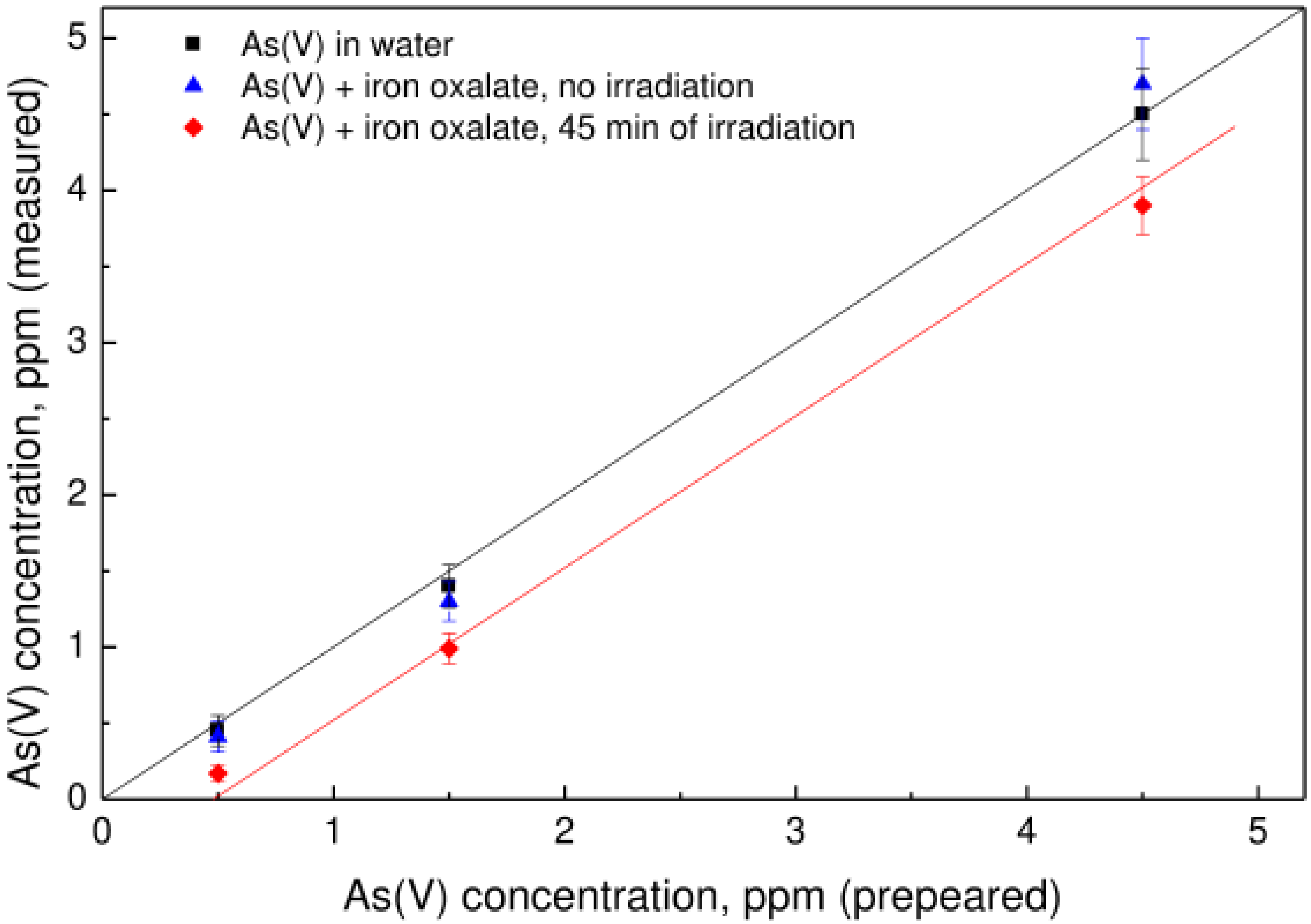
$$\frac{I_0}{I} = \frac{\tau^0_\Delta}{\tau_\Delta} = 1 + k_q[Q]\tau^0_\Delta$$

$$k_\Delta - k^0_\Delta = k_q[Q]$$

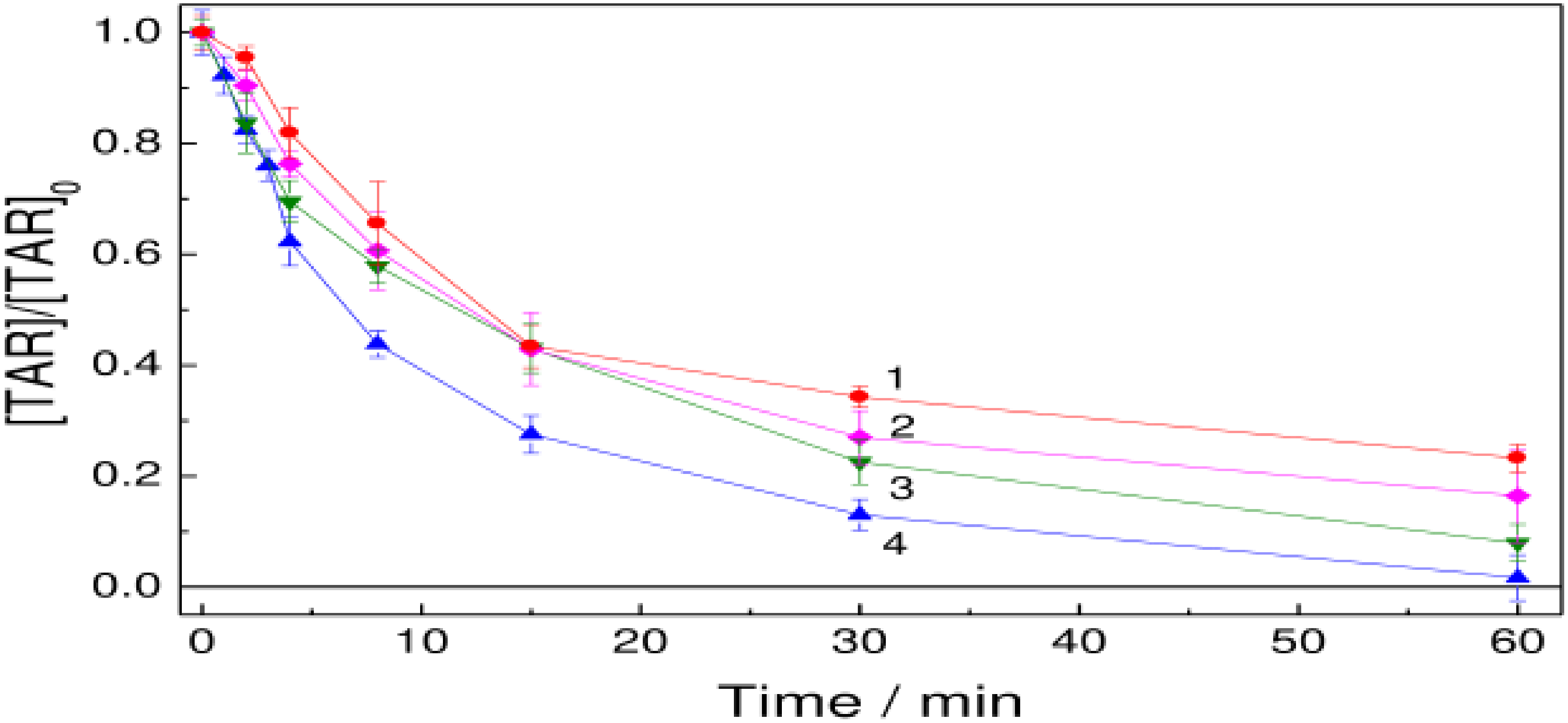
$K_q = 2.4\times10^6\ M^{-1}s^{-1}$

При [p-ASA] < 10^{-3} M синглетный кислород не участвует в фотодеградации

Сорбция As(V) на комплексах железа



Эволюция TAR в ходе стационарного (308 нм) фотолиза



Концентрация оксалата 1.2×10^{-4} M (1), 2.4×10^{-4} M (2), 3.6×10^{-4} M (3) и 5×10^{-4} M (4), соответственно.

Концентрация железа 2×10^{-5} M, p-ASA 6.5 ×10^{-6} M, начальный pH 5.2 – 6.0

При повышении концентрации степень деградации TAR (концентрация общей ароматики) меняется с 80 до 98%.