Influence of gamma irradiation on uranium determination by Arsenazo III in the presence of Fe(II)/Fe(III)

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Highlights
• Accurate measurement of uranium is with great importance in the nuclear fuel cycle.
• Fe(II) added to a gamma irradiated U(VI) solution can give rise to Fenton reaction.
• The induced Fenton reaction can decompose the subsequently added Arsenazo III.
• With γ radiation and ferrous iron, a new U measurement method needs to be developed.

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Abstract
Arsenazo III is a widely used reagent for the concentration measurement of uranium and other actinides in aqueous samples. This study indicates that, for routine aqueous samples, due to the strong complexing ability with Arsenazo III, Fe(III) can significantly decrease the UV–Vis absorbance of the U(VI)-Arsenazo III complex, whereas the influence of Fe(II) on the absorbance is negligible. However, when Fe(II) is present in a gamma-irradiated U(VI) aqueous sample, it can give rise to the Fenton reaction, which produces oxidizing radicals that decompose the subsequently added Arsenazo III, leading to a sharp decrease in the absorbance of the U(VI)-Arsenazo III complex. The decrease in absorbance depends on the iron content and irradiation dose. Furthermore, the oxidizing radicals from the Fenton reaction induced by gamma irradiation can be continually produced. Even if the irradiated solution has been aged for more than one month in the absence of light at room temperature and without the exclusion of oxygen, the reactivity of the radicals did not decrease toward the subsequently added Arsenazo III. This finding demonstrates that the presence of Fe(II) in gamma-irradiated U(VI) aqueous samples can lead to incorrect U(VI) measurement using the Arsenazo III method, and a new method needs to be developed for the quantitative determination of U(VI) in the presence of gamma radiation and ferrous iron.

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1. Introduction
Bisazo-group reagents for the spectrophotometrically identification and concentration determination of elements is simple and selective (Rohwer et al., 1997). In which, Arsenazo III (2,2’-[1,8-dihydroxy-3,6-disulfo-2,7-naphthalene-bis(azo)]dibenzene-sonic acid), a red organic compound that undergoes reactions with a number of elements forming complexes with different colors, is one of the most widely used indicators for the photometric determination of uranium, thorium, plutonium, barium, strontium, hafnium, bismuth, manganese, cobalt and the rare earth elements...
(Savvin, 1963; Zyryanov and Baykov, 2002; Khan et al., 2006; Dedikova et al., 2008). The unique of Arsenazo III is forming strong, stable metal chelate complexes with the elements mentioned above. This makes it important for measuring the concentrations of elements at extreme conditions, such as very basic and acidic media, where hydrolysis reactions could occur and polynuclear species could be formed. Moreover, Arsenazo III is a suitable reagent for coordinating elements with various oxidation states and measuring their concentrations, as is the case for uranium and plutonium.

The ubiquitous of iron on earth makes it co-exist with most of the metal elements. In atmospheric conditions, ferrous ion is oxidized to ferric ion by oxygen in many cases. Due to the strong complexing ability, ferric ion will form complex with Arsenazo III, thus influencing the concentration measurement for those elements mentioned above. To suppress the interference from Fe(III), a chelant is used usually to reduce Fe(III) to Fe(II).

Water radiolysis due to ionizing radiation produces both oxidants (\( \cdot \text{OH}, \text{H}_2\text{O}_2, \text{HO}_2^\cdot \) and 02) and reductants \( (\text{e}^-\text{aq}, \text{H}^+ \) and \( \text{H}_2\text{O}) \) (Nilsson and Jonsson, 2011; Eriksen et al., 2012), and occurs in many situations, e.g., radiotherapy (Schmid et al., 2010), radiosterilization (Maquille et al., 2008), sewage treatment (Guo et al., 2008), food irradiation (Katayama et al., 2006), nuclear waste repository (Jonsson et al., 2007), to name only a few. Many studies have confirmed the effective degradation of refractory organic pollutants by gamma irradiation directly (Gehringer et al., 1988; Arbon et al., 1996; Lee and Lee, 2005; Akiyama et al., 2010; Zheng et al., 2011), and a recent work has demonstrated that the presence of varying concentrations of ferrous sulfate can significantly enhance the degradation (Varghese et al., 2007).

The Fenton reaction is commonly used for advanced oxidation processes (AOPs), in particular with organic compounds (Bouniol, 2010; Nidheesh and Gandhimathi, 2012). The principle of the Fenton reaction is based on a mixture of dissolved iron (Fe(II), catalyst) reacts with hydrogen peroxide (\( \text{H}_2\text{O}_2 \), Fenton reagent) and produces oxidizing radicals in the following manner:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+
\end{align*}
\]

Reaction (1) is the oxidation of ferrous ion Fe(II) to ferric ion Fe(III) by \( \text{H}_2\text{O}_2 \), which produces strongly oxidizing hydroxyl free radicals (\( \cdot \text{OH} \)) and hydroxyl anions (\( \text{OH}^- \)). In reaction (2), Fe(III) is reduced to Fe(II) with the formation of perhydroxyl radicals (\( \text{HO}_2^- \)). The \( \text{HO}_2^- \) radical is a relatively weak oxidant, whereas the hydroxyl free radical (\( \cdot \text{OH} \)) is a strong oxidant that can react non-selectively with most organic compounds (Nidheesh and Gandhimathi, 2012).

Thus, an irradiated solution containing Fe(II, III) or the introduction of Fe(II, III) into a gamma-irradiated solution can lead to the Fenton reactions, which then produce oxidative radicals that can oxidize organic compounds in the solution. To date, there are considerable numbers of studies related to the Fenton reaction, while few studies go to the underlying mechanism of the reaction and the gamma-ray induced reactions are not well-documented (Varghese et al., 2007; Bouniol, 2010).

In this paper, we investigated the gamma ray-Arsenazo III–Fe(II, III) reactions in aqueous solutions and discussed how gamma irradiation can influence the concentration determination of aqueous U(VI) solutions with Arsenazo III spectrophotometric method. We found that the Fenton reaction induced by gamma irradiation can decompose Arsenazo III, leading to a sharp decrease in the absorbance of the U(VI)–Arsenazo III complex. These results will have great influence to the analysis of uranium aqueous solutions from nuclear fuel cycles, and suggest that attention must be paid to the application of organic compounds, such as Arsenazo III, in gamma radiation-exposed samples.

2. Materials and methods

2.1. Chemicals and reagents

All of the reagents used in this study were of analytical grade. Ammonium ferrous sulfate (\((\text{NH}_4)_2\text{FeSO}_4\)) and \(\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}\) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). \(\text{FeCl}_3\cdot 6\text{H}_2\text{O}\) and Arsenazo III were purchased from J&K chemical Ltd. (Beijing, China). The water used was deionized (18.2 MQ).

2.2. Gamma irradiation process

Gamma irradiation of the samples was conducted at room temperature using a \(^{60}\text{Co}\) source in the Fundamental Science Laboratory on Radiochemistry & Radiation Chemistry at Peking University. Solutions of 0.1 mM of \(\text{UO}_2^{2+}\) (pH \(\approx 2.0\)) with and without addition of \((\text{NH}_4)_2\text{FeSO}_4\) or \(\text{FeCl}_3\) were introduced into 10 mL airtight glass vessels and placed into specified positions with different distances from the core of the \(^{60}\text{Co}\) radiation source to achieve desired absorbed doses ranging from 0.15 kGy to 180 kGy. The doses were calibrated with a conventional Fricke dosimeter.

2.3. UV–Vis analyses

After irradiation, 1 mL of the irradiated solution was mixed with 2 mL Arsenazo III solution (0.1% in w/w). The mixture was then diluted to 10 mL with a sulfuric acid solution (pH 2.0) in the presence or absence of the desired concentration of Fe(II). Subsequently, the absorption spectrum was recorded from 450 nm to 700 nm against a blank with a UV–Vis spectrophotometer (Lamda-35, Perkin Elmer Inc., Waltham, MA, USA). The concentrations of Fe(II)/Fe(III) in the irradiated solution were determined by the phenanthroline method, with and without the reduction step by hydroxylamine hydrochloride (Viollier et al., 2000).

2.4. ESI–MS measurements

The substances in the mixtures were determined via electrospray ionization-mass spectrometry (ESI–MS), which is a useful method for identifying the molecular formula to obtain the complex information between Arsenazo III and U(VI). All negative-ion electrospray mass spectra were recorded with a Bruker APEX IV 7.0 T Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, Billerica, MA, USA) equipped with an external ESI source at Peking University. The scan range was from m/z 100 to 1200.

3. Results and discussion

3.1. Influence of Fe(II, III) on the absorbance of U(VI)-Arsenazo III complex

The influence of Fe(II) on the absorption spectra of the Arsenazo III-U(VI)-complex is shown in Fig. 1a. Free Arsenazo III solution exhibits an absorption maximum at 540 nm, whereas its complex with U(VI) shows two intense absorption peaks at 605 and 656 nm (Rowatt and Williams, 1989). It has been reported that a slight shift of the absorption band may occur due to differences in the solution pH and ionic medium used (Rohwer et al., 1997). As observed from Fig. 1a, the influence of Fe(II) on the absorption
spectra of the Arsenazo III-U(VI)-complex is negligible up to 1 mM. While, when the U(VI) solution with 0.03 mM Fe(II) was irradiated before the addition of Arsenazo III, the absorbance peaks at 605 and 656 nm sharply decreased, and the peaks completely disappeared when the Fe(II) concentration was greater than 0.07 mM (Fig. 1b). There was no discernible change in the absorbance for all of the above solutions after standing for 24 h. These results indicate that Fe(II) in a U(VI) solution that had been irradiated by gamma rays will lead to an artificially lower measurement result of the U(VI) concentration using the Arsenazo III method.

Fig. 2 shows the influence of Fe(III) on the absorption spectra of U(VI)-Arsenazo III complex. It indicates that the increase of Fe(III) concentration can significantly decrease the absorbance of the U(VI)-Arsenazo III complex. This is in contrast to a previous observation that Fe(III) can enhance the absorbance of the uranium Arsenazo III complex in 3 M perchloric acid solution (Khan et al., 2006). The reason for this contrast may arise from the difference in solution pH (~2.0) and media (sulfuric acid). Further investigations are needed to understand the underlying mechanism.

A previous study indicated that due to the formation of a complex with Arsenazo III, Fe(III) acts as an interferent for the determination of manganese, bismuth, magnesium and calcium (Reig et al., 1983; Khan et al., 2006). Therefore, to suppress the interference from Fe(III), a reductant such as Ti(II) chloride (Murty et al., 1997) or L-ascorbic acid (Komersová et al., 2001) is commonly used to reduce Fe(III) to Fe(II). While, when there is gamma irradiation, aqueous Fe(II) will be oxidized to Fe(III) due to the strong oxidizing radicals produced by water radiolysis (Trumbore and Hart, 1959), and the final speciation iron in the solution would be mainly ferric iron. Fig. 3 shows the dose-dependence of the decrease in absorbance (left) and the corresponding iron speciation evolution in the irradiated solution (right). The decrease of Fe(II) or the increase of Fe(III) exhibits a linear correlation with the absorbed dose. Due to the competitive complexing of Fe(III) and U(VI) with Arsenazo III, the decrease in absorbance of the gamma irradiated U(VI) + Fe(II) solutions at 605 and 656 nm can be mainly ascribed to the oxidation of Fe(II) to Fe(III).

3.2. Fenton reaction induced by gamma irradiation

To understand the effect of the Fenton reaction on the decrease in absorbance of the U(VI)-Arsenazo III complex, a U(VI) solution was irradiated to a designed absorbed dose and then mixed with Arsenazo III and Fe(II). The color of the mixed solution changed to blue, which is the characteristic color of the U(VI)-Arsenazo III complex. However, the mixed solution lost its color gradually after several minutes. The UV–Vis spectra data of the mixed solution recorded after 24 h is shown in Fig. 4. Fig. 4a shows that the absorbance decrease significantly upon the introduction of Fe(II) into the gamma-irradiated U(VI) solution, and the decrease depends on the Fe(II) concentration. With an absorbed dose of 18 kGy, the absorption at 656 nm disappeared completely in the presence of 0.07 mM Fe(II). Furthermore, Fig. 4b shows that the absorbance decrease is also dose-dependent. To understand the time effect on the reactivity, some irradiated U(VI) solution were allowed to age for 5, 10, 20, and 30 d in the absence of light at room temperature without the exclusion of air, and then mixed with Fe(II) and Arsenazo III. Quite the same phenomena were observed as that shown in Fig. 4a and b, which indicated that even after 30 d, the oxidizing capacity of the gamma irradiated U(VI) solution had no discernable decrease.

Noting that the absorption spectrum in Fig. 4 has a different profile from the one in Fig. 1b, e.g., the absorption originating from Arsenazo III at ~540 nm is decreased simultaneously in Fig. 4, implying the decomposition of the Arsenazo III structure. The same decrease of absorbance at ~540 nm is also observed for the experiments simulating the degradation of Arsenazo III (U(VI) + Arsenazo III + Fe(II) + H2O2) by the Fenton reaction as shown in Fig. 5, indicating the occurrence of the Fenton reaction in the pre-gamma irradiated U(VI) solution with Arsenazo III and Fe(II). Because ferrous iron is consumed more rapidly than it is regenerated during the Fenton reaction process (Zhang et al., 2006; Nidheesh and Gandhimathi, 2012), the absorption decrease in Fig. 4 can be attributed to both the competitive complexing of Fe(III) with Arsenazo III and the decomposition of Arsenazo III by the Fenton reaction. As observed from Fig. 2, the absorbance values at 656 nm are 0.671, 0.378 and 0.234 for the 0.01, 0.03 and 0.05 mM Fe(III),
respectively, whereas Fig. 4 shows lower absorbance values of 0.576, 0.286 and 0.177 for the equivalent concentrations of Fe(II).

The G-value refers to the number of molecules produced or destroyed for every 100 eV dose absorbed by a substance from the ionizing radiation. The G-value for H₂O₂ is 0.76 molecules/100 eV (Draganić et al., 1969). Given the absorbed doses of 1 kGy and 18 kGy, 0.008 and 0.14 mM H₂O₂ are expected to be formed in a 10 mL solution, respectively. Based on the theoretical calculations, we compared the difference in the absorbance decrease between the irradiated solution and the solution without irradiation but with extra H₂O₂.

The effect of H₂O₂ on the decomposition of Arsenazo III by the Fenton reaction was investigated over the range of 0.005–0.1 mM (Fig. 5). Because the decomposition of H₂O₂ is thermodynamically favorable under ambient conditions, the concentration of H₂O₂ was re-calibrated using the KMnO₄ method (Klassen et al., 1994). As shown in Figs. 4b and 5, the absorbances at 656 nm for the 1 kGy and 18 kGy irradiated solutions are comparable with the solutions prepared by adding 0.02 and 0.1 mM H₂O₂. This confirms the reliability of the H₂O₂ production calculations.

With the increase of the H₂O₂ concentration, a significant absorbance decrease at /C24540 nm occurs after the disappearance of the U(VI)-Arsenazo III complex peaks at 605 and 656 nm. Because the symmetrical Arsenazo III molecules contain two groups capable of metal binding and because it can form a 1:1 complex with UO₂⁺ (Rowatt and Williams, 1989; Zyryanov and Baykov, 2002), the results in Figs. 4 and 5 suggest that the complex of Arsenazo III with U(VI) is more susceptible to oxidation.

3.3. Mass spectrometry analysis

ESI-MS, a powerful technique that enables the identification of the molecular formula of complex molecules, was utilized to investigate the binding affinity between Arsenazo III and U(VI). The free Arsenazo III (Fig. 6a) gives rise to a molecular peak at m/z 774.86. After adding 0.01 mM UO₂(NO₃)₂, the ESI-MS spectrum reveals two main ions at m/z 1105.87 and 1042.88, which can be ascribed to [ars+(UO₂NO₃)⁺] and [ars + UO₂⁺], respectively (Fig. 6b). These two ions confirm that Arsenazo III forms a 1:1 complex with U(VI) (Rowatt and Williams, 1989; Khan et al., 2011). Nevertheless, when Arsenazo III was introduced into the gamma-irradiated U(VI) solution (at 1.8 kGy dose) with 0.1 mM Fe(II), the peaks at
m/z 1105.87 and 1042.88, as well as the molecular peak of Arsenazo III at m/z 774.86, disappeared (Fig. 6c). The same result was observed for the Arsenazo III solution that contains 0.1 mM Fe(II), 0.1 mM H2O2 and 0.01 mM U(VI) (Fig. 1d), in which where the Fenton reaction is expected to occur to decompose the Arsenazo III. Therefore, the mass spectral fragmentation patterns further confirm that the Fenton reaction induced in gamma-irradiated solutions in the presence of Fe(II) can decompose subsequently added Arsenazo III reagent.

Based on the discussions mentioned above, the entire process for Fe(II) to influence the measurement of uranium under gamma irradiation can be illustrated as following:

1. Water radiolysis due to ionizing radiation produces oxidants (OH, H2O2 and HO2).
2. Oxidants produced by gamma irradiation oxidize the Fe(II) to Fe(III), and then Fe(III) complexes with Arsenazo III to form Fe(III) + Arsenazo III complex. (The experimental process was: U(VI) + Fe(II) + gamma radiation + Arsenazo III.)
3. The H2O2 produced by gamma irradiation and the thereafter added Fe(II) induce the Fenton reaction. The production OH of the Fenton reaction decomposes Arsenazo III into smaller molecules. (The experimental process was: U(VI) + gamma radiation + Fe(II) + Arsenazo III.)

4. Conclusions
Arsenazo III is a widely used reagent in spectrophotometric analysis of elements. Due to the strong affinity with Arsenazo III, Fe(III) can significantly decrease the UV–Vis absorbance of the U(VI)-Arsenazo III complex. Gamma radiation commonly exists in the nuclear fuel cycle and many other nuclear related occasions, and Fe(III) is ubiquitous in the geosphere. Gamma irradiated solutions containing uranium, ferrous iron and other elements are not few. This study indicates that Fe(II) introduced into gamma-irradiated U(VI) solutions can induce the Fenton reaction, which can decompose Arsenazo III, thus leading to a sharp decrease in the UV–Vis absorbance of the U(VI)-Arsenazo III complex at 605 nm and 656 nm. The decrease in the absorbance is positively related with the iron concentration and the absorbed dose, and the oxidizing radicals from the Fenton reaction that are induced by gamma irradiation can be continually produced within one month when the samples are kept in the absence of light at room temperature and without the exclusion of oxygen. This result suggests that attention must be given to the application of Arsenazo III in gamma radiation-related fields, and new analytical methods need to be developed for the quantitative determination of U(VI) in the presence of gamma radiation and ferrous iron. Moreover, because the Fenton reaction is widely used in the degradation of refractory organic pollutants, this study also provides ideas to investigate the mechanisms in the degradation of refractory organic pollutants. Further investigations on the influence of gamma irradiation to the measurements of other elements with Arsenazo III method are needed. Meanwhile, the influence on the migration behavior of radionuclides in the environment is also essential, for the mobility of radionuclides in the environment may be highly influence by the natural organic matters.

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