Update on Activity 6: Target Solution Chemistry Determination of Iron Sulfate

Chemical Science and Engineering Division

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by

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UPDATE ON ACTIVITY 6: TARGET SOLUTION CHEMISTRY DETERMINATION OF IRON SULFATE

ABSTRACT

Hydrogen peroxide (H_2O_2) is expected to be generated during the irradiation of Subcritical Hybrid Intense Neutron Emitter (SHINE) solutions due to the radiolysis of water. The anticipated concentrations of H_2O_2 could jeopardize the solubility of uranium through uranyl-peroxide precipitation. The formation of this insoluble salt has been validated experimentally. SHINE would introduce small quantities (1–10 ppm) of iron(II)-sulfate into target solutions to mitigate the production of peroxide during radiolysis by catalyzing its autodestruction. The method described here quantifies the concentration of iron in the presence of excess uranyl-sulfate and trace amounts of fission and corrosion products as appropriate for irradiated SHINE solutions. Uranyl sulfate and fission products do not interfere with the method. Excess amounts of chromium(III) relative to iron(II) show some interference.

1 SCOPE

In this task, we are developing a procedure to quantify the concentration of iron in the SHINE target solution. The procedure is necessary to assure that the iron concentration is in the range of 1–10 mg/L, which is required to assure that peroxide autodestruction will be high enough that uranyl peroxide will not precipitate from the target solution during irradiation. The high concentration of uranium (110,000–150,000 mg/L) compared to the iron concentration makes this analysis challenging.

2 MATERIALS AND PROCEDURE

2.1 EQUIPMENT

1. Absorbance spectrometer
 - a. Wavelength range 400–800 nm
 - b. Slit width: 1.000 nm
 - c. Increment: 1.0 nm
2. 2-mL volumetric flask
3. Analytical pipette capable of delivering 100–1000 μL
4. Two 1-cm cuvettes with a detectable volume of 0.7-mL solution.
5. Two small test tubes with caps.

2.2 MATERIALS

1. Bathophenanthroline (Sigma Aldrich) “BPhen.”
 - a. In a 50-mL volumetric flask, weigh ~16 mg and dissolve in 30 mL of pure ethanol. Fill to 50-mL mark with deionized (DI) water.
2. Isoamyl alcohol (Sigma Aldrich) “Iso-OH.”
3. Hydroxylamine (Sigma Aldrich, Trace Metals).
 - a. Prepare 5 g in 50 g of DI water in a separation funnel.
 - b. Add 3 mL of BPhen.
 - c. Add 3 mL of Iso-OH.
 - d. Shake vigorously for 1 minute and allow the phases to separate.
 - e. Drain the lower phase containing the purified hydroxylamine.
4. Sodium Acetate (Sigma Aldrich, Trace Metals).
 - a. Prepare 5 g in 50 g of DI water in a separation funnel.
 - b. Adjust the pH to 9 using ammonium hydroxide.
 - c. Add 3 mL of purified hydroxylamine.
 - d. Add 3 mL of BPhen.
 - e. Add 3 mL of Iso-OH.

- f. Shake vigorously for 1 minute and allow the phases to separate (shown in Figure 1).
 - g. Drain the lower phase containing the purified sodium acetate.
5. Uranyl-sulfate solution.
- a. pH 1.
 - b. 140 g/L U with corrosion and fission products.

2.3 PROCEDURE

1. To the 2-mL volumetric flask, add 100 μ L of uranyl-sulfate.
2. Add 100 μ L of hydroxylamine.
3. Add 300 μ L of sodium acetate.
4. Add 1000 μ L of BPhen.
5. Gently shake the volumetric flask to mix the BPhen.
6. The solution should change to a red-orange color.
7. Add DI water to the 2-mL mark.
8. Mix the solution using a transfer pipette and transfer the solution to a test tube. The pH of this solution should be approximately 6.
9. Take 1000 μ L of the solution and transfer it to the second test tube.
10. Add 1000 μ L of Iso-OH to the second test tube.
11. Shake the second test tube rigorously for 1 minute and allow the phases to separate.
12. Prepare a cuvette containing neat Iso-OH for baseline measurement.
13. Separate the top alcohol phase from the second test tube to a 1-cm cuvette. This phase should be a light pink to red color. Measure the sample.
14. The absorbance at 800 nm should be zero or at least 0.01. If the solution exhibits absorbance at 800 nm, agitate the sample or change the cuvette.

FIGURE 1 An Extraction of Fe(II)BPhen into Iso-OH from a Sodium Acetate Solution (The red Fe(II)BPhen complex can be seen in the top layer.)

15. The concentration of iron(II) in the original uranyl-sulfate solution is given by the absorbance (A) at 533 nm ($\text{ppm} \pm 5\%$):

$$[Fe(II)] = \left(\frac{2000 \mu L}{100 \mu L} \right) \times (3.5 \text{ ppm}) \times (A_{533nm}) = (70 \text{ ppm}) \times (A_{533nm})$$

16. If the solution's absorbance saturates the detector ($A > 3$), then the organic phase can be quantitatively diluted with Iso-OH. Take 500 μL of the loaded phase and dilute it with 500 μL of neat Iso-OH. Adjust the above equation to $140 \text{ ppm} \times A_{533nm}$.

3 DEVELOPMENT OF THE METHOD

3.1 PEROXIDE DESTRUCTION

Hydrogen peroxide undergoes disproportionation, particularly when in contact with a metal surface:

The half reactions are as follows:

The reduction standard potentials for equations (2) and (3) are +1.78 V and +0.70 V, respectively (Shriver and Atkins 2006). Thus, any redox reactions with a standard potential within this region could potentially decompose H_2O_2 . A candidate for H_2O_2 decomposition in solution is the Fe(II/III) redox couple ($E^0 = +0.77$ V) (Shriver and Atkins 2006). The reduction of Fe^{3+} by H_2O_2 is shown in the following equation:

The E^0 for this reaction is +0.07 V and thus thermodynamically favorable (Shriver and Atkins 2006). There is also the oxidation of Fe^{2+} :

which is also thermodynamically favorable ($E^0 = 1.01$ V).

3.2 COLORIMETRY AND METHOD

Both Fe(II) and Fe(III) absorb visible light with relatively strong intensities. There exist several methods of quantification that use colorimetry. *Vogel's Textbook of Quantitative Chemical Analysis* (Jeffery et al. 1989) reports two methods that uniquely quantify both Fe(II) and Fe(III). Quantification of Fe(III) utilizes thiocyanate to give intensely red-colored compounds without interference from Fe(II). However, the presence of sulphate anions can significantly complex the Fe(III). For quantification of Fe(II), 1,10-phenanthroline (phen) complexes form a red-orange solution that exhibits a maximum absorbance at 515 nm ($\epsilon = 11,100 \text{ M}^{-1}\text{cm}^{-1}$). Fe(III) is also complexed by this ligand; however, its maximum absorbance is observed at 396 nm, which directly overlaps in absorbance with U(VI). The presence of additional transition metals such as silver, bismuth, copper, nickel, and cobalt can seriously interfere with and affect the absorbance when using phen. Derivatives of this ligand have demonstrated a competitive edge for iron quantification in solution. Smith et al. (1952) and Gahler et al. (1961) reported the use of

the ligand 4,7-Diphenyl-1,10-phenanthroline (BPhen; see Figure 2) for Fe(II) quantification in the concentration range of 0.0001 to 2%. The reported extinction coefficient for Fe(II) with BPhen is $22,400 \text{ M}^{-1}\text{cm}^{-1}$ at 533 nm. A sample containing $10 \text{ }\mu\text{M}$ of Fe(II)-BPhen would exhibit an absorbance of approximately 0.2, which is an acceptable quantification for most spectrometers.

The procedure for iron quantification with BPhen, however, requires additional manipulations and separations. A generalized procedure follows; concentrations and volumes are omitted:

1. Prepare iron-containing solutions in a volumetric flask.
2. Add hydroxylamine to reduce Fe(III) to Fe(II).
3. Add sodium acetate solution for buffering.
4. Add excess BPhen.
5. Adjust pH of solution if necessary.
6. Contact the aqueous phase with isoamyl alcohol (Iso-OH; see Figure 3.).
7. Shake solutions and allow the phases to separate.
8. Separate the iron-containing organic phase into a cuvette.
9. Having corrected for background subtraction, measure the absorbance spectra at 533 nm.
10. Repeat the process using standardized solutions of Fe(II) and generate a calibration curve within the concentration region of interest.
11. Introduce the appropriate contaminants and test the reliability.

FIGURE 2 4,7-Diphenyl-1,10-phenanthroline (BPhen)

FIGURE 3 Isoamyl Alcohol (Iso-OH)

3.3 SPECIATION

Speciation diagrams for Fe (II), uranyl ion, and phen based on the stability constants of phen (not BPhen) with selected metals reported in the National Institute of Standards and Technology (NIST) database are shown in Figure 4 (NIST 2004). The literature concerning complexation of BPhen is limited. The stability constant for the U(VI)-phen complex was

FIGURE 4 Speciation Diagram of Fe(II) and U(VI)-phenanthroline (The diagram on the left shows the species formation relative to Fe(II). The diagram on the right shows the speciation with respect to phenanthroline.)

substituted with that of Nd(III)-phen. This assumption should be regarded with caution but was used nonetheless due to the scarce literature concerning U(VI)-phen. The diagram on the left-hand side of Figure 4 shows the speciation of iron(II) in the presence of excess BPhen and U(VI) as a function of pH. Beyond pH 4, the majority of the iron(II) is complexed by phen.

3.4 CALIBRATION CURVE

A 10% (w/w) solution of hydroxylamine (99.999% Trace analysis, Sigma-Aldrich) and sodium acetate (Sigma-Aldrich) was prepared using milli-pore deionized water. Each solution was purified of iron contaminants as reported in Smith et al. (1952).

A solution of BPhen (>99%, Fluka) was prepared by dissolving 19.5 mg in 25 mL of ethanol and filling to volume (50 mL) of deionized water. A stock solution of Fe(II) was prepared by dissolving Fe(NH₄)₂(SO₄)₂·6H₂O in dilute H₂SO₄. Iso-amyl alcohol (Sigma-Aldrich) was used without purification.

A Cary 5E UV-Vis-NIR spectrometer was used for absorption measurements. The absorption range was between 800 and 400 nm. The incremental wavelengths were 1 nm and the slit width was 1 nm. A reference solution containing hydroxylamine and sodium acetate was used. Temperatures of the solutions were in the range of $20 \pm 2^\circ\text{C}$.

Aqueous solutions of Fe(II)BPhen were prepared in 2 mL volumetric flasks according to Smith et al. (1952). Upon addition of excess BPhen, a vibrant red complex appeared. The concentrations of Fe(II) in the volumetric flask were in the range of 0.7–10.4 ppm. The pH of the solutions was estimated to be in the range of 4–6 as measured using pHydrion paper (2-12). One milliliter of aqueous solution was contacted with 1 mL of Iso-OH and vortexed for one minute. The solutions were centrifuged and separated. The organic phase was taken for measurement. A

calibration curve is shown in Figure 5. The concentration range of Fe(II) demonstrated a linear relationship with the absorbance at 533 nm. From Figure 5, the Fe(II) concentration is equal to 3.5 ppm times the absorbance at 533 nm (1-cm path length).

3.5 POTENTIAL INTERFERENCES

A solution containing uranyl-sulfate, chromium-sulfate, and a cocktail of fission products was tested for interferences in the Fe(II)-BPhen absorbance. The method above was tested in the presence of 0.1 M uranyl-sulfate (pH 1, depleted uranium) that was diluted from a 0.6 M uranyl-sulfate stock. The pH of the solution was adjusted to 6. There was no visible evidence that uranium was extracted into the alcohol with no characteristic uranyl peaks at 400 nm (see Figure 6 for a photograph of a typical extraction experiment). It should be noted that the uranyl-sulfate stock solution already contained appreciable amounts of Fe(II). The method was repeated as a function of uranyl-sulfate concentration. The Fe(II) concentration exhibited a linear dependence with increasing concentrations of uranium, as seen in Figure 7. From this linearity, the initial concentration of Fe(II) present in the stock solution was calculated to be 80 ± 3 ppm. The linear dependence plateaued above 0.06 M uranyl-sulfate due to the low pH (<2) and competition for the BPhen ligand.

FIGURE 5 Calibration Spectra for Fe(II)-BPhen in the Range of 0.7–10.4 ppm (The insert shows the relationship between the Fe(II) concentration and the absorbance at 533 nm.)

Chromium-sulfate was tested as a potential corrosion contaminant. Chromium (III) sulfate hydrate ($\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, 99.999% Sigma Aldrich) was dissolved in dilute sulfuric acid. The dark-green solution was submitted for ICP-MS to determine the concentration of chromium. Five samples containing 0, 9.1, 21.3, 33.4, and 45.7 ppm Cr(III) were prepared in the presence of 5.8 ppm iron-sulfate standard. The pH was adjusted to 6 using NH_4OH . The solutions containing 9.1–33.4 ppm Cr(III) did not interfere. However, solutions containing 45.7 ppm (nearly 8 times the concentration of iron) decreased the absorbance at 533 nm as shown in Figure 8. The effective cationic charges for the Cr(III) and Fe(II) ions are 4.8 and 3.1, respectively (Shannon 1976). From these values, we anticipate the stability constant for the Cr(III)-BPhen complex to be significant and competitive with Fe(II), although steric dependency may affect this. The stability constant for the Cr(III)-phen complex is not reported in the NIST database (NIST 2004). There was no evidence that this complex was extracted into the alcohol solvent. It should be mentioned that the presence of Cr(III) in solution would likely indicate an excess of iron due to stainless-steel corrosion.

FIGURE 6 The Two-Phase Extraction of Fe(II)-BPhen (top red layer) from a Solution of Uranyl-Sulfate (bottom yellow layer)

The method was tested in the presence of a surrogate PUREX raffinate solution. This cocktail contained the rare-earth elements and selected transition metal fission products dissolved in 3 M HNO_3 . The solution was dark brown and the concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS). The final concentrations after dilution are listed in Figure 9. An aliquot was diluted and tested in the presence of 5 ppm Fe(II) sulfate standard. The pH of the solution was adjusted to 6 using NH_4OH . The absorbance at 533 nm was not affected, as shown in Figure 9.

The literature suggests that other metal ions may interfere, but many of these elements are not anticipated through uranium fission. Cu(II) and Co(II) may interfere, according to Smith et al. (1952). The stability constants for these divalent cations with BPhen are orders of magnitude higher than Fe(II) (Irving and Mellor 1962). However, Smith et al. (1952) reported that these cations can be separated from Fe(II)-BPhen during the extraction if the pH of the aqueous solution is adjusted to more acidic conditions ($4 \leq \text{pH} < 6$). Gahler et al. (1961) used a similar method to the one reported here and demonstrated that V(V), Mn(II), and Ni(II) interfered. This is contrary to Smith et al. (1952), whose method more closely reflects our method. Trace amounts of Ni(II) are to be expected with corrosion of 316 stainless steel but should be overwhelmed by the more abundant Fe(II) concentration in the steel. Tellurates will be reduced to the metallic form by hydroxylamine but should not be extracted into the alcohol solvent and are expected to be present in <1 ppm quantities.

FIGURE 7 The Absorbance of Fe(II)-BPhen in the 0.6 M Uranyl-Sulfate Stock Solution (The concentration of uranyl-sulfate was tested in the range of 0.01–0.1 M. From the linear trendline in the insert, the concentration of Fe(II) in the uranyl-sulfate stock solution was determined to be 80 ± 3 ppm. At high concentrations of uranyl-sulfate, the spectrometer was saturated with Fe(II) and unusable. U(VI)-BPhen complexes were not extracted.)

FIGURE 8 The Absorbance of 5 ppm Fe(II)-BPhen in the Presence of Cr(III) (At 45.7 ppm Cr(III) there was significant interference. Cr(III)-Bphen complexes were not extracted into the alcohol.)

FIGURE 9 The Absorbance of 5 ppm Fe(II)-BPhen in the Presence of a PUREX Raffinate

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