INL/EXP-22-68458-Revision-0

Characterizing Radiation-Induced Chromium Redox Chemistry

August 2022

Changing the World's Energy Future

Emma Grace Danaher, Gregory P Horne, Jacy Kathleen Conrad

Idaho National Laboratory

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Overall Goal

- To use UV-Visible spectroscopy methods to analyze aqueous chromium ions to elucidate their redox behavior in nuclear environments.

Background

- The formation of different chromium oxidation states can occur through gamma radiolysis of chromium solutions

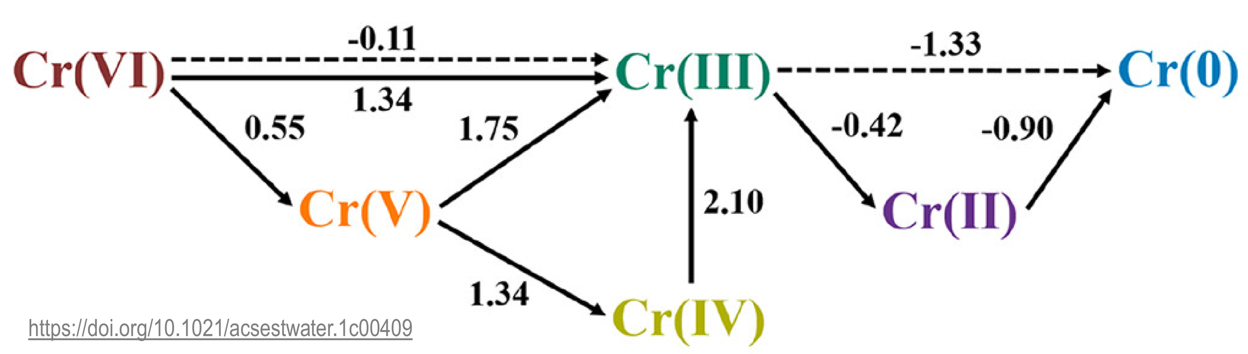

Fig. 1. Standard redox potentials of various Cr species

- Chromium can make its way into the primary coolant of reactors because of corrosion of stainless steel reactor components.
- Cr speciation is important in industrial wastewaters in general because Cr(VI) is toxic and not suitable for environmental release.

Methods

- To collect accurate doses, Fricke dosimetry was performed.
- Calibration curves and extinction coefficients were obtained by: Direct Cr, Cr(III)-EDTA complex, and Cr(VI)-DPC complex.

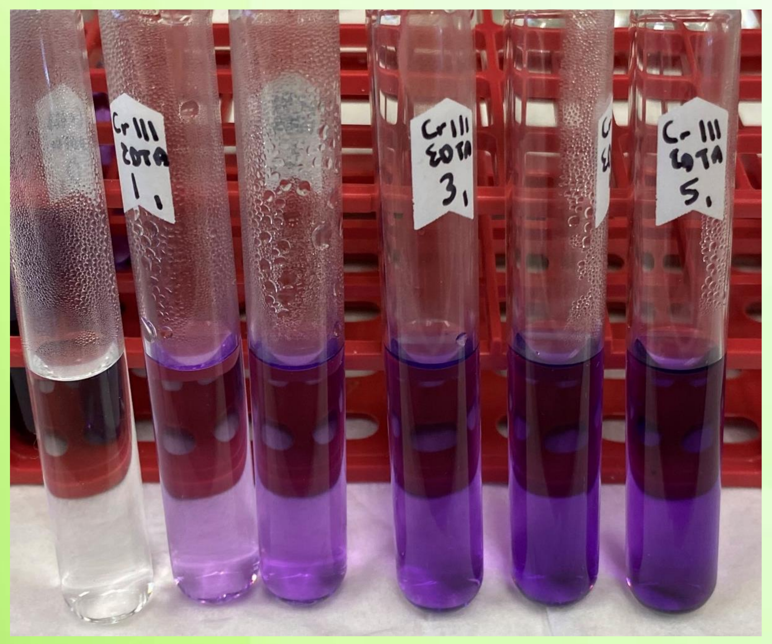

Fig. 2. Cr(III)-EDTA complex solutions ranging from 0 to 6.24 mM

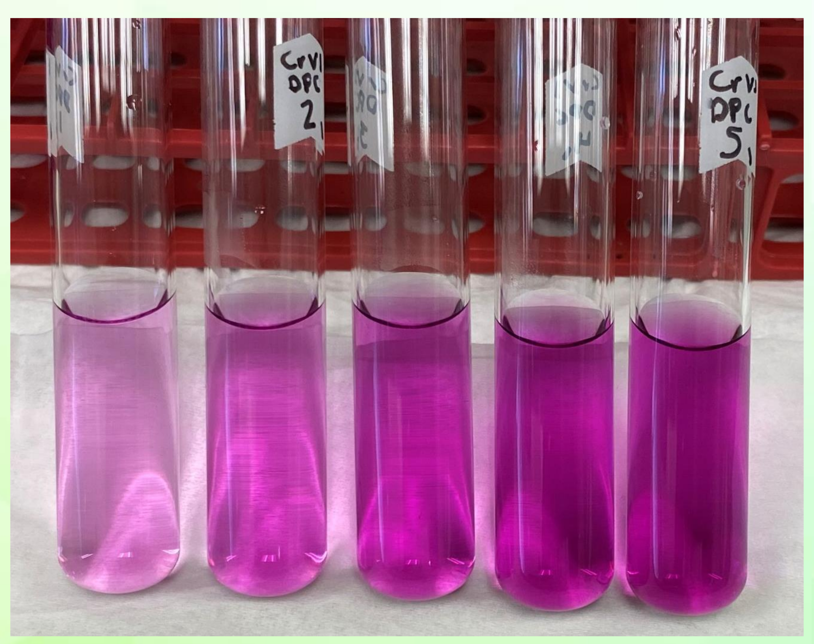

Fig. 3. Cr(VI)-DPC complex solutions ranging from 8.05 to 40.2 μM

- Chromium samples were irradiated using a Cobalt-60 gamma irradiator, and analyzed with UV-Vis.

Methods

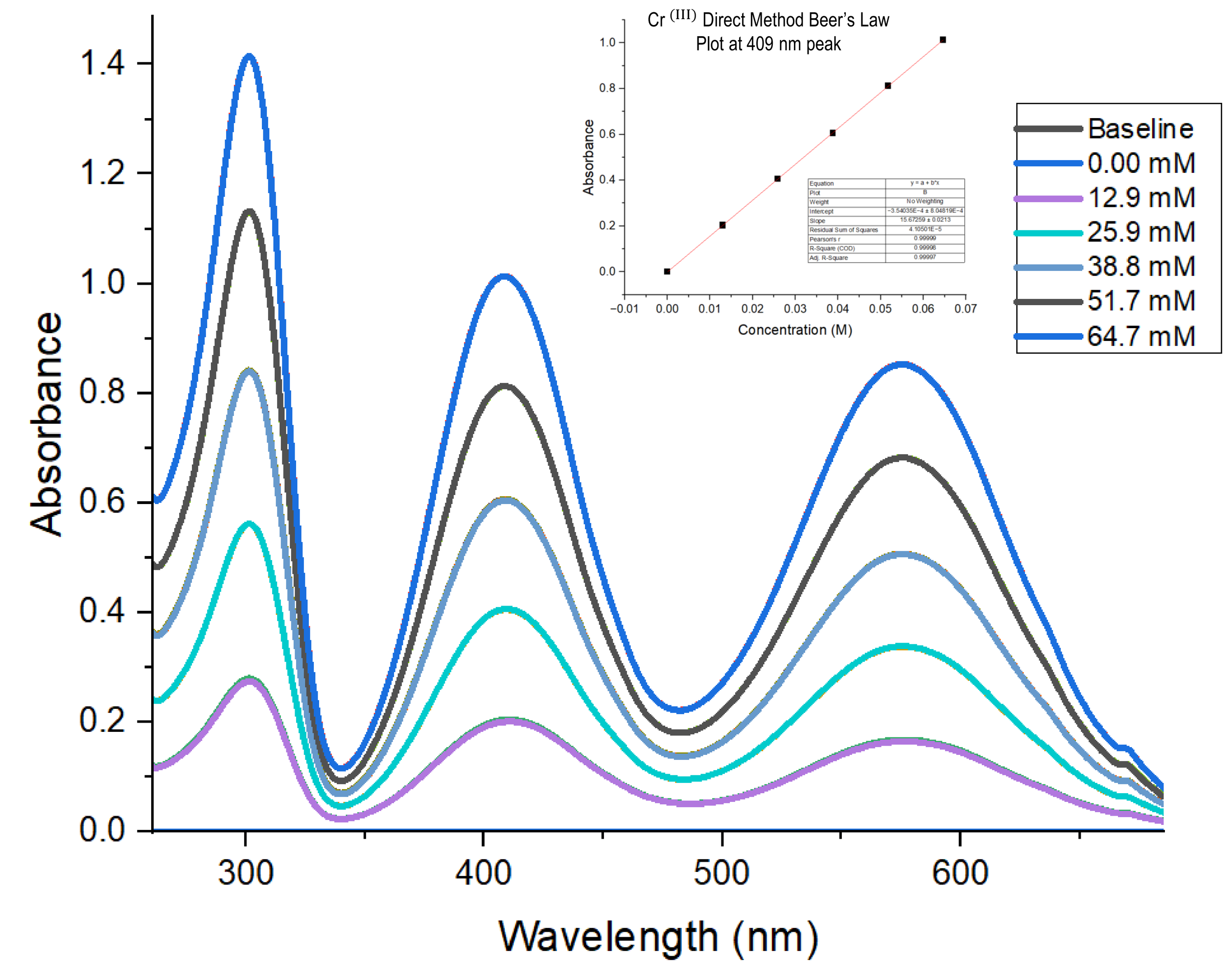

Fig. 4. Cr(III) Direct Method Spectrum for Calibration Curve (Duplicates)

Results

Extinction coefficients (L mol $^{-1}$ cm $^{-1}$):

Cr(III) Direct:
575 nm: 13.192
409 nm: 15.673
301 nm: 21.884

Cr(III) EDTA complex:
544 nm: 196.97
393 nm: 114.72

Cr(VI) Direct (Acidic):
350 nm: 1570.8
257 nm: 2067.9

Cr(VI) Direct (Basic):
373 nm: 4656.9
274 nm: 3553.2

Cr(VI) DPC complex:
542 nm: 33831

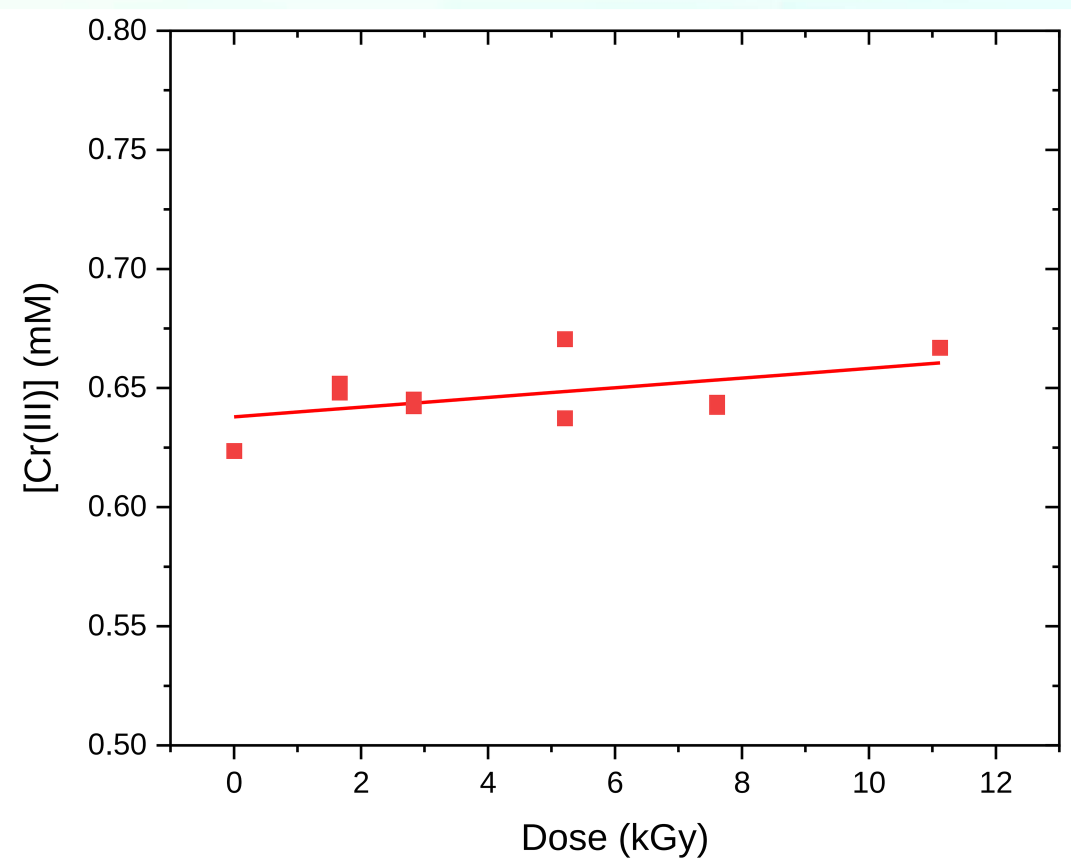

Fig. 5. No Loss of 0.6 mM Cr(III) and no formation of Cr(VI) at pH 6 at 390 nm with EDTA method

Results

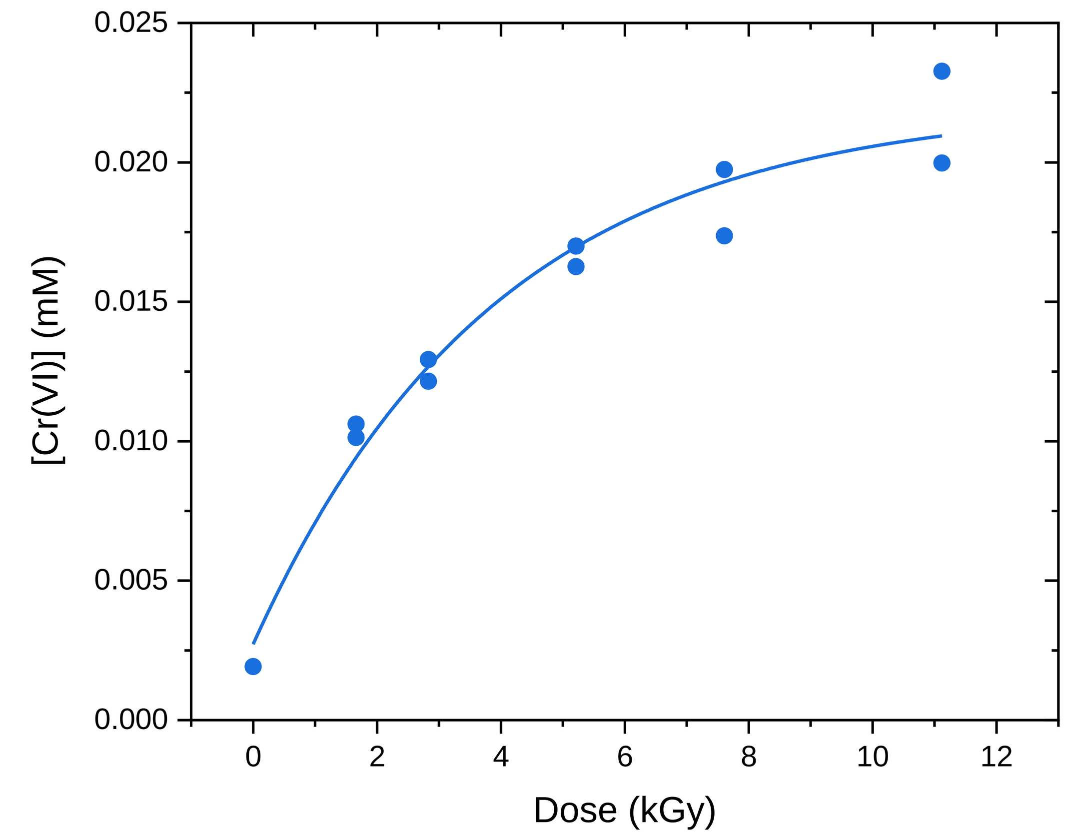

Fig. 6. Loss of 0.1 mM Cr(III) and formation of Cr(VI) at pH 6 at 372 nm

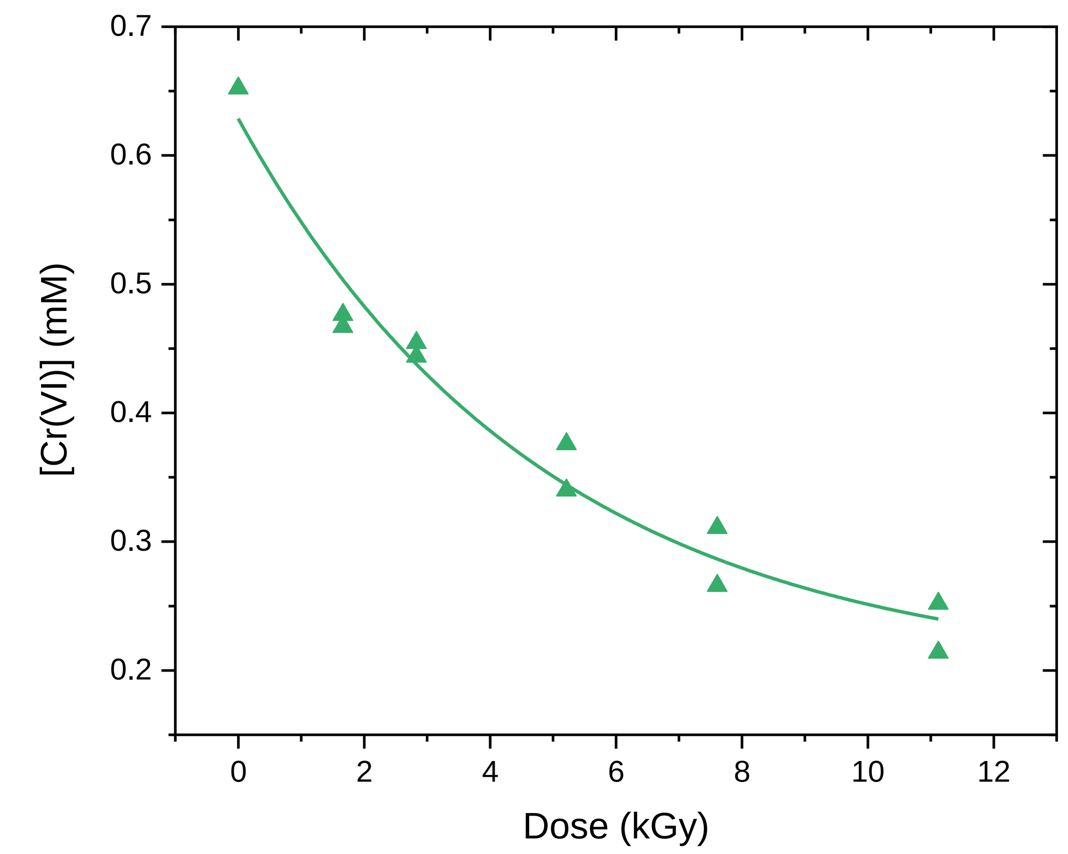

Fig. 7. Loss of 0.6 mM Cr(VI) and formation of Cr(III) at pH 2 at 542 nm with DPC method

Radiation-induced redox chemistry occurred under the following conditions:

- Cr(III), 0.6 mM, pH 4
- Cr(III), 0.6 mM, pH 6
- Cr(III), 0.1 mM, pH 6
- Cr(VI), 0.6 mM, pH 2

Conclusion

- Results show that Cr(III) can easily be oxidized to Cr(VI) and vice versa, but only under specific conditions.
- Cr(III) acidic solutions with a pH less than 2 showed no change.
- Continuation of this project includes collecting more data with additional conditions to develop a complimentary model.

Salisbury UNIVERSITY

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