Redox Chemistry of Np in Irradiated Solution

INEST Fuel Cycle Meeting
Oregon State University
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Bruce J. Mincher et al.
Idaho National Laboratory, USA

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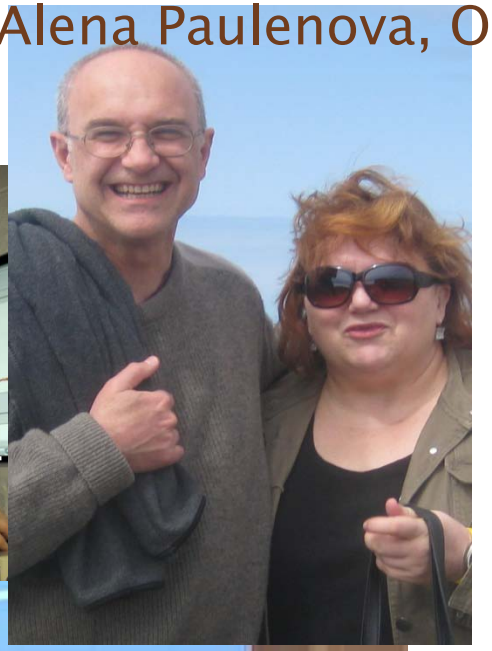
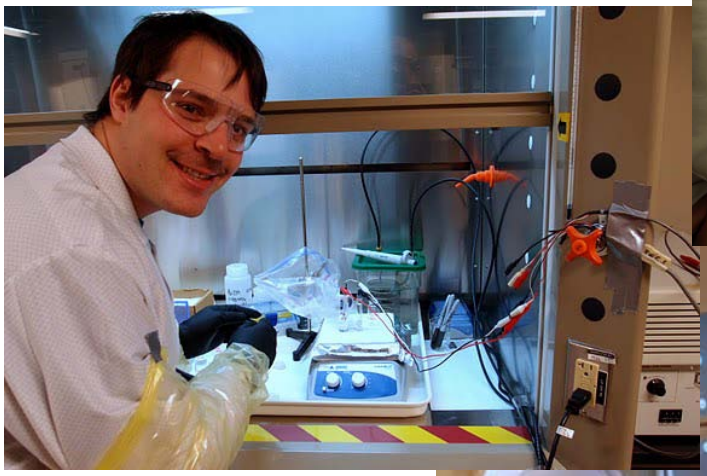
Thanks collaborators..

Alena Paulenova, OSU



Leigh Martin, INL



Martin Precek, OSU

Steve Mezyk, CSULB

Gracy Elias, INL

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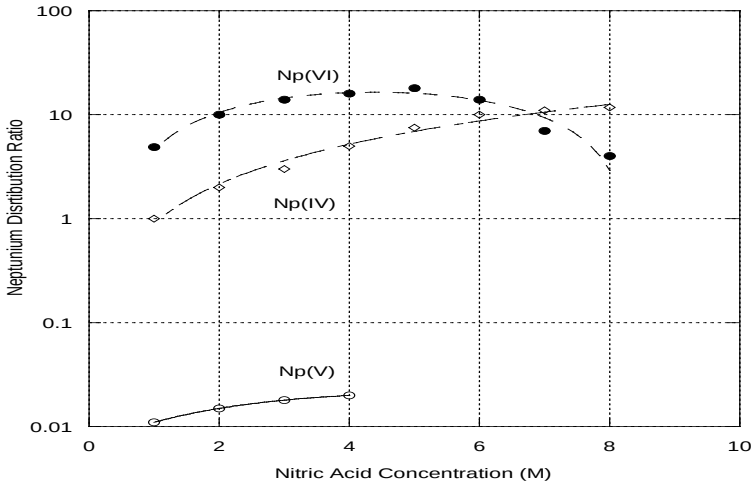
Neptunium Redox Chemistry

- Np^{4+} , NpO_2^{+} or NpO_2^{2+}
- For a reliable co-extraction of Np, the oxidation state must be known and maintained.



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Np valence is controlled by HNO_2

- $NpO_2^+ + 3/2\ H^+ + ½\ NO_3^- \leftrightarrow NpO_2^{2+} + ½\ HNO_2 + H_2O$
- (Siddall and Dukes 1959)

- Nitrous acid should favor Np^V
- Yet Siddall and Dukes found Np oxidation upon small additions of HNO_2?
- They proposed an undefined "activated state"!

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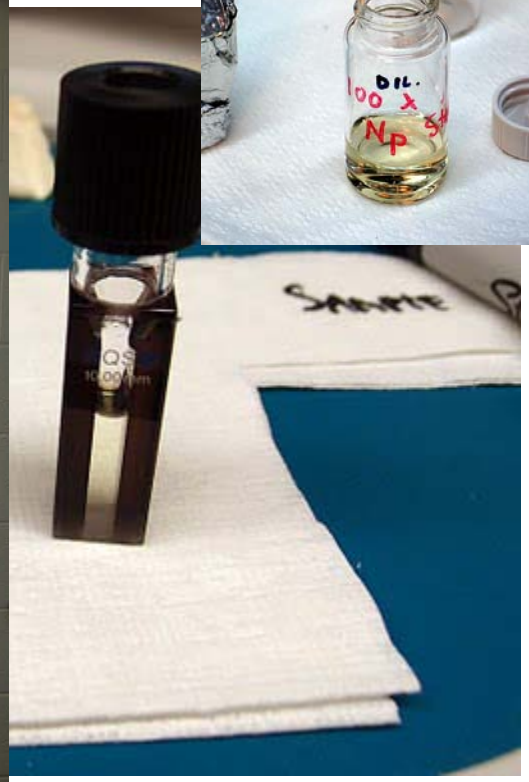
Nitrogen oxide chemistry is complicated…

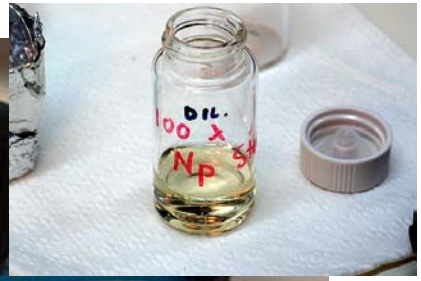
- $HNO_2 + HNO_3 \leftrightarrow N_2O_4 + H_2O \leftrightarrow \cdot NO_2 + \cdot NO_2$

- Tochiyama et al. (1995) proposed that $\cdot NO_2$ was the real oxidizing agent.
- Where does HNO_2 come from?

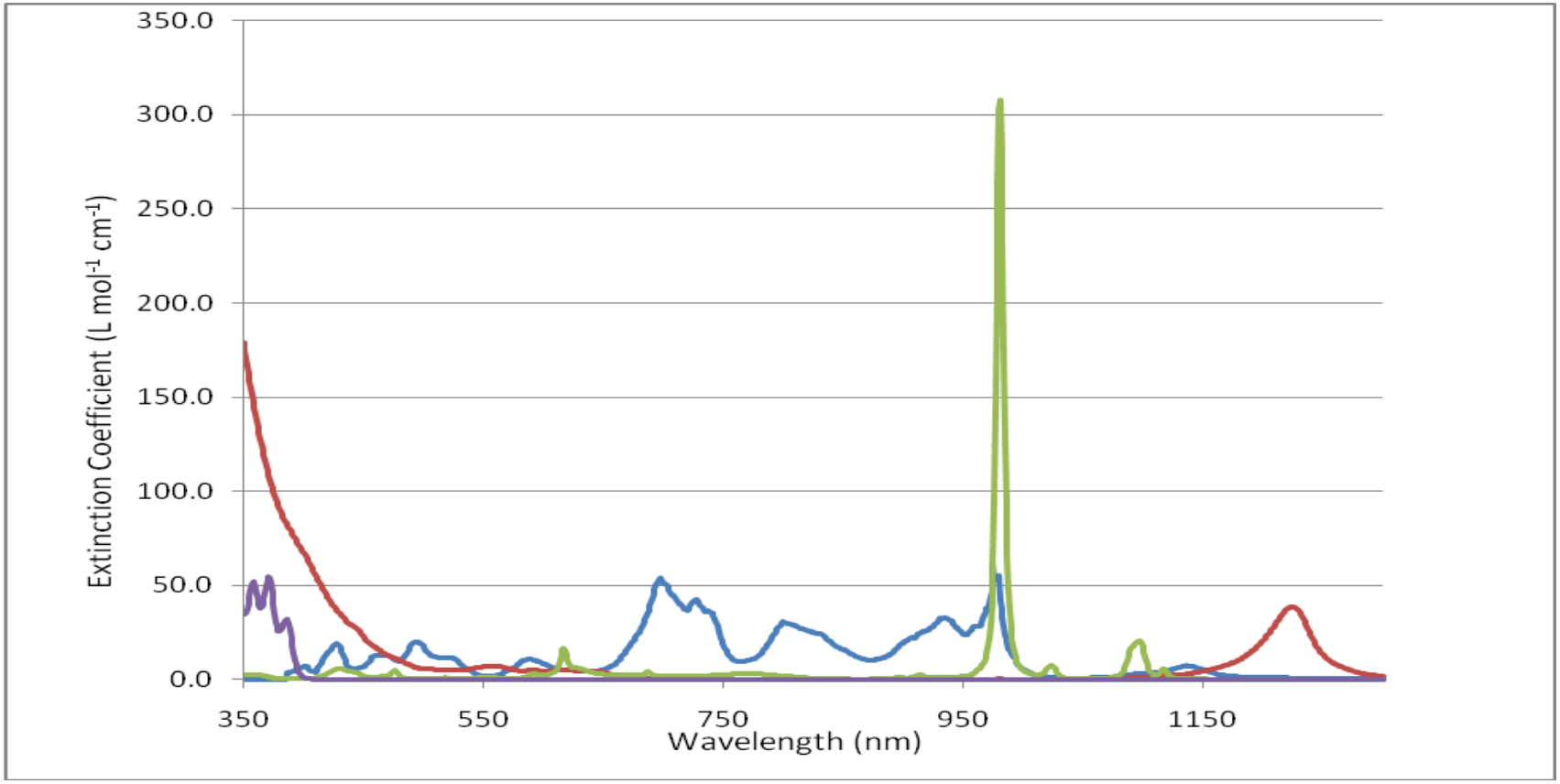
- HNO_3 –ww→ $\cdot O + HNO_2$

Np sample irradiations…





Np valence determined by UV/Vis spectroscopy



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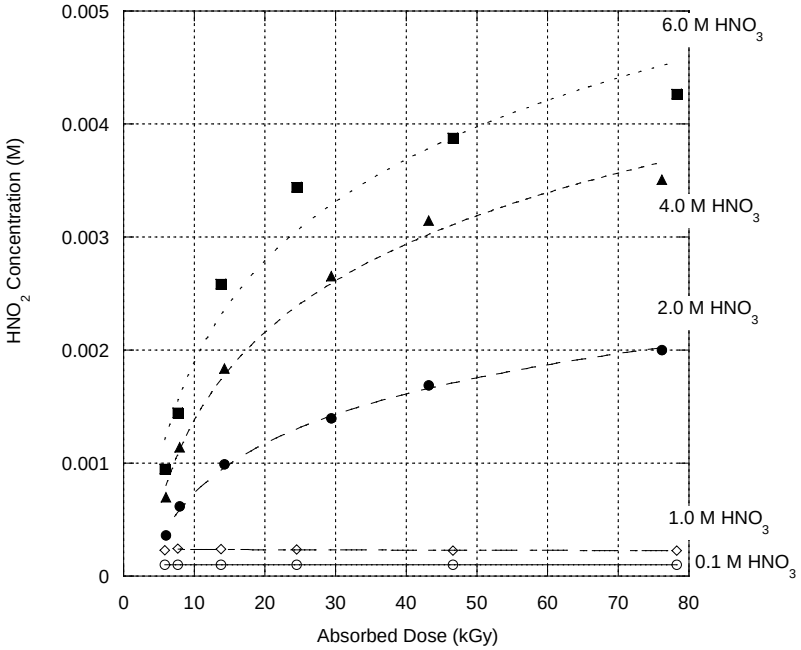
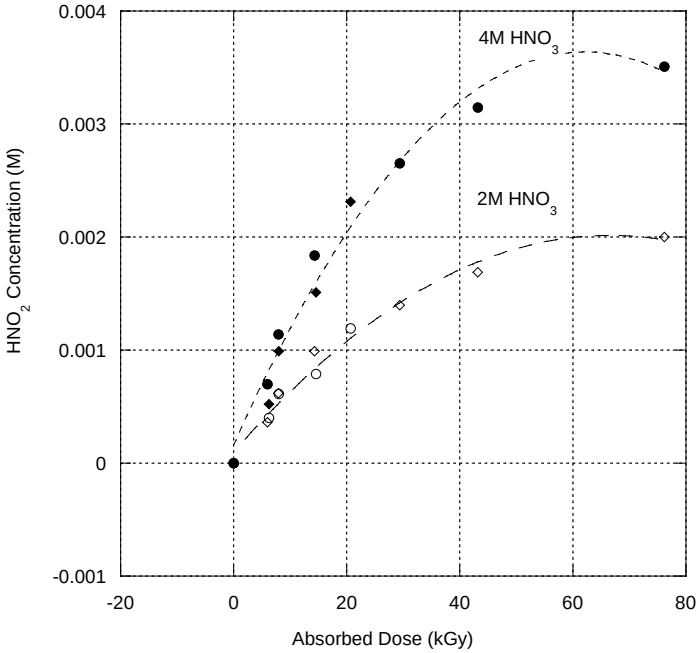
Nitrous Acid generation by radiolysis





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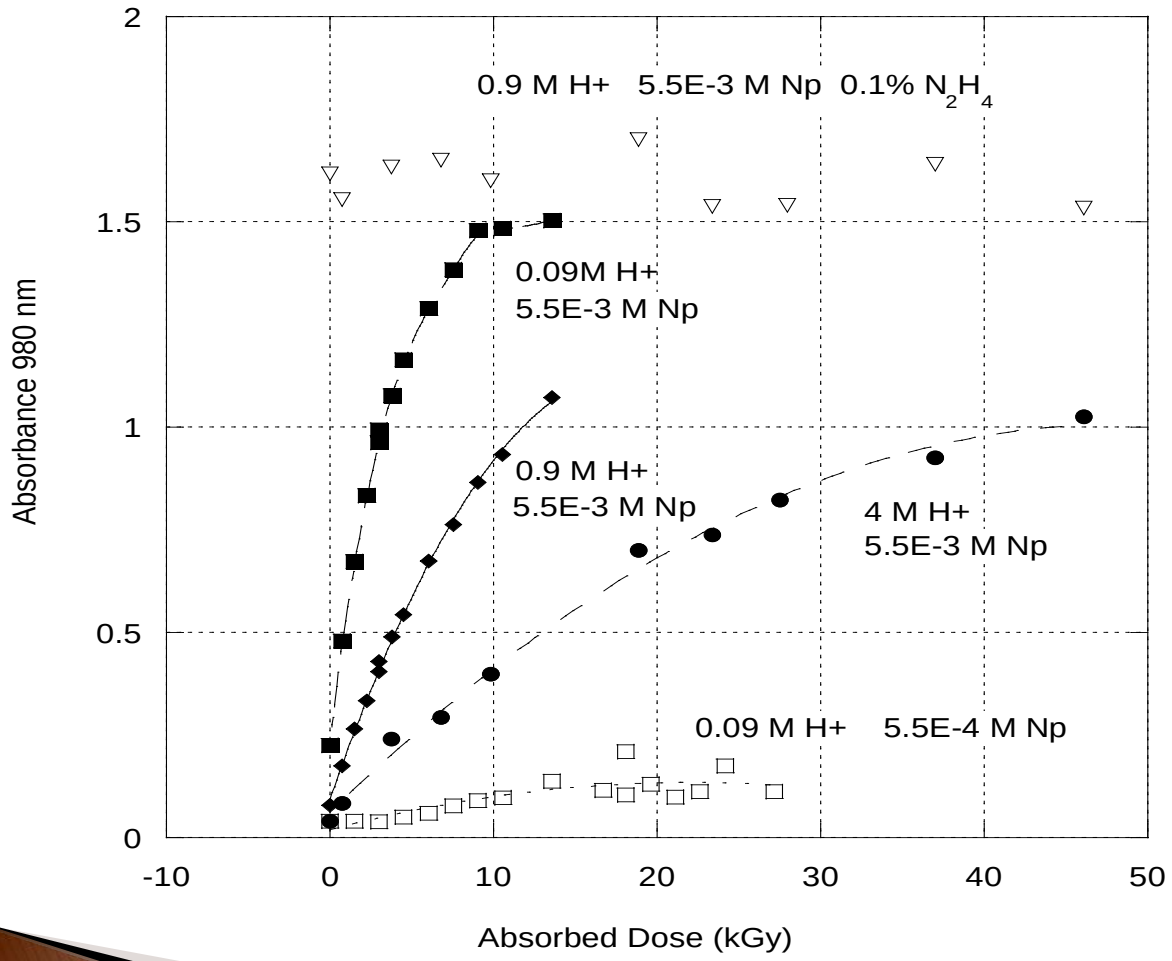

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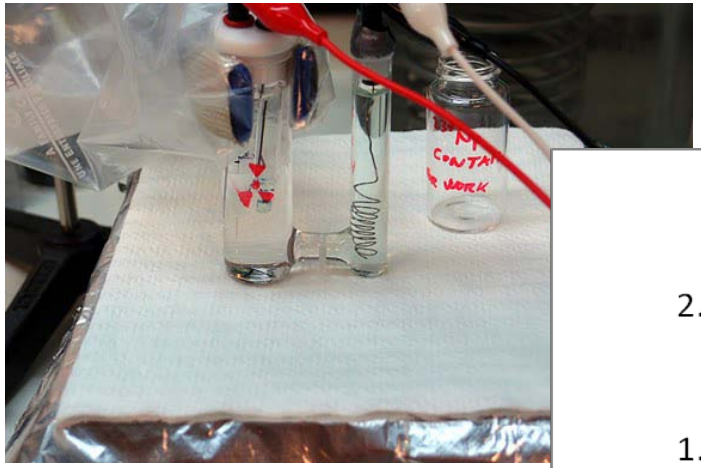
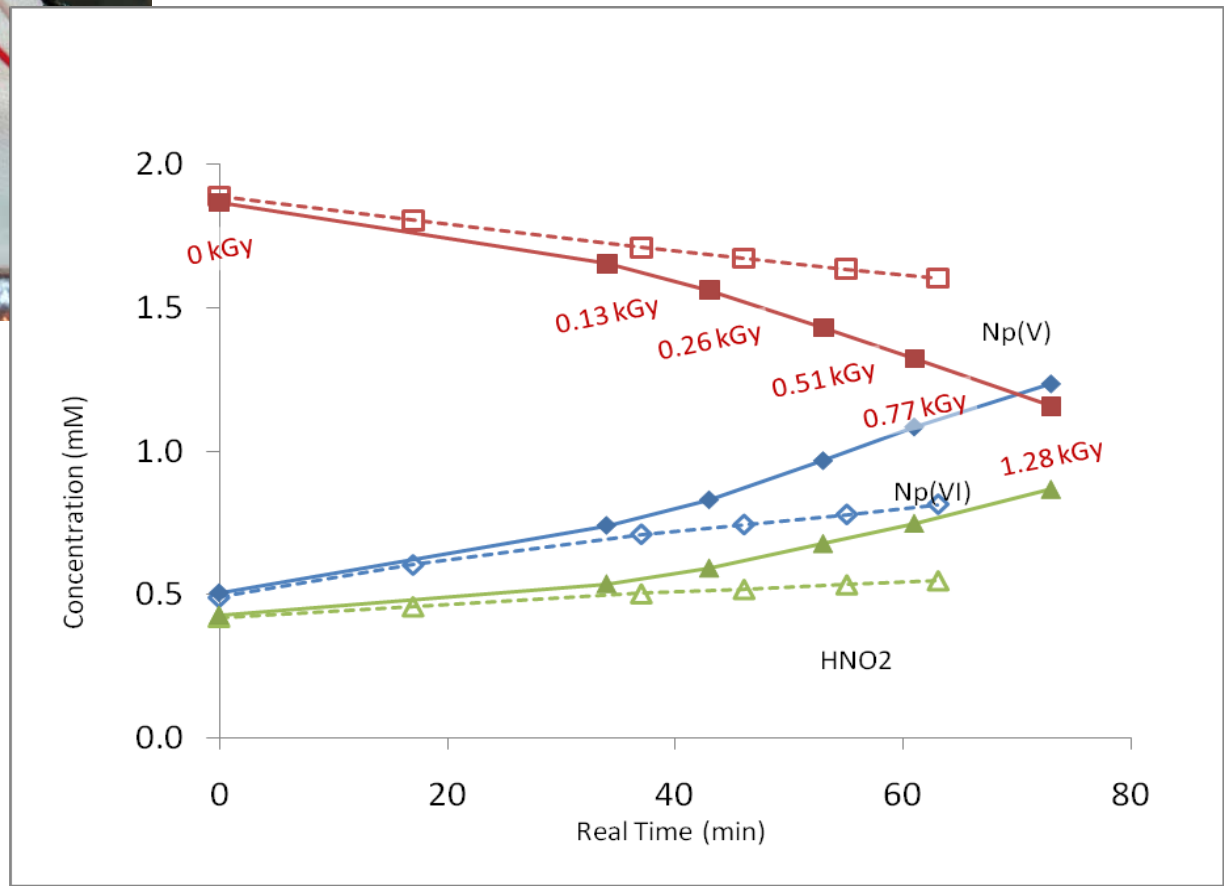
Starting with Np^V



- Preparation of Np^V is difficult in 4 M HNO_3
- Initially got 80% Np^V



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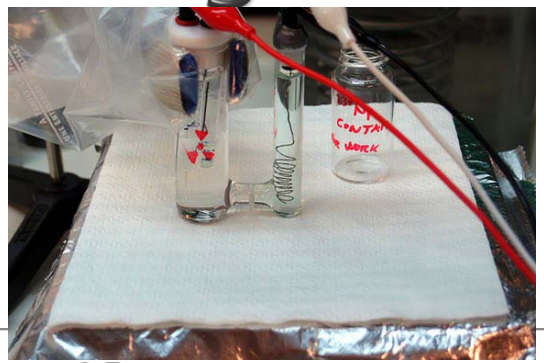
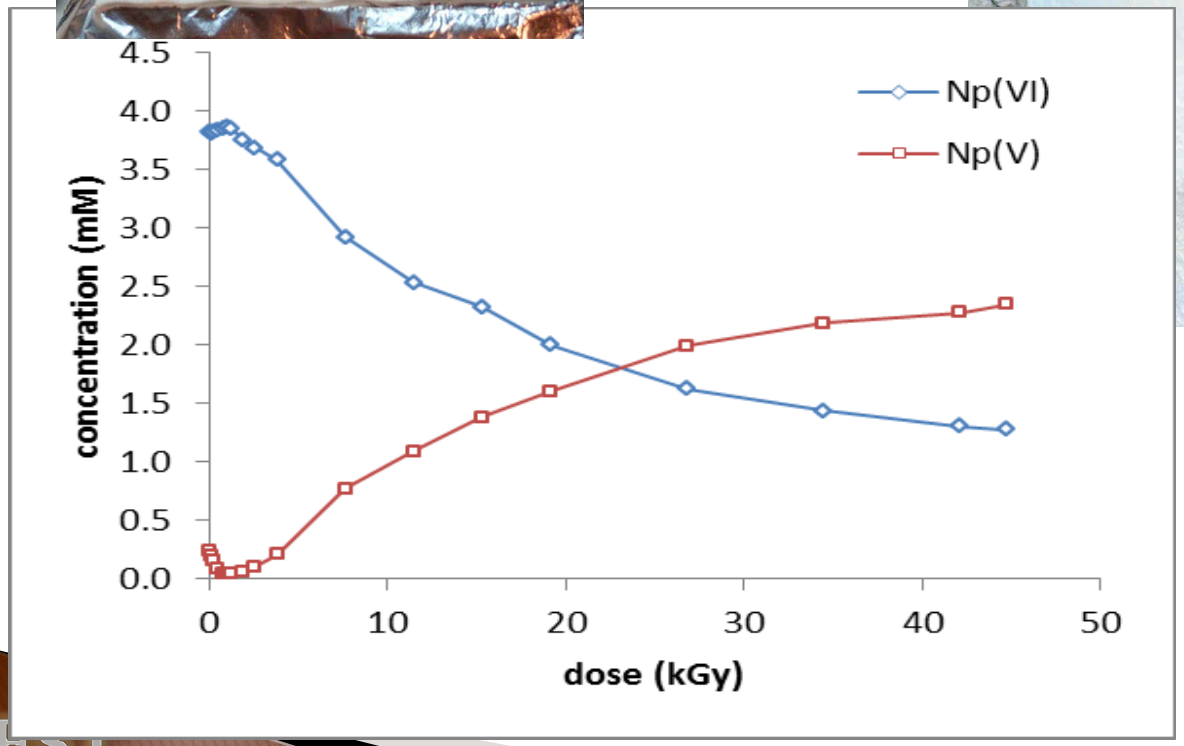
Starting with Np^{VI}



- Initially 94% Np^{VI} in 4M HNO_3



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Let's recap:

- HNO_3 oxidizes Np^{V} to Np^{VI}
- HNO_2 reduces Np^{VI} to Np^{V}
- Irradiation produces an amount of HNO_2 that depends on $[HNO_3]$
- The oxidation of Np^{V} by HNO_3 also produces HNO_2
- No matter what you start with, an equilibrium will be achieved as first reported by Siddall and Dukes:

- $NpO_2^{+} + 3/2\ H^{+} + ½\ NO_3^{-} \leftrightarrow NpO_2^{2+} + ½\ HNO_2 + H_2O$

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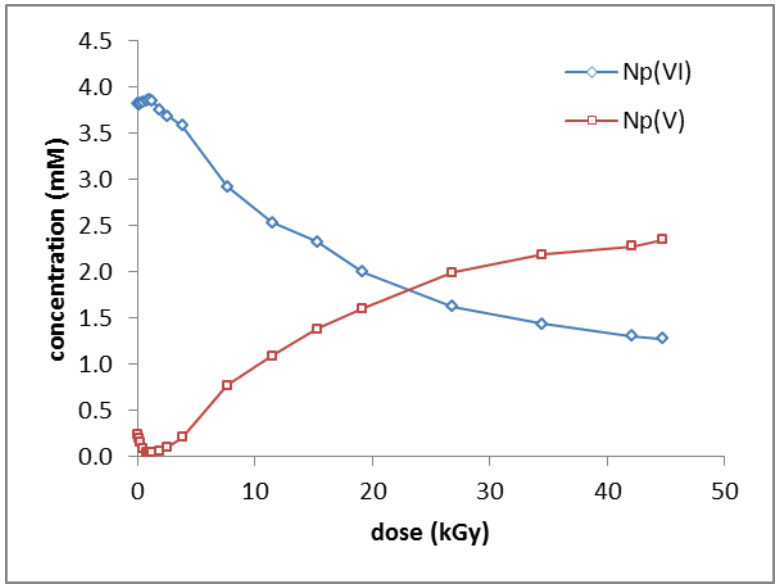
Where does the initial oxidation come from?



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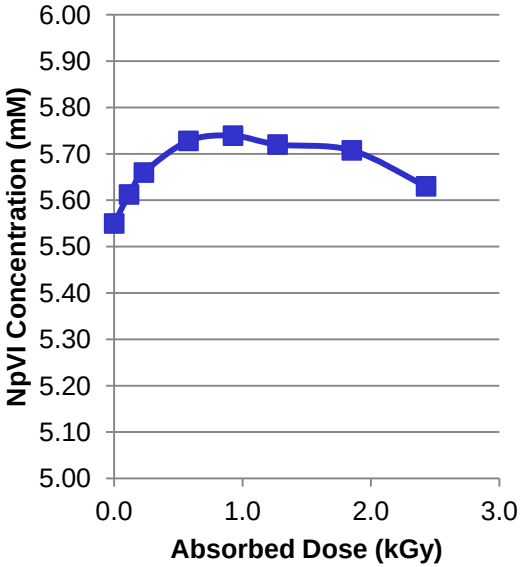
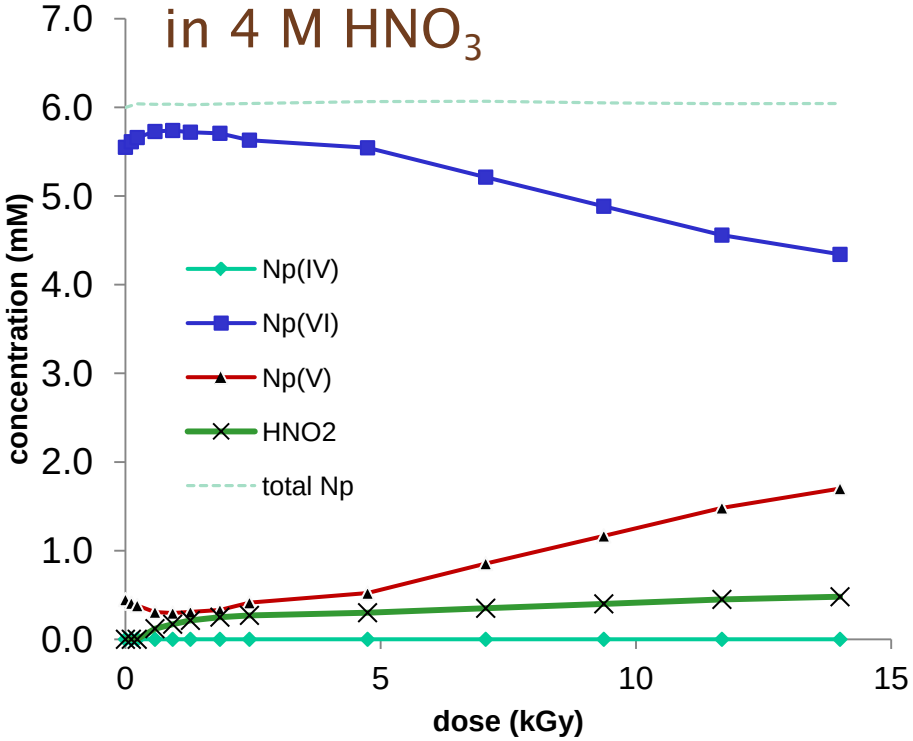
Where does the initial oxidation come from?



Initially 75% Np^{VI}– long-term equilibrium for 6 mM Np in 4 M HNO_3



Initial solution is air saturated

- H_2O –\/\/\→ $\cdot OH + e^-_{aq} + H\cdot + H_2O_2 + H_3O^+ + H_2$

- $e^-_{(aq)} + O_2 \rightarrow O_2^-$ $k = 1.9 \times 10^{10}\ M^{-1}\ s^{-1}$
  - $e^-_{(aq)} + H^+ \rightarrow \cdot H$ $k = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}$
  - $\cdot H + O_2 \rightarrow \cdot HO_2$ $k = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$
- Oxygen is scavenged in the first few kilogray, chemistry switches to reducing.

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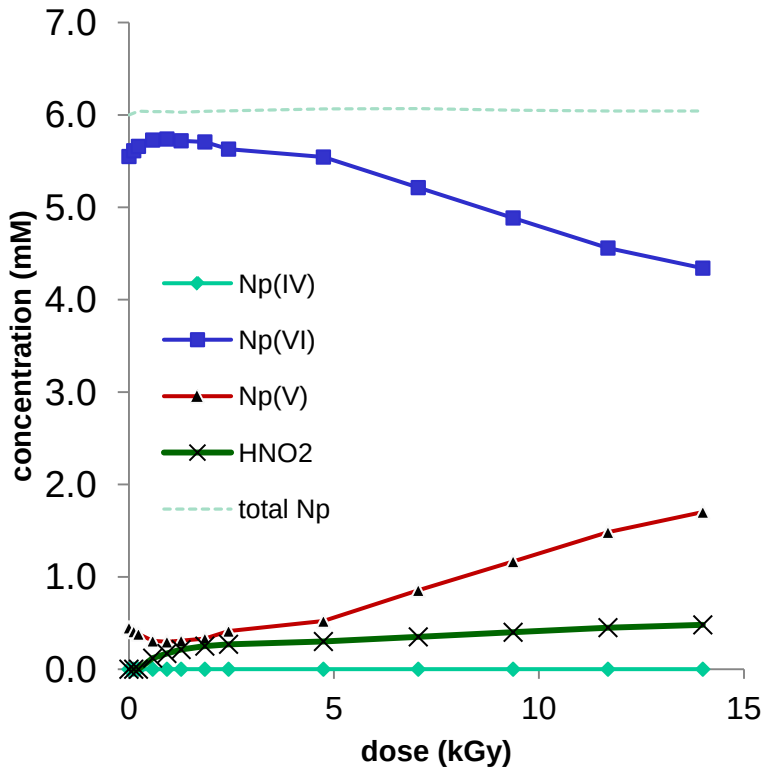
Oxygen plays an important role ?



- HNO_2 grows in during the oxidizing phase– but it is not reacting with Np^{VI}
- As soon as O_2 is gone HNO_2 begins to react with Np^{VI}
- An artifact of our experiment? The process is aerated?

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Can we encourage an oxidizing solution?

- N_2O is used in radiation chemistry to encourage oxidizing conditions…
- $N_2O + H \rightarrow OH + N_2$ $\quad k = 2.1 \times 10^6\ M^{-1}\ s^{-1}$
- $N_2O + e^- + H_2O \rightarrow N_2 + OH^- + \cdot OH$

$k = 9.1 \times 10^9\ M^{-1}\ s^{-1}$

- N_2O sparging should also remove the initial dissolved O_2

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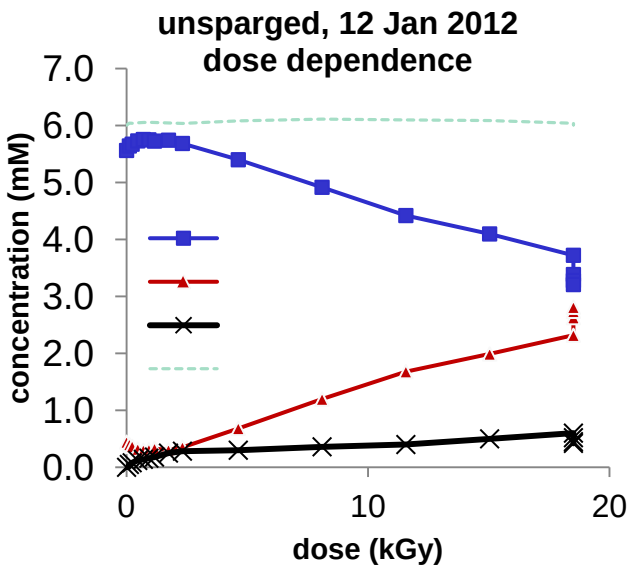
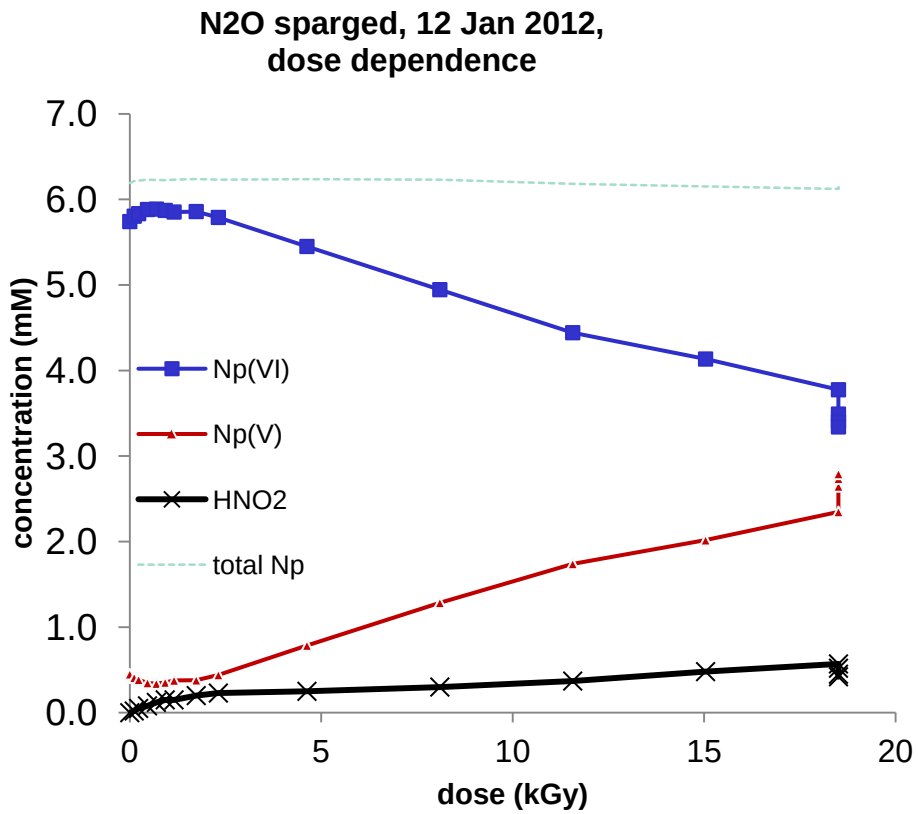
N_2O made no difference at all?

This suggests that neither reducing free radicals or O_2 have anything to do with this chemistry!





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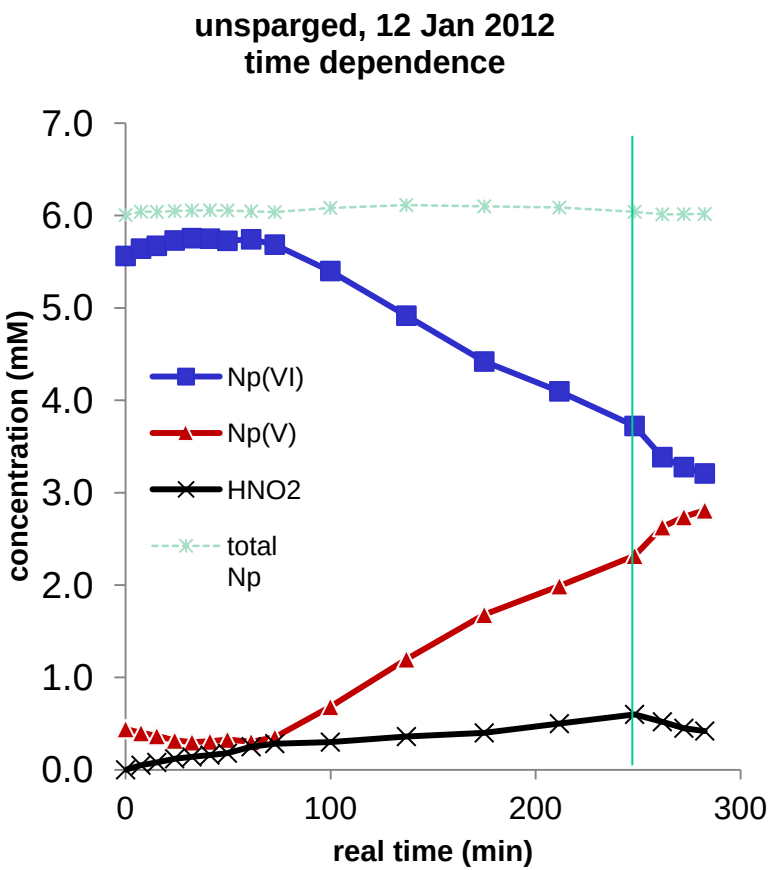
And another thing…

Same data as previous slide, versus time rather than dose.



- Reduction of Np^{VI} continues after the end of the irradiation, expected if its HNO_2.
- The rate of reduction a bit higher? Loss of oxidizing radicals?
- HNO_2 declines after irradiation, lost to Np^{VI} reduction.

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Conclusions

- Rad-produced HNO_2 reduces Np^{VI} in the long run. No evidence of Np^{IV}.
- This effect is limited by scavenging of HNO_2 by rad-produced oxidizing agents, and their oxidation of Np^{V}.
- At low doses, prior to production of sufficient HNO_2, oxidation of Np^{V} predominates. This may also explain Siddall and Dukes observations at very low [HNO_2] where it is the radical source.

Future work

- NO_2 sparging of samples to see if this radical is capable of oxidizing Np^{V}.
- Irradiations in the presence of the organic phase (Np^{IV}?).
- Ultimately, a radiation chemical model is desirable.