REACTOR BASED STUDY OF ALPHA RADIOLYSIS OF EXTRACTION SOLVENTS

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Why Study Radiolysis?

- Chemical methods for separation of fission products from useful actinides are being both developed and used for nuclear fuel recycling and high level waste processing.
- New chemicals may need to be selected for greater efficiency and lower costs.
- Viability of these methods and future selections depends on understanding their behavior in intense radiation fields of the fuel and products to be separated. This radiation includes gamma, beta, and alpha.

Key Recent Review

The Effects of Radiation Chemistry on Solvent Extraction: 1. Conditions in Acidic Solution and a Review of TBP Radiolysis.

Bruce J. Mincher, Gioseppe Modolo and Stephen Mezyk***, Solvent Extraction and Ion Exchange***, 27, 1-25, 2009.

"Only a few studies have been done using high LET radiation"

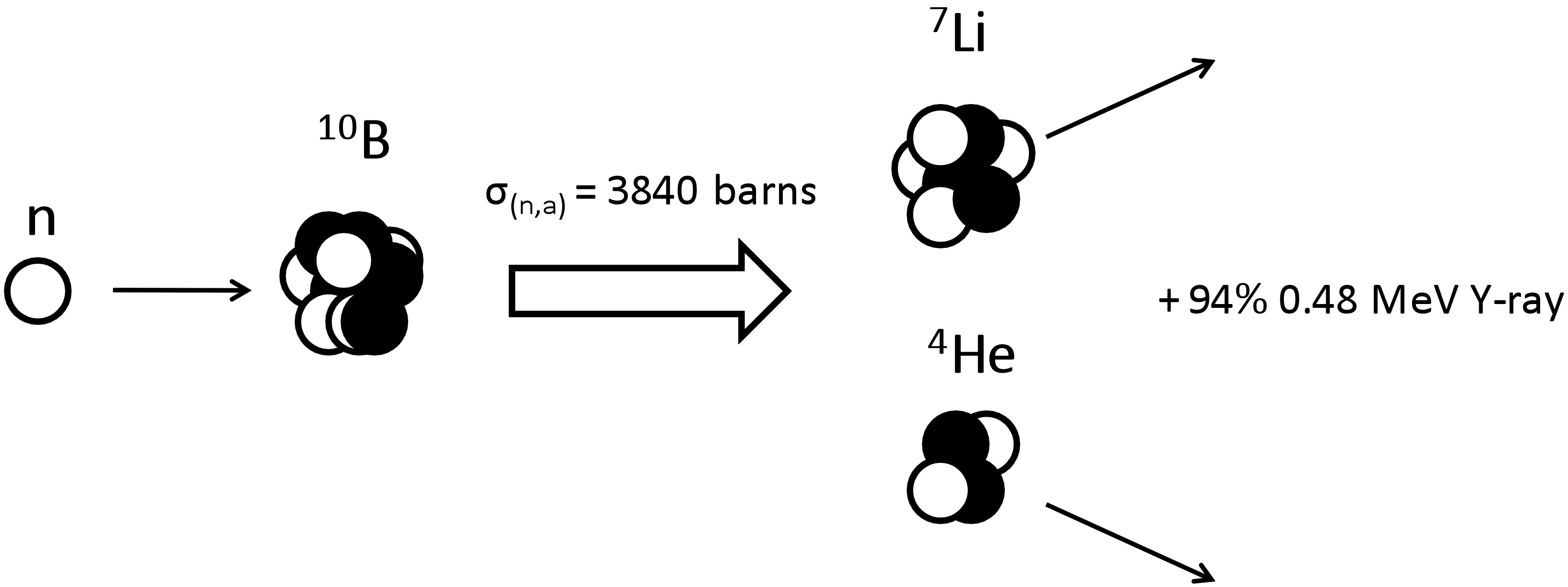
Goals of Our Studies

- 1. Can we reproduce earlier results for alpha radiolysis in aqueous solutions (mostly from 1950's)?
- 2. What are the complications and limits of methods to be used?
- 3. Can radiolysis products from these methods be identified and mechanisms and kinetics evaluated?

Traditional Dosimeter – Fricke (1927-35) Still the best method!

- Oxidation of Fe^{2+} to Fe^{3+} in aqueous solution
- $[Fe^{3+}]$ measured by spectrophotometer at 304 nm
- Solution contains ferrous sulfate, 0.4 M sulfuric acid.
- Can be aerated or de-aerated.
- G = reaction molecules per 100 eV absorbed = 15.5 for γ radiation in aerated water solution.

Add boron (boric acid – H_3BO_3) and irradiate with neutrons



n

^{10}B

$\sigma_{(n,a)} = 3840$ barns

^{7}Li

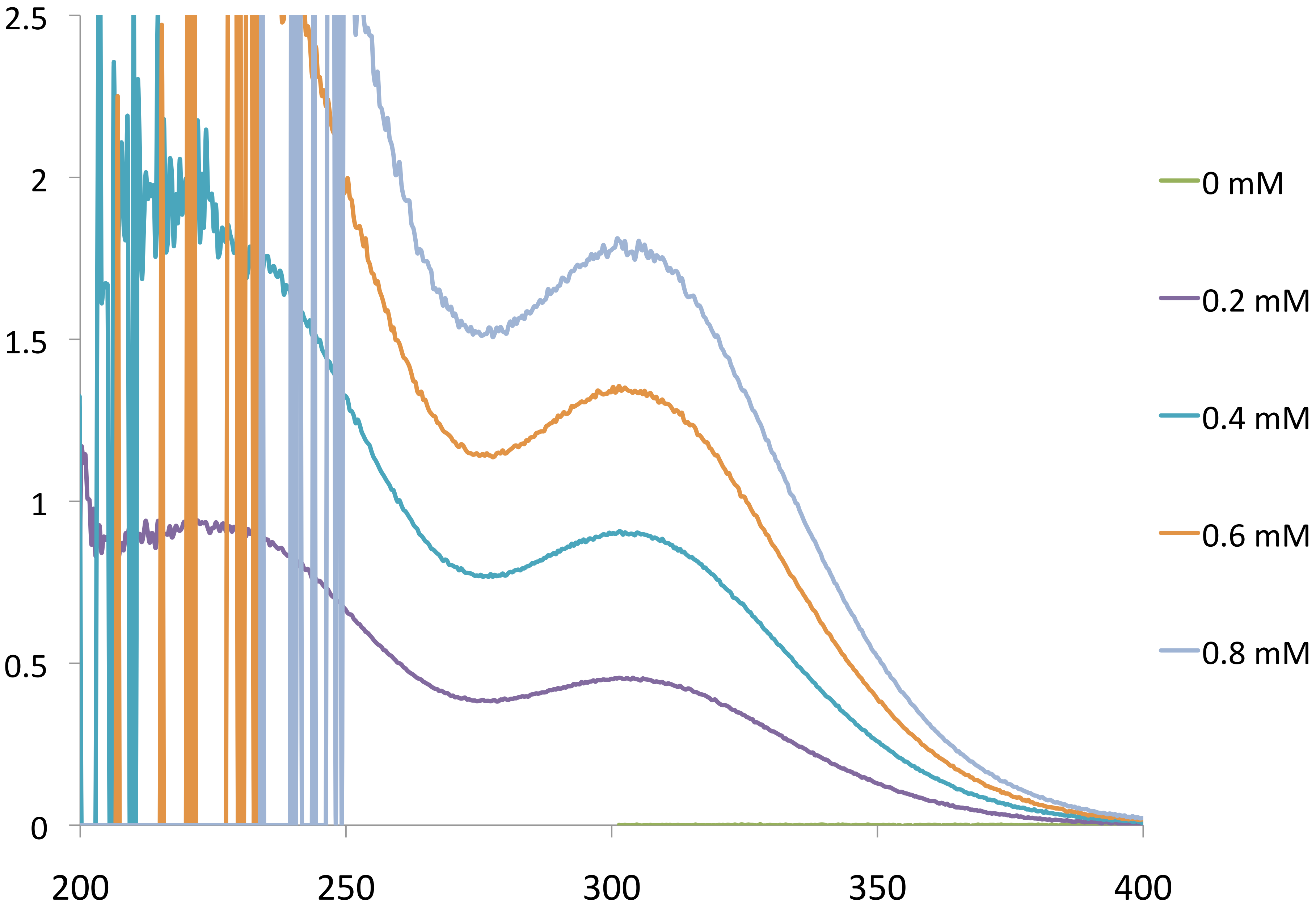
^{4}He

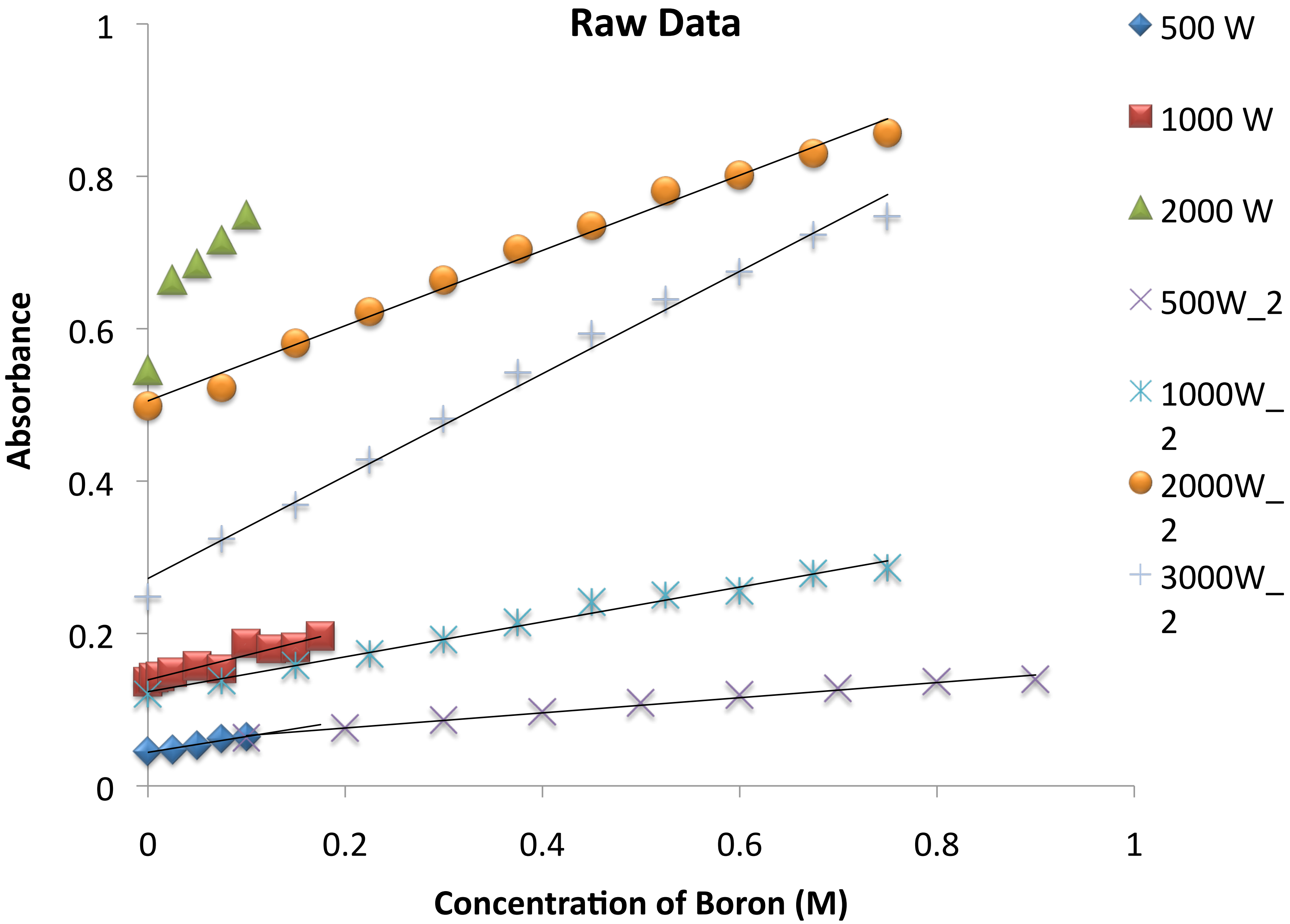
+ 94% 0.48 MeV Y-ray

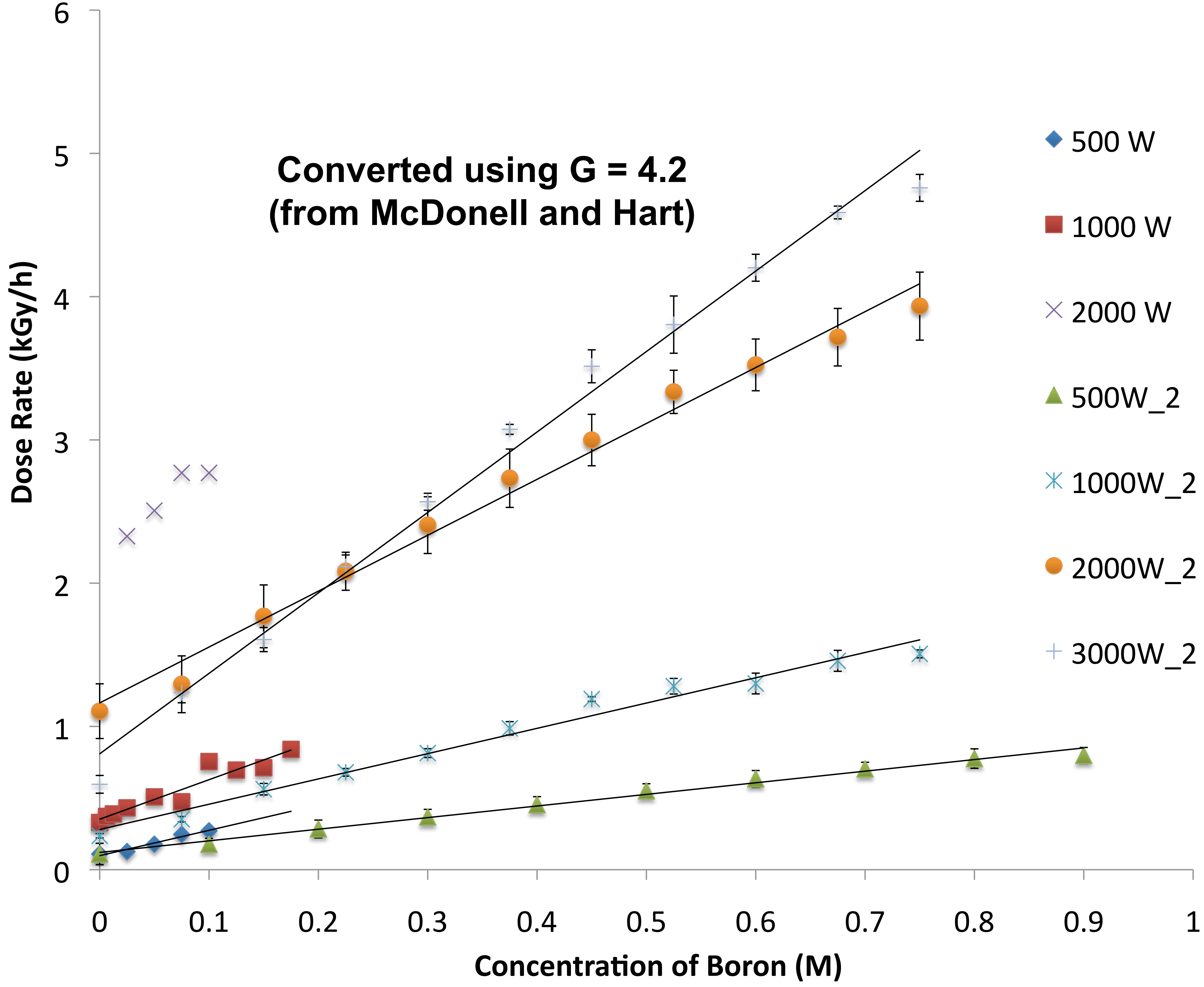
Energy release is 2.79 MeV total

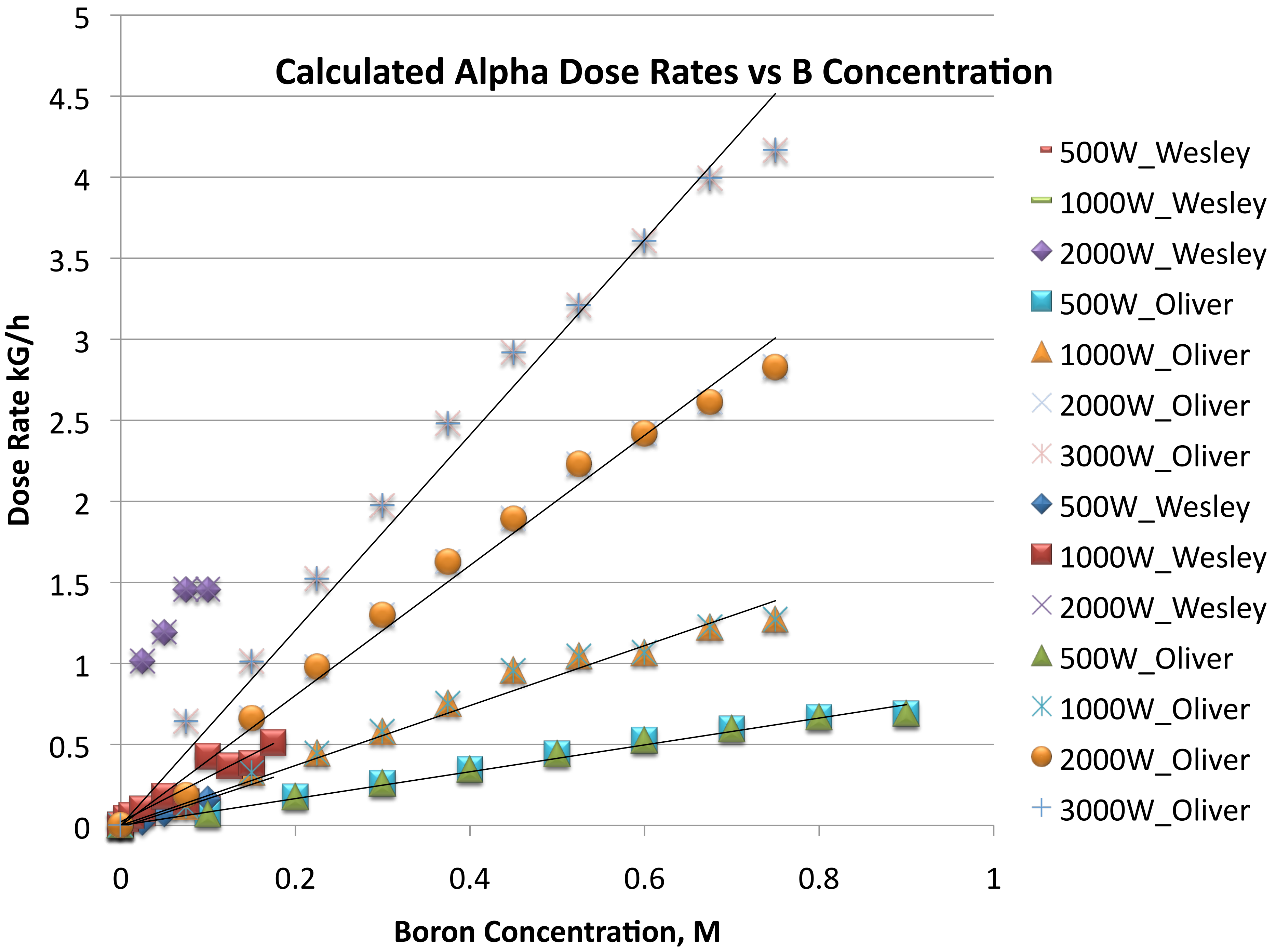
Experimental

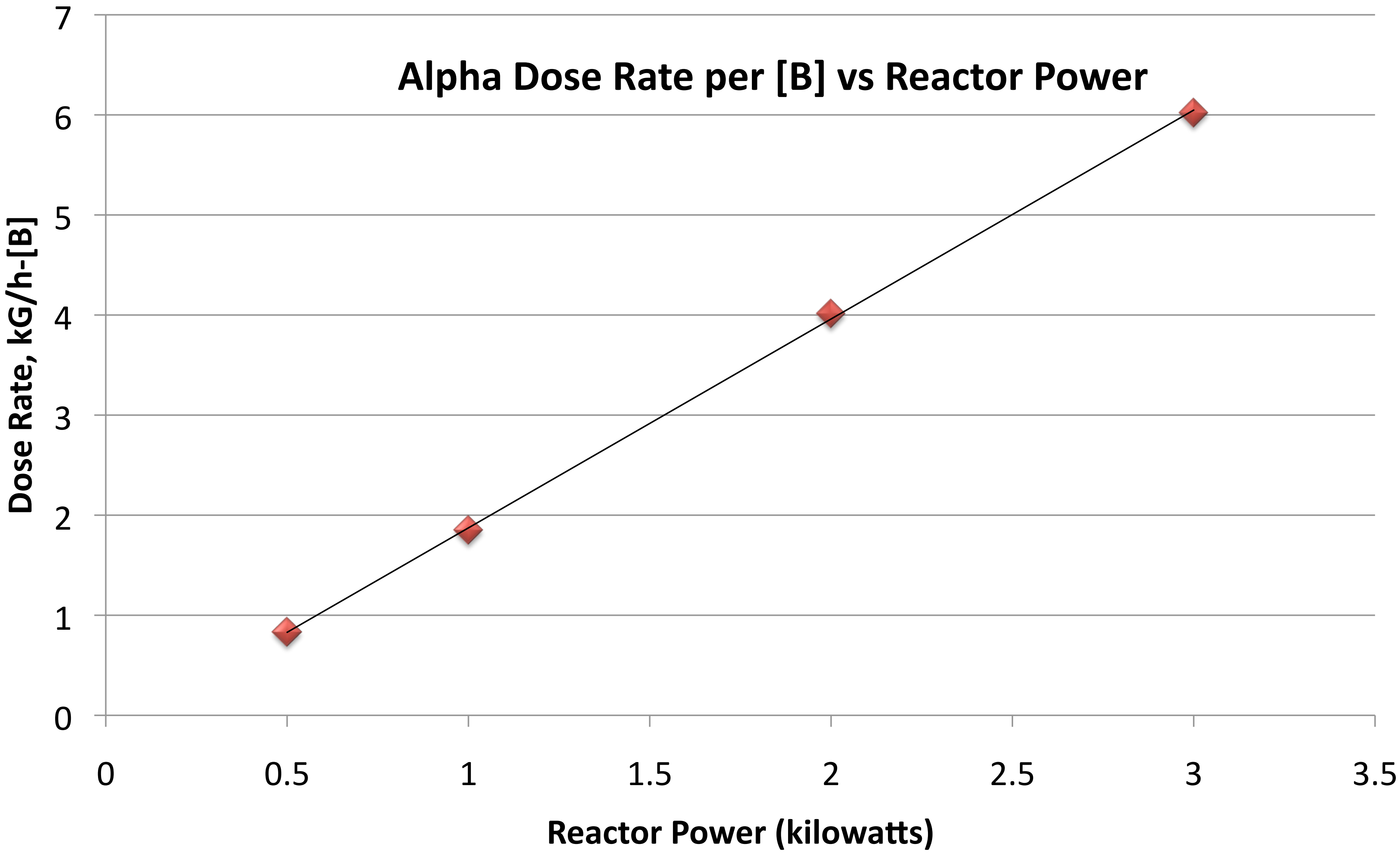
- Solutions made with varying boric acid molarity, otherwise identical
- Solutions placed in small sealed polyethylene vials – but air not excluded
- In Rotating Specimen Rack of TRIGA reactor
- All conducted for 7 minutes at different power levels.


2.5
2
1.5
1
0.5
0
200
250
300
350
400
0 mM
0.2 mM
0.4 mM
0.6 mM
0.8 mM


Raw Data
Absorbance
Concentration of Boron (M)
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
500 W
1000 W
2000 W
500W_2
1000W_2
2000W_2
3000W_2


Converted using G = 4.2
(from McDonell and Hart)
Dose Rate (kGy/h)
0
1
2
3
4
5
6
Concentration of Boron (M)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
◆ 500 W
■ 1000 W
× 2000 W
▲ 500W_2
✳ 1000W_2
● 2000W_2
+ 3000W_2


Calculated Alpha Dose Rates vs B Concentration
Dose Rate kG/h
Boron Concentration, M
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
500W_Wesley
1000W_Wesley
2000W_Wesley
500W_Oliver
1000W_Oliver
2000W_Oliver
3000W_Oliver
500W_Wesley
1000W_Wesley
2000W_Wesley
500W_Oliver
1000W_Oliver
2000W_Oliver
3000W_Oliver


Alpha Dose Rate per [B] vs Reactor Power
Dose Rate, kG/h-[B]
0
1
2
3
4
5
6
7
0
0.5
1
1.5
2
2.5
3
3.5
Reactor Power (kilowatts)

Effects Discovered

1. Increasing neutron rate or fluence increases alpha radiolysis rate or amount.
2. Increasing boron concentration increases alpha radiolysis rate
3. Gamma background contribution can be subtracted successfully
4. Gamma background varies greatly with reactor run status
5. Some correction likely for self absorption at high boron concentrations

Basic Information

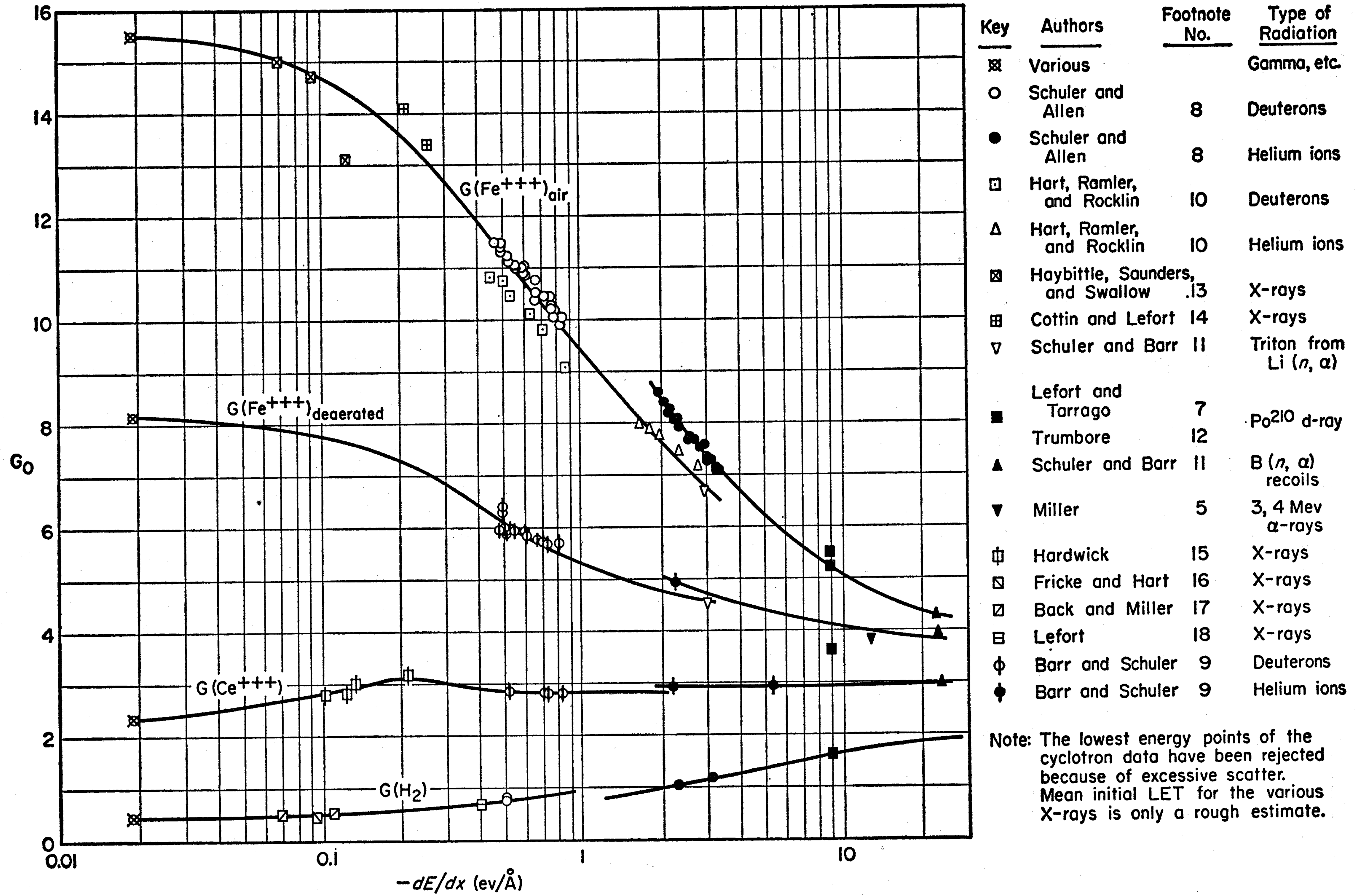
Neutron Flux: 1000 w ≈ 3×10^{9} n-cm^{-2}-sec^{-1}

Fluence (7 min) = 1.3×10^{12} neutrons

Alpha Dose rates in the region of a few kG/hr are readily attained

Advantage of the TRIGA Reactor

- Rotating rack – many specimens equal fluence
- Readily controlled at low power
- If low operating schedule – background can be lower.



Key	Authors	Footnote No.	Type of Radiation
⊠	Various		Gamma, etc.
○	Schuler and Allen	8	Deuterons
●	Schuler and Allen	8	Helium ions
⊡	Hart, Ramler, and Rocklin	10	Deuterons
△	Hart, Ramler, and Rocklin	10	Helium ions
⊠	Haybittle, Saunders, and Swallow	13	X-rays
⊞	Cottin and Lefort	14	X-rays
▽	Schuler and Barr	11	Triton from Li (n, α)
■	Lefort and Tarrago Trumbore	7 12	Po^{210} d-ray
▲	Schuler and Barr	11	B (n, α) recoils
▼	Miller	5	3, 4 Mev α-rays
◫	Hardwick	15	X-rays
⧅	Fricke and Hart	16	X-rays
⧄	Back and Miller	17	X-rays
⊟	Lefort	18	X-rays
ϕ	Barr and Schuler	9	Deuterons
●	Barr and Schuler	9	Helium ions

Note: The lowest energy points of the cyclotron data have been rejected because of excessive scatter. Mean initial LET for the various X-rays is only a rough estimate.

Influence of LET on water radiolysis (Allen)

Continued work

- Close work with NMR analysis to look at products and effects on separation/extraction reactions.
- Effects may not be the same as much studied gamma radiolysis.

REFERENCES TO EARLY WORK

1. Fricke, H and S. Morse, Am J. Roentgenol. Radium Therapy, 1927. 18, p 430.
2. McDonell, W.R. and E.J. Hart, *Oxidation of Aqueous Ferrous Sulfate Solutions by Charged Particle Radiations.* Journal of the American Chemical Society, 1954. **76**(8): p. 2121-2124.
3. Schuler, R.H. and N.F. Barr, *Oxidation of Ferrous Sulfate by Ionizing Radiations from (n, α) Reactions of Boron and Lithium.* Journal of the American Chemical Society, 1956. **78**(22): p. 5756-5762.