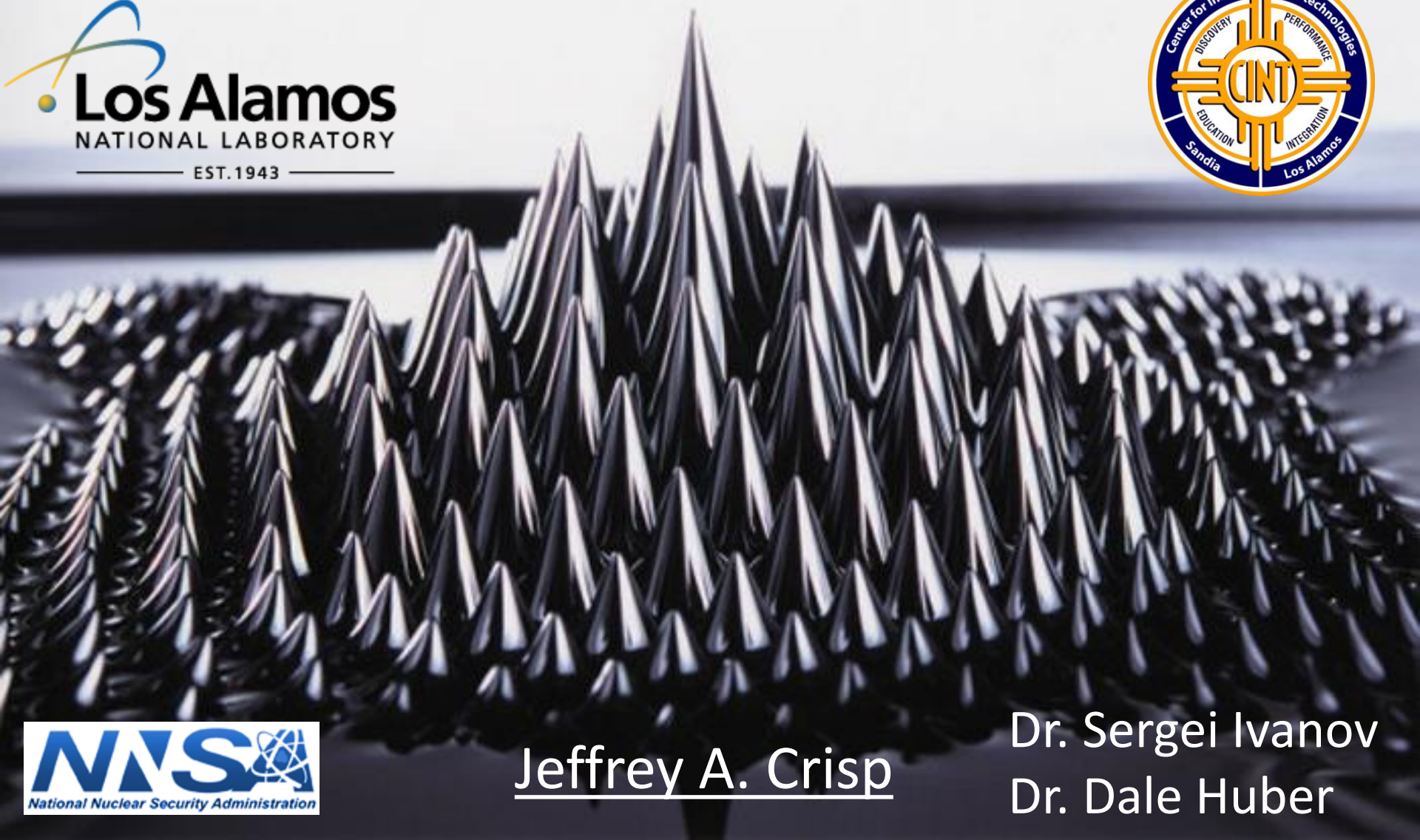


# Synthesis of Magnetite Nanoparticles through Select Iron(III) Carboxylate Precursors

SAND2013-3730C

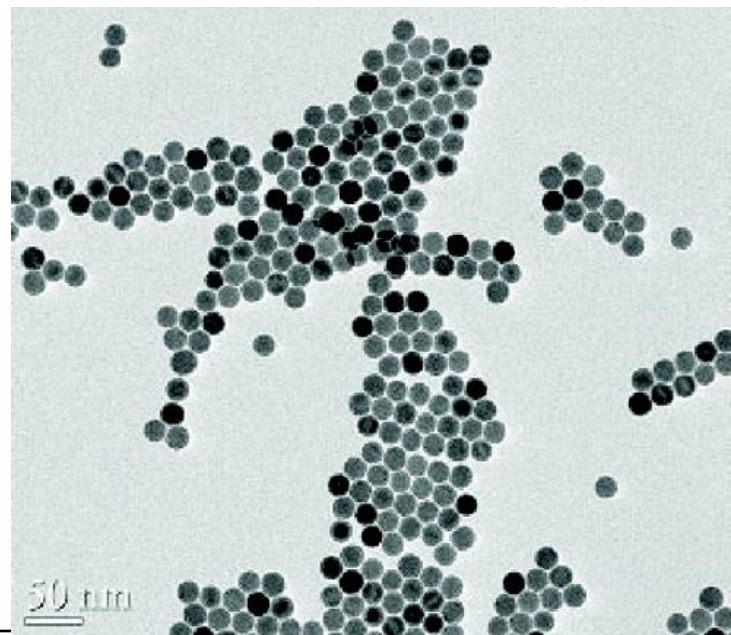


Jeffrey A. Crisp

Dr. Sergei Ivanov  
Dr. Dale Huber

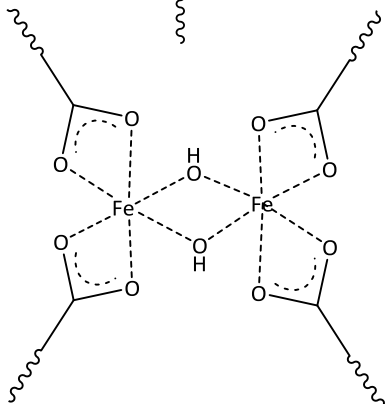
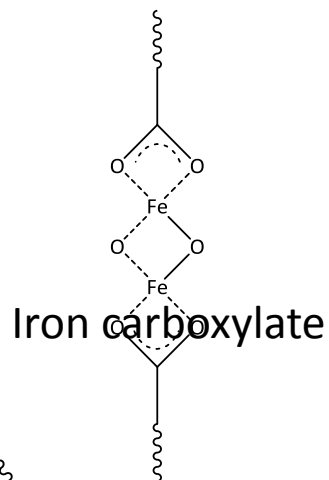
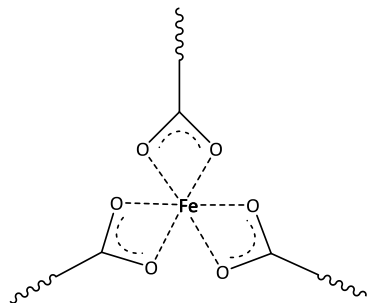
# Usefulness of Magnetite Nanoparticles

- Ferrofluids
- MRI contrast agents
- Magnetic data storage
- Magnetic field assisted cancer detection



(Oswald, P. *et al*; *Magnetic Resonance Imaging* **1997**)  
(Frolov, G. I.; *Tech. Phys.* **2001**)  
(Jordan, A. *et al*; *J. Magn. Magn. Mater.* **1999**)

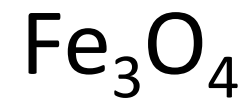
# General Synthesis of Magnetite

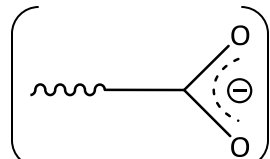


Thermodynamic decomposition  
inert atmosphere



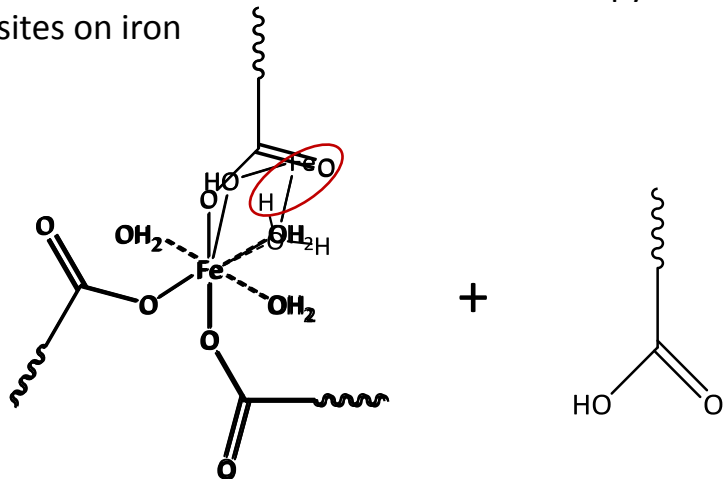
Gentle oxidation



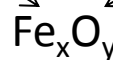
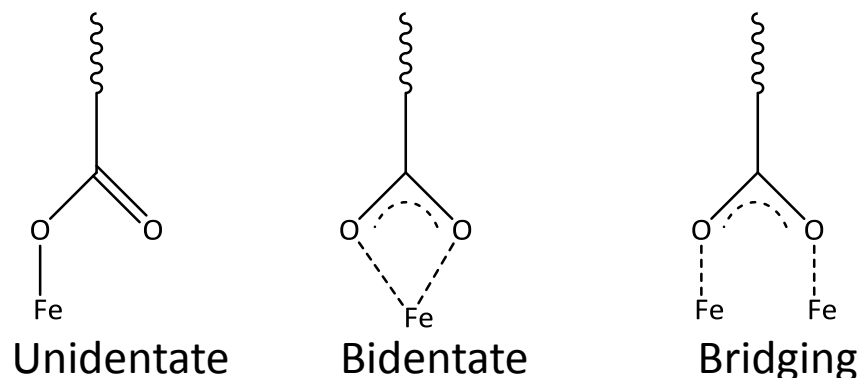
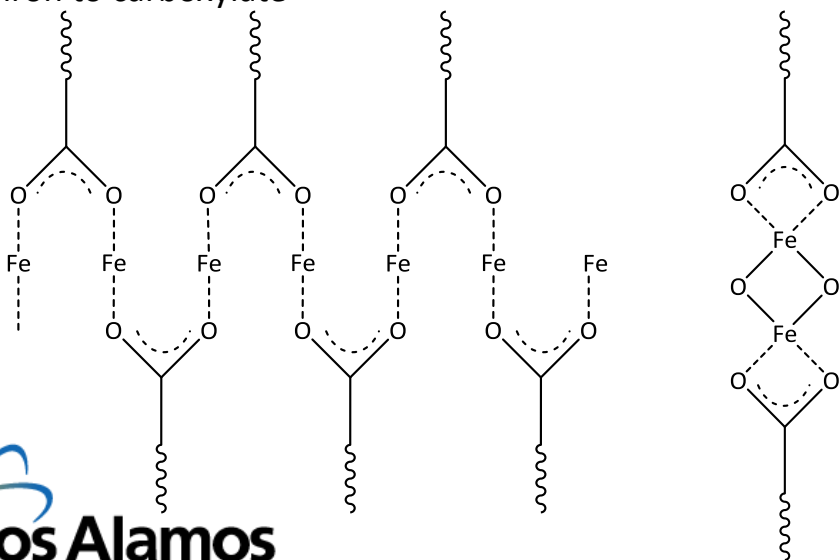
Where  is typically a long chain carboxylate

# Carboxylate Coordination to Iron

- Promote unidentate coordination: occupy coordination sites on iron

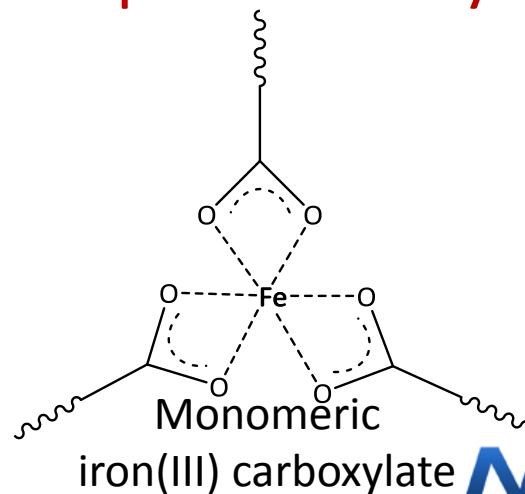


- Promote bridging coordination: high concentration of iron to carboxylate

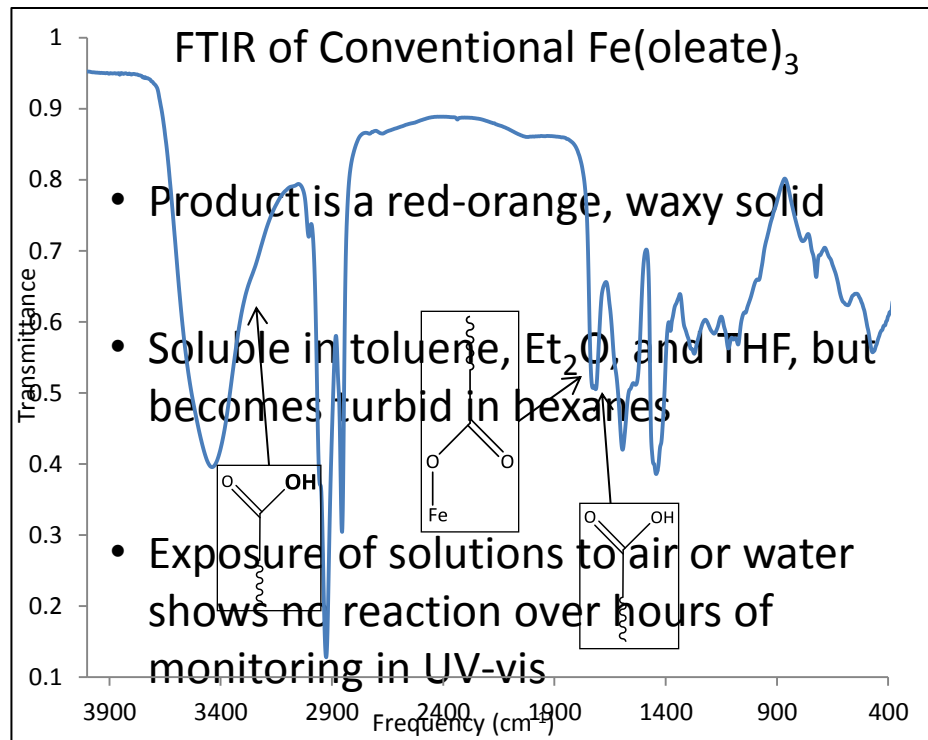
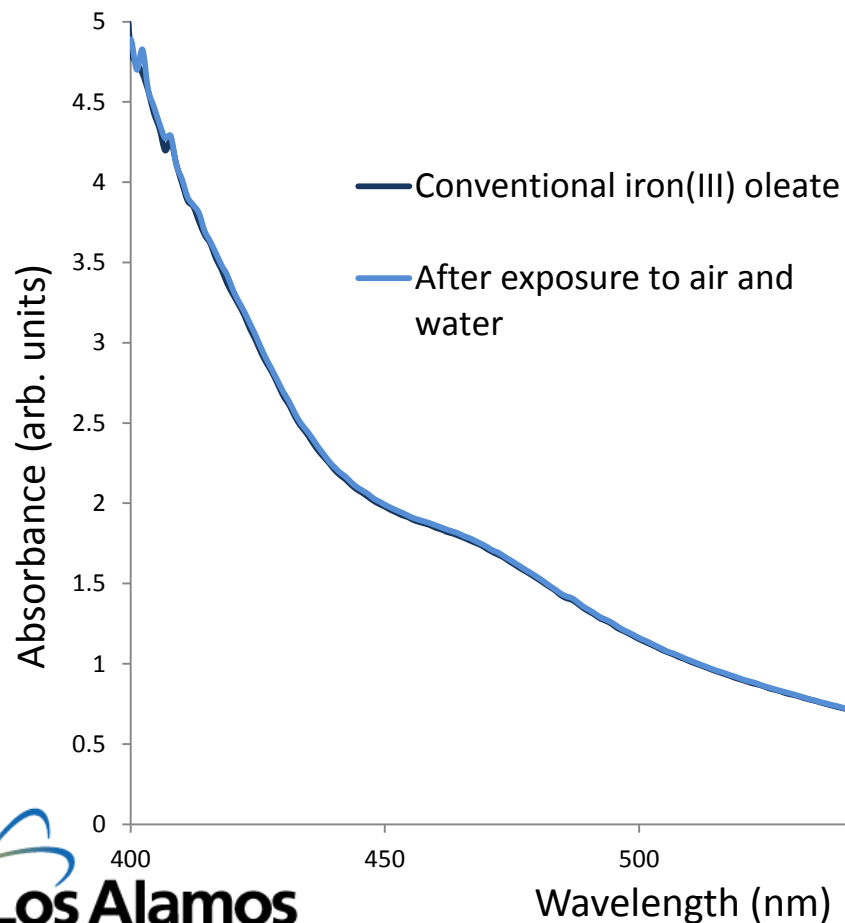
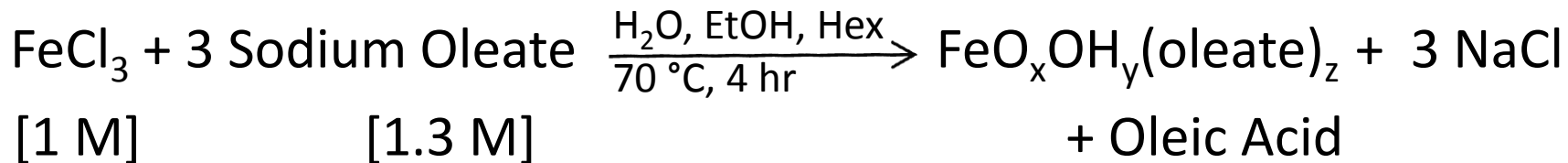


Why do we care about coordination mode?

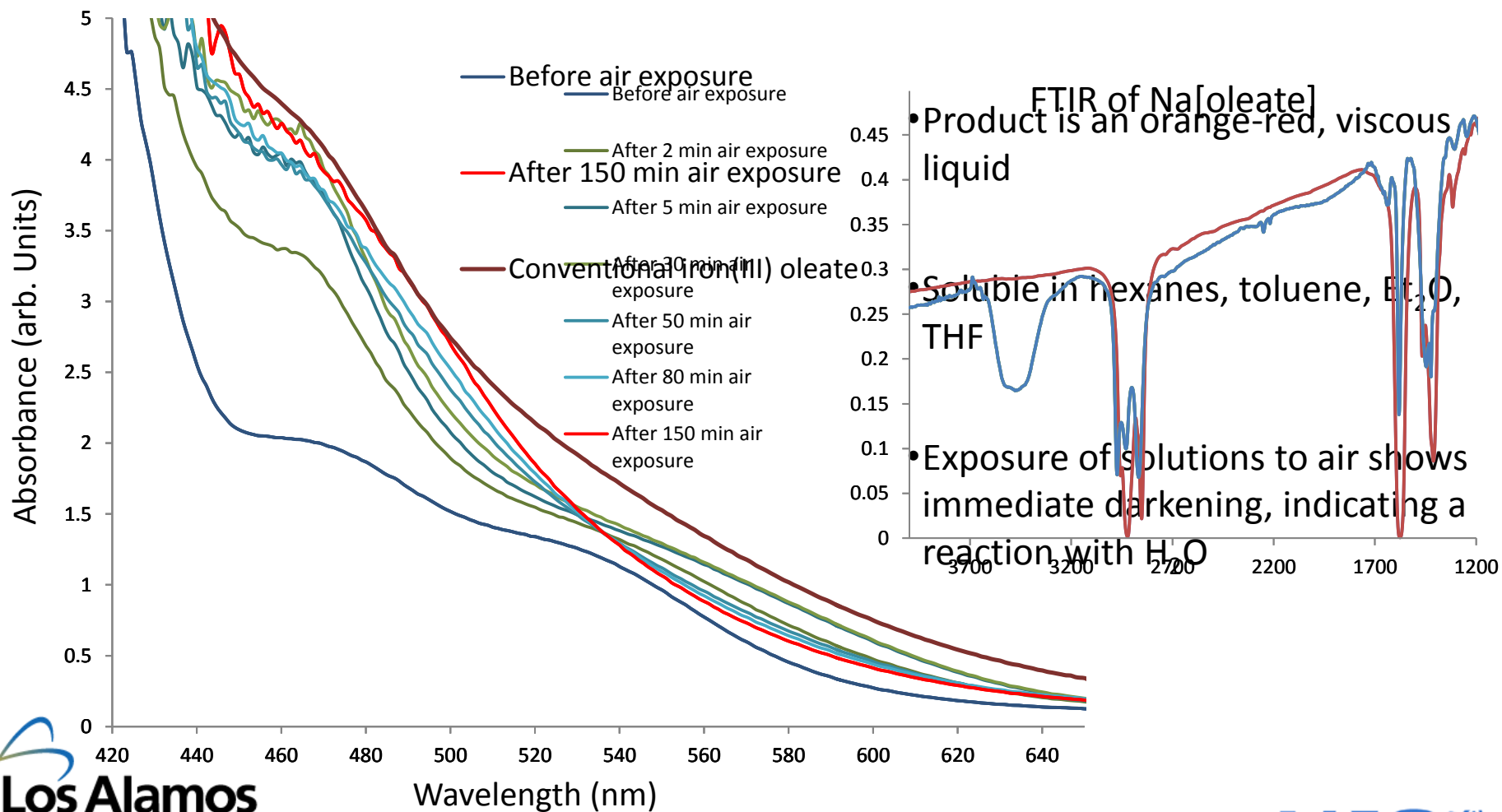
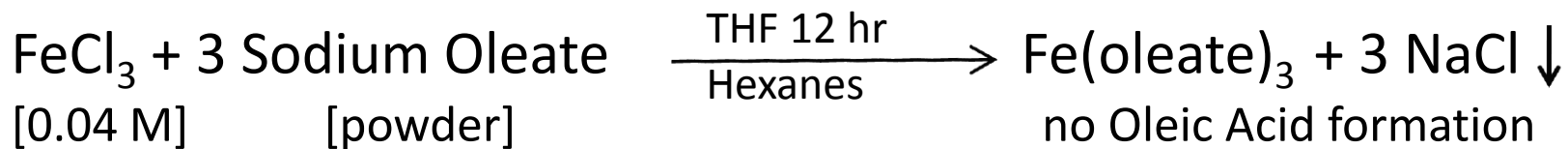
**Reproducibility!**



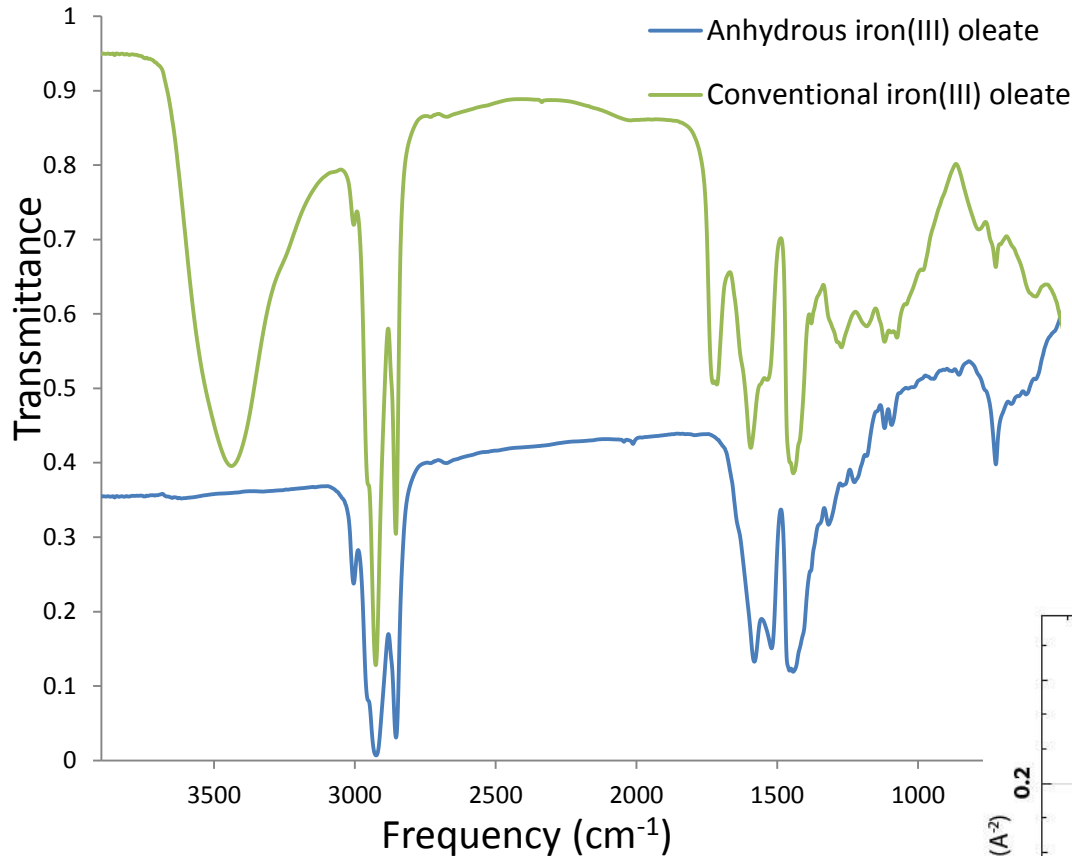
# Conventional Synthesis of Iron(III) oleate



# Anhydrous Synthesis of Iron(III) oleate

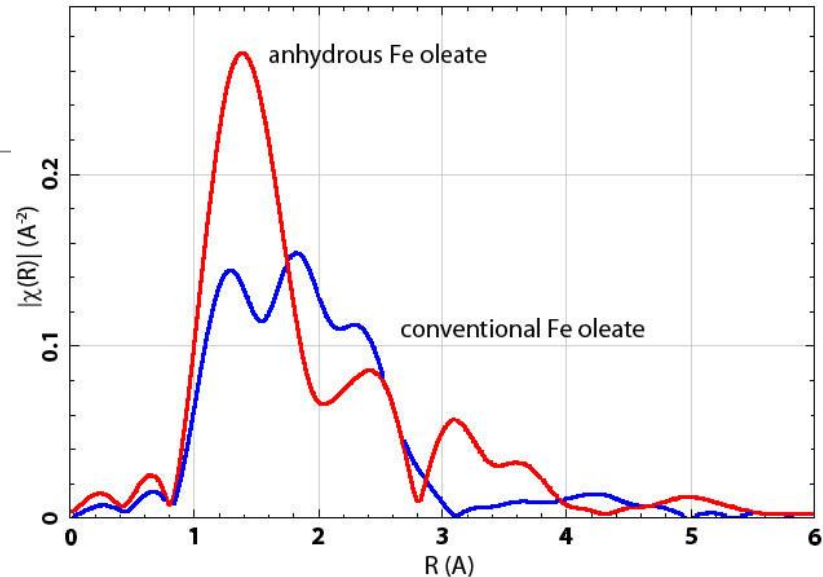


# FTIR and XAFS of Iron(III) oleate

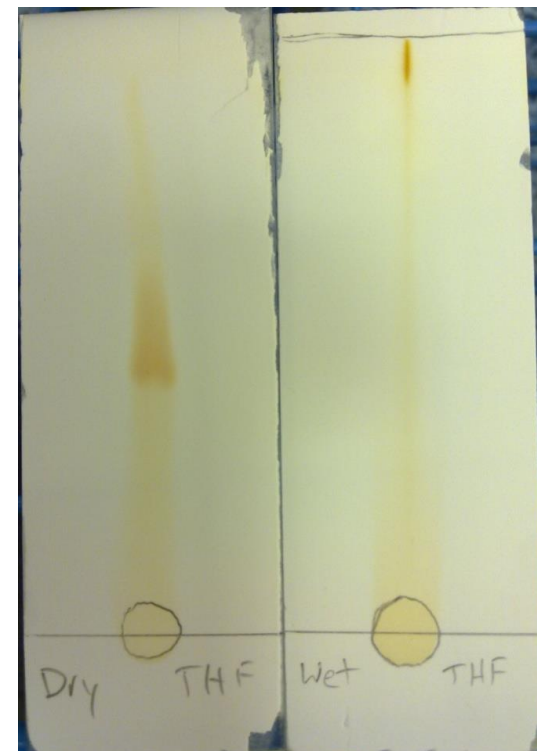
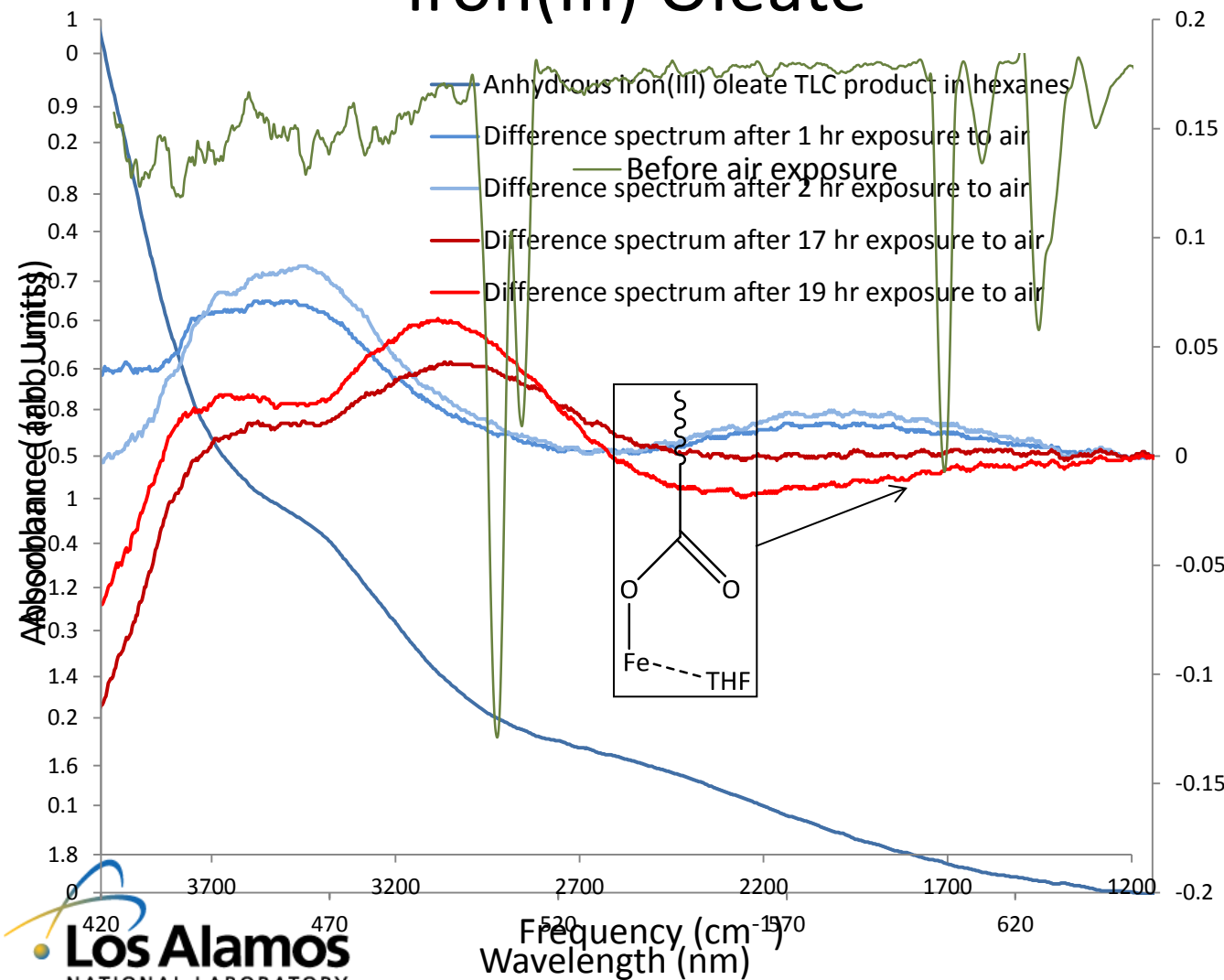


*Preliminary XAFS data shows a consistency with a single type of Fe–O distance for the anhydrous material; however, the data for the conventional material point to multiple Fe–O distances.*

FTIR of anhydrous iron(III) oleate shows no indication of free oleic acid, unidentate oleate coordination, or iron hydroxide bonding.

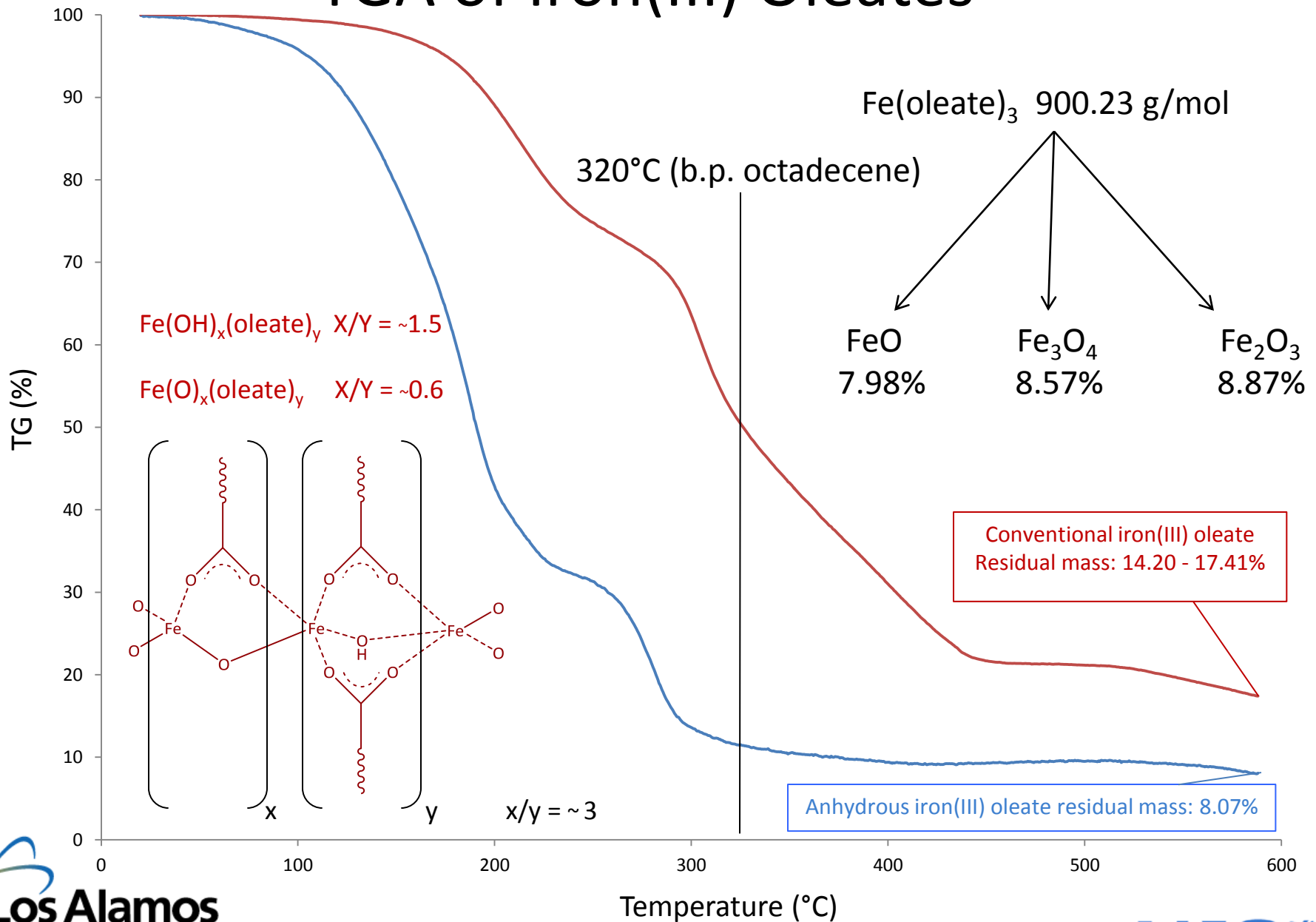


# Absorbance and FTIR Spectroscopy of Preparative TLC Product of Anhydrous Iron(III) Oleate

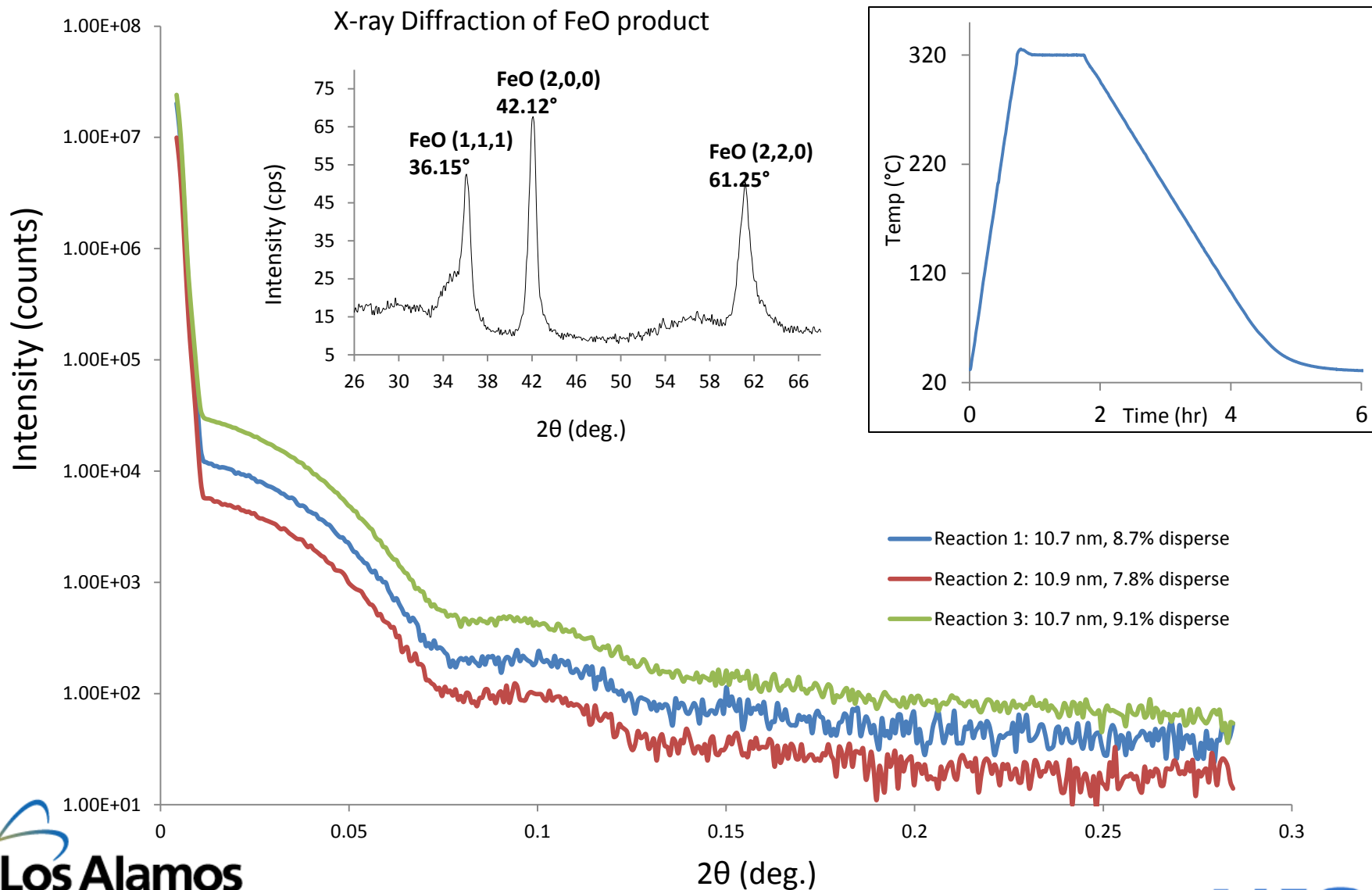


- RF = 0.5  
(anhydrous  $\text{Fe}(\text{oleate})_3$ )
- RF = 1  
(conventional  $\text{Fe}(\text{oleate})_3$ )
- After 15 min of exposure to air prior to TLC, both the anhydrous and conventional  $\text{Fe}(\text{oleate})_3$  have an RF = 1.

# TGA of Iron(III) Oleates



# Size Analysis using Small Angle X-ray Scattering



# Conclusions

- Iron(III) carboxylate compositions are difficult to reproduce when synthesized in water due to the oxophilicity of iron and the resultant side reactions.
- Water and oxygen-free syntheses of iron(III) carboxylates yield consistent products without hydroxide or oxide bridges.
- Anhydrous iron(III) oleate decomposes at lower temperatures, allowing for more solvent systems.
- Anhydrous iron(III) carboxylates yield iron oxide products with a higher batch to batch reproducibility than the conventional counterpart.



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