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Lanthanide surrogate development for actinide aerosol waste

Timothy J. Boyle, Josh Hubbard,

Xavier J. Robinson, Fernando (NMI) Guerrero, Taylor Setteceri

Sandia National Laboratories
Advanced Materials Laboratory
1001 University Blvd SE
Albuquerque, NM 87106
tjboyle@sandia.gov

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“Red Oil” explosions have occurred in liquid-liquid extraction of actinide wastes

Six explosions have occurred world wide:

- Hanford Site (1953)
- Savannah River Site (1953 and 1975)

- Tomsk-7 Seversk Russia (1993)

$UO_2(NO_3)_2$ + TBP/kerosene ⟶

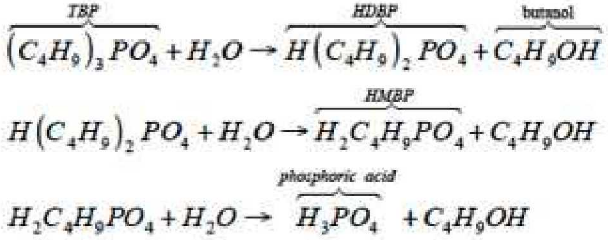
Defense Nuclear Facilities Safety Board “CONTROL OF RED OIL EXPLOSIONS IN DEFENSE NUCLEAR FACILITIES 2003” (DNFSB/TECH-33) Randall N. Robinson, David M. Gutowski, William Yeniscavich (2003).

- red oil: a substance of nonspecific composition formed when an organic phase consisting of TBP and diluent is in contact with concentrated nitric acid is heated above 120°C under reflux.

- The red color imparted to the organic phase is believed to be nitrated organic species.

- produced in contact with less than 10 M nitric acid, but only at temperatures above 137°C (Enos, 2002)

- Red oil can also be produced with pure TBP in contact with boiling 14.9 M nitric acid under total reflux.



$$\overbrace{(C_4H_9)_3PO_4}^{TBP} + H_2O \rightarrow \overbrace{H(C_4H_9)_2PO_4}^{HDBP} + \overbrace{C_4H_9OH}^{butanol}$$

$$H(C_4H_9)_2PO_4 + H_2O \rightarrow \overbrace{H_2C_4H_9PO_4}^{HMBP} + C_4H_9OH$$

$$H_2C_4H_9PO_4 + H_2O \rightarrow \overbrace{H_3PO_4}^{phosphoric\ acid} + C_4H_9OH$$

Conditions for Runaway Red Oil Explosion

- The presence of TBP in organic phase
- Organic phase in contact with nitric acid greater than 10 M
- Solution temperature greater than 130°C
- Insufficient venting area

Exacerbators

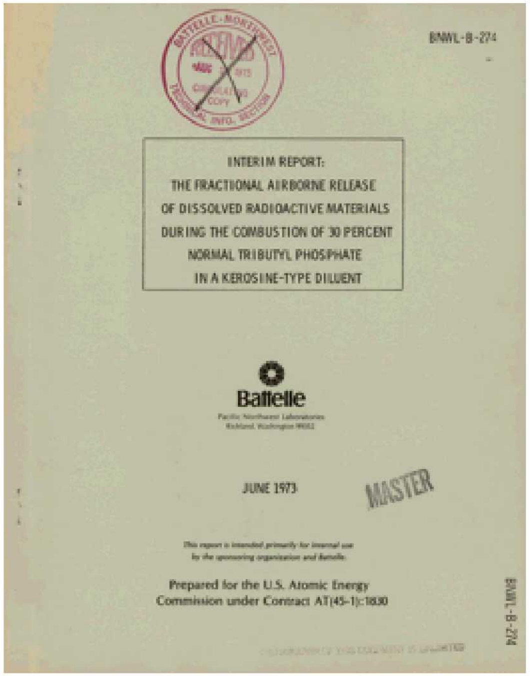
- The presence of a diluent
- The presence of metal ions in the aqueous phase that can solvate with TBP in the organic phase and cause phase inversion

Controls

- Temperature: maintain at less than 130°C.
- Pressure: provide a sufficient vent for the process.
- Mass: remove organics from the process.
- Concentration: maintain nitric acid less than 10 M.

BNWL-B-274 report from 1973 is the basis of actinide aerosol particulate waste release data.

BNWL-B-274 describes the original experimental apparatus (1973). Shown below.



BATTELLE-NORTHWEST RECEIVED 1973 CIRCULATING COPY TECHNICAL INFO. SECTION

BNWL-B-274

INTERIM REPORT:
THE FRACTIONAL AIRBORNE RELEASE
OF DISSOLVED RADIOACTIVE MATERIALS
DURING THE COMBUSTION OF 30 PERCENT
NORMAL TRIBUTYL PHOSPHATE
IN A KEROSINE-TYPE DILUENT

Battelle
Pacific Northwest Laboratories
Richland, Washington 99352

JUNE 1973

MASTER

This report is intended primarily for internal use by the sponsoring organization and Battelle.

Prepared for the U.S. Atomic Energy
Commission under Contract AT(45-1):1830

BNWL-B-274

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

- The fractional airborne release of the isotopes evaluated was < 1 % except for ^{131}I (lost up to the time of self-extinguishment (~65 %)).
- Iodine sublimes at 84 ^{O}C and methyl iodide boils at 42.5 ^{O}C, high releases are not surprising.
- The fractional release of the remaining materials - U, Cs, Ce, Zr - were low.
- Ce appears to be the most readily entrained but considerable variations can be found in the measured release for a l l materials.
- U tends to remain with the n-TBP which is less mobile than the kerosine.
- The fractional release of U is an order of magnitude less up to the point of self-extinguishment than for the other elements.
- Up to the point of extinguishment the TBP appears to be little involved in the burning process.

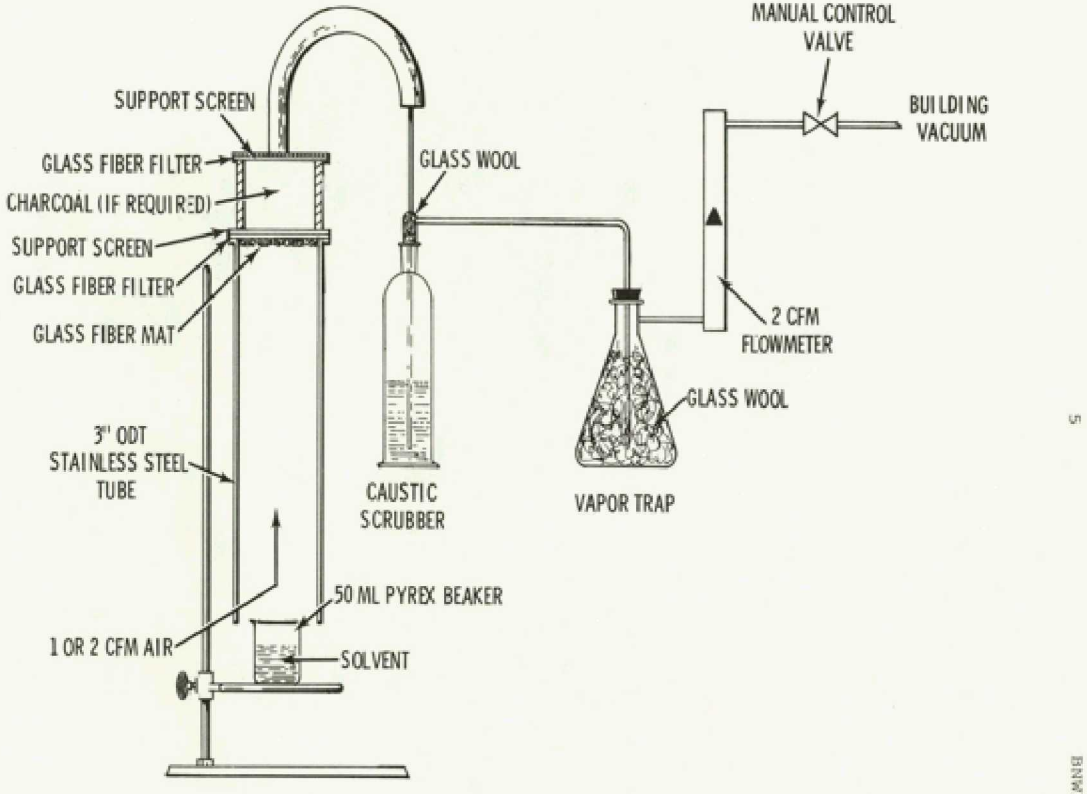


FIGURE 1b

SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

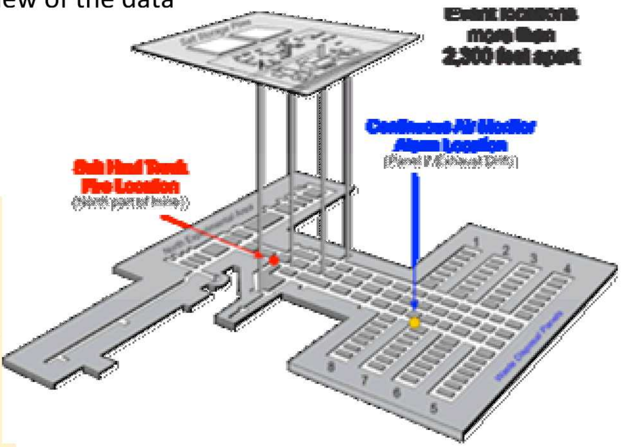
2014 WIPP radiation release has brought up old concerns about actinide aerosol behavior.

2014 Radiological Event at the WIPP: On February 14, 2014, a radiation release occurred at the WIPP from a compromised drum of contact-handled transuranic waste emplaced underground in the WIPP facility. The drum contained nitrate salts, processed and emplaced at the WIPP in late 2013. The Department of Energy Accident Investigation Board determined the cause of the radiation release was an exothermic reaction due to the use of incompatible, **organic sorbent material instead of inorganic sorbents** for absorbing free liquids in sludge waste containers.

EPA Response to 2014 Radioactive Release at the Waste Isolation Pilot Plant (WIPP)
EPA was in regular contact with DOE, the New Mexico Environment Department and the Carlsbad Environmental Monitoring and Research Center. EPA's review of the data collected indicated that:

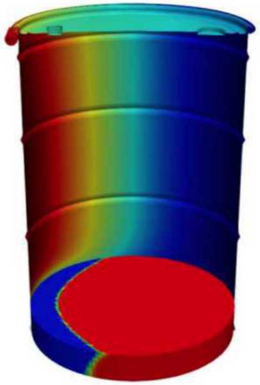
- The radiation releases did not pose a public health concern.
- DOE followed the procedures previously approved by EPA.
- The WIPP facility remains in compliance with EPA regulations.

When the CAM alarmed, two dampers were automatically closed in the exhaust duct, redirecting the exhaust through high efficiency particulate air (HEPA) filters that remove radioactive particles. next day, an aboveground exhaust air monitor on the WIPP site detected very low levels of airborne radioactive contamination. It is believed that a small amount of radioactivity went through the exhaust duct dampers. The exhaust duct dampers are large "butterfly" valves that are designed to close and cut off the air flow through the exhausters. However, the valves do not fully seal the exhaust ducts and still allowed a small amount of unfiltered air to escape.

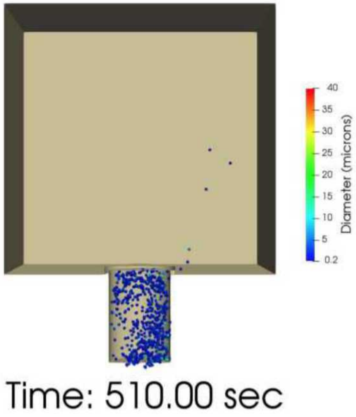


Images taken from http://www.wipp.energy.gov

Sandia’s modeling efforts have supported work on the DOE Handbook 3010[1]



- SNL’s Fire Sciences and Technology department simulated a variety of contaminant release scenarios using Computational Fluid Dynamics (SIERRA/FUEGO) tools
- Contaminant entrainment/release has been the focus of previous studies:
  - **- Benchtop (“beaker”) fires**
  - **- Gasoline fuel fires**
  - **- Drum fires**



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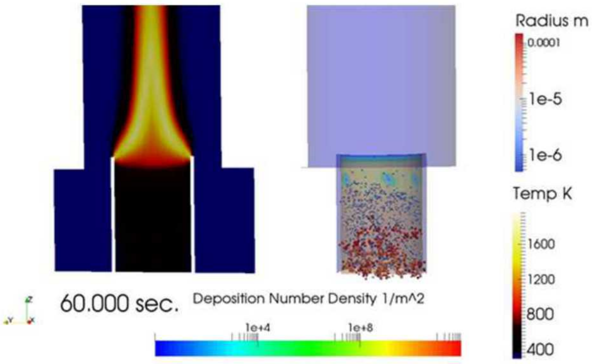
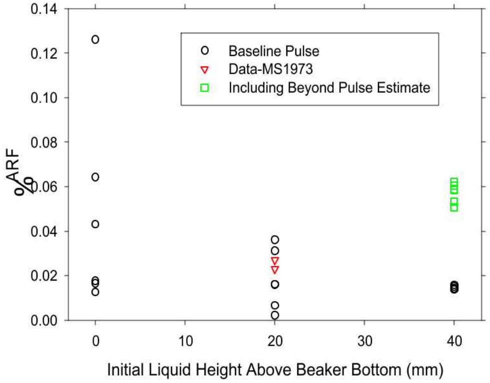
1. Department of Energy, “DOE HANDBOOK: Airborne Release Fractions/Rates and Respirable Fractions for Nonreactor Nuclear Facilities”, Volume 1 and 2, U.S. Department of Energy, DOE-HDBK-3010-94, Reaffirmed 2013, (2013).



- Beaker fire experimental effort modeling a solvent heated to boiling point and ignited
- Focused primarily on d-U release from kerosene with 30% TBP.
- Experimental repetition appear challenging
- Code enhancements were made to better track composition of entrained particles



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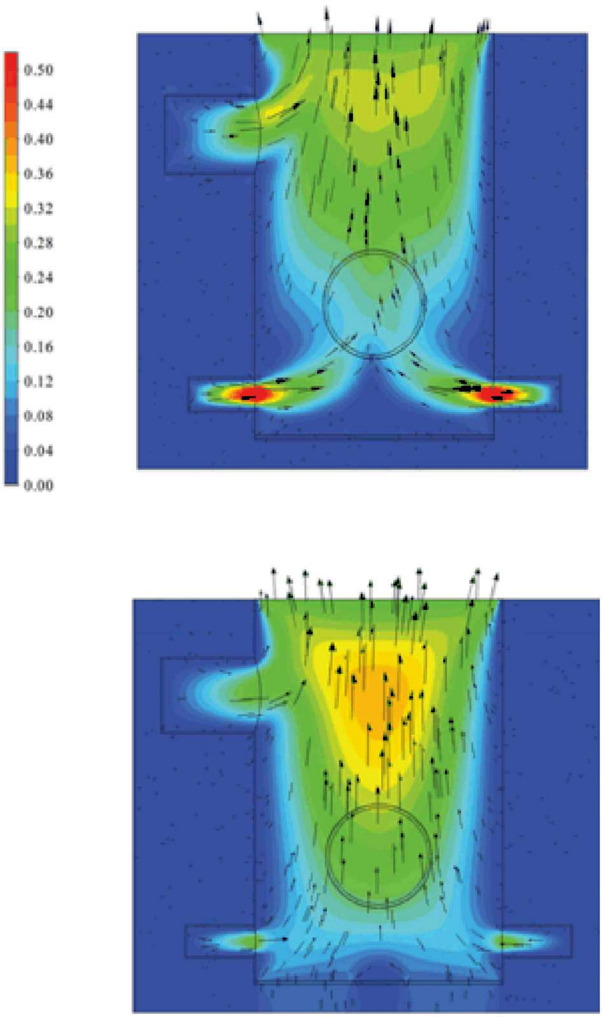
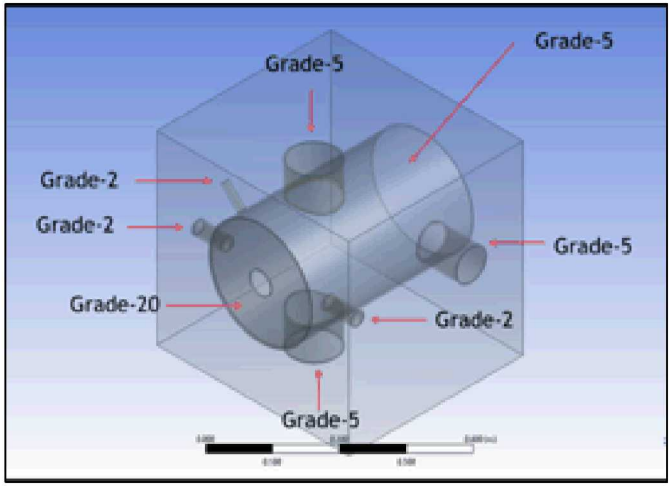
1. Brown, A. L., and Louie, D. L. Y., "Contaminant Entrainment in a Liquid Fuel Fire," TFESC-12948, 1st Thermal and Fluid Engineering Summer Conference, New York, NY, August 9-12, 2015.
2. Brown, A. L., Zepper, E. T., Louie, D. L. Y., and Restrepo, L. “Contaminant Entrainment from a Gasoline Pool Fire,” SAND2015-7185C, September 2015, Sandia National Laboratories.
3. Zepper, E. T., Brown, A. L., Pierce, F., Voskuilen, T., and Louie, D. L. Y., “Contaminated Fuel Fires: Parametric Sensitivity of Resuspension and Boiling Particle Evolution”, TFEC-IWHT2017-17709, Proceedings of the 2nd Thermal and Fluid Engineering Conference, Las Vegas, NV, April 2-5, 2017.

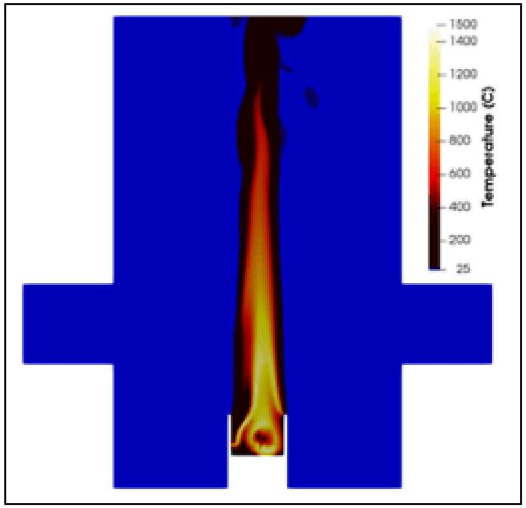
Computational modeling of flame aerosol production lead to the design of the burn chamber.

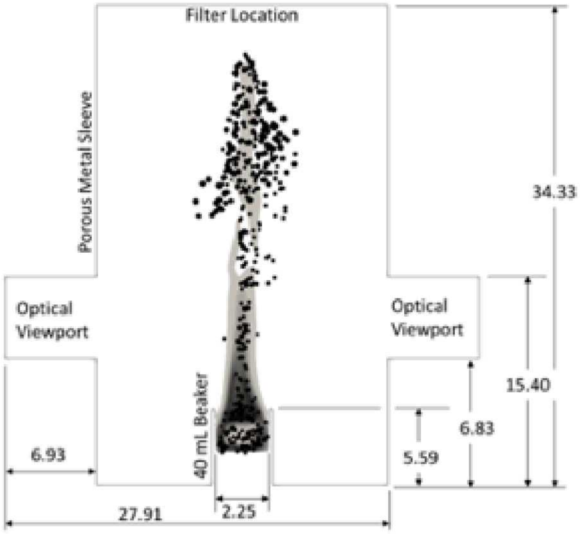


Combustion simulation, and CFD, were used to determine the size and amount of air flow needed.

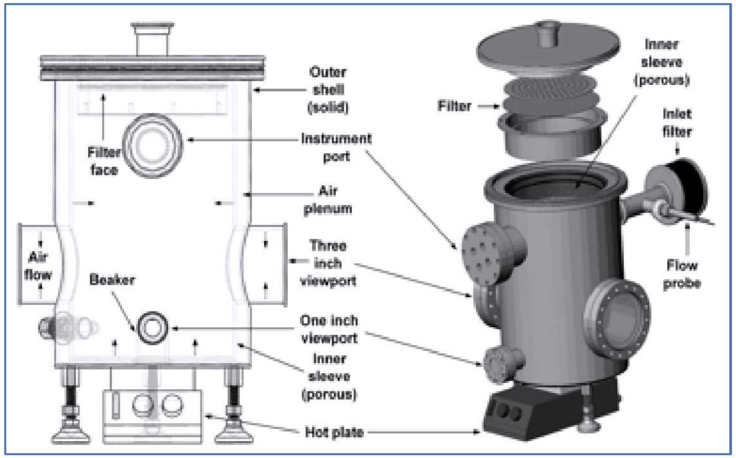


Dilution air is brought in from all surfaces surrounding the fire, to sweep particulate up to the filter.

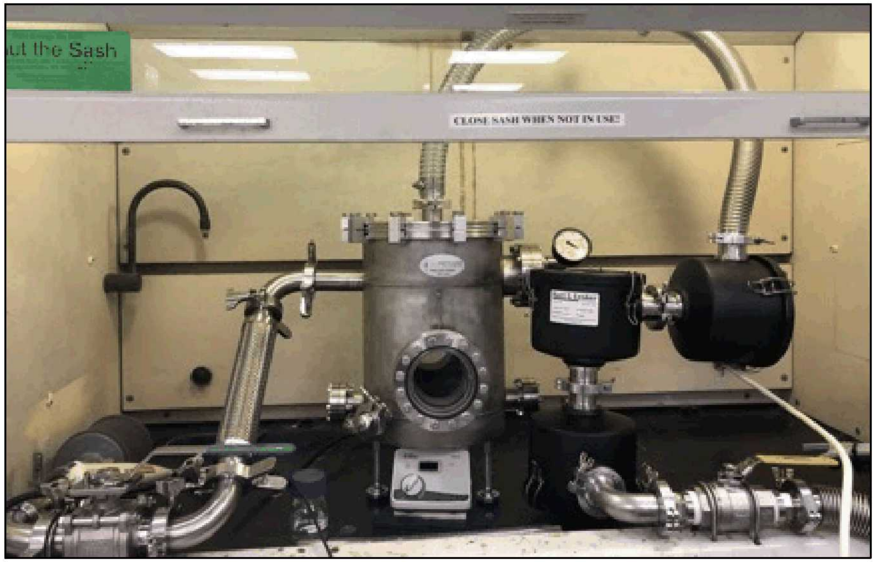




Can surrogate modeling (e.g., drum fires), extend the results to the An-contaminant (d-U), aiding in safety assertions?



- Tests were conducted in order to use extractive sampling techniques in order to characterize particles close to real-time
- Tests were conducted where all particulate was captured on the filter at the top of the chamber and filters were analyzed destructively with ICP-MS (ARF)



The ideal simulant for aerosol particulate have led (not surprising) to the Ln cations, but favor late Ln.

- Simulating experiments conducted in 1973 by Mishima and Schwendiman
  - DOE Handbook 3010 Section 3.3.1 “Burning of Small Volume/Surface Area 30% TBP-Kerosene Solutions, No Vigorous Boil-off”
  - Process solution from PUREX liquid-liquid extraction, actinides, kerosene, tri-butyl phosphate (plus fission products)
- Ideal simulant
  - Density of resultant particle similar (nitrate vs. oxide), does the particle get hot enough to undergo calcination?
  - Solubility of surrogate metal similar to solubility of uranium (~120 grams per liter).
  - Concentration of metal in solution will have a substantial effect on resultant particle size.
- Ideal simulant depends on the process being simulated (e.g., PUREX waste, metal fabrication, spent fuel)
- Focused on TBP (or TPhP)/kerosene experiments.

Actinides

Element	Oxide	Density (g/cm^3)
Th	ThO_2	10
U	UO_2	10.97
	U_3O_8	8.3
Pu	PuO_2	11.5

Transition metals

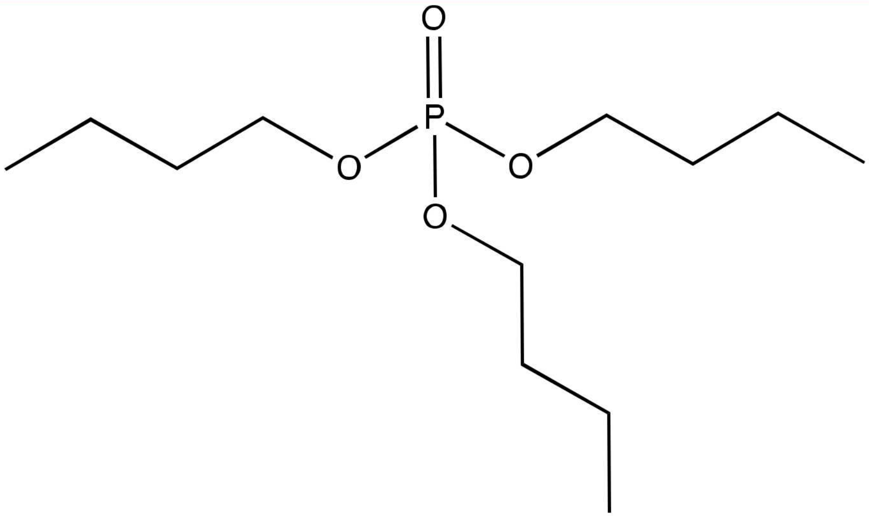
Element	Oxide	Density (g/cm^3)
W	WO_2	10.8
	WO_3	7.16
Bi	Bi_2O_3	8.9
Hf	HfO_2	9.68

Lanthanides

Element	Oxide	Density (g/cm^3)
La	La_2O_3	6.51
Ce	Ce_2O_3	6.2
	CeO_2	7.215
Pr	Pr_2O_3	6.9
	Pr_6O_{11}	6
Nd	Nd_2O_3	7.24
Pm	Pm_2O_3	6.85
	Pm_2O_3	7.48
	Pm_2O_3	7.62
Sm	Sm_2O_3	8.347
Eu	Eu_2O_3	7.42
	Eu_2O_3	7.42
Gd	Gd_2O_3	7.07
Tb	Tb_2O_3	7.91
	Tb_4O_7	7.3
Dy	Dy_2O_3	7.8
Ho	Ho_2O_3	8.1
Er	Er_2O_3	8.64
Tm	Tm_2O_3	8.6
Yb	Yb_2O_3	9.17
Lu	Lu_2O_3	9.42

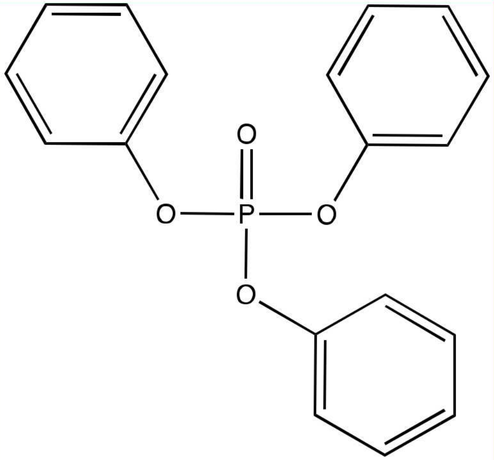
The system explored was metal nitrate hydrates dissolved in a 30% organophosphate/kerosene solution.

$$[\mathrm{M}[(\mathrm{NO_3})_3\bullet\, n\,\mathrm{H_2O}] + (\mathrm{xs})\ \mathrm{O{=}P(OR)_3} \xrightarrow{\text{kerosene}}$$



tributyl phosphate

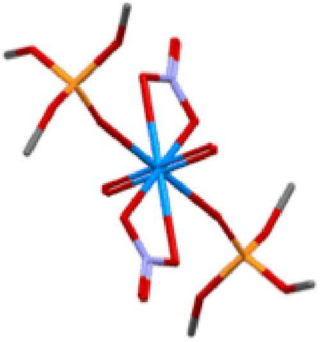
TBP



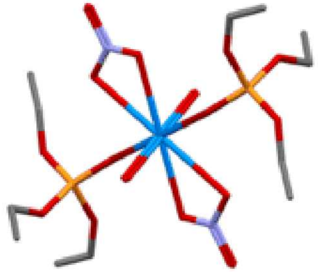
triphenyl phosphate

TPhP

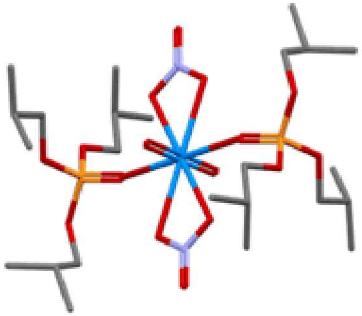
Literature uranyl nitrate organophosphate structures reported are monomeric or dimeric.



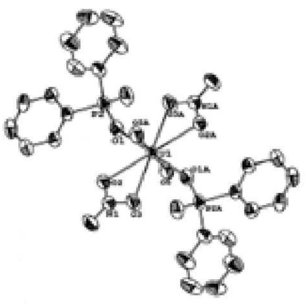
BIZXUD: Uranyl nitrate trimethylphosphate
Agostini et al. ICA, 62 (1982) 237.
DOI: 10.1016/S0020-1693(00)88507-2



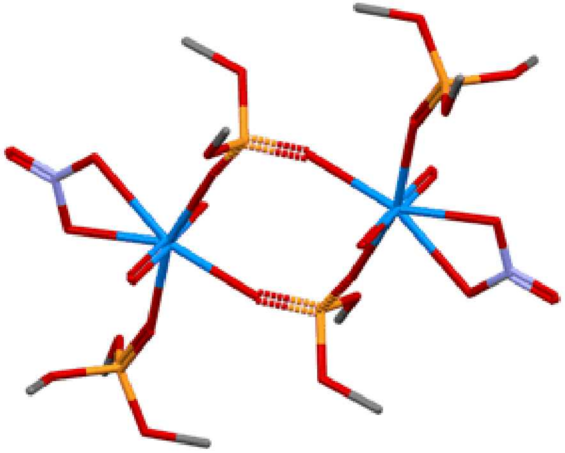
UNOEPO: Uranyl nitrate triethylphosphate
Fleming and Lynton Chem. Ind. (1960) 1415.
UNOEPO01: Kanellakopulos et al. Z. Anorg. Allg. Chem. 619 (1993) 593.
DOI: 10.1002/zaac.19936190327



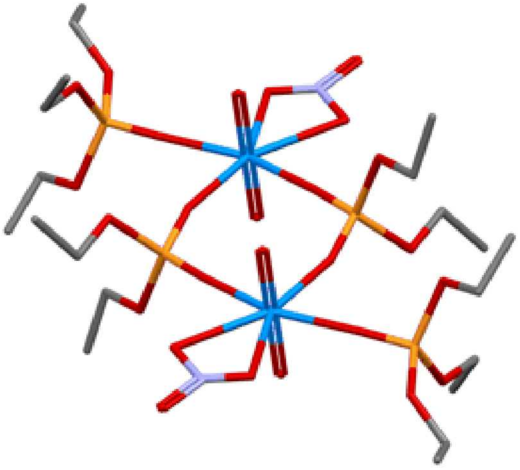
DEFMEG: Uranyl nitrate triisobutylphosphate
Burns et al. Acta Cryst. C 41 (1985) 1446.
DOI: 10.1107/S0108270185008125



Uranyl nitrate methyldiphenyl phosphine oxide
Martin et al. J. Nucl. Sci. Tech. (2002) 453-456.
DOI: 10.1080/00223131.2002.10875505



LIDTEZ: Uranyl nitrate bis(trimethylphosphate)
Charushnikova et al. Radiochim Acta, (2012) 173.
DOI: 10.1524/ract.2012.1899

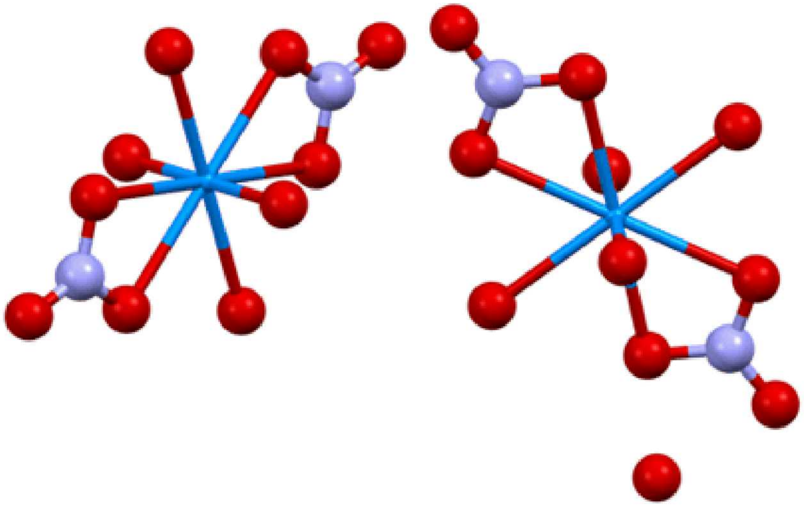


WEWXAX: Uranyl nitrate bis(triethylphosphate)
Kanellakopulos et al. Z. Anorg. Allg. Chem. (1993) 593.
DOI: 10.1002/zaac.19936190327
WEWXAX01: Charushnikova et al. Radiochim. Acta (2012) 173.
DOI: 10.1524/ract.2012.1899

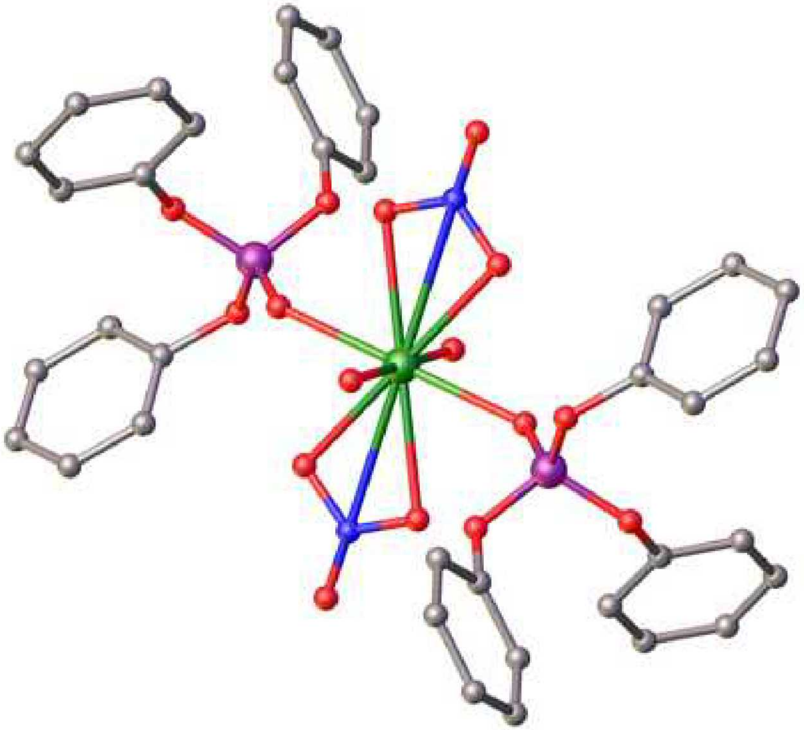
Single crystal X-ray diffraction reveals for U-TPhP a monomer w/ two phosphate, two nitrates, two oxides.

$$U^0 + \text{(aq) } HNO_3 \longrightarrow 2\,[U(O)_2(NO_3)_2(H_2O)_2] \bullet H_2O$$

$$[U(O)_2(NO_3)_2 \bullet 6\,H_2O] + \text{(xs) } O{=}P(OR)_3 \xrightarrow{\text{kerosene}}$$



2 $[U(O)_2(NO_3)_2(H_2O)_2] \bullet H_2O$



$[U(O)_2(NO_3)_2(TPhP)_2]$

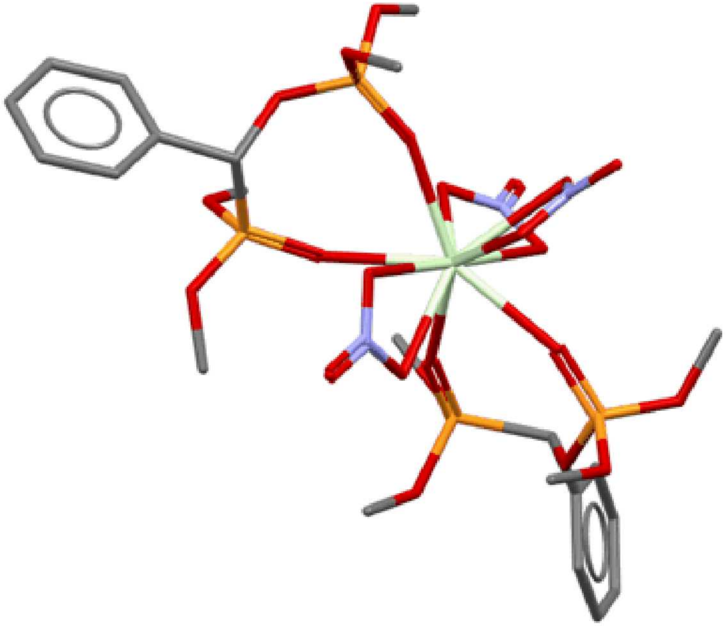
Understanding the lanthanide nitrate hydrates dissolved in a 30% organophosphate/kerosene solution was of interest.

$$[\mathrm{Ln}[(\mathrm{NO_3})_3\text{•}6\ \mathrm{H_2O}] + (\mathrm{xs})\ \mathrm{O{=}P(OR)_3} \xrightarrow{\text{kerosene}}$$

TBP TPhP

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
●	●	●	●	●	●	●	●	●	●	●	●	●	●

A dozen Ln-OP(OR)$_3$ structures reported but only one is a nitrate!

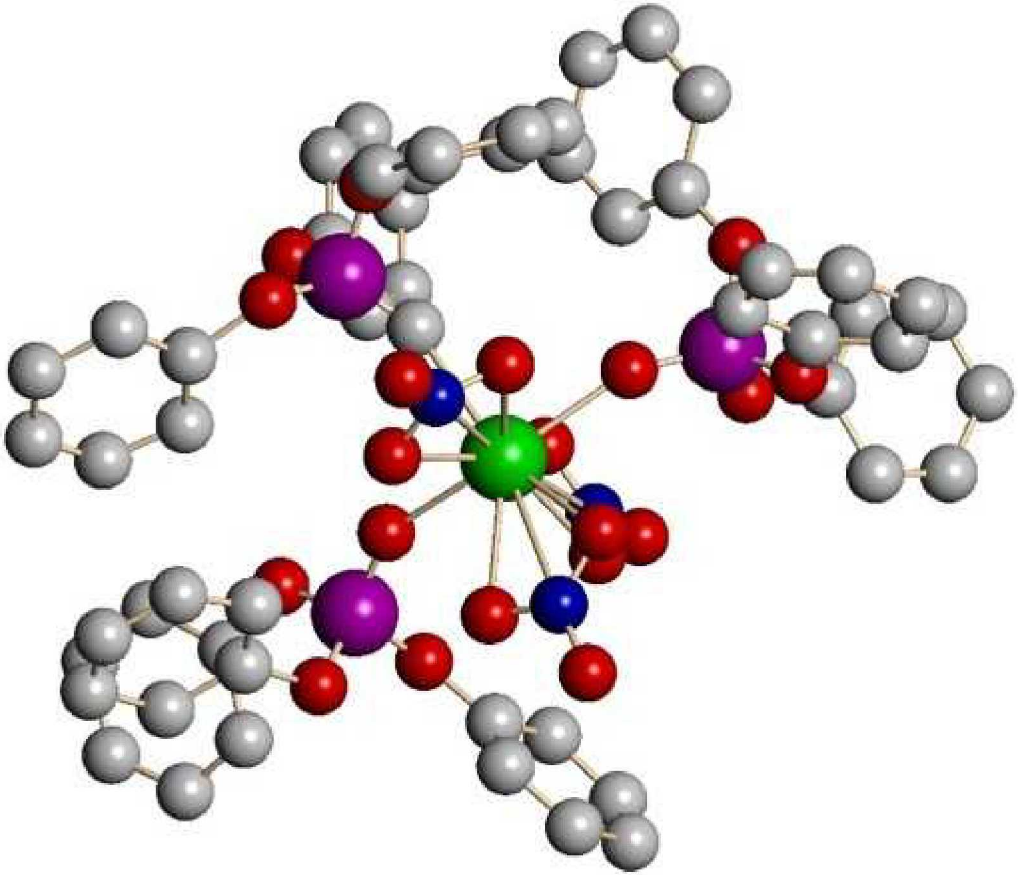


POPJAF: Praseodymium tris(nitrato-O,O')-bis(bis(dimethylphosphonato)phenylmethanol)
Platt et al. ICA 223 (1994) 223.
DOI: 10.1016/0020-1693(94)03988-7

Single crystal X-ray diffraction reveals for Ln-TPhP system monomers w/ three phosphate and three nitrates isolated . .

$$[\mathrm{Ln}[(\mathrm{NO_3})_3 \cdot 6\,\mathrm{H_2O}] \;+\; (\mathrm{xs})\ \mathrm{O{=}P(OR)_3} \xrightarrow{\text{kerosene}} \xrightarrow{\text{acetone}}$$

- √ ● La
- √ ● Ce
- √ ● Pr
- √ ● Nd
- √ ● Sm
- √ ● Eu
- √ ● Gd
- √ ● Tb
- √ ● Dy
- √ ● Ho
- √ ● Er
- √ ● Tm
- √ ● Yb
- √ ● Lu



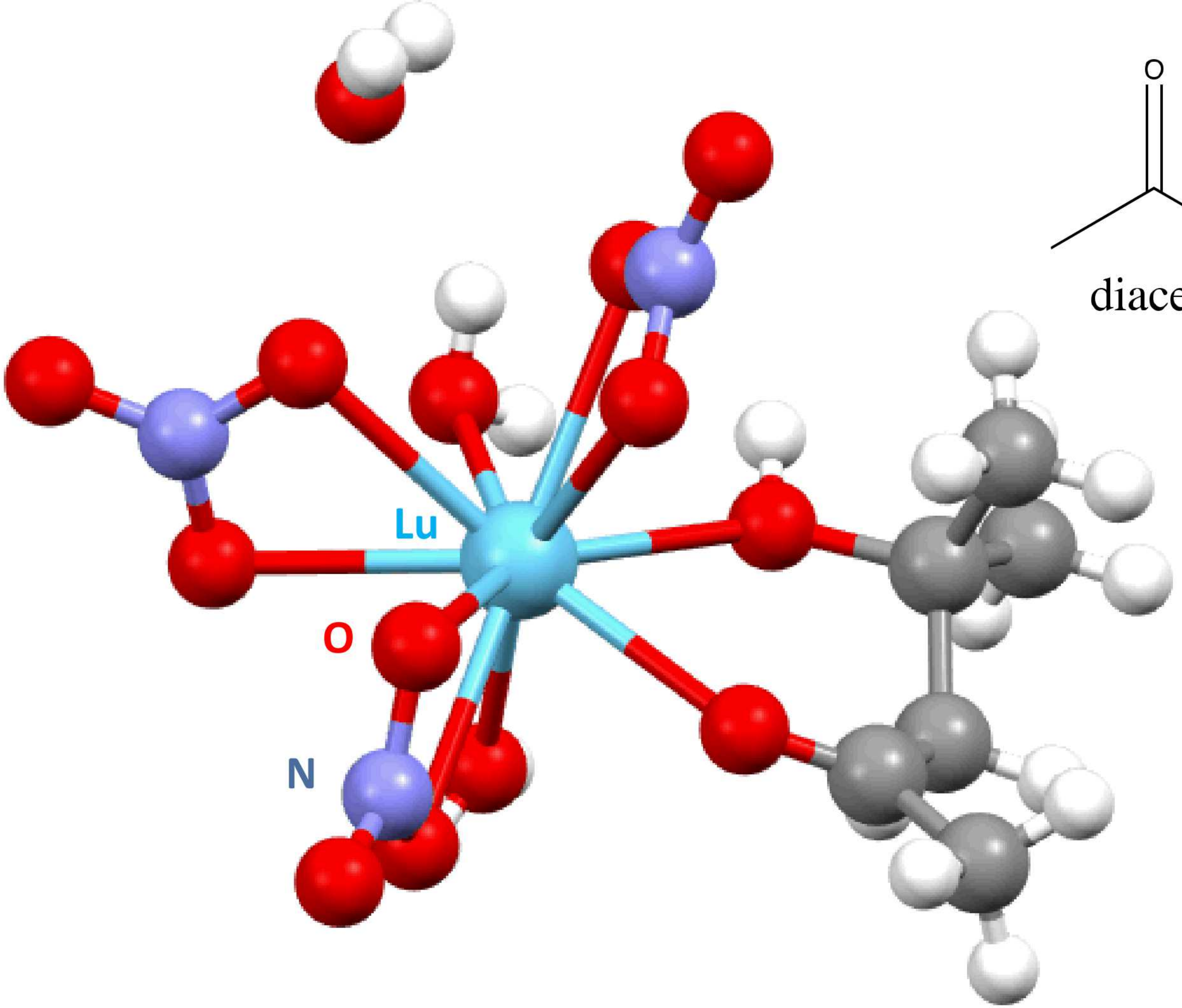
$[\mathrm{Ln}(\mathrm{NO_3})_3(\mathrm{TPhP})_3]$

. . when crystallization from acetone a different product was isolated, where acetone was reduced to H-DAA.

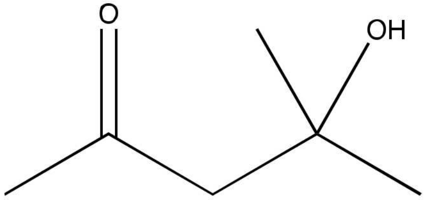
$[Ln[(NO_3)_3 \bullet 6\,H_2O] \xrightarrow{\text{acetone}}$

RT		50°C
	La	√
Mix	Ce	√
Mix	Pr	√
	Nd	
√	Sm	
	Eu	√
	Gd	√
√	Tb	√
√	Dy	√
√	Ho	√
√	Er	√
√	Tm	√
√	Yb	√
√	Lu	√

Mix: Ln-DAA and $Ln(NO_3)_3 \bullet 6H_2O$



$[Ln(k^2\text{-}NO_3)_3(H_2O)_x(k^2\text{-}DAA)] \bullet n\ H_2O$

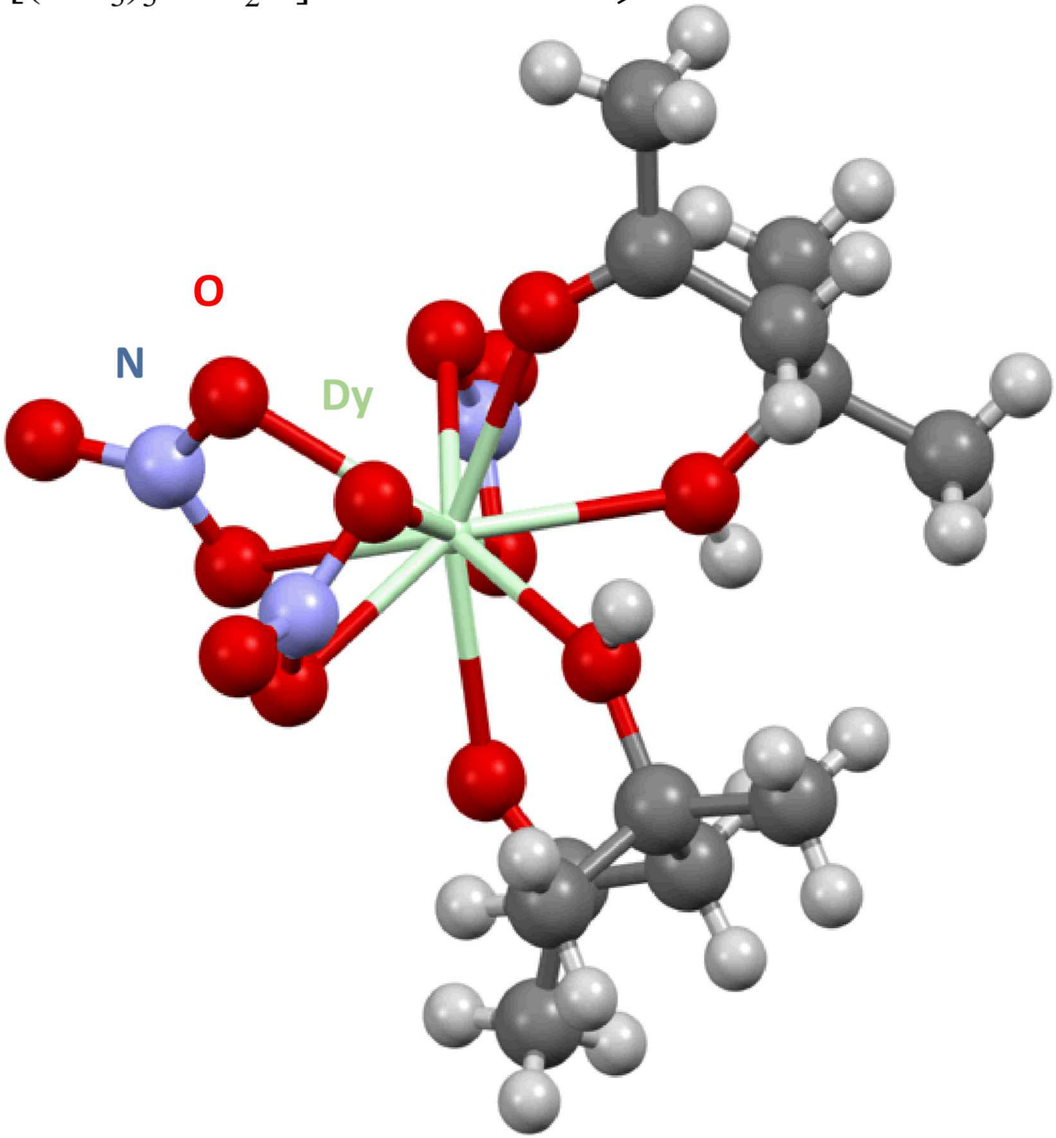


diacetone alcohol
(DAA)

Other dual-substituted DAA derivatives were isolated , too.

$[Ln[(NO_3)_3 \cdot 6\ H_2O] \xrightarrow{\text{acetone}}$

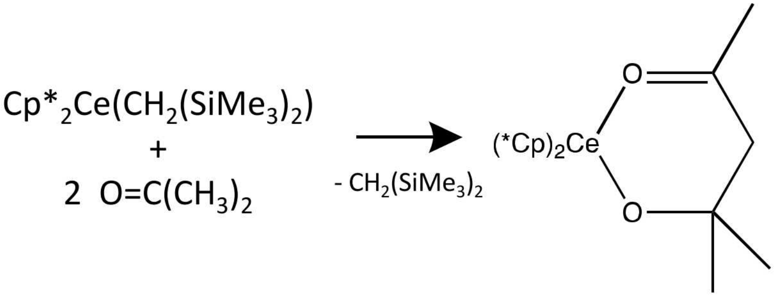
RT		50°C
	● La	√*
	● Ce	√*
	● Pr	
√	● Nd	
	● Sm	√
√	● Eu	
	● Gd	
	● Tb	
	● Dy	
	● Ho	
	● Er	
	● Tm	
	● Yb	
	● Lu	



$[Ln(k^2\text{-}NO_3)_3(k^2\text{-}DAA)_2]$

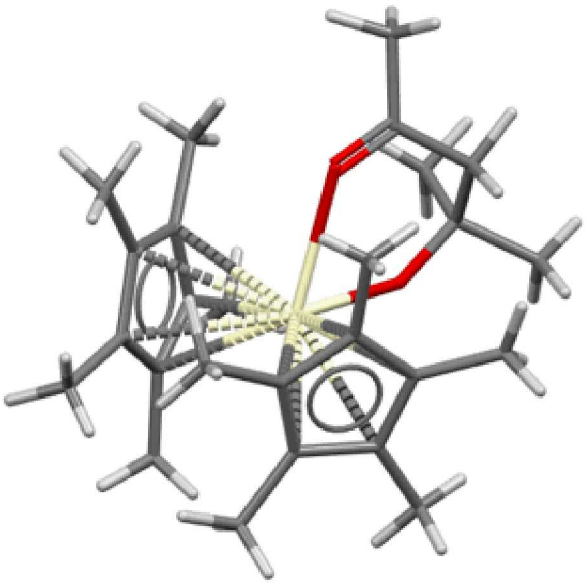
*only observed after boiling in acetone

Ln-DAA-like structures reported: 1 from reduction of acetone to form the alkoxide; others H-DAA coordination

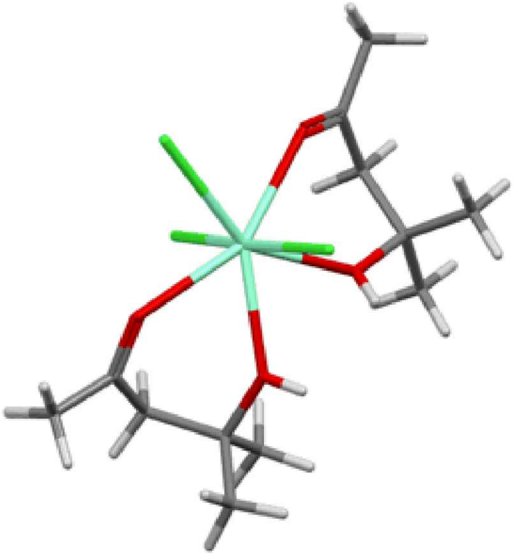


$$Cp^*_2Ce(CH_2(SiMe_3)_2) + 2\ O{=}C(CH_3)_2 \xrightarrow[- CH_2(SiMe_3)_2]{}$$

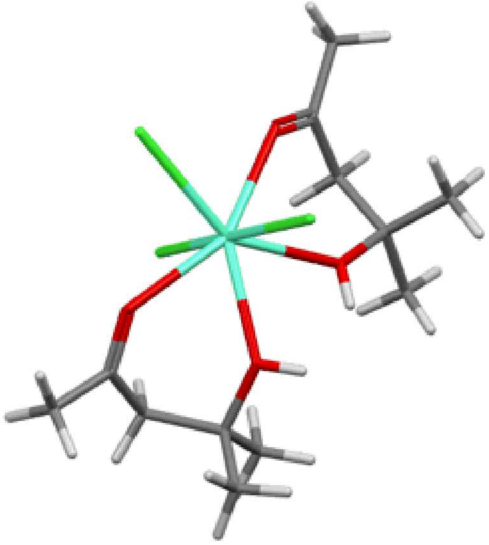
$$LnCl_3 + 2\ \mathbf{DAA} \xrightarrow[Ln = Sm,\ Eu]{} [LnCl_3(DAA)_2]$$



JOLYAK: **Cerium bis(h5-Pentamethyl-cyclopentadienyl)-(4-hydroxy-4-methyl-2-pentanonato-O,O')**



OFULEG: **Samarium trichloro bis(4-Hydroxy-4-methyl-2-pentanone)**



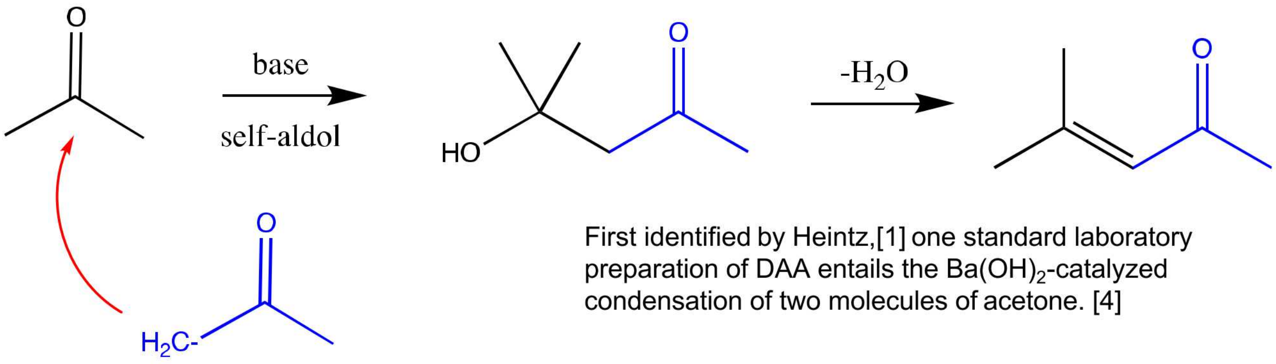
OFULEG: **Europium trichloro bis(4-Hydroxy-4-methyl-2-pentanone)**

Heeres et al. Organomet. 11 (1992) 350.
DOI: 10.1021/om00037a059

Li et al. Z. Anorg. Allg. Chem. 628 (2002) 933.
DOI: 10.1002/1521-3749(200206)628:5<933::AID-ZAAC933>3.0.CO;2-O

Most reports on DAA from $O=C(CH_3)_2$ requires strong base

Diacetone alcohol can be prepared from acetone by the Soxhlet extraction of acetone using alkali (NaOH or KOH) and alkaline earth metal hydroxides[1]: calcium hydroxide [2] < barium hydroxides[3].



First identified by Heintz,[1] one standard laboratory preparation of DAA entails the $Ba(OH)_2$-catalyzed condensation of two molecules of acetone. [4]

Diacetone alcohol (DAA) is mainly used as a solvent in industrial and professional applications in coatings, cleaning, oil and gas filed drilling, lubricants, metal working fluids, polymer processing and water treatment. It is found in a number of consumer products such as adhesives, inks, paints, household cleaners and agrochemicals. The substance is also a chemical intermediate for the preparation of other compounds. It is used in cellulose ester lacquers, particularly of the brushing type, where it produces brilliant gloss and hard film and where its lack of odor is desirable. It is used in lacquer thinners, dopes, wood stains, wood preservatives and printing pastes; in coating compositions for paper and textiles; permanent markers; in making artificial silk and leather; in imitation gold leaf; in celluloid cements; as a preservative for animal tissue; in metal cleaning compounds; in the manufacture of photographic film; and in hydraulic brake fluids. **https://en.wikipedia.org/wiki/Diacetone_alcohol**

US20170158591A1 "Synthesis of diacetone alcohol and meistyl oxide"

Disclosed herein are processes for synthesizing diacetone alcohol. In some embodiments, an exemplary process for synthesizing diacetone alcohol includes contacting acetone with a neutral heterogeneous catalyst (metal aluminosilicates) at a temperature of less than 100° C (20° C. to about 25° C), to provide diacetone alcohol. [5]

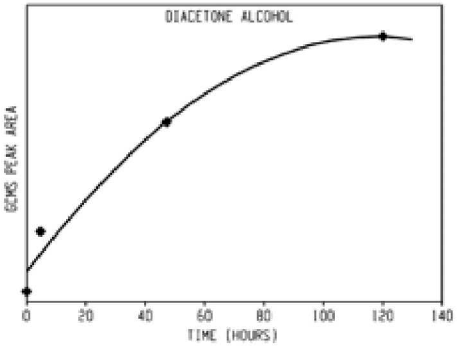


Fig. 2

FIG. 2 is a graphical representation of formation of DAA from acetone over time according to an exemplary process of the present disclosure.

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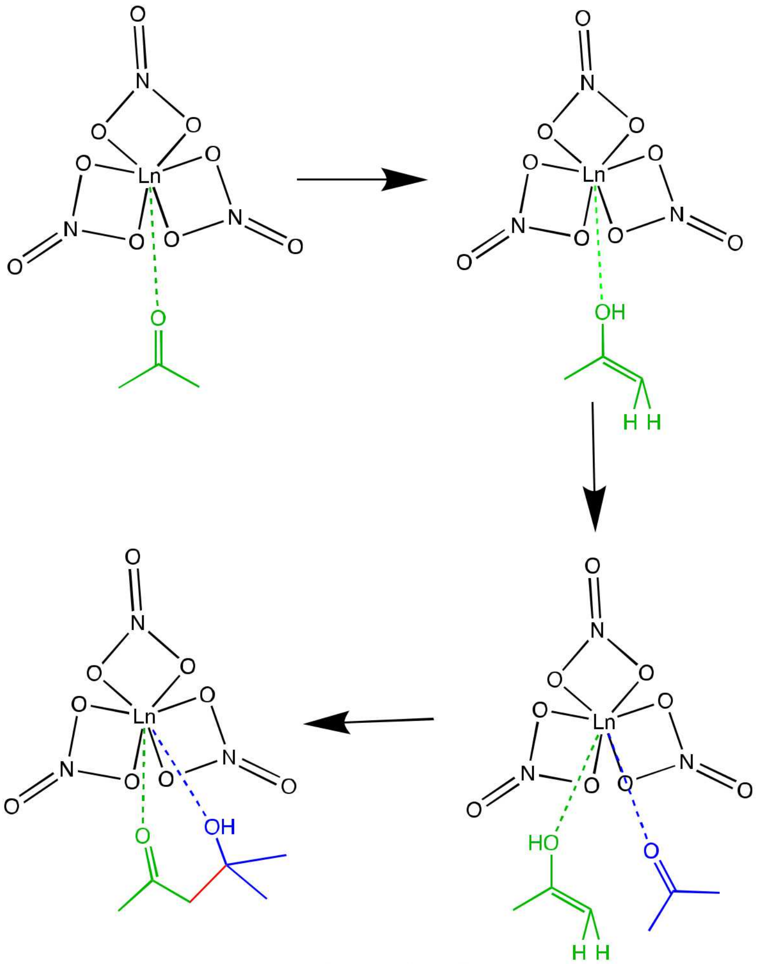
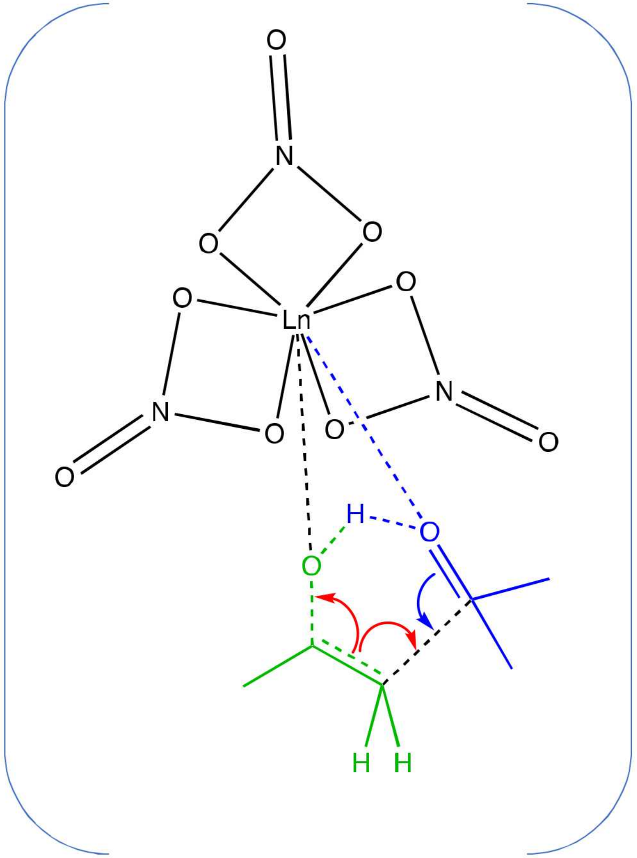
1. Heintz, Ann. **169**, 114 (1873); Locquin, Ann. Chim. (9) **19**, 32 (1923); Thomson, U. S. pat. 1,654,103 [C. A. **22**, 787 (1928)]; Ellis, U. S. pat. 1,701,473 [C. A. **23**, 1419 (1929)].
2. Hoffman, Ger. pat. 229,678 [Frdl. **10**, 998 (1910–12)]; U. S. pat. 1,082,424 [C. A. **8**, 788 (1914)]; Edmonds, U. S. pat. 1,550,792 [C. A. **20**, 51 (1926)].
3. Kyriakides, J. Am. Soc. **36**, 534 (1914).
4. Conant, J. B.; Tuttle, N. (1921). "Diacetone Alcohol". Organic Syntheses. **1**: 45. doi:10.15227/orgsyn.001.0045.
5. Osei-Twum et al, U.S. pat **US20170158591A1** "Synthesis of diacetone alcohol and meistyl oxide" Jun. 8, 2017.

Proposed acid catalyzed reduction of $O{=}C(CH_3)_2$ by $Ln(NO_3)_3{\bullet}6H_2O$

$$[Ln(NO_3)_3{\bullet}6\ H_2O] \xrightarrow[\text{acetone}]{\text{acetone}} [Ln(NO_3)_3(DAA)]$$



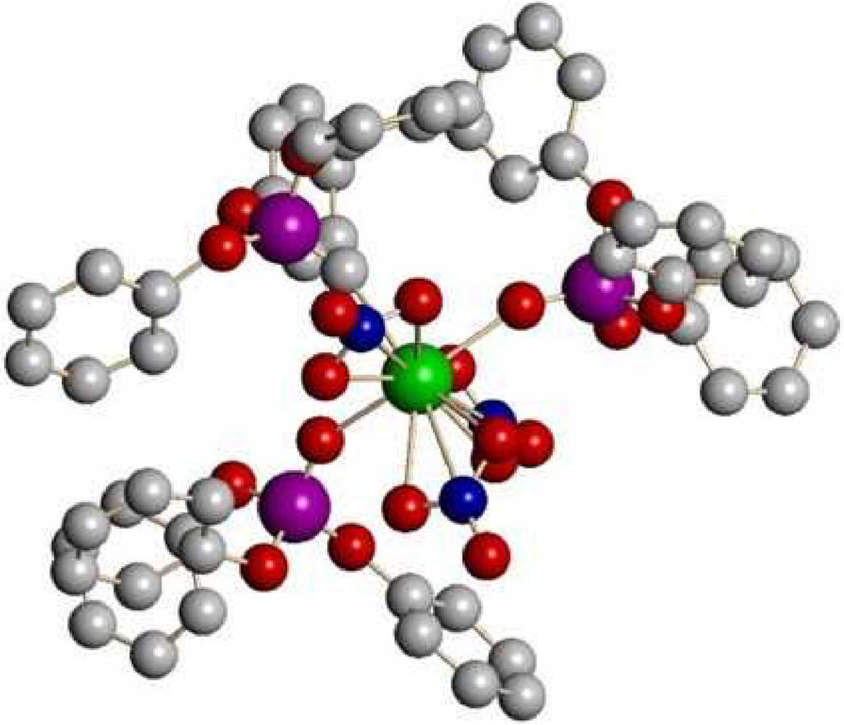
Waters not shown for clarity



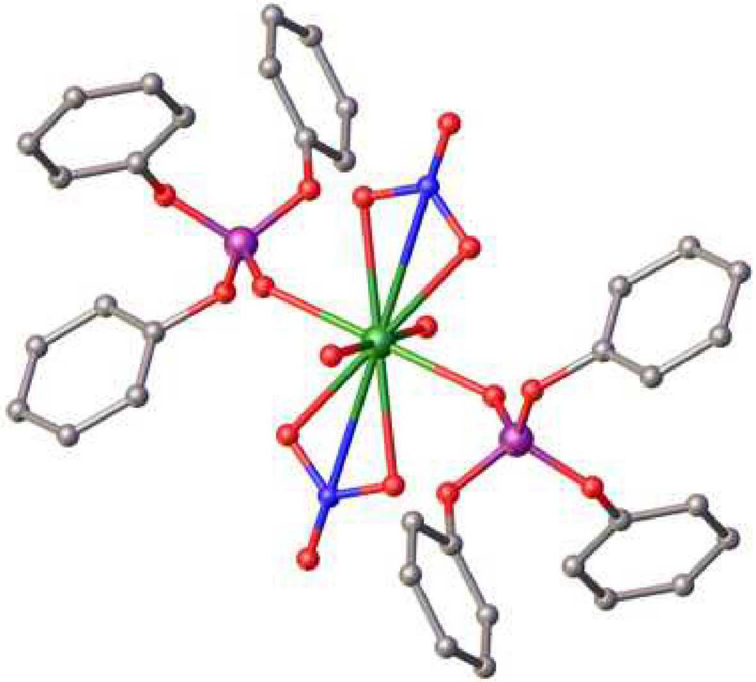
intermediate

Single crystal X-ray diffraction reveals for Ln-TPhP system monomers w/ three phosphate and three nitrates isolated.

$$[\mathrm{Ln}[(\mathrm{NO}_3)_3\cdot 6\ \mathrm{H}_2\mathrm{O}] + (\mathrm{xs})\ \mathrm{O{=}P(OR)}_3 \xrightarrow{\text{kerosene}}$$



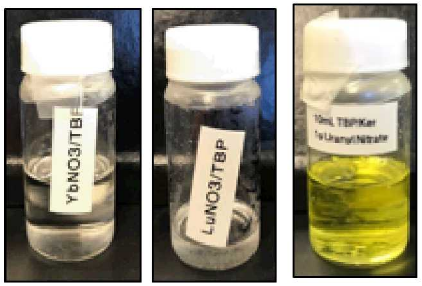
$[Ln(NO_3)_3(TPhP)_3]$



$[U(O)_2(NO_3)_2(TPhP)_2]$

With solutions in hand, beaker heating of surrogates were undertaken

- **PUREX**
  - Solvent-solvent extraction
  - 30% TBP in Kerosene
  - TBP molecule binds to U and Pu

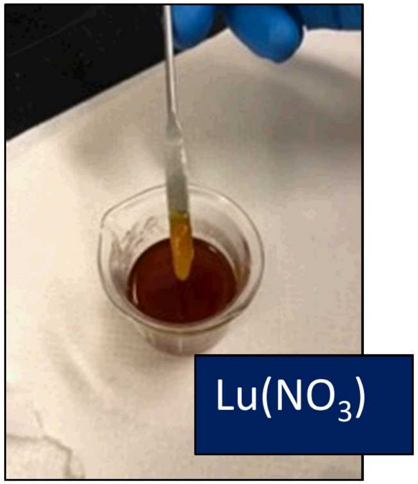


Metal	Assumed Oxide	Density (g/cm^3)	Solution (g/mL)	Notes
Ce	CeO_2	7.2	N/A	Common surrogate, not tested here
Ho	Ho_2O_3	8.1	N/A	Insoluble
Sm	Sm_2O_3	8.3	0.1	
Er	Er_2O_3	8.6	0.1	
Yb	Yb_2O_3	9.2	0.1	Better surrogate
Lu	Lu_2O_3	9.4	0.1	Better surrogate
Th	ThO_2	10.0	-	Not yet tested
U	UO_2	11.0	0.1	99.7% 238-U

- **What metals?**
  - Soluble in TBP/Kerosene to similar level as U (~120 g/L)
  - High particle density so transport is similar
  - Lanthanides often used as alternatives due to their similar size, electronics, densities, and additional inherent properties

Non-combustion heating to determine rates and the probability that boiling conditions were attained during airborne release fraction (ARF) measurements.

Heating up to 110°C when no metal-nitrates were present



Heating up to 110°C caused phase separation

Test Chamber designed for optimal burning

Distinguishing feature – porous walls and chamber bottom which bring in dilution air and prevents aerosol deposits.

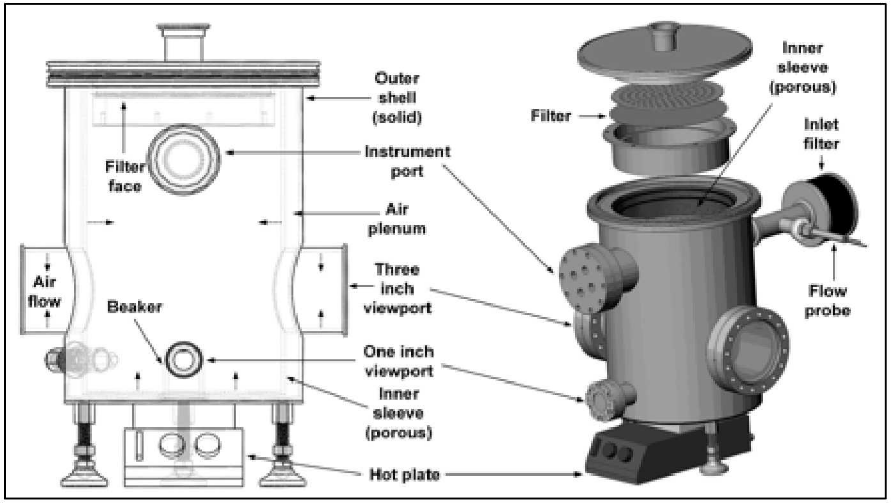
CO_2 purge – fire extinguishing system

Materials are completely enclosed – enables work with radioactive materials.

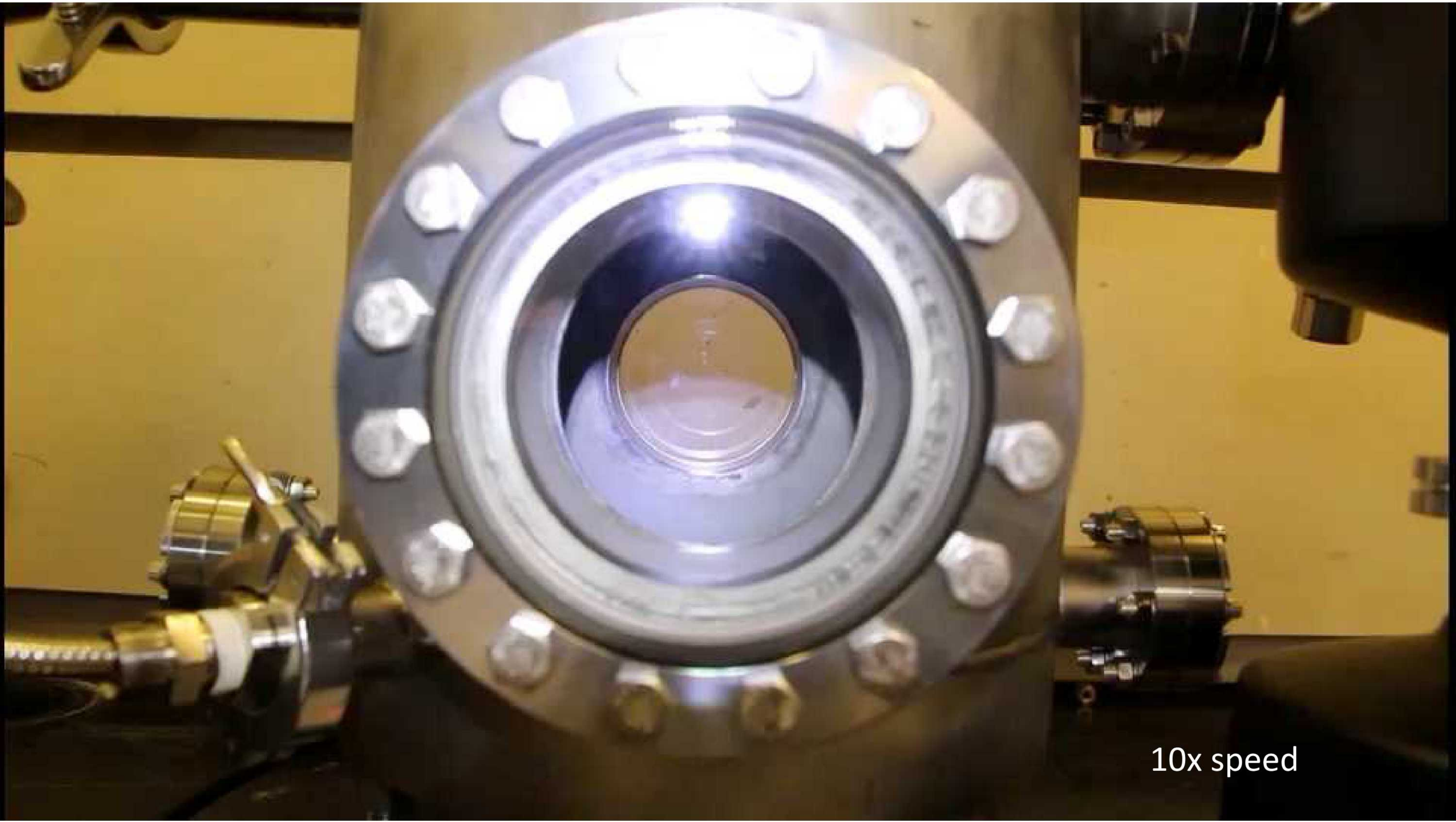
System sits inside a fume hood for secondary containment.

Metal, HEPA, and carbon filters downstream of aerosol capture filter visualization and instrumentation ports.

Aerosols are captured at the top of the chamber on EPM-2000 glass fiber filters, leached, and quantified with Inductively Coupled Plasma Mass Spectrometry (ICP-MS)



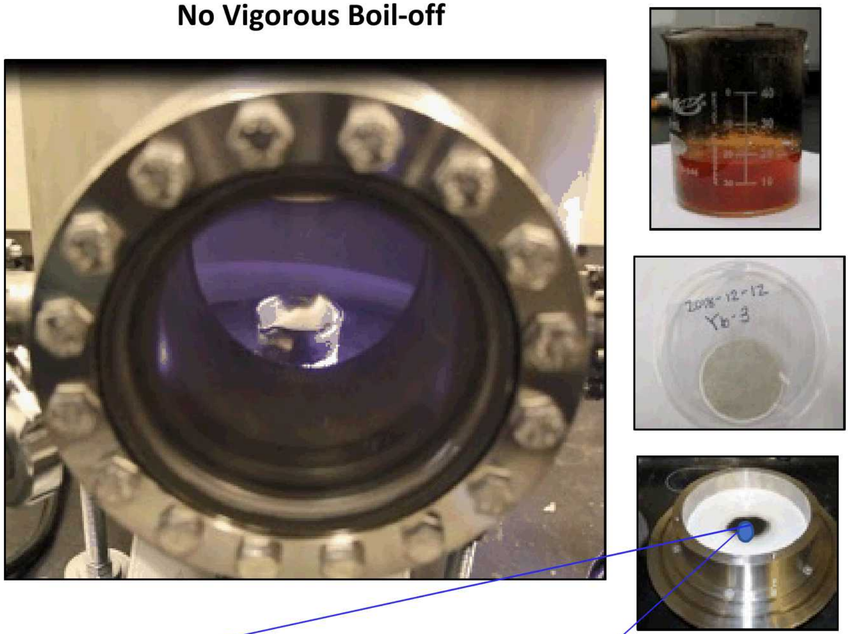
Sample burning shows continuous flame and soot production.



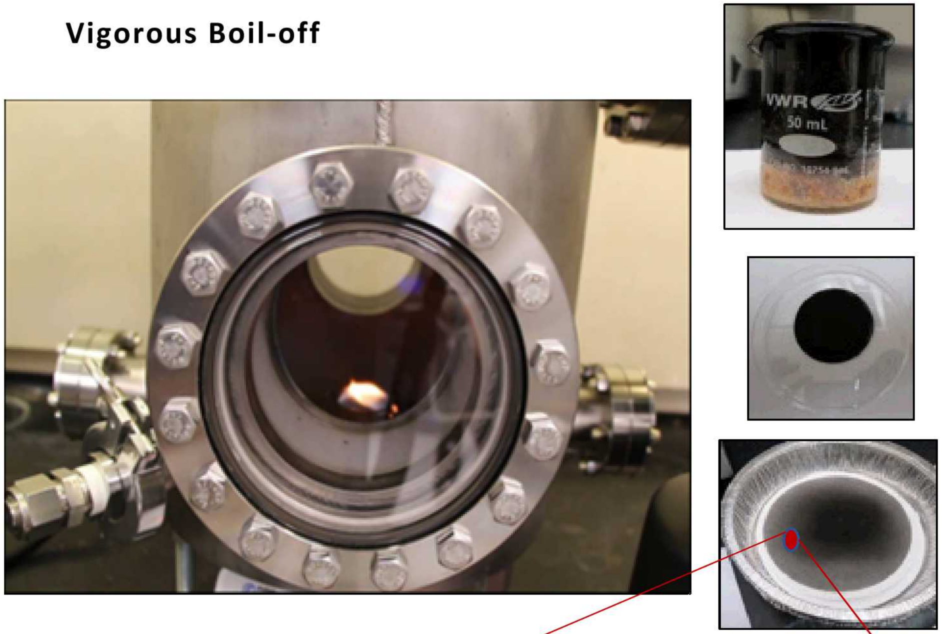
- No metal nitrate
- 20 mL in beaker, warmed at 400 ^{0}C continuously
- Flame extinguished by shutting off air flow to chamber

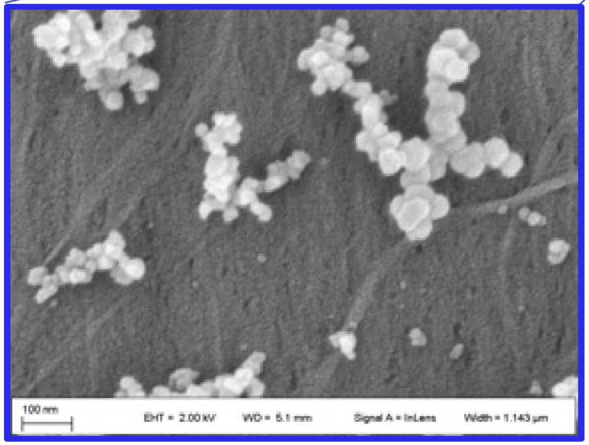
Real time testing of burned samples of the Ln surrogate solutions

No Vigorous Boil-off

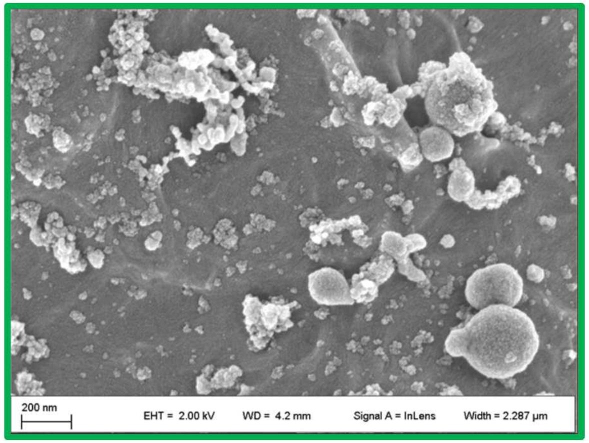


Vigorous Boil-off

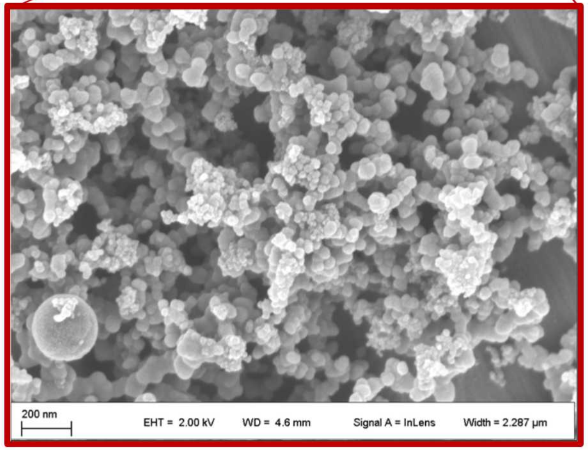




Fuel: 30% TBP in kerosene,
no metal nitrate

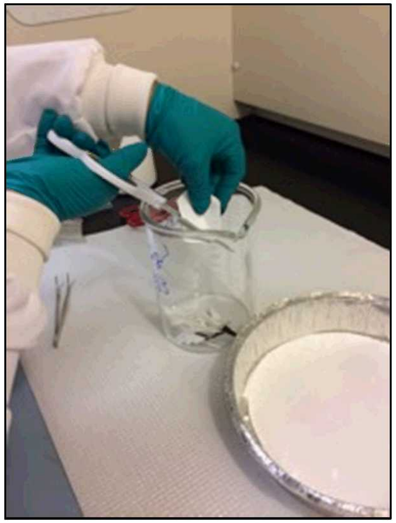


Fuel: 30% TBP in kerosene,
0.1 g/mL lutetium nitrate

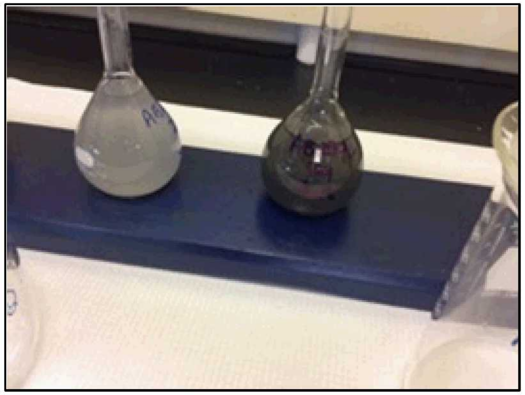


Fuel: 30% TBP in kerosene,
0.1 g/mL ytterbium nitrate

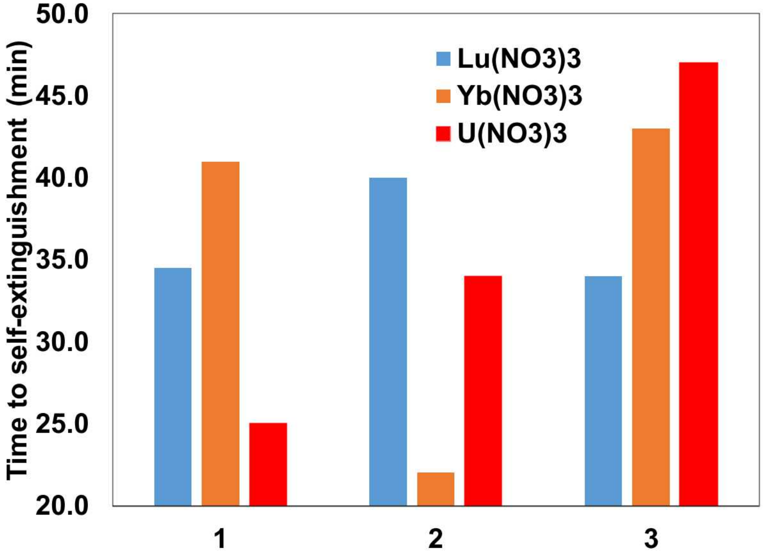
Filter Analysis used EPA standards to extract metal particulates (ARF) from filter paper

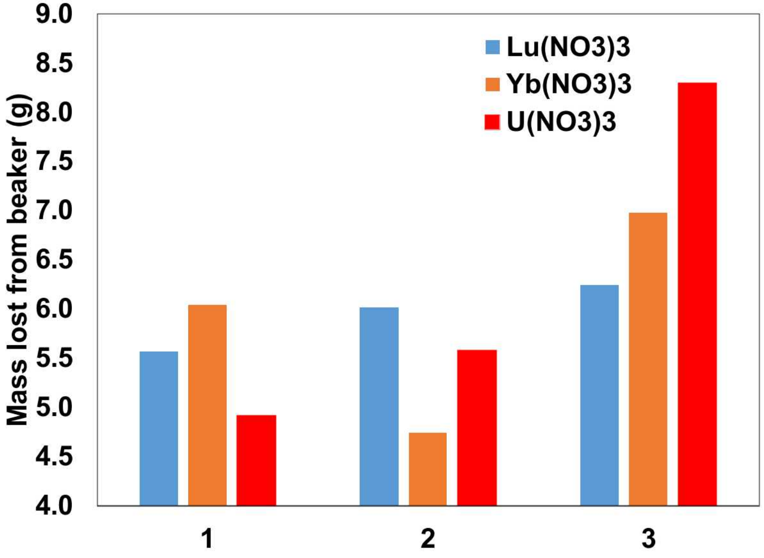


- 3 runs for each precursor (lutetium nitrate, ytterbium nitrate, and uranium nitrate)
- Filters collected for destructive analysis
- Leached metals from particulate, and performed Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to quantify mass of metal on filters

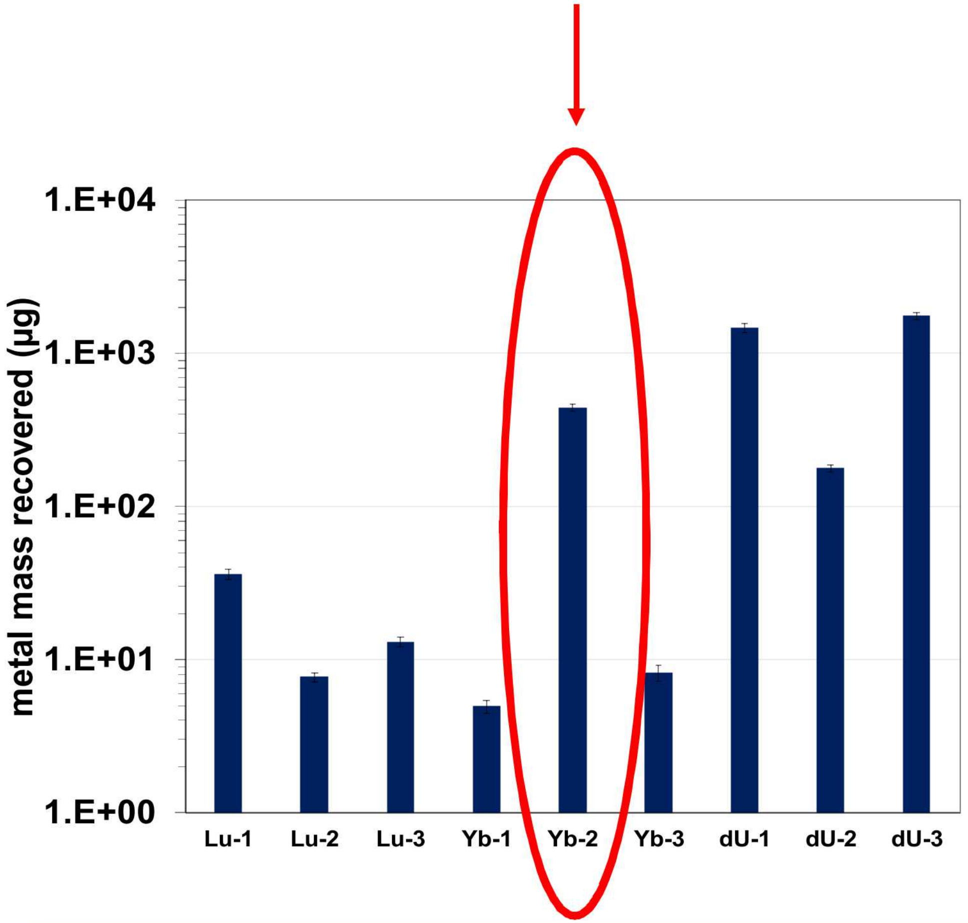


Mass Loss and Time to Self Extinguishment





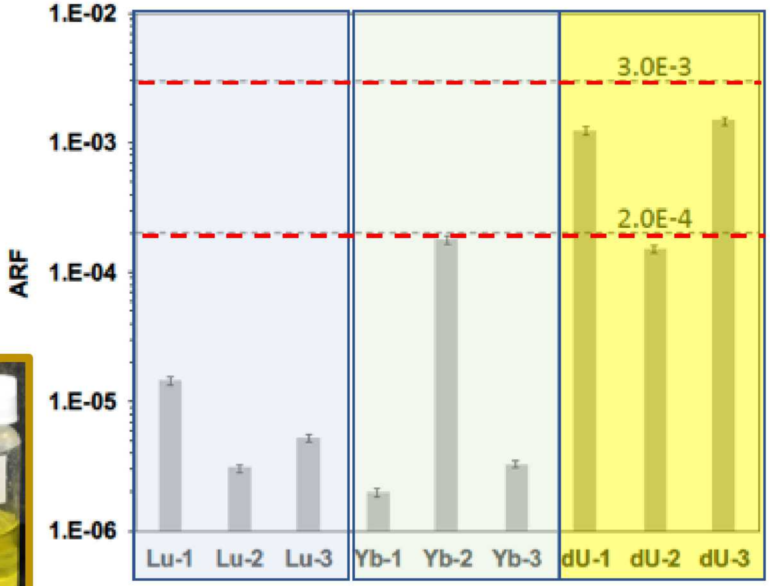
25 mL sample took ~ 40 min to ignite with many additional periods of heating, flame appeared to undulate more than other experiments with $Yb(NO_3)_3$



Analyzing ICP-MS data, uncertainties, and ARF

Lower ARF of Yb and Lu appear to be correlated to "additional heating intervals" - poor surrogates!

Metal	Experiment	Mass pre- (g)	Mass loss (g)	mass loss (%)	Time to ignition (min)	Add heat intervals (-)	Time to self-extinguish (min)	Filt. Mass recovered (µg)	ARF (-)
Lu	1	22.4	5.6	24.8	17.0	1	34.5	36	1.4E-05
Lu	2	22.4	6.0	26.9	9.5	0	40.0	8	3.1E-06
Lu	3	22.4	6.2	27.9	24.0	2	34.0	13	5.2E-06
Yb	1	22.1	6.0	27.3	17.0	1	41.0	5	2.0E-06
Yb	2	22.1	4.7	21.5	47.0	4	22.0	440	1.8E-04
Yb	3	22.2	7.0	31.5	17.0	1	43.0	8	3.3E-06
U	1	22.3	4.9	22.1	22.0	1	25.0	1468	1.2E-03
U	2	22.4	5.6	24.9	30.0	2	34.0	178	1.5E-04
U	3	22.3	8.3	37.3	11.0	1	47.0	1750	1.5E-03

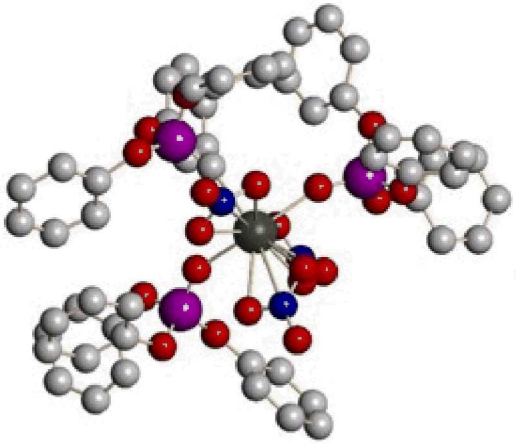


"Uranium ARFs range from 2E-4 to 3E-3, an uncertainty of approximately an order of magnitude"

DOE Handbook 3010 Section 3.3.1 -- Burning of Small Volume / Surface Area 30% TBP-Kerosine Solutions, No Vigorous Boiloff

Processing of the Ln-NO_3- $O=P(OR)_3$ do not form the expected oxide but instead form the phosphate

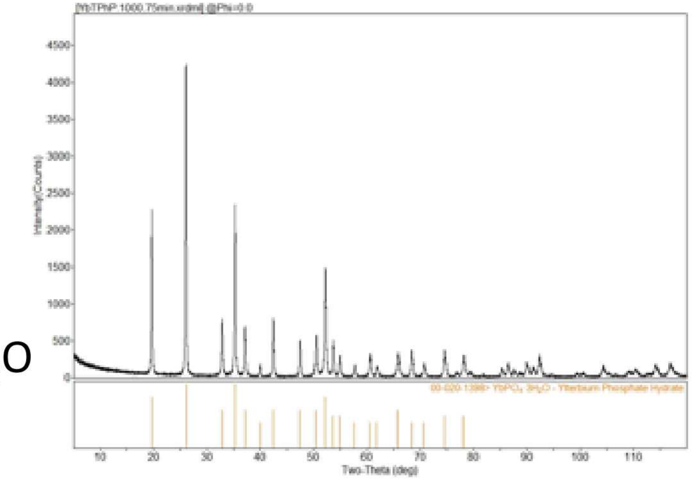
$$[Ln[(NO_3)_3\cdot 6\,H_2O] + (xs)\ O=P(OR)_3 \xrightarrow{\text{kerosene}}$$

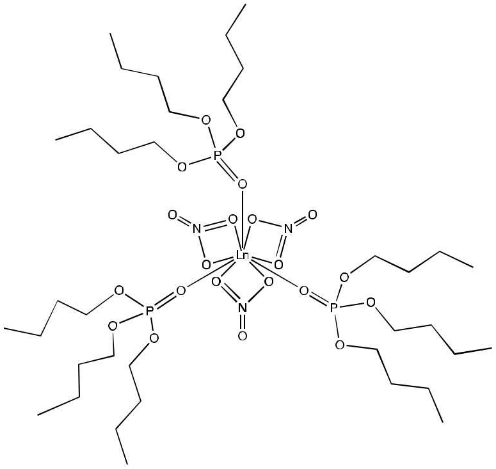


[$Ln(NO_3)_3(TPhP)_3$]

$\longrightarrow$ $\cancel{Ln_2O_3}$

$\longrightarrow$ $LnPO_4\bullet 3H_2O$

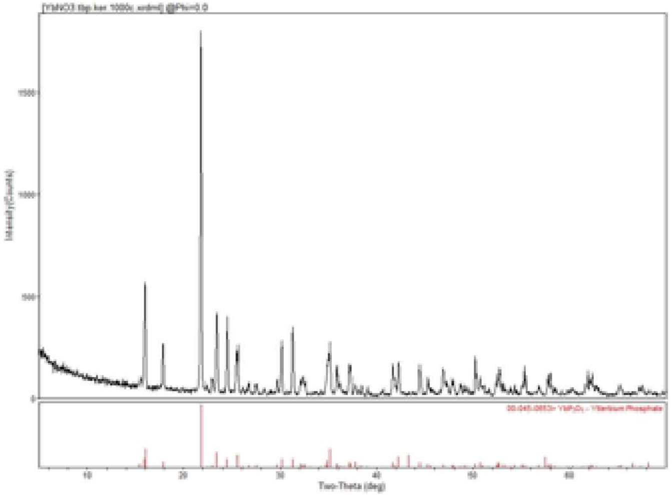




"$Ln(NO_3)_3(TBP)_3$"

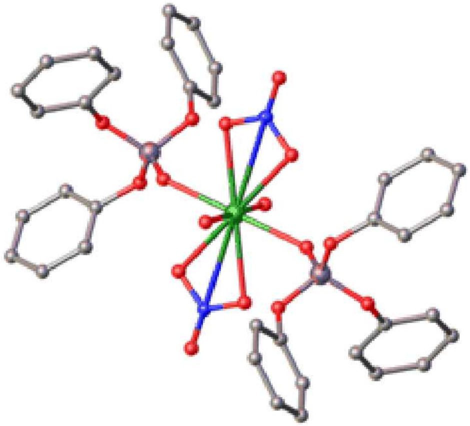
$\longrightarrow$ $\cancel{Ln_2O_3}$

$\longrightarrow$ LnP_3O_9



$U(O)_2(NO_3)_2$•$6H_2O$ in the presence of $O{=}P(OR)_3$ also found to unexpectantly form the phosphate phase

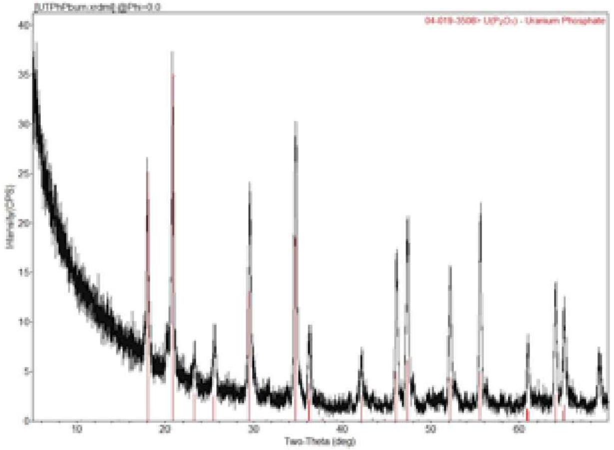
$$[U[(NO_3)_3\bullet 6\ H_2O] + (xs)\ O{=}P(OR)_3 \xrightarrow{\text{kerosene}}$$

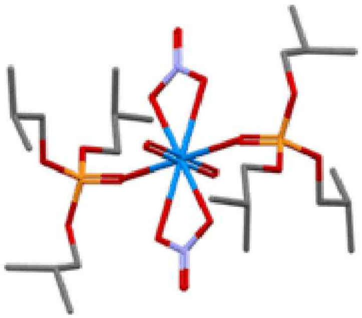


$[U(O)_2(NO_3)_2(TPhP)_2]$

$\longrightarrow \cancel{UO_x}$

$\longrightarrow U(P_2O_7)$

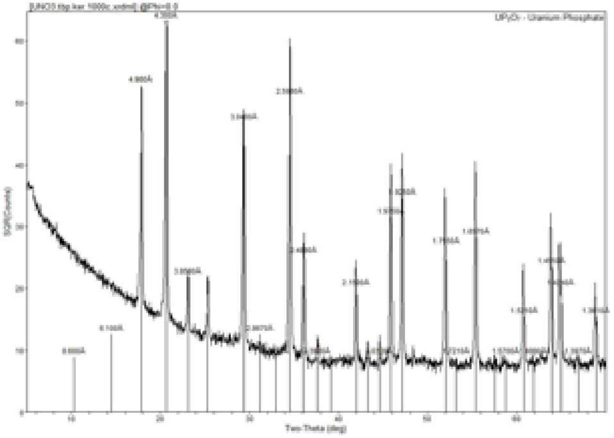




$[U(O)(NO_3)_2(TBP)_2]$

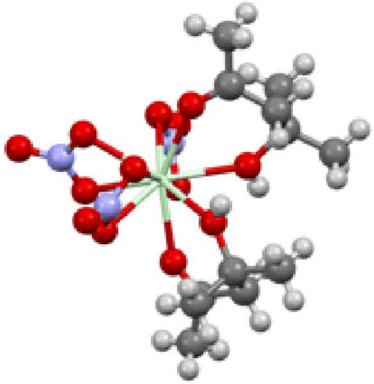
$\longrightarrow \cancel{UO_x}$

$\longrightarrow U(P_2O_7)$



DEFMEG: Uranyl nitrate triisobutylphosphate
Burns et al. Acta Cryst. C 41 (1985) 1446.
DOI: 10.1107/S0108270185008125

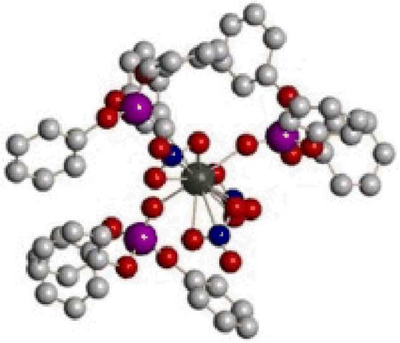
Summary and Conclusions



[Ln(κ^2-NO_3)$_3$(κ^2-DAA)$_2$]

- Solubility of Ln show useful surrogate – heavier Ln of interest for aerosol studies.
- Coordination chemistry of [Ln$(NO_3)_3$$(TPhP)_3$] determined (^{31}P and SCXRD).

- **H-DAA formed from [Ln$(NO_3)_3$$(H_2O)_6$] in acetone.**
- **Acid catalyzed room temperature conversion?**



[Ln(κ^2-NO_3)$_3$(TPhP)$_3$]

- Burning showed similar particulates and burn parameters for U- and Ln- system.
- Lower ARF for Ln-system: high temp solubility issues.
- Processing showed Ln-phosphate formed (but so did U-system)!