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Direct Extraction of Lanthanide Oxides and Nitrates in Tributyl Phosphate

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September 2023

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PREFACE OR ACKNOWLEDGEMENTS

We express our gratitude to Chandra Lamberth of the SRNL Glass Shop for the fabrication of our custom designed reactor vessel.

EXECUTIVE SUMMARY

This work investigated the dissolution rate of lanthanide oxides and nitrates in a 30 vol % TBP-*n*-paraffin solvent (pre-equilibrated with various nitric acid concentrations) using visible (Vis) spectroscopy over time. Some dissolution mechanics were observed, such as an aqueous layer forming, considerably longer dissolution times for the heavier lanthanides (hours) vs. the lighter lanthanides (minutes), and the impacts of mixing lanthanide oxides or nitrates during dissolution. Neodymium, samarium, holmium, and erbium were selected due to their unique spectroscopic signatures and to represent the lighter (neodymium and samarium) and heavier (holmium and erbium) lanthanides. Even though europium does not have a strong absorbance in the range studied, europium was used in some instances to also represent the lighter lanthanides. Cerium oxide was used to representant dissolution of tetravalent lanthanides.

TABLE OF CONTENTS

LIST OF TABLES	viii
LIST OF FIGURES	viii
1.0 INTRODUCTION	10
2.0 EXPERIMENTAL	11
2.1 Metal Oxide and Nitrate Dissolution.....	11
2.1.1 Solvent Extraction Run Using a Loaded Organic Solution	12
2.2 Preparation of Uranium-Neodymium Oxides	14
3.0 RESULTS AND DISCUSSION.....	15
3.1 Lanthanide Oxide/Nitrate Dissolution.....	15
3.2 Lanthanide Oxide Conversion and Nitrate Dissolution Kinetics	24
3.3 X-Ray Fluorescence (XRF) of Europium and Cerium.....	27
3.4 Solvent Extraction Directly from Loaded Organic Solvent in Mini Mixer Settlers to Improve Purification Efficiency	28
4.0 CONCLUSIONS.....	29
5.0 FUTURE WORK.....	29
6.0 REFERENCES	30

LIST OF TABLES

Table 1: Dissolution conditions of neodymium oxide (Nd_2O_3) and nitrate ($\text{Nd}(\text{NO}_3)_3$).....	17
Table 2: Dissolution conditions of samarium oxide (Sm_2O_3) and nitrate ($\text{Sm}(\text{NO}_3)_3$).....	19
Table 3: Dissolution conditions of erbium oxide (Er_2O_3) and nitrate ($\text{Er}(\text{NO}_3)_3$).....	21
Table 4: Dissolution conditions of holmium oxide (Ho_2O_3) and nitrate ($\text{Ho}(\text{NO}_3)_3$)	23
Table 5: Conversion rates of some oxides	25

LIST OF FIGURES

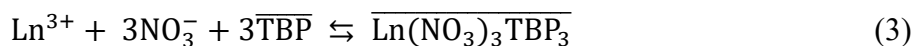
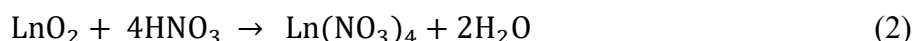
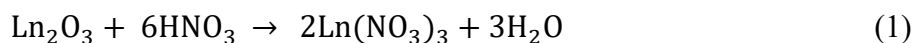
Figure 1: The <i>in-situ</i> dip probe monitoring neodymium oxide (left) and single pass transmission monitoring holmium oxide (right) in an organic solution.	12
Figure 2: Spectrum of neodymium nitrate and europium nitrate in loaded organic solution.	13
Figure 3: Loaded organic solution being fed into miniature mixer-settler bank.....	14
Figure 4: Calcined product of uranium-neodymium solids.	15
Figure 5: Neodymium oxide added to 30 vol % TBP with no acid (left) and pre-equilibrated with 10 M nitric acid (right).....	16
Figure 6: Vials of converted neodymium oxide and nitrate (numbered from Table 1).	17
Figure 7: Final spectra of neodymium oxide and nitrate: Solutions 1 (—), 2 (—), 3 (—), 4 (—), 5 (—), 6 (—), and 7 (—) (numbered from Table 1). Inset is a closeup of 500 – 550 nm for clarity.	18
Figure 8: The aqueous phase (circled) observed during direct extraction of neodymium oxide.	19
Figure 9: Vials of converted samarium oxide and nitrate (numbered from Table 2).....	20
Figure 10: Final spectra of samarium oxide and nitrate: Solutions 1 (—), 2 (—), 3 (—), 4 (—), and 5 (—) (numbered from Table 2). Inset is a closeup of 375 – 400 nm for clarity. .	20
Figure 11: Vials of converted erbium oxide and nitrate (numbered from Table 3).....	21
Figure 12: Final spectra of erbium oxide and nitrate: Solutions 1 (—), 2 (—), 3 (—), 4 (—), and 5 (—) (numbered from Table 3). Inset is a closeup of 500 – 600 nm for clarity.	22
Figure 13: The additional phase (circled) that was observed during conversion of the erbium oxide to erbium nitrate.....	23
Figure 14: Vials of converted holmium oxide and nitrate (numbered from Table 4).....	24
Figure 15: Final spectra of holmium oxide and nitrate: Solutions 1 (—), 2 (—), 3 (—), 4 (—) (numbered from Table 4).	24

Figure 16: Direct extraction of holmium oxide being monitored using an <i>in-situ</i> dip probe (left) and single pass transmission (right).	25
Figure 17: Comparison of Er_2O_3 and Ho_2O_3 dissolution.	26
Figure 18: Comparison of europium oxide (Eu_2O_3), erbium nitrate ($\text{Er}(\text{NO}_3)_3$), and holmium nitrate ($\text{Ho}(\text{NO}_3)_3$).....	27
Figure 19: XRF of europium and cerium oxide in an organic solution	28
Figure 20: SRNL Glass Reactor Vessel for Co-Precipitated Oxides.	29

1.0 INTRODUCTION

Approximately 5% of the initial uranium in nuclear fuel for a power reactor will fission or transmute after an irradiation cycle, creating used nuclear fuel (UNF) [1]. The transmuted elements, transuranics, can be recovered and fabricated into fuels or targets. A reprocessing facility that can recycle UNF is expensive using current technology. H-Canyon is the only facility that exists in the United States with this capability. A potentially more cost effective alternative is to voloxidize the UNF (for tritium removal) and then directly extract (or directly dissolve) the formed oxides or nitrates in an organic solution containing an extractant like tributyl phosphate (TBP) [2]. This organic solution can then be sent through a conventional solvent extraction process to recover desired elements [3].

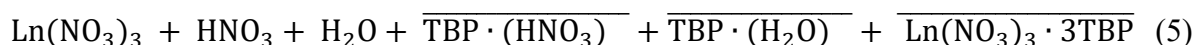
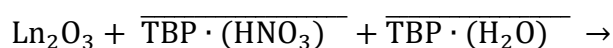
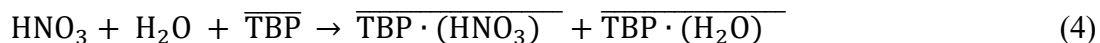
While metal nitrates complex with TBP within minutes, metal oxides are limited by the amount of nitric acid present in the organic phase [4-6]. Metal oxides cannot dissolve in an organic solution like 30 vol % TBP because TBP does not complex with metal oxides. An acid is necessary to convert the metal from an oxide to a compound that can complex with TBP, such as a lanthanide nitrate (Equations 1 and 2). The Ln-NO₃-TBP complex will most likely be 1:3:3, as shown in Equation 3 [7, 8].



However, nitric acid does not freely dissociate in organic solutions. Instead, it complexes with TBP via hydrogen bonding. The nitric acid is added to the organic solution during a pre-equilibration step where TBP extracts nitric acid and reaches equilibrium prior to metal transfer studies. It was of interest to determine how the dissolution kinetics change if the oxide dissolves in an aqueous solution of nitric acid or an organic solution containing nitric acid.

An intriguing phenomenon to consider is that by pre-equilibrating TBP with nitric acid, water also goes into the organic phase (Equation 4) [9]. Chiarizia and Briand indicated that an organic solution of 0.73 M TBP pre-equilibrated with 10 M HNO₃ will also contain approximately

0.075 M H₂O [9]. Due to Le Chatelier's principle, as the oxide dissolves and consumes nitric acid, the water would dissociate from the TBP to maintain the equilibrium. It was found that when enough water is dissociated from the TBP and generated during metal oxide dissolution, then an aqueous phase was formed. The formed aqueous phase will then strip nitric acid from the TBP to maintain chemical equilibrium. Additionally, because the trivalent lanthanide nitrates weakly complex with TBP, they will strip into the aqueous phase (Equation 5).



Rudisill et al. dissolved surrogate used nuclear fuel in an organic solution to determine the distribution of actinide and fission products [3] but did not probe the dissolution kinetics or mechanics, especially for the lanthanide fission products. This work investigated the dissolution rate of lanthanide oxides and nitrates in a 30 vol % TBP-*n*-paraffin solvent (pre-equilibrated with various nitric acid concentrations) using visible (Vis) spectroscopy over time. Some dissolution mechanics were observed: an aqueous layer forming, longer dissolution times for the heavier lanthanides, and the impacts of mixing lanthanide oxides or nitrates during dissolution. Neodymium, samarium, holmium, and erbium were selected due to their unique spectroscopic signatures and to represent the lighter (neodymium and samarium) and heavier (holmium and erbium) lanthanides. Even though europium does not have a strong absorbance in the range studied, europium was used in some instances to also represent the lighter lanthanides. Cerium(IV) oxide was used to represent dissolution of tetravalent lanthanides.

2.0 EXPERIMENTAL

2.1 Metal Oxide and Nitrate Dissolution

The organic solutions were prepared by pre-equilibrating 30 vol % TBP (diluted in *n*-paraffin) with various nitric acid concentrations twice. The solutions were vigorously mixed for at least two minutes with a 2:1 vol. ratio of the aqueous to organic, respectively. The oxides of cerium, europium, neodymium, samarium, holmium, and erbium, and the nitrate-hydrates of

europium, neodymium, samarium, holmium, or erbium were added to the organic solution. A stir bar vigorously mixed the solution at room temperature. The target concentrations of the dissolved lanthanide ranged from 0.01 to 0.05 M. To clarify, the lanthanide oxide concentrations represent the measured amount of the oxide for a given volume of solution and not the anticipated concentration of their nitrate form (Equation 1). This nomenclature was used because the all the oxide may not convert to its nitrate form. The dissolution rate was monitored by using an *in-situ* dip probe or single pass transmission, Figure 1, connected to an Avantes spectrometer. An Avantes model AvaSpec-ULS3648 spectrometer with a VB grating, 10- μ m slit and wavelength range of 365 to 914 nm was used for all experimentation. The light source is an Avantes Xe flash lamp, and the optical absorbance probe is an Equitech International 1/4" retro-reflecting dip probe with 2.5-mm optical pathlength.



Figure 1: The *in-situ* dip probe monitoring neodymium oxide (left) and single pass transmission monitoring holmium oxide (right) in an organic solution.

2.1.1 Solvent Extraction Run Using a Loaded Organic Solution

A solution of 30 vol % TBP diluted in *n*-paraffin was pre-equilibrated with 4 M nitric acid as previously described. After pre-equilibration, final target concentrations of 0.02 M neodymium oxide and 0.02 M europium oxide were added and the solution was vigorously mixed. Figure 2 shows the final spectrum of the neodymium and europium in solution, referred to as the loaded organic solution. This solution was a feed solution for subsequent solvent extraction experiments.

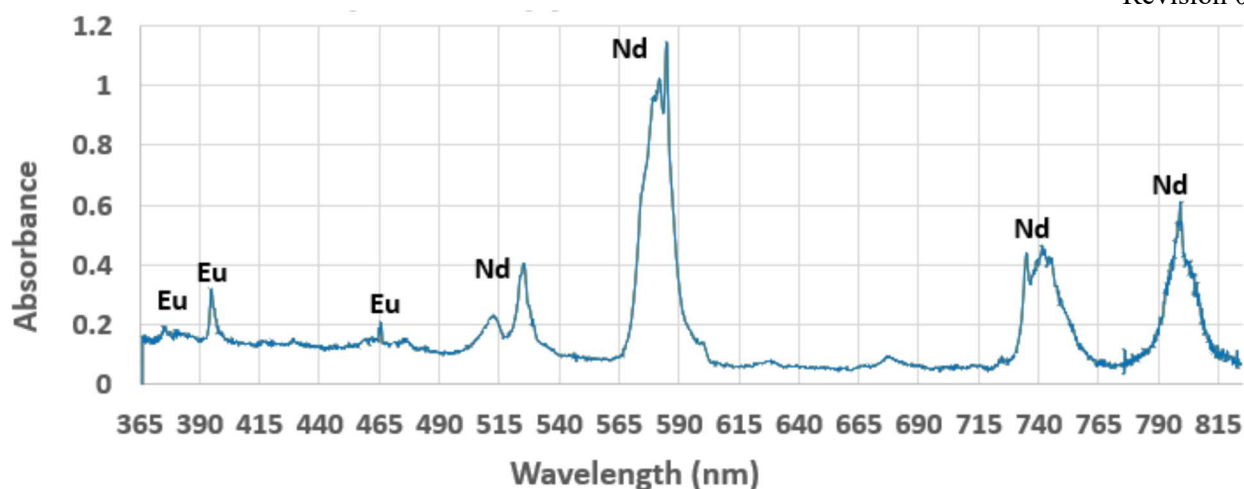


Figure 2: Spectrum of neodymium nitrate and europium nitrate in loaded organic solution.

Miniature mixer-settler equipment was used for the solvent extraction experiment. In the mixing compartment of a stage the aqueous and organic phases are vigorously mixed to transfer metals between the phases thereby establishing equilibrium conditions. The emulsion then flows to the settling compartment where phase disengagement occurs. The separated organic and aqueous phases flow to the next mixing compartment of the next stage in a countercurrent arrangement. The miniature mixer-settler bank was first filled with the scrub solution (1 M nitric acid) by using large transfer pipettes. Next, the mixers and aqueous pump were started to establish fluid flow. Once steady aqueous flow was achieved, the organic pump was started. The loaded organic solution was fed counter-current to a scrub solution into a miniature mixer-settler bank with sixteen stages, Figure 3. This experiment did not include an extraction phase and so was exclusively a scrub phase (i.e., sixteen scrub stages). The counter-current flow resulted in the aqueous waste and scrubbed organic coming out the right and left sides of the bank, respectively. Pump flow rates were slightly adjusted to achieve steady state of the two phases.

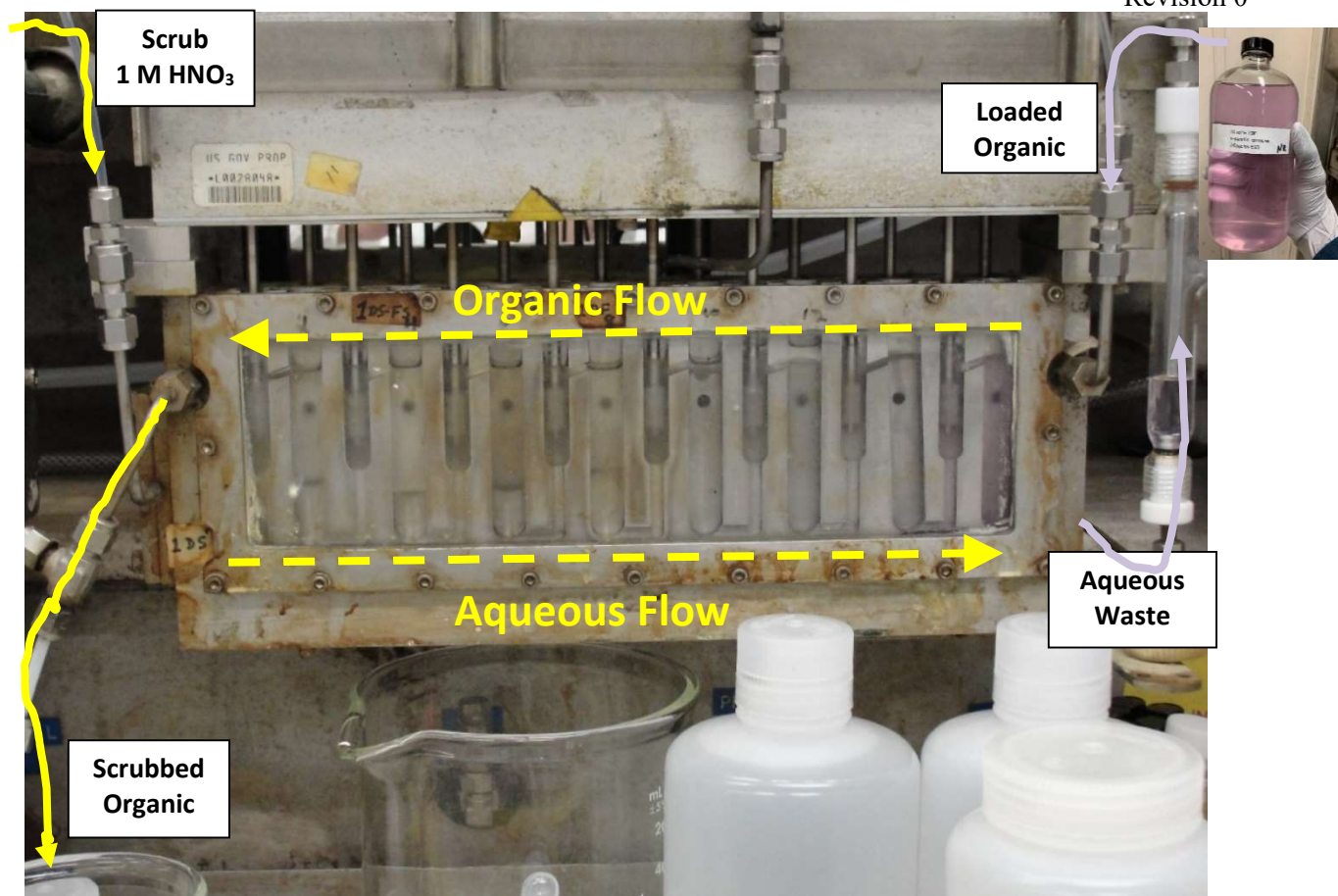


Figure 3: Loaded organic solution being fed into miniature mixer-settler bank.

2.2 Preparation of Uranium-Neodymium Oxides

The uranium-neodymium oxide was prepared using the following method. A diluted solution of ammonium hydroxide (4.7 M) was slowly added to an acidic solution containing neodymium nitrate and uranyl nitrate. An excess of ammonium hydroxide (approximately 2.5x) was used to ensure complete conversion of uranyl nitrate to ammonium diuranate [10]. The solution was diluted with water and well mixed to ensure complete precipitation. The resulting slurry was filtered to remove the aqueous solution prior to the calcination step. The co-precipitated solids were first heated at 110 °C for at least 30 min and then calcined at 600 °C for two hours. The calcined solids are shown in Figure 4.



Figure 4: Calcined product of uranium-neodymium solids.

3.0 RESULTS AND DISCUSSION

3.1 Lanthanide Oxide/Nitrate Dissolution

It was uncertain if lanthanide oxides can directly extract into TBP without nitric acid present. Neodymium oxide was added to an organic solution not pre-equilibrated with acid and another organic solution pre-equilibrated with acid (Figure 4). Spectroscopic analysis showed that the neodymium oxide added to the pre-equilibrated TBP had peaks like its nitrate form, indicating that the oxide was converted to a nitrate (Equation 1). Additionally, this can be visually confirmed in Figure 4 because neodymium oxide is blue whereas neodymium nitrate is purple. The neodymium oxide did not complex with the TBP and settled to the bottom of the vial when the mixing was stopped. The organic solutions need to be pre-equilibrated with nitric acid prior to the addition of a lanthanide oxide for the conversion to nitrate to occur. It was later confirmed that all the lanthanide oxides used had spectral peaks like their respective nitrate forms when dissolved in the organic solutions pre-equilibrated with acid.



Figure 5: Neodymium oxide added to 30 vol % TBP with no acid (left) and pre-equilibrated with 10 M nitric acid (right).

Several dissolution experiments were done for each oxide to compare different dissolution conditions and determine if there was a minimum amount of acid needed to convert the oxide. The neodymium dissolution conditions, visual appearance of the solution, and final spectra are shown in Table 1, Figure 5, and Figure 6, respectively. Solution 1 was a control to demonstrate that no acid was needed to allow the neodymium nitrate hexahydrate to bind to the TBP. Also, the absorbance is approximately half that of the organic solutions containing acid with converted neodymium oxide (Solutions 2 and 3). This occurs due to Equation 1, one mole of metal oxide converts to two moles of the nitrate. It is uncertain why the absorbances for Solutions 2 and 3 do not completely overlap, perhaps due to the different acidities or another complex forming. Even though Solutions 2 – 4 have approximately the same concentrations of neodymium, the absorbance of Solution 4 is distinctly lower. The reason is due to incomplete dissolution of the neodymium oxide as all the available acid was used to convert the oxide to the nitrate. Equation 1 indicates that six moles of nitric acid are needed to convert one mole of neodymium oxide to neodymium nitrate. A TBP solution pre-equilibrated with 1 M nitric acid contains approximately 0.1 M nitric acid, which is available to convert oxide to nitrate (Solution 4), but the 0.05 M neodymium oxide would have needed 0.3 M nitric acid.

The spectrum of Solution 5 was taken when the neodymium oxide solids had settled (Figure 5) after vigorous mixing (Figure 1). The Solution 5 spectrum showed a significant baseline offset but otherwise no characteristic neodymium nitrate nor oxide peaks. The experiment with Solution 5 further demonstrated that the metal oxide does not bind to the TBP but needs to convert to its nitrate form to bind to the TBP. Solution 6 included cerium(IV) oxide, which does not readily

dissolve in nitric acid and was used as a surrogate for plutonium oxide. Unfortunately, neither cerium(IV) oxide nor cerium(IV) nitrate have distinct spectroscopic peaks within the spectral measurement range, so it is more difficult to determine the cerium oxide that converted using Vis spectroscopy. However, the presence of solids at the bottom (Figure 5) indicates that the cerium oxide did not readily dissolve in the organic solution. Solution 7 is an aqueous nitric acid solution with dissolved neodymium oxide. Comparing the spectrum of Solution 7 with the spectrum taken of the organic solutions in Figure 6 shows a bathochromic shift, most likely due to complexation with TBP.

Table 1: Dissolution conditions of neodymium oxide (Nd_2O_3) and nitrate ($\text{Nd}(\text{NO}_3)_3$)

Solution #	$\text{Nd}(\text{NO}_3)_3$			Nd_2O_3			
	1	2	3	4	5	6	7
Neodymium Added (M)	0.048	0.050	0.049	0.050	0.049	0.021 + 0.024 CeO_2	0.012
Pre-equilibrated with # M HNO_3	0	10	4	1	0	10	No Org/ 1 M HNO_3
Solids	No	No	No	Yes	Yes	Yes	No

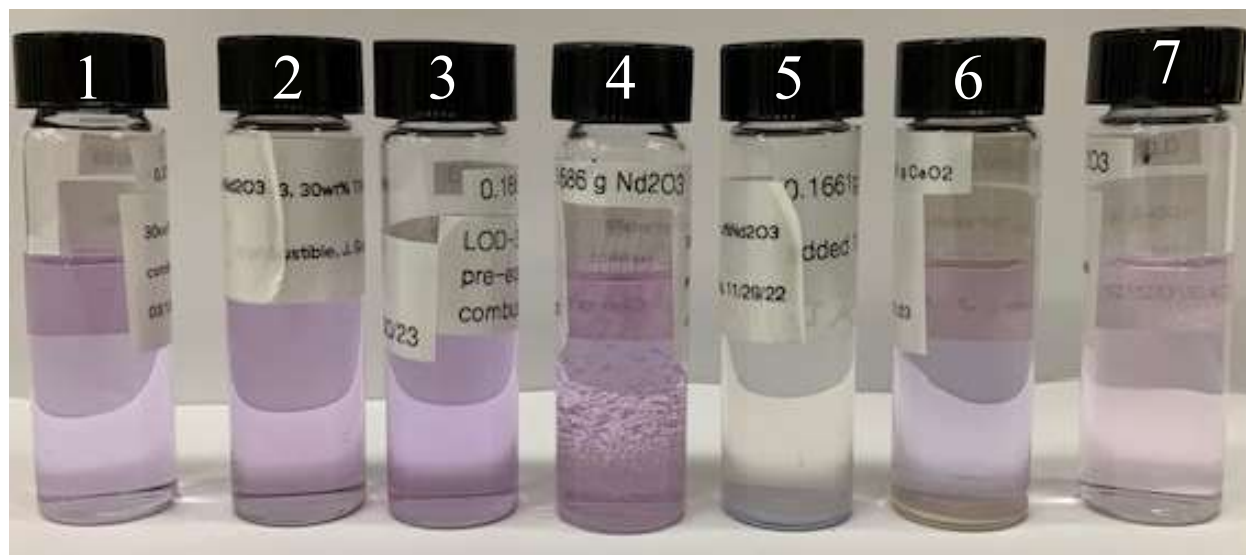


Figure 6: Vials of converted neodymium oxide and nitrate (numbered from Table 1).

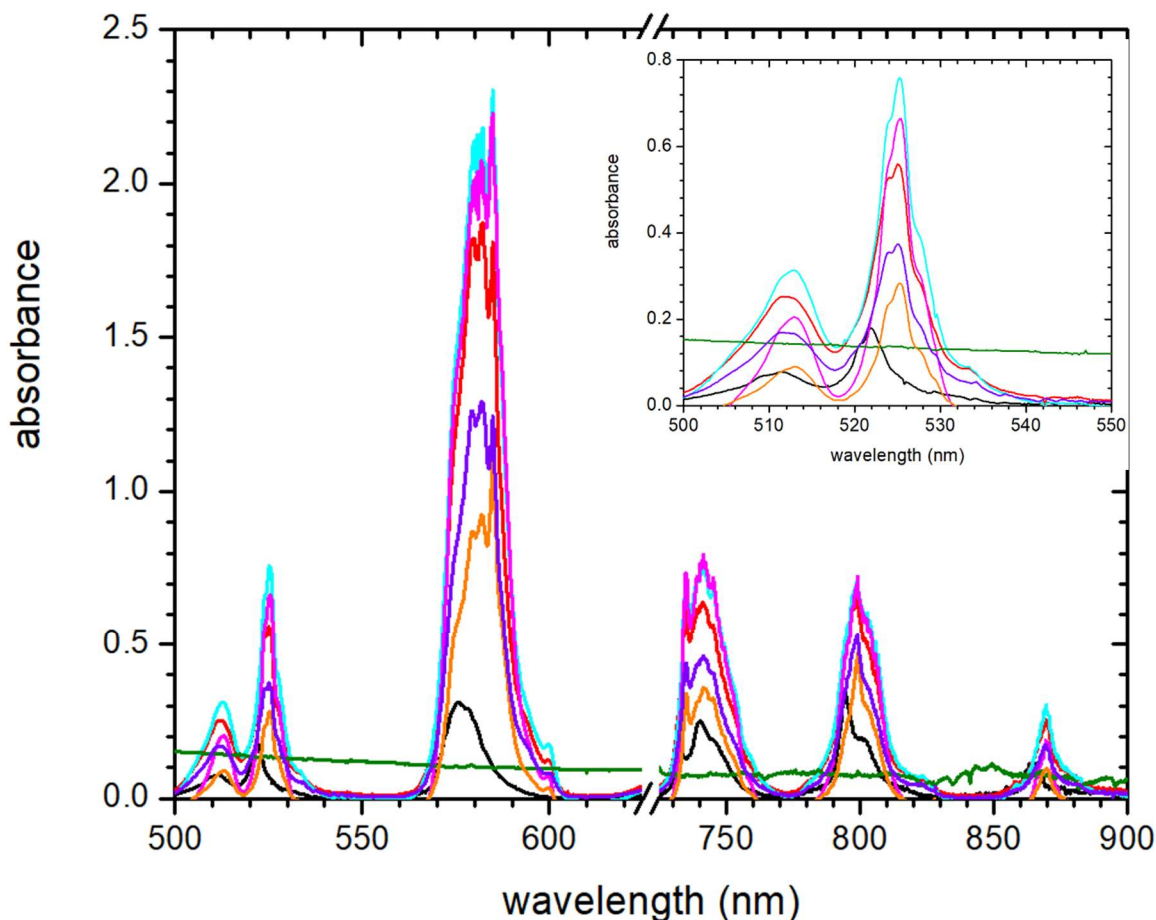


Figure 7: Final spectra of neodymium oxide and nitrate: Solutions 1 (—), 2 (—), 3 (—), 4 (—), 5 (—), 6 (—), and 7 (—) (numbered from Table 1). Inset is a closeup of 500 – 550 nm for clarity.

Note that direct extraction of neodymium nitrate in the organic phase will not be analogous to direct extraction of neodymium oxide. The neodymium nitrate is hydrated and will add water to the organic phase, slightly perturbing the equilibrium, whereas the neodymium oxide will consume nitric acid to convert to its nitrate form and generate water. The vials shown in Figure 5 contained 10 mL of solution. It was found that by scaling the volume to 50 mL and keeping the same metal concentration, a distinct aqueous layer is formed (Figure 7). According to Equation 1, the conversion of 0.9170 g of Nd_2O_3 to $\text{Nd}(\text{NO}_3)_3$ generates 1030 μL of water. However, the volume of the formed aqueous layer is expected to vary due to water dissociating from the TBP to maintain chemical equilibrium (Equation 5).

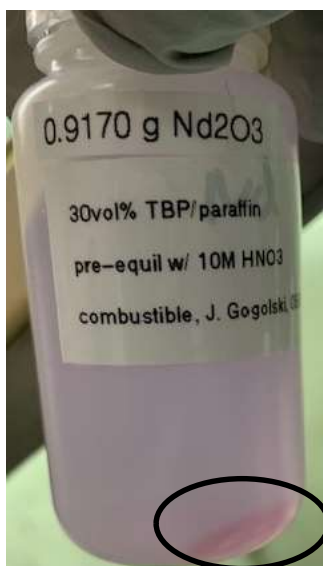


Figure 8: The aqueous phase (circled) observed during direct extraction of neodymium oxide.

Similar dissolution experiments done for neodymium were also done for samarium. The samarium dissolution conditions, visual appearance of the solution, and final spectra are shown in Table 2, Figure 8, and Figure 9, respectively. The samarium oxide shared the same characteristics as the neodymium oxide: conversion within minutes, inadequate nitric acid concentration leaving unconverted oxide in the vial, and a spectral shift between aqueous and organic solutions.

Table 2: Dissolution conditions of samarium oxide (Sm_2O_3) and nitrate ($\text{Sm}(\text{NO}_3)_3$).

Solution #	$\text{Sm}(\text{NO}_3)_3$	Sm_2O_3			
	1	2	3	4	5
Samarium Added (M)	0.049	0.050	0.050	0.049	0.012
Pre-equilibrated with # M HNO_3	0	10	4	1	No Org/ 1 M HNO_3
Solids	No	No	No	Yes	No

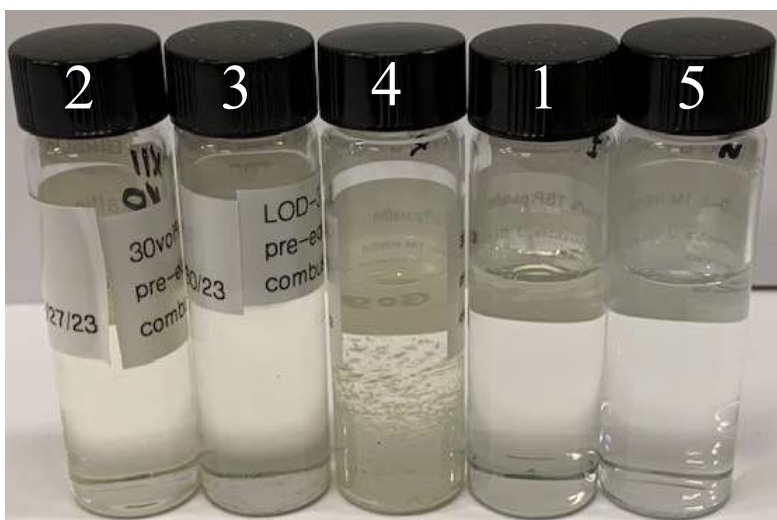


Figure 9: Vials of converted samarium oxide and nitrate (numbered from Table 2).

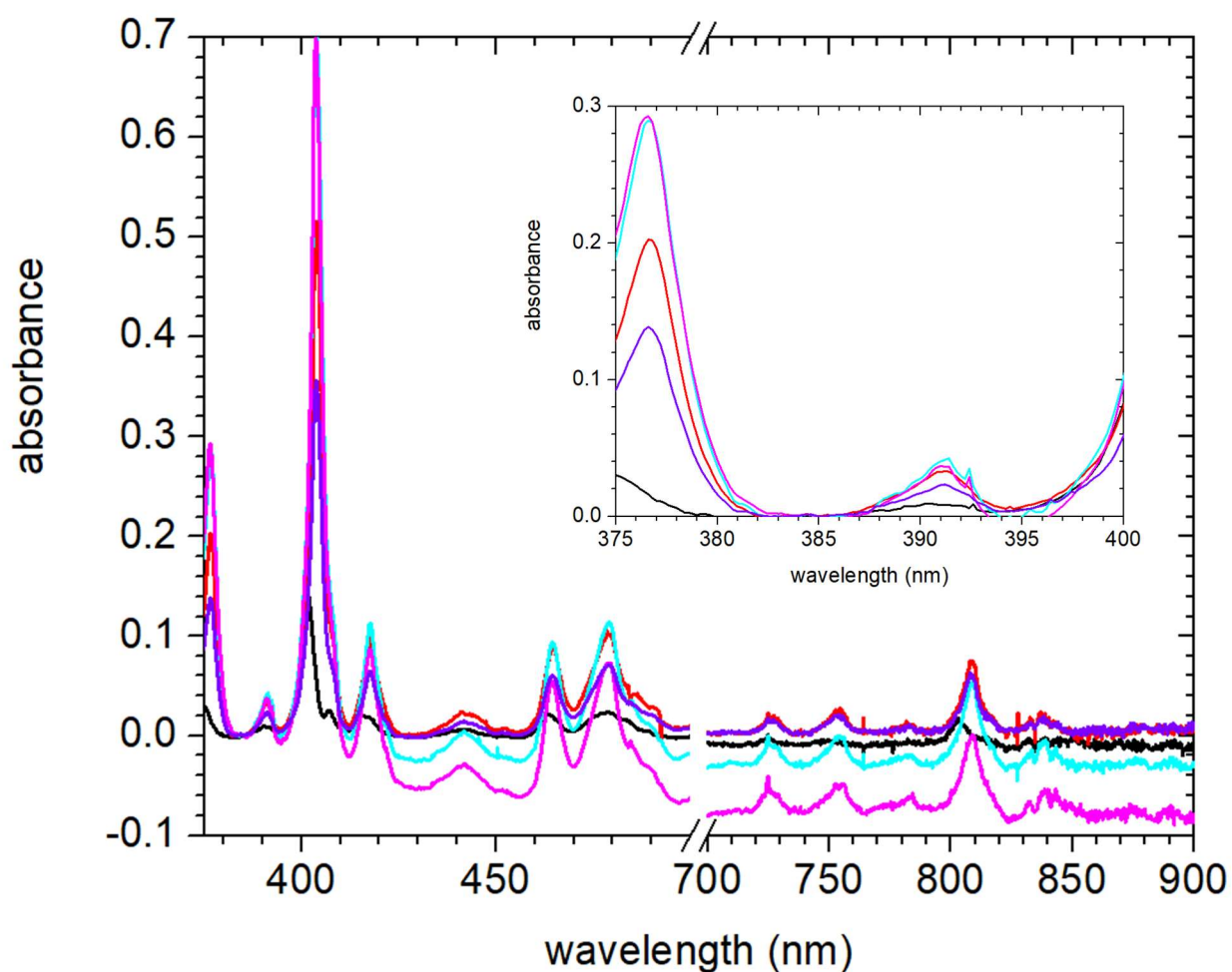


Figure 10: Final spectra of samarium oxide and nitrate: Solutions 1 (—), 2 (—), 3 (—), 4 (—), and 5 (—) (numbered from Table 2). Inset is a closeup of 375 – 400 nm for clarity.

The erbium dissolution conditions, visual appearance of the solution, and final spectra are shown in Table 3, Figure 10, and Figure 11, respectively. Unlike neodymium and samarium oxides, the erbium oxide needed at least several hours to completely convert to its nitrate form. The slower conversion rate of a heavier lanthanide oxide (erbium) was previously observed [6]. Additionally, it seemed that the lower acid concentration also affected the conversion rate. As the stoichiometric ratio of the oxide to nitric acid needed for dissolution is the same for all trivalent lanthanides, it is unclear what would cause a slower conversion rate (seconds to minutes vs. hours). Also, contrary to the lighter lanthanides, Solution 2 formed a distinct diluent rich phase as well. The absorbance of Solution 2 in Figure 11 was quite high due to the *in-situ* dip probe taking spectra of the heavier organic phase.

Table 3: Dissolution conditions of erbium oxide (Er_2O_3) and nitrate ($\text{Er}(\text{NO}_3)_3$)

Solution #	$\text{Er}(\text{NO}_3)_3$		Er_2O_3		
	1	2	3	4	5
Erbium Added (M)	0.057	0.051	0.011	0.019 + 0.018 CeO_2	0.009
Pre-equilibrated with # M HNO_3	0	10	4	10	No Org/ 1 M HNO_3
Solids	No	No	No	Yes	No



Figure 11: Vials of converted erbium oxide and nitrate (numbered from Table 3)

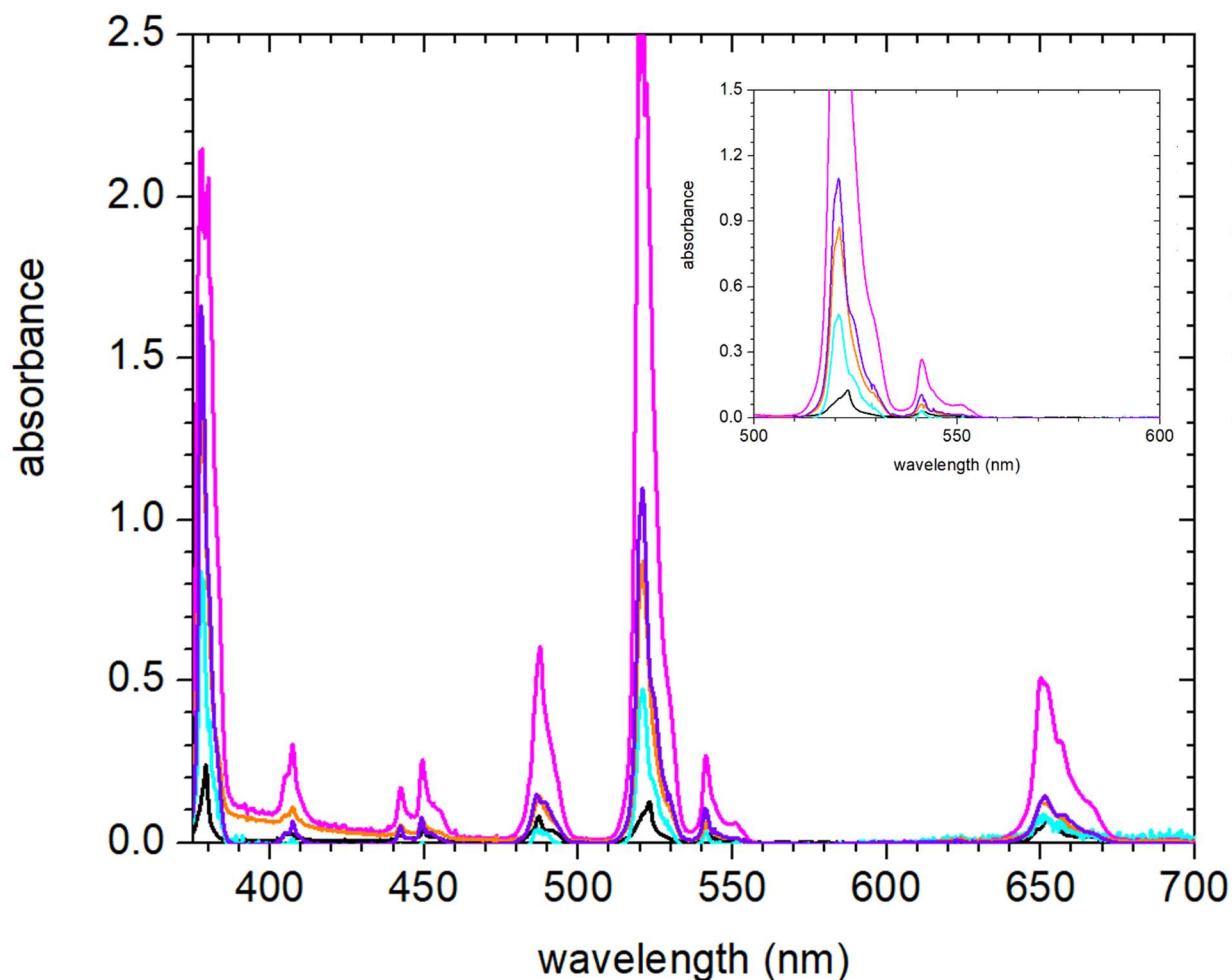


Figure 12: Final spectra of erbium oxide and nitrate: Solutions 1 (—), 2 (—), 3 (—), 4 (—), and 5 (—) (numbered from Table 3). Inset is a closeup of 500 – 600 nm for clarity.

Similar conditions that created the aqueous phase for the neodymium oxide experiment (Figure 7) were repeated with erbium oxide (Figure 12). A key difference is that the aqueous phase formed before complete conversion of the erbium oxide and coated the erbium oxide powder. The newly formed aqueous phase will strip nitric acid from the TBP and continue converting the erbium oxide to erbium nitrate. If enough acid is present and given enough time, then the erbium oxide will be fully converted to its nitrate form.

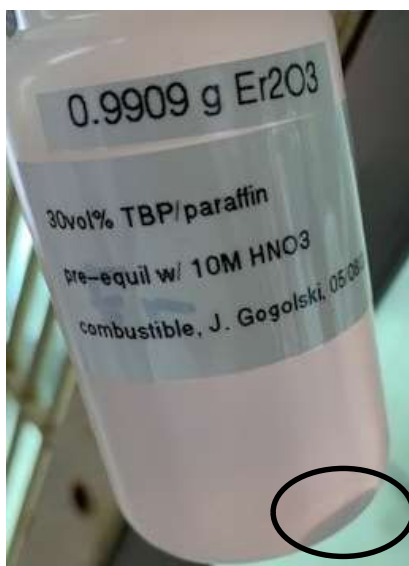


Figure 13: The additional phase (circled) that was observed during conversion of the erbium oxide to erbium nitrate.

The conversion experiments for holmium oxide differed slightly from previous experiments by including a spike of an aqueous phase during the conversion process (Solution 3). The aqueous spike was used to help determine if the holmium oxide would convert faster with an aqueous phase present from the beginning. The holmium conversion conditions, visual appearance of Solutions 2 and 3, and final spectra are shown in Table 4, Figure 13, and Figure 14, respectively. The holmium oxide shared the same characteristics as the erbium oxide: conversion taking several hours and the split of the organic phases. The aqueous spike did not seem to impact the conversion rate but did change the equilibrium of the organic phase. The organic phase split but the metal-rich phase was smaller (Figure 13), likely due to excess holmium nitrate going into the aqueous phase.

Table 4: Dissolution conditions of holmium oxide (Ho_2O_3) and nitrate ($\text{Ho}(\text{NO}_3)_3$)

Solution #	$\text{Ho}(\text{NO}_3)_3$	Ho_2O_3		
	1	2	3	4
Holmium Added (M)	0.048	0.049	0.050	0.012
Pre-equilibrated with # M HNO_3	0	10	10 *with 0.1 vol% H_2O added	No Org/ 1 M HNO_3
Solids	No	No	No	No

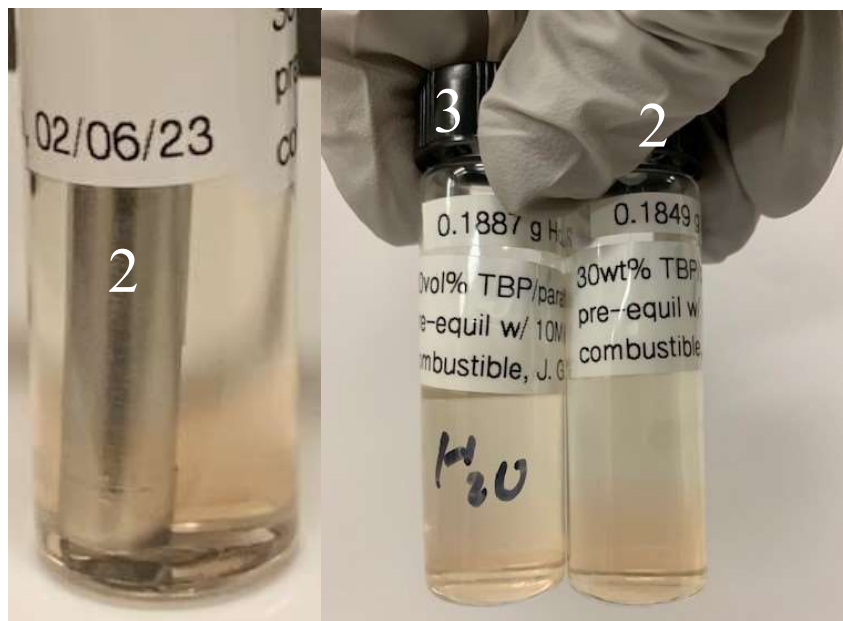


Figure 14: Vials of converted holmium oxide and nitrate (numbered from Table 4).

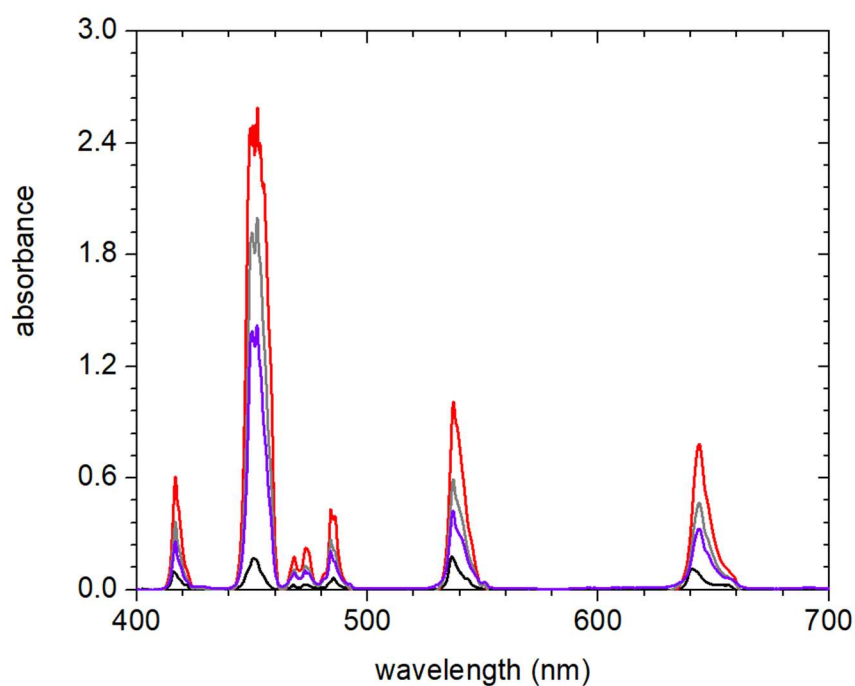


Figure 15: Final spectra of holmium oxide and nitrate: Solutions 1 (———), 2 (———), 3 (———), 4 (———) (numbered from Table 4).

3.2 Lanthanide Oxide Conversion and Nitrate Dissolution Kinetics

The initial goal of these experiments was to monitor the conversion rate of the lanthanide oxides using Vis spectroscopy. It was found that the oxide powder would settle on the reflective surface of the *in-situ* dip probe (Figure 15) and block the light when the conversion rate was too

slow (aspect of the heavier lanthanides) or when higher concentrations of the lanthanides (heavy and light) were used. A single pass transmission was used instead for monitoring the dissolution rates; however, too much oxide in solution still caused high baseline issues. Figure 15 also shows how fine the particles are in solution with vigorous mixing.



Figure 16: Direct extraction of holmium oxide being monitored using an *in-situ* dip probe (left) and single pass transmission (right).

$$\text{Peak} = A_0 + A(1 - e^{-b(t-t_0)}) \quad (6)$$

The conversion rate was calculated using Equation 6: t_0 is determined from the time when the baseline offset deviated from ~ 0 , A_0 is assumed equal to 0, $-b$ is dissolution rate, and A is the absorbance at given time t . It is uncertain why the conversion rates for the lighter lanthanides (Nd, Sm, and Eu) were two orders of magnitude faster than for the heavier lanthanides (Ho and Er), reported in Table 5. The dissolution rates for Nd and Sm are not reported because the exponential fit did not match well, indicating that either multiple species are forming or there is a potentially irregular conversion rate of the oxide.

Table 5: Conversion rates of some oxides

Oxide	Concentration (mM)	-b (min ⁻¹)
Eu	21.2	0.385
Ho	19.3	0.0043
Er	31.0	0.0032

Figure 16 emphasizes the slower dissolution rate of the heavier lanthanides. Monitoring of the experiment was terminated after several hours before the conversion reaction was completed, as evidenced due to the slope not leveling off.

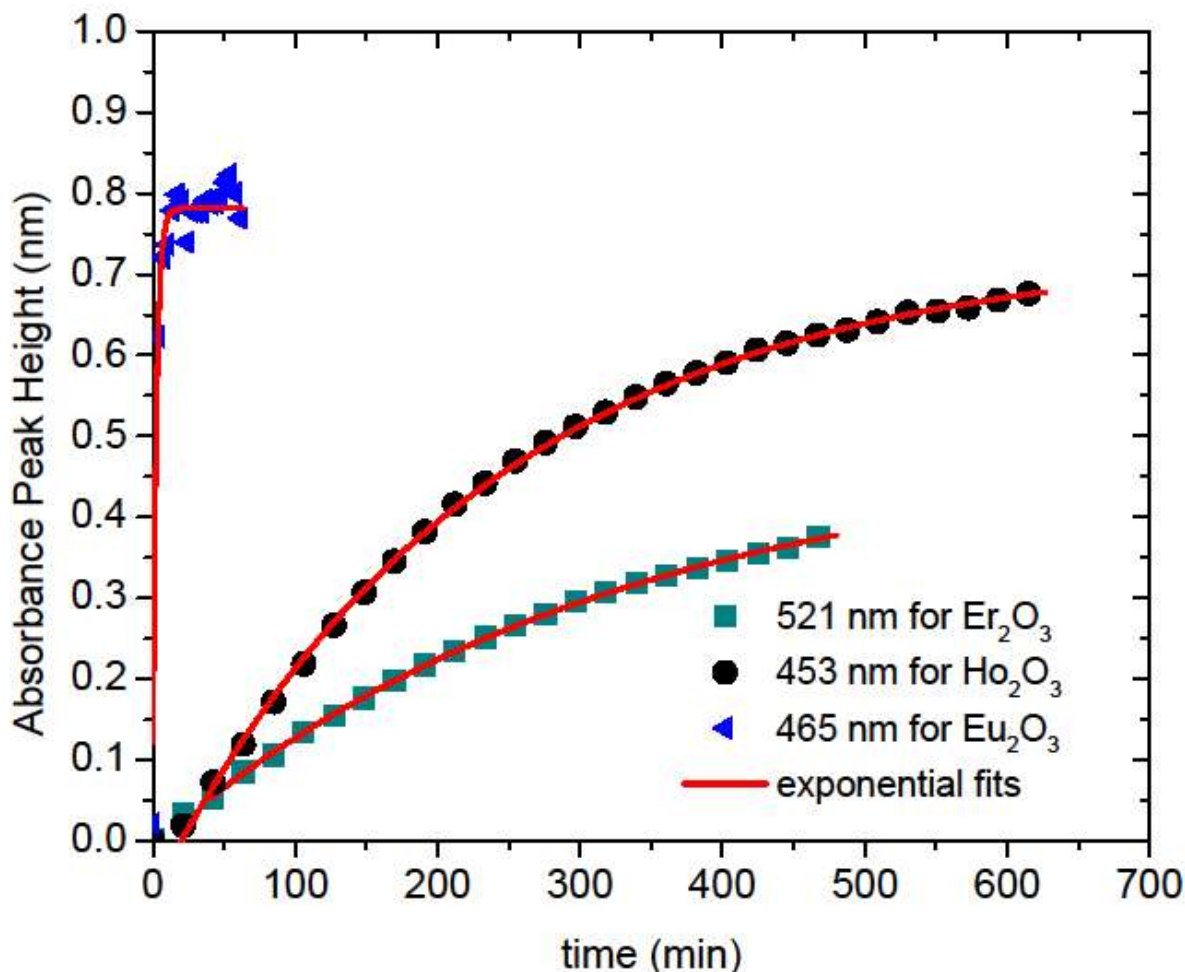


Figure 17: Comparison of Er_2O_3 and Ho_2O_3 dissolution.

Intriguingly, the conversion rates of the lighter lanthanide oxides were not only like their nitrate forms, but also the heavier lanthanide nitrates, Figure 17. This observation suggests that once the nitrate salt is formed, the lanthanide nitrate readily binds to TBP. Also, that the conversion from an oxide to nitrate is the limiting factor. This was additionally explored by dissolving the heavier lanthanide oxides in acidic aqueous solutions and comparing their dissolution rates to the experiments with the organic solutions.

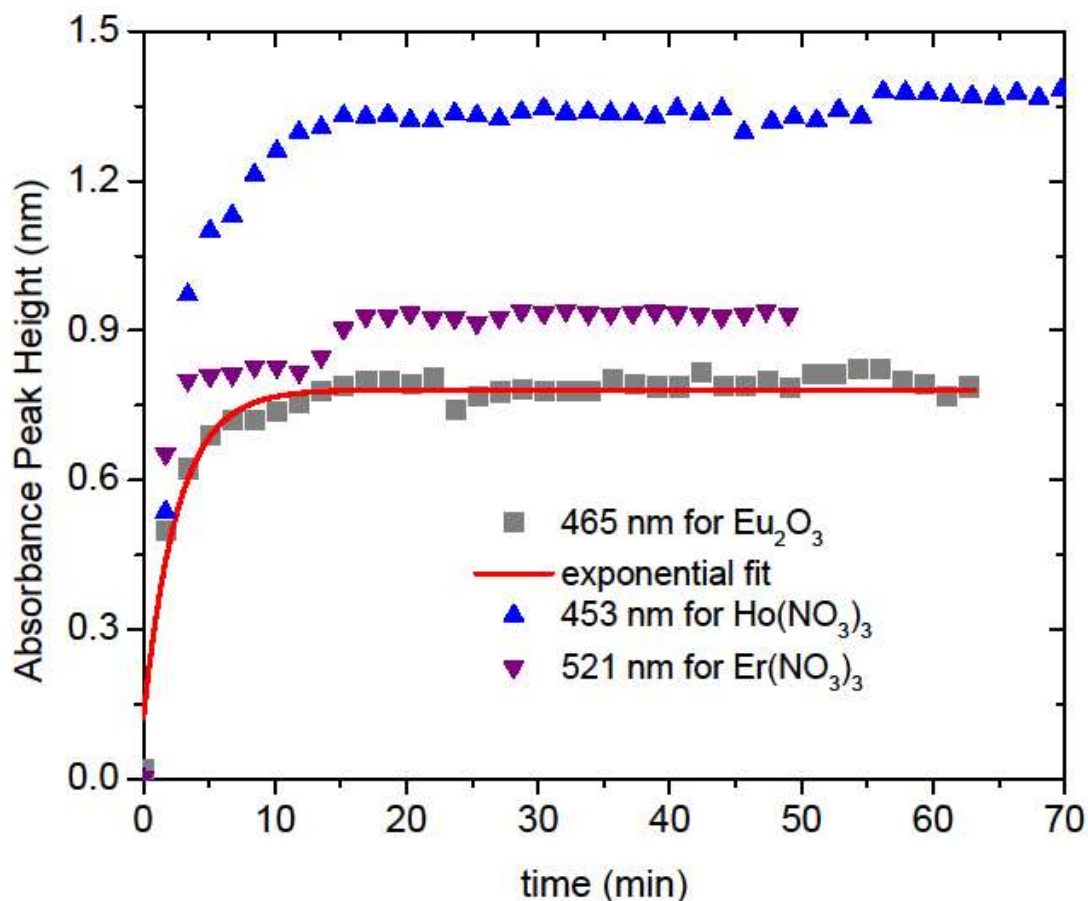


Figure 18: Comparison of europium oxide (Eu_2O_3), erbium nitrate ($\text{Er}(\text{NO}_3)_3$), and holmium nitrate ($\text{Ho}(\text{NO}_3)_3$).

3.3 X-Ray Fluorescence (XRF) of Europium and Cerium

Since europium and cerium oxides are not as spectroscopically unique as the other lanthanide oxides studied, XRF was briefly used to determine the ease of quantitative analysis. A major drawback to this method is the loss of solution over time. Aliquots of the solution are used for sample analysis but cannot be returned to the original solution. Therefore, if solids were still present in the organic solution, then the solids are lost. This issue became apparent when studying the slowly converting cerium oxide. This method will work if the conversion is complete or equilibrium reached because then the metals can be accurately quantified.

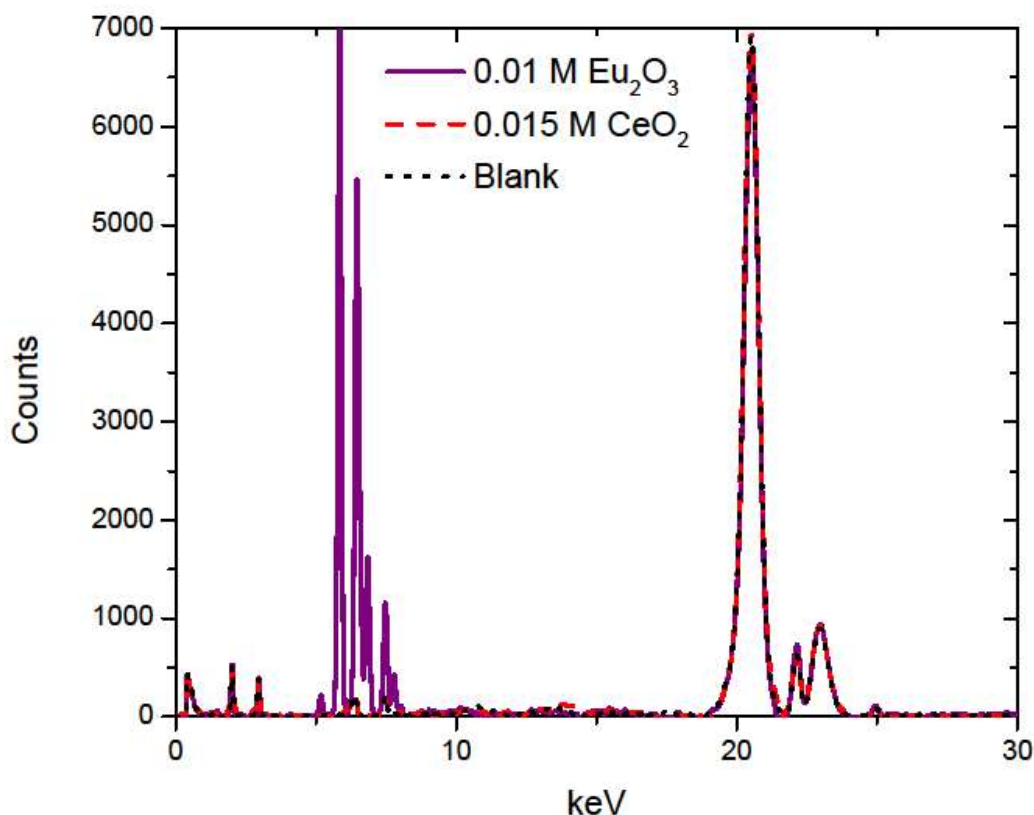


Figure 19: XRF of europium and cerium oxide in an organic solution

3.4 Solvent Extraction Directly from Loaded Organic Solvent in Mini Mixer Settlers to Improve Purification Efficiency

Solvent extraction equipment was used to observe the effects of a loaded organic feed from the direct extraction of neodymium and europium oxides (preparation described in Section 2.1.1) being scrubbed with 1 M nitric acid [11]. Figure 3 shows a purple hue in Stages 16 and 15. Unsurprisingly, the neodymium nitrate from the dissolved oxides readily stripped from the organic phase, as evidenced by neodymium nitrate's purple color shifting from the loaded organic solution to be present in the aqueous waste. The europium nitrate was most likely readily stripped along with neodymium nitrate. Since there was no extraction section, this flowsheet would have a low recovery of a desired element in the loaded organic, like uranyl nitrate. If a higher recovery of uranium was desired then the loaded organic would need to be introduced elsewhere in the bank (e.g., at Stage 8) and a fresh organic stream would be introduced into Stage 16. The fresh organic stream would re-extract uranium from the aqueous phase and minimize losses.

4.0 CONCLUSIONS

Lanthanide metal oxides need nitric acid to be converted to their nitrate form, which will readily bind to TBP. That nitric acid can be provided by TBP that is pre-equilibrated with nitric acid. Nonetheless, sufficient nitric acid in the organic phase is needed for complete conversion of oxide to nitrate, otherwise the lanthanide oxides will remain undissolved. This research indicates there is little to no difference in the oxide dissolution rate between an aqueous or organic phase. Heavy or light lanthanide oxides will convert to their nitrate forms at different rates. The lighter lanthanide oxides convert within minutes to nitrates but the heavier lanthanide oxides take at least several hours. Because the heavier lanthanide oxides convert slower, longer residence times (minutes vs. days) in contact with pre-equilibrated TBP would be required for complete conversion. Water was visually observed at higher metal concentrations (> 0.05 M in 10 mL) or volumes (> 0.02 M in 50 mL).

5.0 FUTURE WORK

The next phase of this work is to dissolve multiple oxides at once, specifically co-precipitated oxides. Additionally, the co-precipitated oxides would be added to the organic solution in a specially made glass reactor vessel, Figure 19. The organic solution will be pumped, after being filtered to remove solids, through a flow cell for spectroscopic analysis. The organic solution would then return to the main solution.

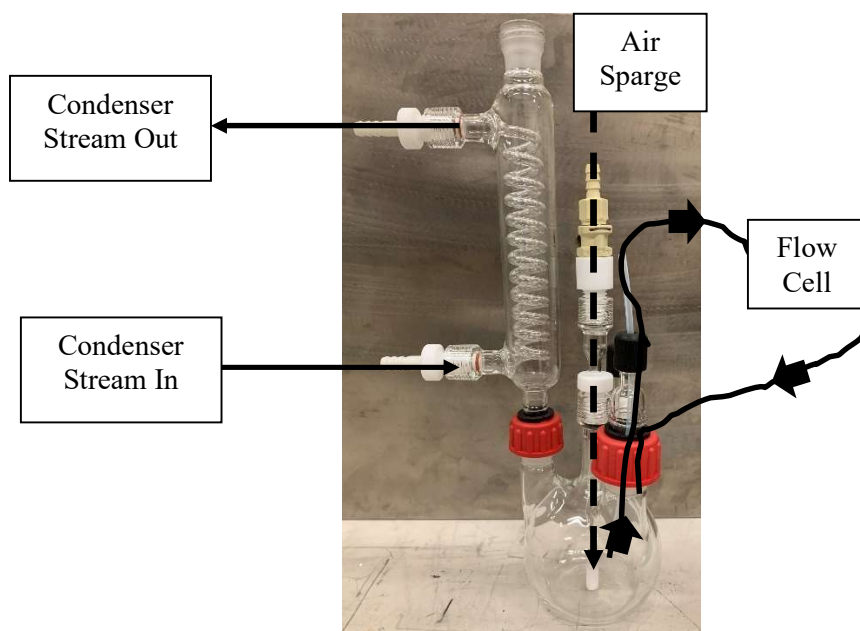


Figure 20: SRNL Glass Reactor Vessel for Co-Precipitated Oxides.

6.0 REFERENCES

- [1] Choppin, G. R., Liljenzin, J., & Rydberg, J. *Radiochemistry and Nuclear Chemistry*. Butterworth-Heinemann, 2001; pp 593.
- [2] DelCul, G. D., Hunt, R. D., Spencer, B. B., & Jubin, R. T. *Demonstrate complete NO₂-based tritium-pre-treatment process with simulated fission products at kilogram scale* (FCRD-MRWFD-2015-000397). Oak Ridge National Laboratory. 2015.
- [3] Rudisill, T. S., Shehee, T. C., Jones, D. H., & DelCul, G. D. Dissolution of used nuclear fuel using a TBP/n-paraffin solvent. *Sep. Sci. Technol.*, 2019,
- [4] Dorda, F. A., Lazarchuk, V. V., Matyukha, V. A., Sirotkina, M. V., & Tinin, V. V. Kinetics of UO₃ dissolution in nitric acid saturated 30% TBP in a hydrocarbon diluent. *Radiokhimiya*, 2010, 52(5), 469-471.
- [5] Hiroshi, T., Kazushige, T., & Yoshimi, O. (1966). *Direct dissolution of water-insoluble uranium compounds by contact with neutral organic solvents pretreated with nitric acid* (Patent 3,288,568).
- [6] Gogolski, J. M., O'Rourke, P. E., Lascola, R. J., & Rudisil, T. S. *Preliminary result from the dissolution of neodymium and erbium oxide in a tributyl phosphate solvent* (SRNL-RP-2022-00681). Savannah River National Laboratory. 2022.
- [7] Peppard, D. F. Liquid-Liquid extraction of the actinides. *Annual Review of Nuclear Science*, 1971, 21(1), 365-396.
- [8] Wang, Z., Liu, T., He, X., Zhu, L., & He, H. Competitive complexation of solid lanthanide nitrates with tri-n-butyl phosphate in n-hexane. *Journal of Radioanalytical and Nuclear Chemistry*, 2017, 311, 483-489.
- [9] Chiarizia, R., & Briand, A. Third phase formation in the extraction of inorganic acids by TBP in n-octane. *Solvent Extraction and Ion Exchange*, 2007, 25, 351-371.
- [10] Woolfrey, J. L. *The preparation and calcination of ammonium uranates-a literature survey* (AAEC/TM476). Research Establishment of the Australian Atomic Energy Commission, Lucas Heights. 1968.
- [11] Vogle, J. L., Fara, R. E., Crowder, M. L., & Gogolski, J. M. *Solvent extraction directly from loaded organic solvent in mini mixer settlers to improve purification efficiency* (SRNL-RP-2023-00834). Savannah River National Laboratory. 2023.

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