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Preliminary Result from the Dissolution of Neodymium and Erbium Oxide in a Tributyl Phosphate Solvent

Nuclear Technology Research and Development

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SUMMARY

This work demonstrated that visible absorbance spectroscopy can track the dissolution of neodymium and erbium oxide in an organic solution containing tributyl phosphate and nitrates. The formation of an aqueous phase was unexpected but an important phenomenon to consider when developing a metal oxide dissolution in organic solution flowsheet. Since the metal oxide appeared to completely dissolve into either the organic or newly formed aqueous phase, dissolution (extraction) rates should be easier to determine.

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PRELIMINARY RESULT FROM THE DISSOLUTION OF NEODYMIUM AND ERBIUM OXIDE IN A TRIBUTYL PHOSPHATE SOLVENT

1. INTRODUCTION

When used nuclear fuel (UNF) is removed from a reactor, approximately 95% of the initial U is still present in the fuel [1]. The fuel also contains heavier actinides (e.g., Np, Pu, Am, and Cm) that can be recovered, fabricated into fuels or targets, and used to generate additional energy. However, construction of a large-scale reprocessing facility with the capability to completely recycle UNF has exorbitant costs. Simplified flowsheets that reduce the equipment footprint and facility size are needed to improve the economic viability of complete recycle. To address this issue, a hybrid process was demonstrated on a laboratory-scale that combines the dissolution of pretreated UNF (for tritium removal) in a tributyl phosphate (TBP) containing solvent with two cycles of solvent extraction required for the recovery of the actinide and lanthanide elements [2]. The hybrid process would be used to dissolve the lanthanide fission products and actinides directly into TBP. The minor actinides (Am and Cm) and lanthanide fission products could then be scrubbed from the solvent using dilute nitric acid. Additional solvent extraction processes would be used to recover and purify the desired products.

The tritium removal process, which involves the voloxidation of UNF with a mixture of nitrogen dioxide and oxygen gases, produces either a U nitrate or oxide depending on the process temperature and time [3]. In the nitrate form, U can be dissolved (extracted) directly into TBP. The direct dissolution of U oxide into TBP can also be achieved by using TBP pre-equilibrated with nitric acid [4]. Although the direct dissolution of both U nitrate and oxides into TBP has been demonstrated [5], the extent of dissolution of other components of UNF into a TBP solvent has not been thoroughly investigated. The U(VI), Pu(IV), Np(IV), and Np(VI) are extracted into TBP as their electro-neutral nitrate salts [6, 7]. The nitrates of the trivalent actinides and lanthanides do not readily complex with TBP. However, under high nitrate salting conditions (salting-out effect), these species will extract (dissolve) into the organic phase [3]. The Ln-NO_3-TBP complex will most likely be a 1:3:3, Equation 1 [8, 9].

$$Ln^{3+} + 3NO_3^- + 3\overline{TBP} \leftrightarrows \overline{Ln(NO_3)_3TBP_3} \quad (1)$$

Laboratory data are available for the distribution of the actinide and lanthanide fission product elements between a TBP solvent and undissolved solids [2], however, the kinetics for the dissolution are not well established, especially for the lanthanide fission products. To address this gap in the data, a methodology was demonstrated to measure the rate of dissolution of selected elements across the lanthanide series. Visible (Vis) spectroscopy was used to measure the concentration of the lighter (Nd) and heavier (Er) lanthanides in a 30 vol % TBP-dodecane solvent (pre-equilibrated with 10 M HNO_3) as the lanthanide oxides dissolved in the organic solution over time.

2. EXPERIMENTAL

The organic solution was prepared by washing 30 wt % TBP (diluted in dodecane) with 4 wt % sodium bicarbonate (twice with a 1:1 vol. ratio), re-acidified in 0.1 M HNO_3 (once with a 1:1 vol. ratio), and then pre-equilibrated with 10 M HNO_3 (twice with a 2:1 vol. ratio of the aqueous to organic, respectively). The 10 M HNO_3 is the upper limit before the organic phase will split into two phases [10]. The neodymium or erbium oxide (99.9% purity and obtained from Sigma Aldrich) was then added to the organic solution. A stir bar gently mixed the solution at room temperature. The target concentration of dissolved Nd and Er oxide was 0.05 M and 0.025 M, respectively. The dissolution rate was monitored by using an optical fiber-coupled dip probe, Figure 1, for several hours.

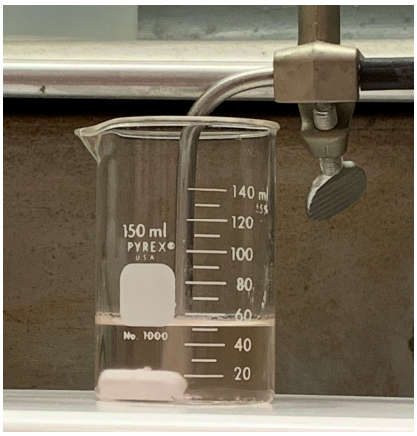

Figure 1: The apparatus during the Er_2O_3 kinetic dissolution experiment.

An Avantes model AvaSpec-ULS3648 spectrometer with a VB grating, 10-µm slit and wavelength range of 365 to 914 nm was used to monitor the dissolution experiments. 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. The spectrophotometer control software was written at SRNL and uses the AS5216_APP driver to control the Avantes hardware and write raw intensity spectra to the Avantes_Model_D.xlsm Excel macro spreadsheet. The macro spreadsheet calculates the correction from the raw intensity for dark signal, non-linear response, and stray light. Each intensity corrected spectrum is wavelength calibrated by identifying Xe peaks and fitting their peak channels to the known Xe wavelengths. Wavelength calibrated spectra are then interpolated to a common, evenly spaced wavelength scale using a least-squares five-point quadratic spline fit. Spectrophotometric accuracy from 0 to 2.0 AU was verified by measuring a set of Starna Neutral Density Filters, #33649 (94563_5N, 95668_N3, 92592_N1).

Operating conditions were 15-ms exposure, 400 exposure average, and 1 Xe flash per exposure. Maximum intensity was adjusted using an iris diaphragm at the light source to keep the intensity counts below 60,000 counts with the probe in the organic solution before the addition of metal oxide. Before each dissolution experiment, a dark spectrum and a blank spectrum from the organic solution were collected and stored to allow the calculation and display of real-time absorbance spectra from the dissolution experiment. Spectra were measured and displayed at approximately six-second intervals, and every tenth spectrum was saved to a data file.

3. RESULTS AND DISCUSSION

3.1 Neodymium Oxide Dissolution

As soon as the neodymium oxide (Nd_2O_3) was added to the organic solution, spectra peaks similar to $Nd(NO_3)_3 \cdot TBP_3$ in *n*-hexane [9] could be distinguished within seconds. As shown in Figure 2, several peaks were higher than 0.5 absorbance at the target concentration of 0.05 M. Interestingly, the spectra do not show distinct peaks associated with other Nd-containing species, specifically Nd_2O_3 [11]. The dissolution of the Nd seems to be two rapid steps of conversion from its oxide to nitrate form and complexation with the TBP as $Nd(NO_3)_3 \cdot TBP_3$ (Equation 1).

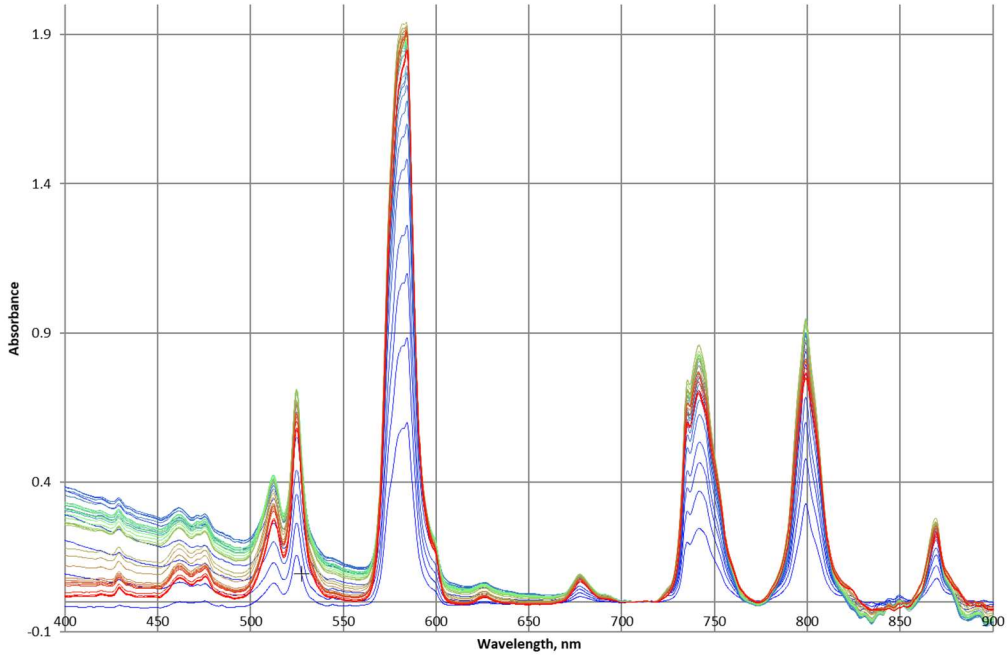

Figure 2: The spectra of Nd complexing with TBP over time (3.5 h).

A second derivative of Figure 2 was made to remove the baseline offsets, which are especially apparent for the 400 to 550 nm range (Figure 3). The transformed peaks help emphasize peak shifts and shoulder formations that could indicate the formation of a second complex as the relative concentrations of lanthanide, nitrate, and TBP change over time. The derivatization was done with limited smoothing to reduce the chance of suppressing these sometimes subtle spectral changes.

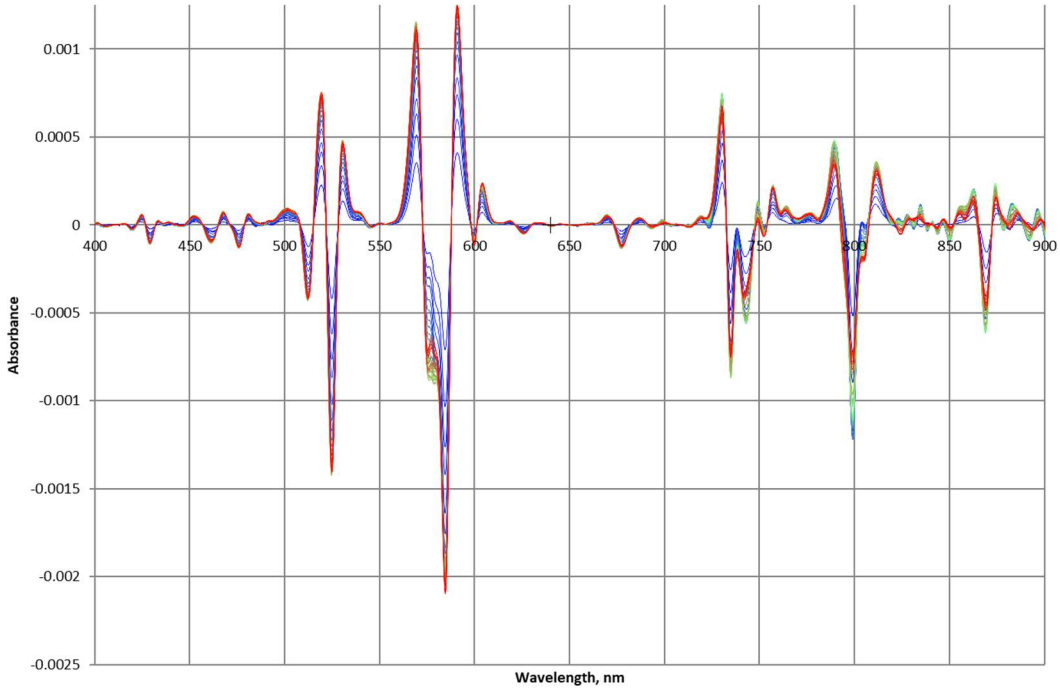

Figure 3: The second derivative of the spectra with Nd complexing with TBP over time.

Curiously, an additional phase was observed after approximately 2 h, shown in Figure 4. The new phase was pipetted out into a separate container and diluted readily when water was added, which means that an aqueous phase was formed and not a second organic layer (third phase). Rudisill et al. observed an aqueous phase forming when they dissolved uranium oxides in TBP, Figure 4 [2]. The aqueous phase has not yet been sampled but based on the observed color and that no Nd_2O_3 powder could be seen in solution, most likely contains $Nd(NO_3)_3$ in dilute nitric acid. This phenomenon may indicate that a hydrated $Nd(NO_3)_3$ is a brief intermediate step during Nd_2O_3 dissolution in TBP that cannot be otherwise seen on the spectra. Once the TBP is fully loaded with the $Nd(NO_3)_3$, the excess $Nd(NO_3)_3$ coalesces to form a distinct phase.

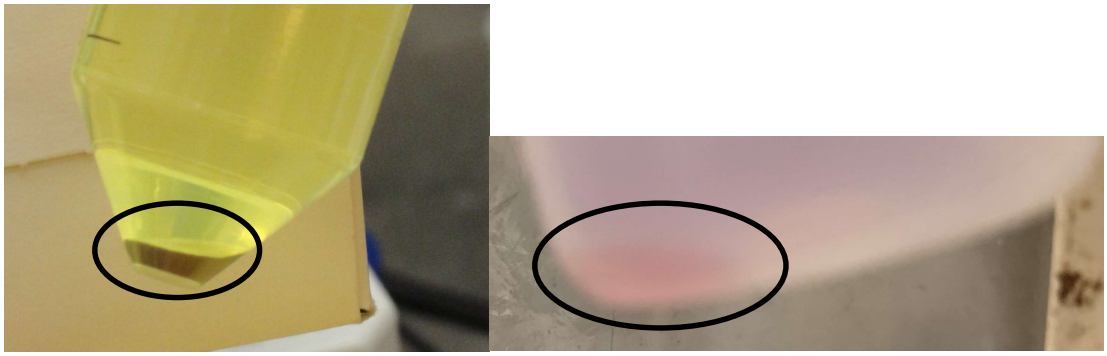

Figure 4: The additional phase (circled) that was observed during U_3O_8 (left) the Nd_2O_3 (right) dissolution.

3.2 Erbium Oxide Dissolution

The solution immediately clouded after adding the erbium oxide (Er_2O_3), and the rate of growth of Er-related absorbance peaks was slow. However, the peaks got stronger after approximately an hour (Figure 5), with the solution developing a pink hue, shown in Figure 1. (The Er_2O_3 powder is pink.) Since an additional phase formed during the Nd_2O_3 experiment, the concentration of the Er_2O_3 was halved to reduce metal loading of the organic phase. Curiously, despite the lower concentration of Er, the Er_2O_3 was not completely converted to $Er(NO_3)_3 \cdot TBP_3$ after seven hours in the organic solution.

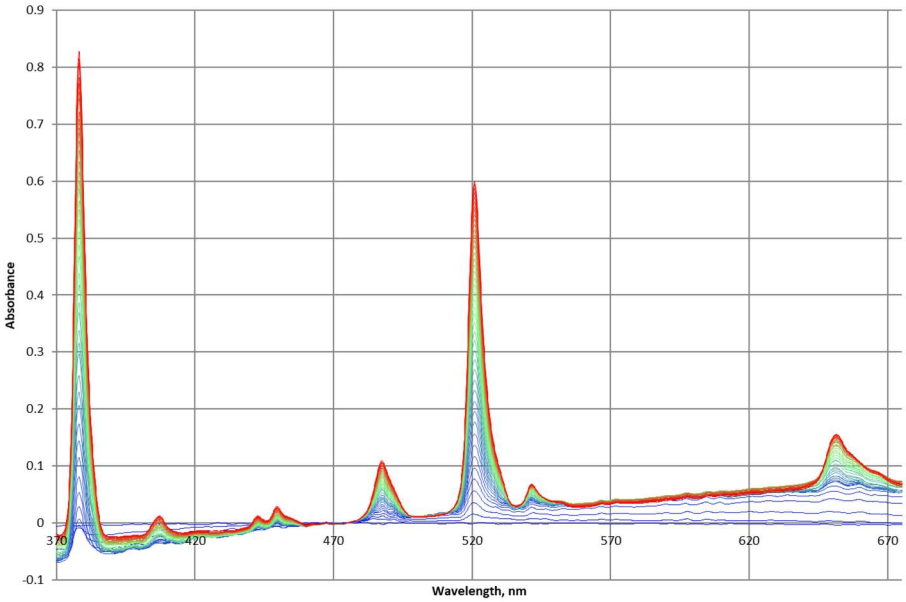

Figure 5: The spectra of Er complexing with TBP over time (7 h).

The second derivative of Figure 5 was taken to compensate for baseline offsets associated with the increased turbidity, Figure 6. However, the baseline offset might be disguising species conversion. The solution was left to sit over the weekend with the Er_2O_3 powder and formed an aqueous phase like the Nd solution. Since the Er_2O_3 powder could no longer be seen, the Er was assumed to have gone completely into solution (organic and aqueous phases). It is unclear if the decreased Er concentration had any effect on the aqueous phase forming.

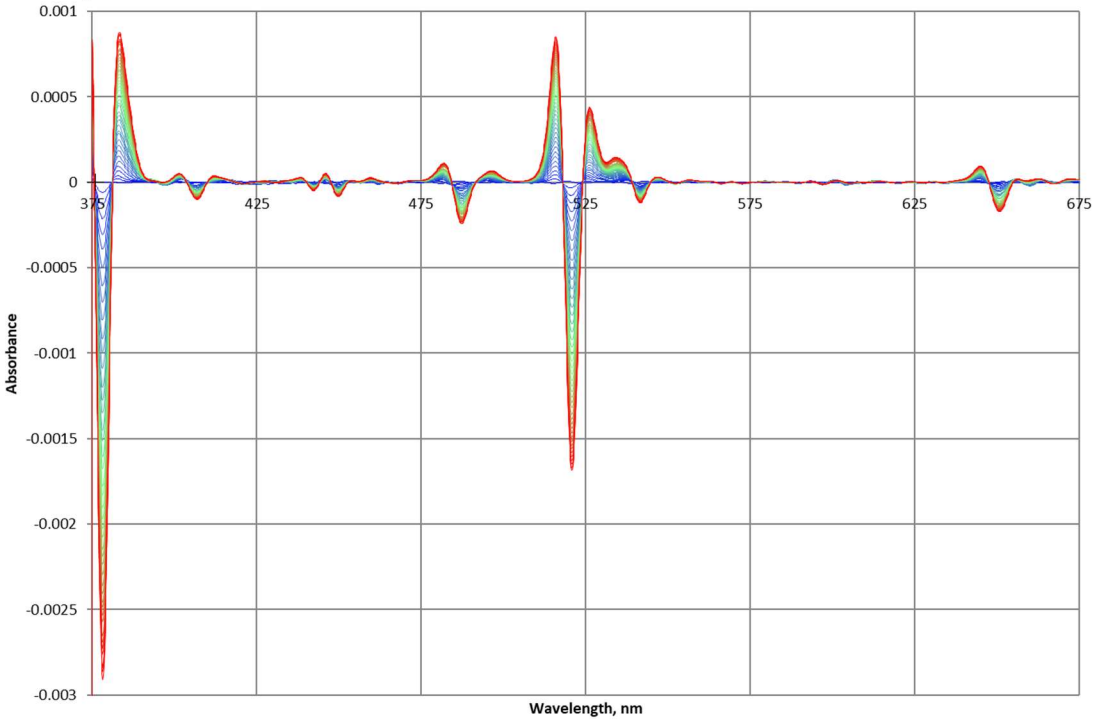

Figure 6: The second derivative of the spectra with Er complexing with TBP over time.

4. CONCLUSIONS

Unsurprisingly, the Nd and Er oxides readily dissolved into the organic solution that was preequilibrated with a high nitric acid concentration. The dissolution rate is uncertain at this time because of the unknown amount of the lanthanide that went into the aqueous phase. Although, it is likely that the observed aqueous phase contains the rest of the lanthanide in its nitrate form, in which case, a mass balance of the organic and aqueous phase will yield a dissolution rate in the organic phase. A multivariate analysis method could have been used to determine the dissolution rate if the solids had fully dissolved in the organic phase. Figures 2 and 5 indicate that only one main organic complex was formed, $Ln(NO_3)_3TBP_3$.

5. FUTURE WORK

The Nd and Er oxides will be dissolved in a range of pre-equilibrated (4, 6, 8, and 10 M HNO_3) 30 and 50 vol % TBP. The preliminary findings showed that the oxide concentrations will have to be fine-tuned to develop a calibration curve at each dissolution condition. The calibration curve will quantitatively define the dissolution over time. While the *in-situ* dip probe could only measure the Vis range, it was able to capture the rapid dissolution of Nd_2O_3 and when the peaks formed during the Er_2O_3 dissolution. Using UV and Raman spectroscopy will help determine if any other complexes are forming but would only provide infrequent snapshots of the dissolution process.

Samarium oxide should behave similarly to Nd oxide, but another heavier lanthanide oxide like Ho_2O_3 might need to be included to help understand why the Er_2O_3 did not fully go into the organic phase at twice the time it took Nd_2O_3. This observation might indicate a competitive complexation between the heavier and lighter lanthanides, as was seen for Nd and Ho [9]. This study could expand to consider dissolving multiple oxides at once, in which case taking the second derivative of the spectra can help resolve the lanthanide oxide dissolution kinetics [12].

Cerium and Eu will be dissolved using the same procedure as the Nd, Er, Ho, and Sm, but due to the lack of spectral peaks in the visible range for Ce and Eu, those lanthanides will be additionally analyzed with X-ray absorption and fluorescence spectroscopy. To confirm that additional species were not forming and that the lanthanide oxides converted to their nitrate form and were then directly complexing with TBP, the respective lanthanide nitrates should be dissolved in the organic solution as a reference. Any aqueous phases that form during experimentation will be sampled separately to help determine how the equilibrium changes with the addition of the oxides.

6. REFERENCES

[1] Choppin, G. R., Liljenzin, J., & Rydberg, J. (2001). *Radiochemistry and Nuclear Chemistry*. Butterworth-Heinemann, 593.

[2] Rudisill, T. S., Shehee, T. C., Jones, D. H., & DelCul, G. D. (2019). Dissolution of used nuclear fuel using a TBP/n-paraffin solvent. *Separation Science and Technology*.

[3] DelCul, G. D., Hunt, R. D., Spencer, B. B., & Jubin, R. T. (2015). *Demonstrate complete NO_2-based tritium-pre-treatment process with simulated fission products at kilogram scale* (FCRD-MRWFD-2015-000397). Oak Ridge National Laboratory.

[4] Dorda, F. A., Lazarchuk, V. V., Matyukha, V. A., Sirotkina, M. V., & Tinin, V. V. (2010). Kinetics of UO_3 dissolution in nitric acid saturated 30% TBP in a hydrocarbon diluent. *Radiokhimiya*, *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] Hyder, M. L., Perkins, W. C., Thompson, M. C., Burney, G. A., Russel, E. R., Holcomb, H. P., & Landon, L. F. (1979). *Processing of irradiated, enriched uranium fuels at the Savannah River Plant* (DP-1500). Savannah River Site.

[7] Morss, L. R., Edelstein, N. M., & Fuger, J. (2006). *The Chemistry of the Actinide and Transactinide Elements* (3rd ed., Vol. 24). 2646.

[8] Peppard, D. F. (1971). Liquid-Liquid extraction of the actinides. *Annual Review of Nuclear Science*, *21*(1), 365-396.

[9] Wang, Z., Liu, T., He, X., Zhu, L., & He, H. (2017). Competitive complexation of solid lanthanide nitrates with tri-n-butyl phosphate in n-hexane. *Journal of Radioanalytical and Nuclear Chemistry*, *311*, 483-489.

[10] Chiarizia, R., & Briand, A. (2007). Third phase formation in the extraction of inorganic acids by TBP in n-octane. *Solvent Extraction and Ion Exchange*, *25*, 351-371.

[11] Runowski, M., Stopikowska, N., & Lis, S. (2020). UV-Vis-NIR absorption spectra of lanthanide oxides and fluorides. *Dalton Transactions*, *49*, 2129-2137.

[12] Wang, N., Jiang, W., Xu, X., Si, Z., Bai, H., & Tian, C. (2002). Visible absorption spectra of the 4f electron transitions of neodymium, praseodymium, holmium and erbium complexes with fleroxacin and their analytical application. *Analytical Sciences*, *18*.