SACSESS
WP1.2 Performance Optimisation of Chemical Systems

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Performance Optimisation of Chemical Systems

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- Improve the understanding and optimise selected An / Ln extraction systems for safe and efficient operation
- Study of coupled mass transfer / interfacial kinetics
- Rotating Diffusion Cell (RDC)
  - Derived from Lewis Cell
  - Monitor both physical (diffusion, low to high sheer convection) and chemical (interfacial) kinetics
  - Possibility to study separations based on kinetic selectivity (high sheer, low residence) rather than thermodynamic (low sheer, high residence) and the transition between the two regimes

Rotating Diffusion Cell
- Apparatus

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- Twin compartment for two separate solution phases
- Solution flux generated by rotation
- Defined interface area determined by membrane

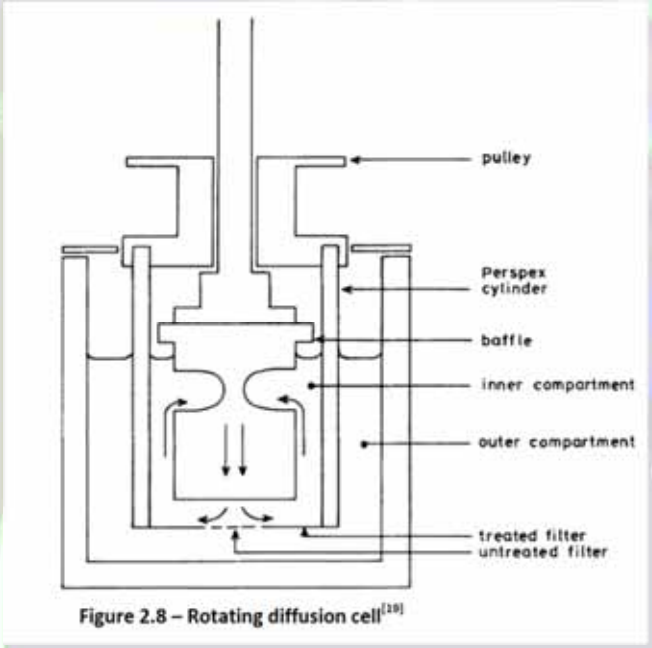
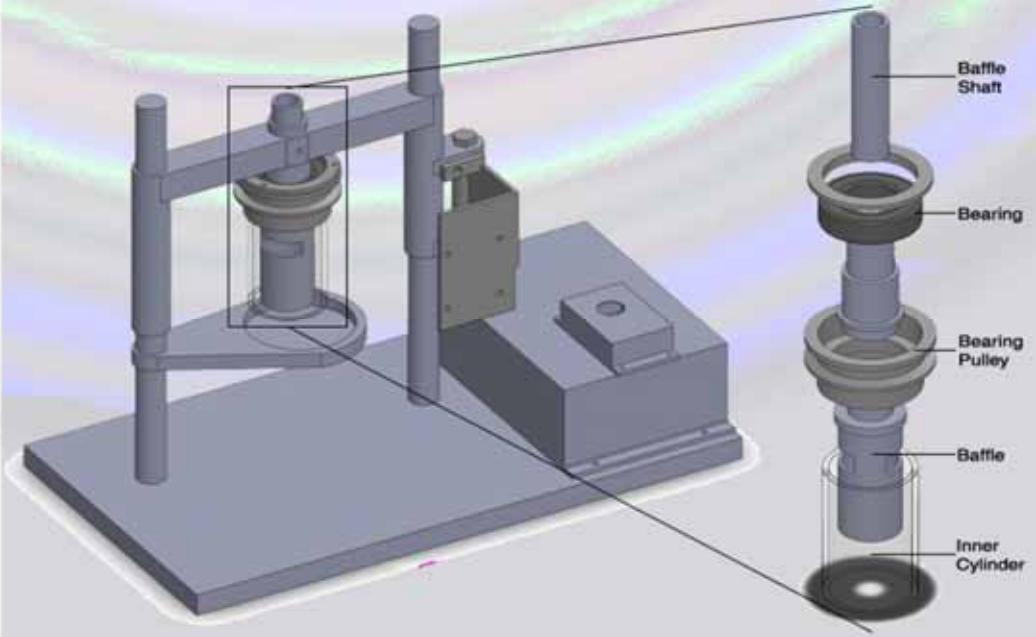


Figure 2.8 – Rotating diffusion cell[19]



Rotating Diffusion Cell

- Modifications

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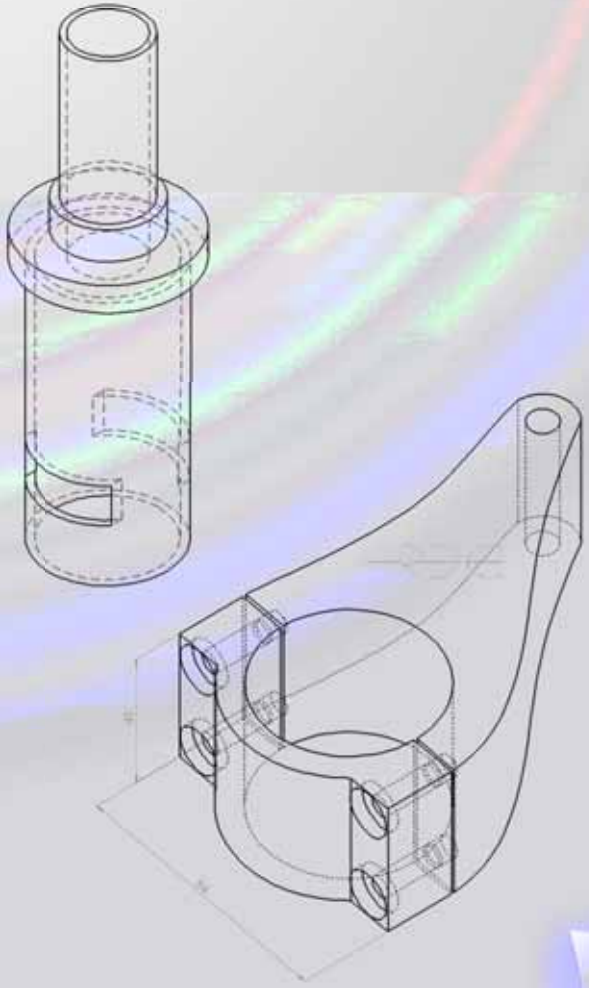
- Commissioning & troubleshooting
  - Eliminate pulley vibrations
  - Redesign motor arm for stability
  - Redesign PTFE baffle for improved solution flow and incorporated sampling port
- Augmentation
  - Variable speed motor control
  - Optical encoder & Arduino setup to provide live readout of motor shaft rotation speed (RPM & Hz)



Rotating Diffusion Cell
- Membrane Mounting

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- Millipore GSWP nitrocellulose membranes
  - Range of pore sizes and thicknesses available
  - Vary effective interface and flow rate
- Membrane mounted on RDC cylinder
  - Methyl methacrylate-based adhesive
  - Highly effective; membrane perimeter encased
- Appropriate mounting essential
  - Avoid leakage through perimeter edge
  - Resist application of damaging clearing solvent

Rotating Diffusion Cell

- Membrane Pore Closure

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- Porous structure of the nitrocellulose collapsed with clearing solvent
  - 33.3% n-hexane
  - 33.3% 1,2-dichloroethane
  - 33.3% 1,4-dioxane
- Applied by pipette onto rotating membrane
  - Defines porous interface area
  - Treated area is transparent and non-porous
  - Resulting membrane is under tension, aiding stability during rotation
  - Variation of interface diameter allows for tuning of transfer rates through membrane

Rotating Diffusion Cell

- Trans-membrane Ce Extractions

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- Millipore GSWP047 nitrocellulose membrane mounted on RDC
  - 0.2 μm pore size; 150 μm thickness; flow rate of 18 ml/min x cm^2
  - Rotation speeds of 0 – 10 Hz
  - 3 porous interface diameters examined
- Ce(IV) extraction by TBP
  - Aqueous phase – 10 mM Ce(IV) $(SO_4)_2$ in 1 M nitric acid
  - Organic phase – 0.2 M TBP in kerosene
- Ce(III) extraction by TODGA
  - Aqueous phase – 10 mM Ce_2(III) $(SO_4)_3$ in 1 M nitric acid
  - Organic phase – 0.2 M TODGA in 5% octanol : 95% kerosene

TODGA Synthesis

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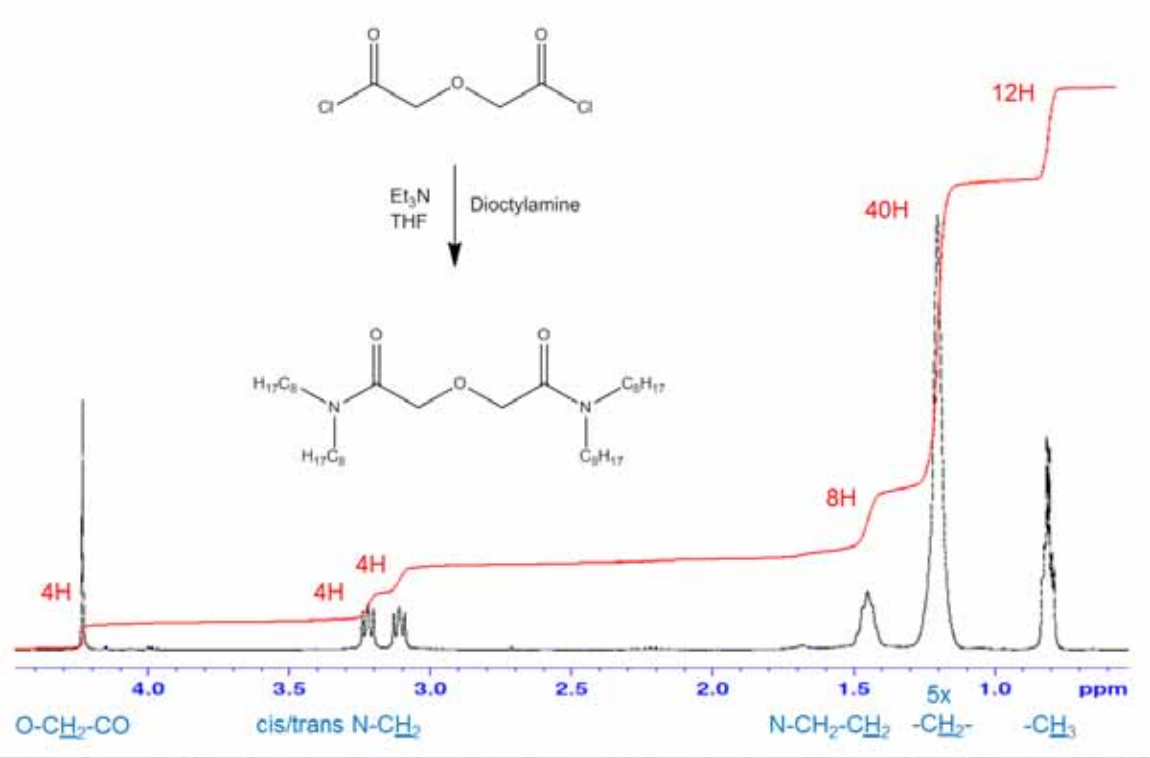
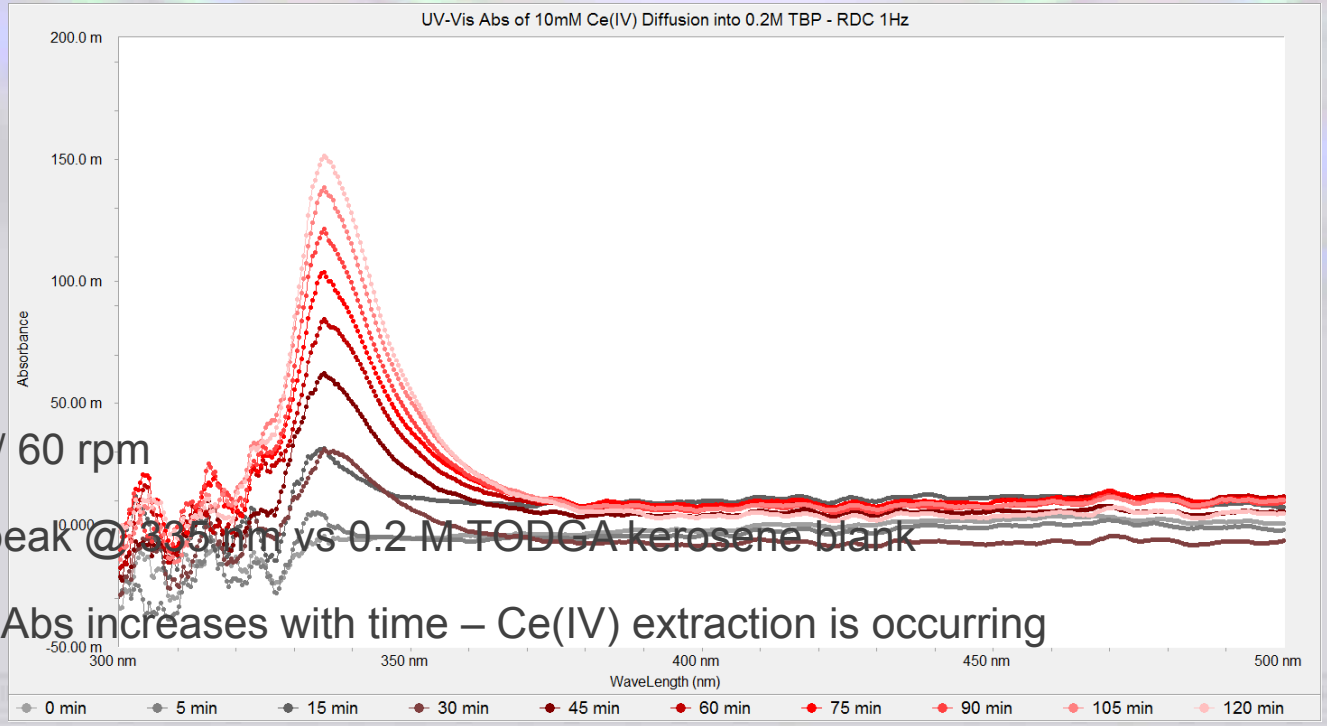
- In house manufacture
  - (Dr Dominic Laventine)
- 80% yield
- Substantial cost reduction
  - Technocomm £2000 (€2770) / 100 g
  - Lancaster £315 (€436) / 100 g



RDC – Ce(IV)/TBP Extraction

- Varied Rotation Speed

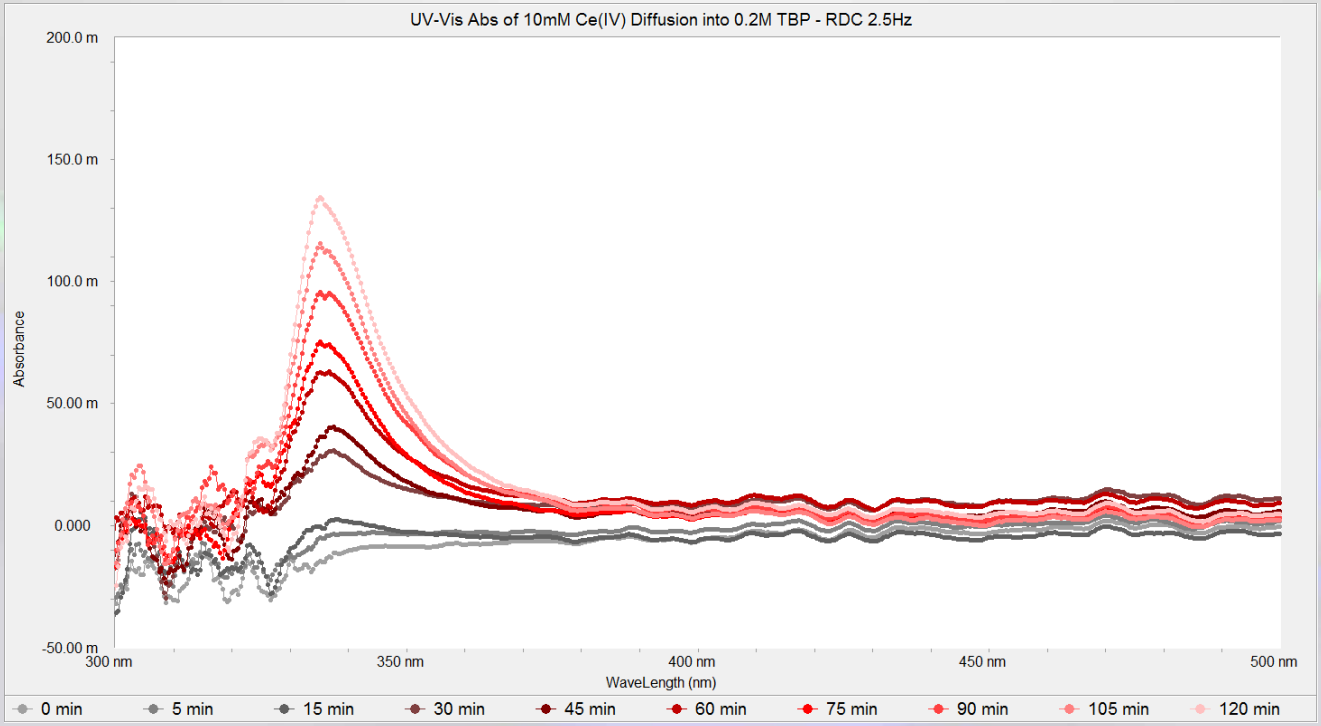
- Conditions
  - 10 mM Ce(IV)
  - 0.2M TBP in kerosene
  - Interface diameter 20 mm
  - 0-10 Hz rotation
  - UV-Vis Abs monitoring



- 1 Hz / 60 rpm
- Abs peak @ 335 nm vs 0.2 M TODGA kerosene blank
- Peak Abs increases with time – Ce(IV) extraction is occurring

RDC – Ce(IV)/TBP Extraction

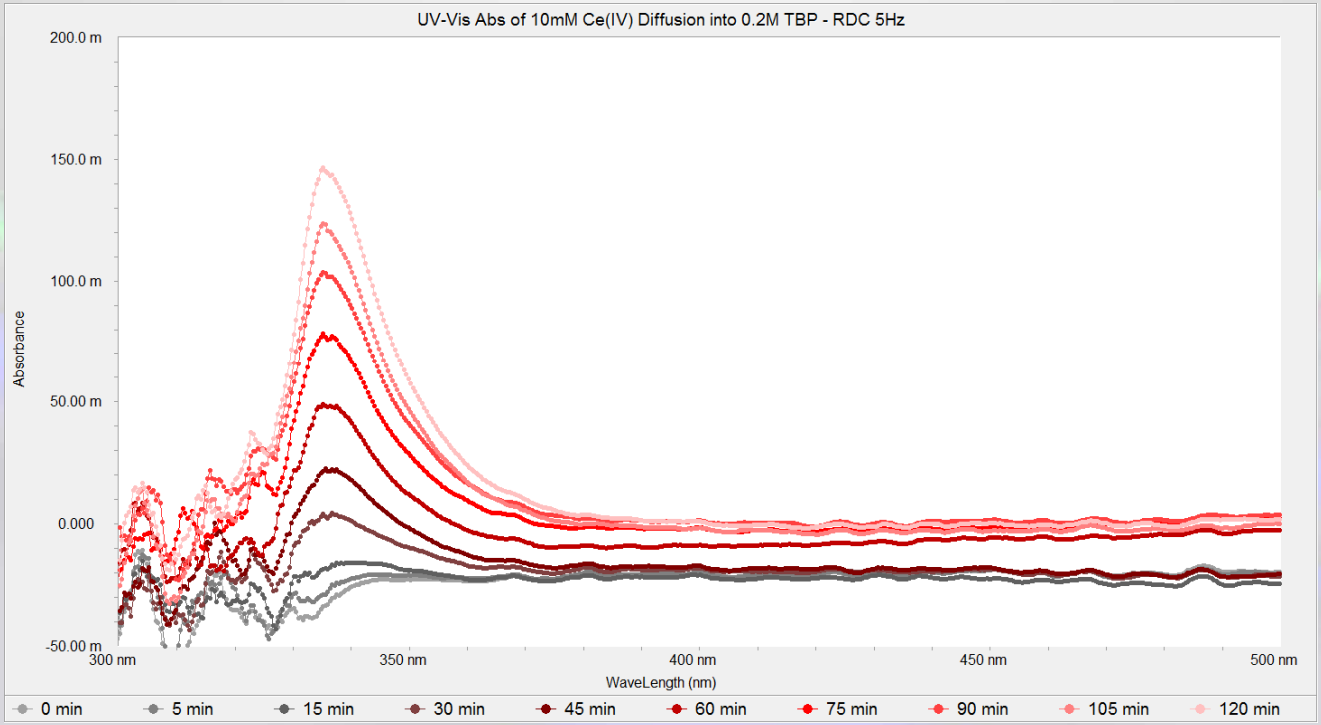
- Varied Rotation Speed



- 2.5 Hz / 150 rpm
- Abs peak @ 335 nm vs 0.2 M TODGA kerosene blank
- Peak Abs decreases as rotation speed increases

RDC – Ce(IV)/TBP Extraction

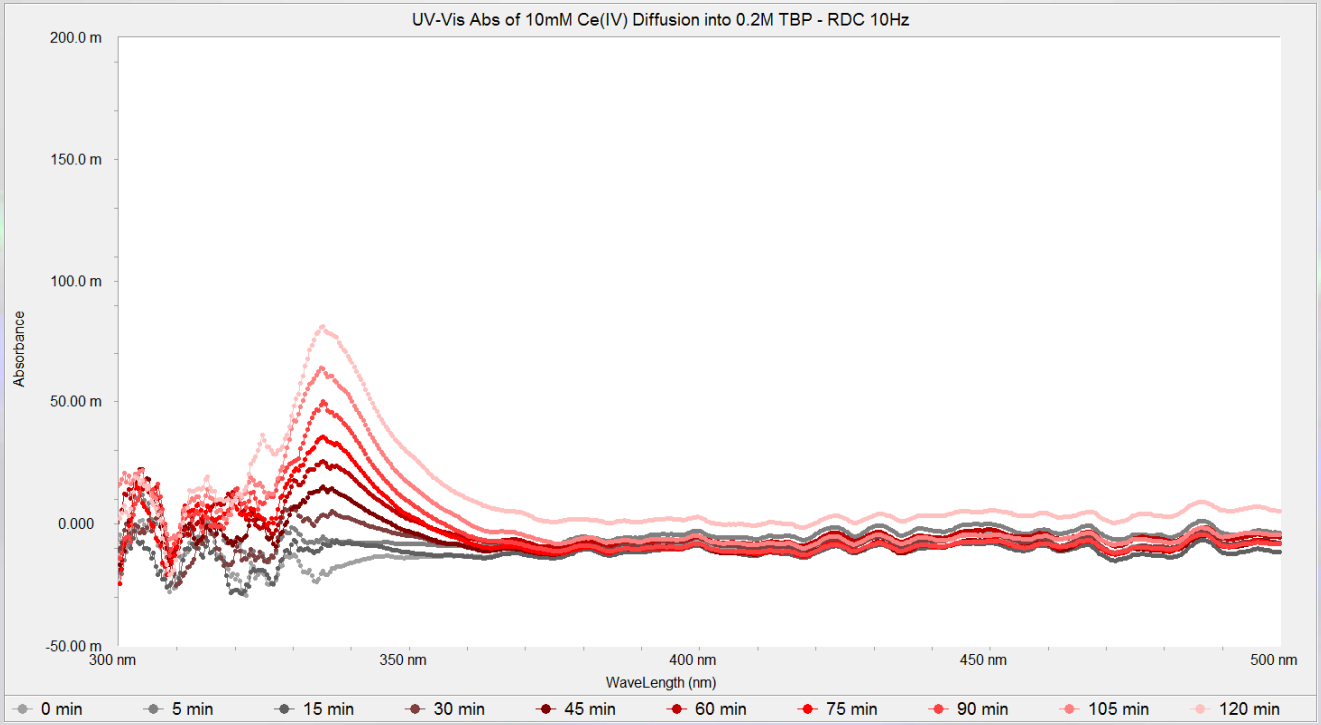
- Varied Rotation Speed



- 5 Hz / 300 rpm
- Abs peak @ 335 nm vs 0.2 M TODGA kerosene blank
- Peak Abs decreases as rotation speed increases

RDC – Ce(IV)/TBP Extraction

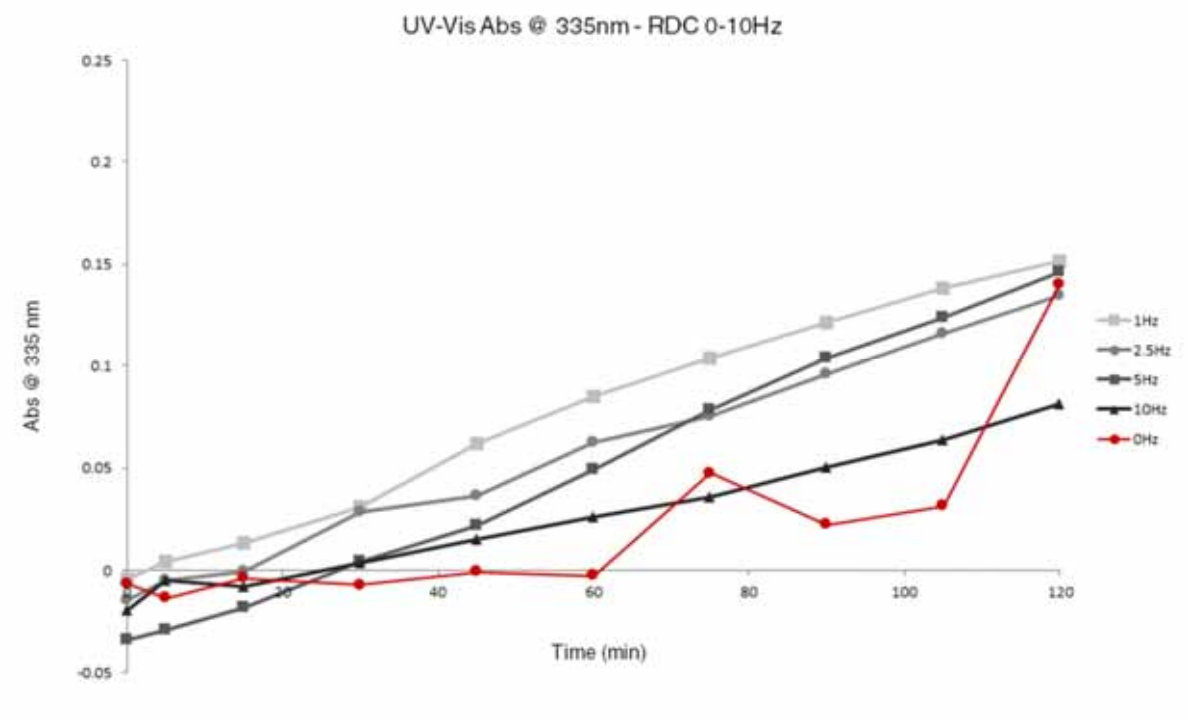
- Varied Rotation Speed



- 10 Hz / 600 rpm
- Abs peak @ 335 nm vs 0.2 M TODGA kerosene blank
- Peak Abs decreases as rotation speed increases
- Counter-intuitive – increased flux expected to increase extraction rate

RDC – Ce(IV)/TBP Extraction

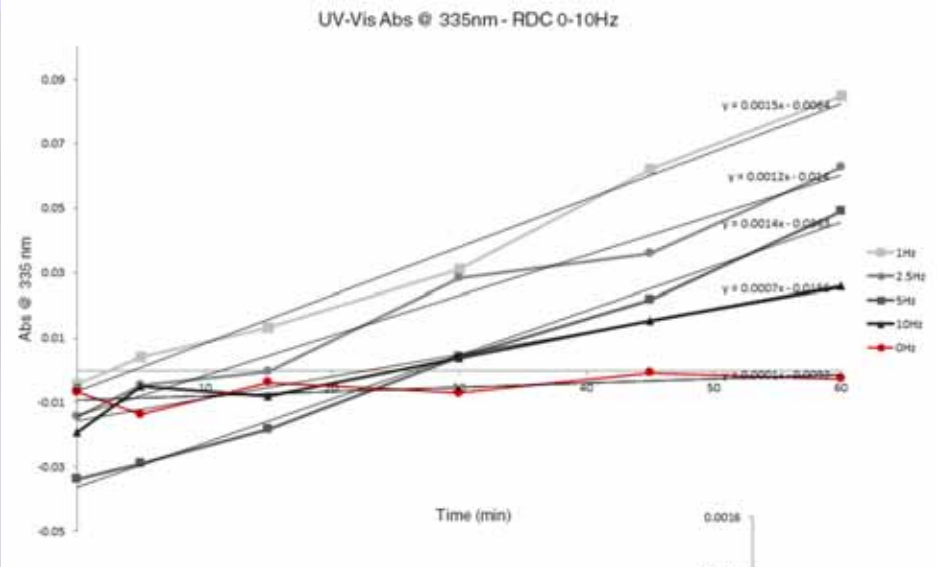
- Varied Rotation Speed



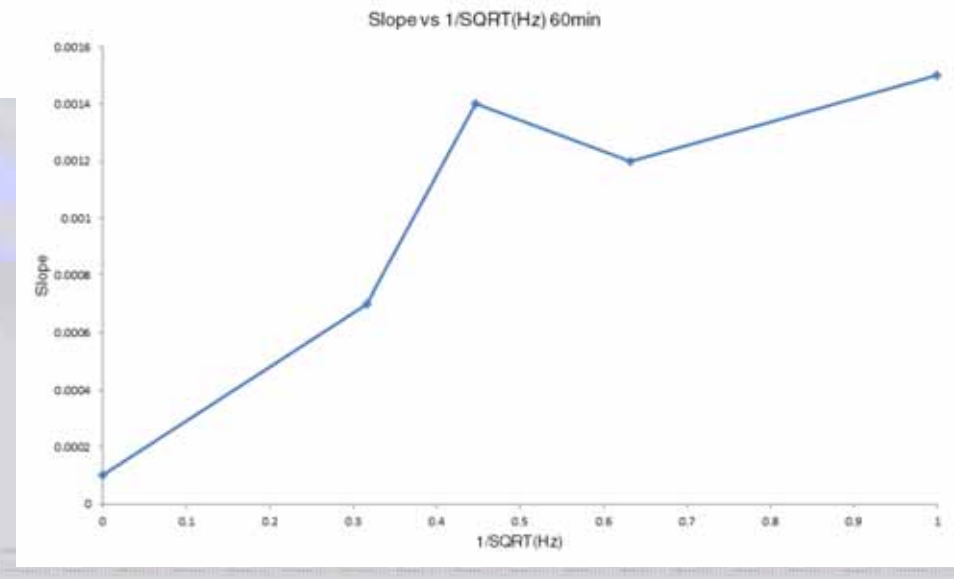
- Very little extraction at 0 Hz – no rotational flux
- Peak Abs, hence $[Ce(IV)]_{aq}$, decreases as rotation speed increases
- No indication of saturation in extraction up to 120 min
  - Indicative of high D-value for extraction OR extraction not reached completion

RDC – Ce(IV)/TBP Extraction

- Varied Rotation Speed



- Slope data from 0-60 min
  - Interfacial flux
- Plot interfacial flux vs 1/SQRT(Hz)
- Approximate linearity

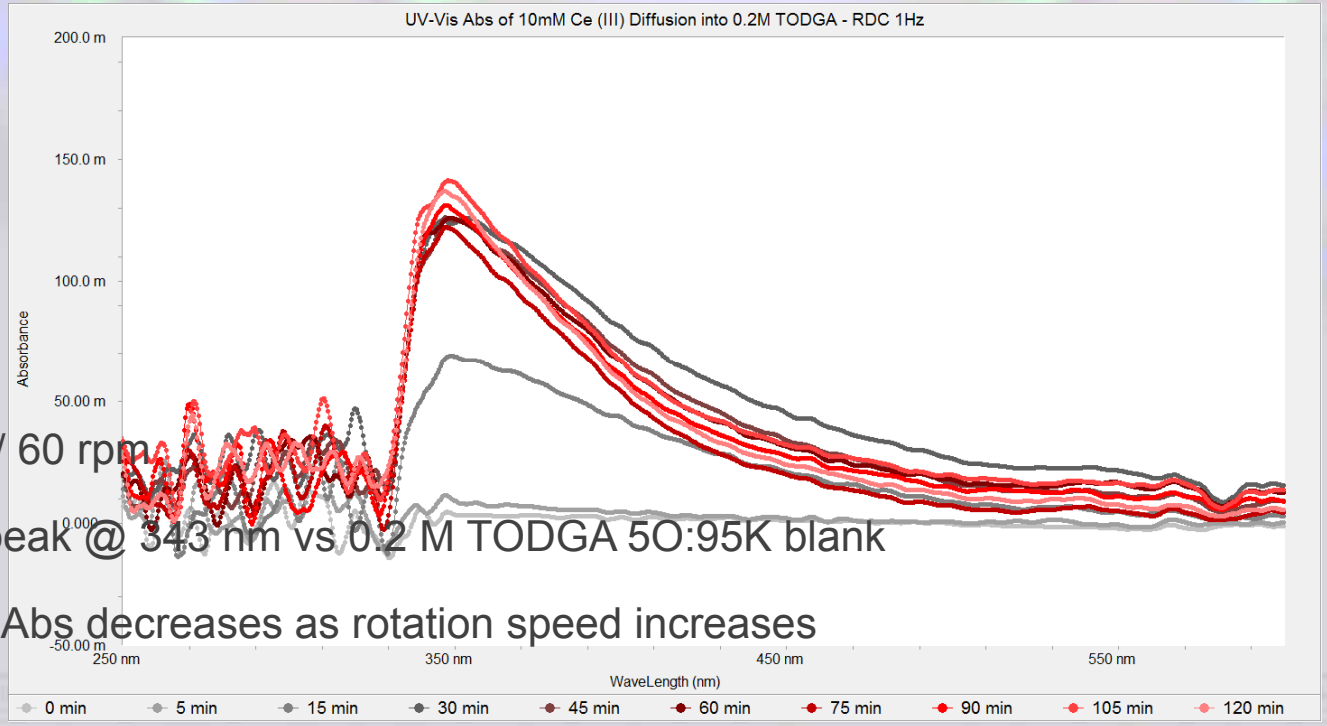


- Diffusion layer thickness, X_D, increases with 1/SQRT(Hz)
- Extraction rate indicates Ce captured from diffusion layer
- Extractant diffusion into aqueous phase

RDC – Ce(III)/TODGA Extraction

- Varied Rotation Speed

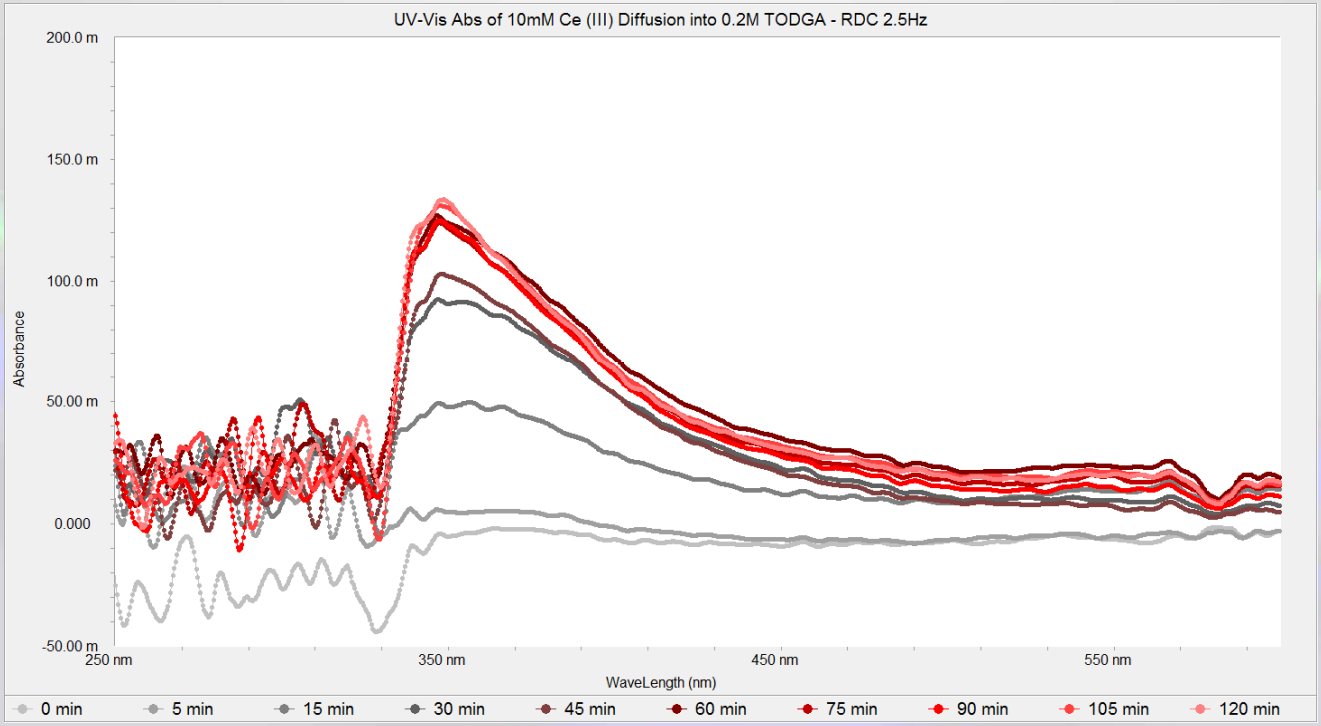
- Conditions
  - 10 mM Ce(III)
  - 0.2M TODGA in 5O:95K
  - Interface diameter 20 mm
  - 0-10 Hz rotation
  - UV-Vis Abs monitoring



- 1 Hz / 60 rpm
- Abs peak @ 343 nm vs 0.2 M TODGA 5O:95K blank
- Peak Abs decreases as rotation speed increases

RDC – Ce(III)/TODGA Extraction

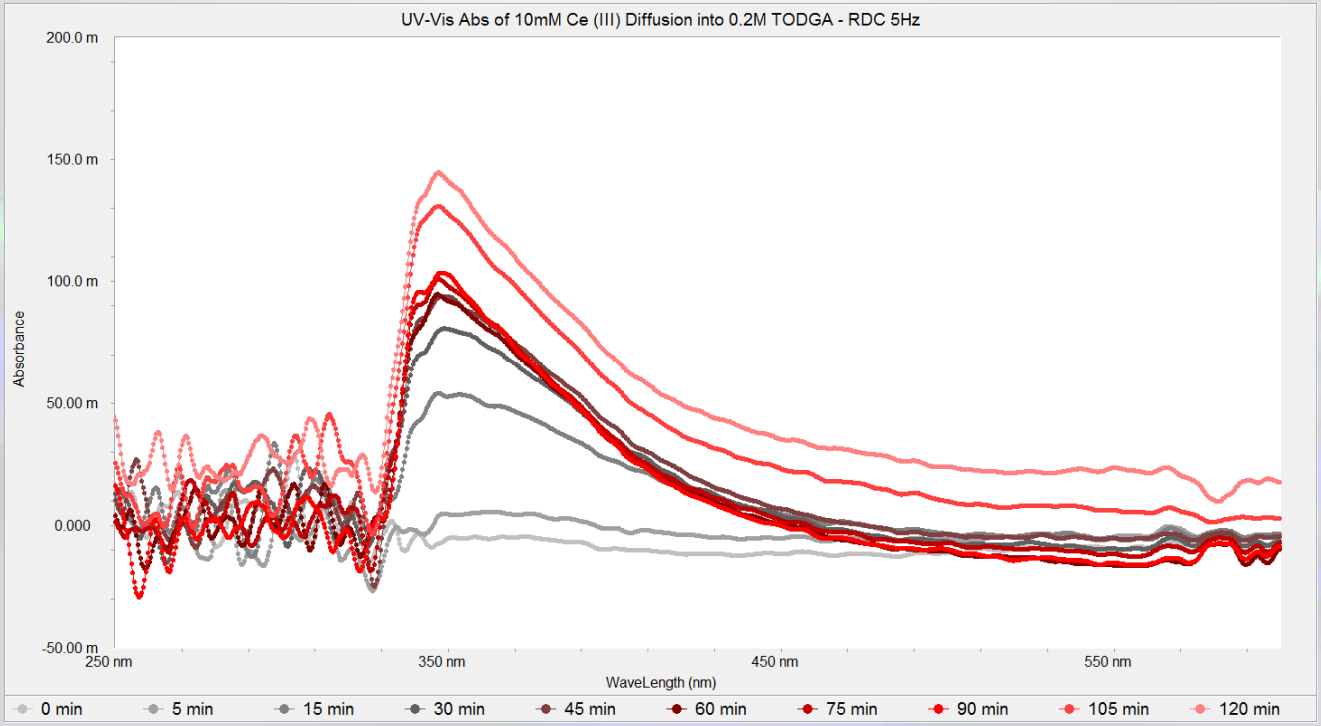
- Varied Rotation Speed



- 2.5 Hz / 150 rpm
- Abs peak @ 343 nm vs 0.2 M TODGA 5O:95K blank
- Peak Abs decreases as rotation speed increases

RDC – Ce(III)/TODGA Extraction

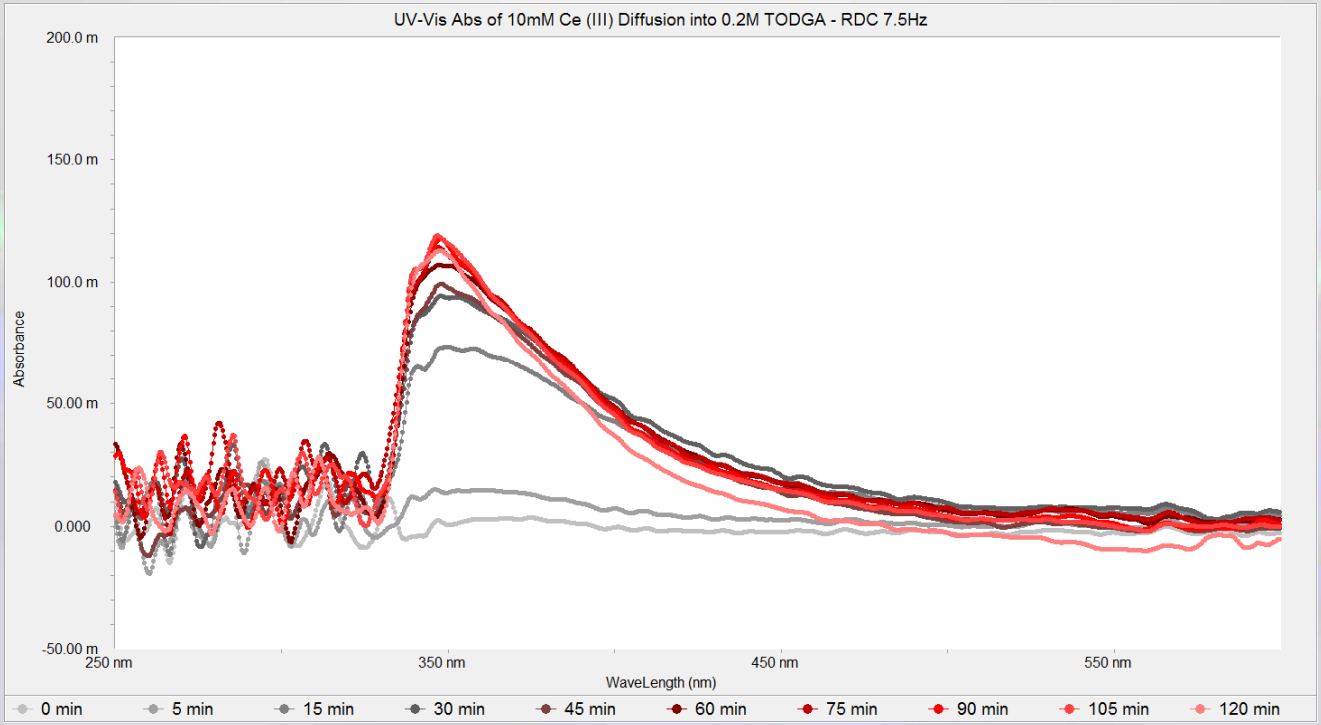
- Varied Rotation Speed



- 5 Hz / 300 rpm
- Abs peak @ 343 nm vs 0.2 M TODGA 5O:95K blank
- Peak Abs decreases as rotation speed increases

RDC – Ce(III)/TODGA Extraction

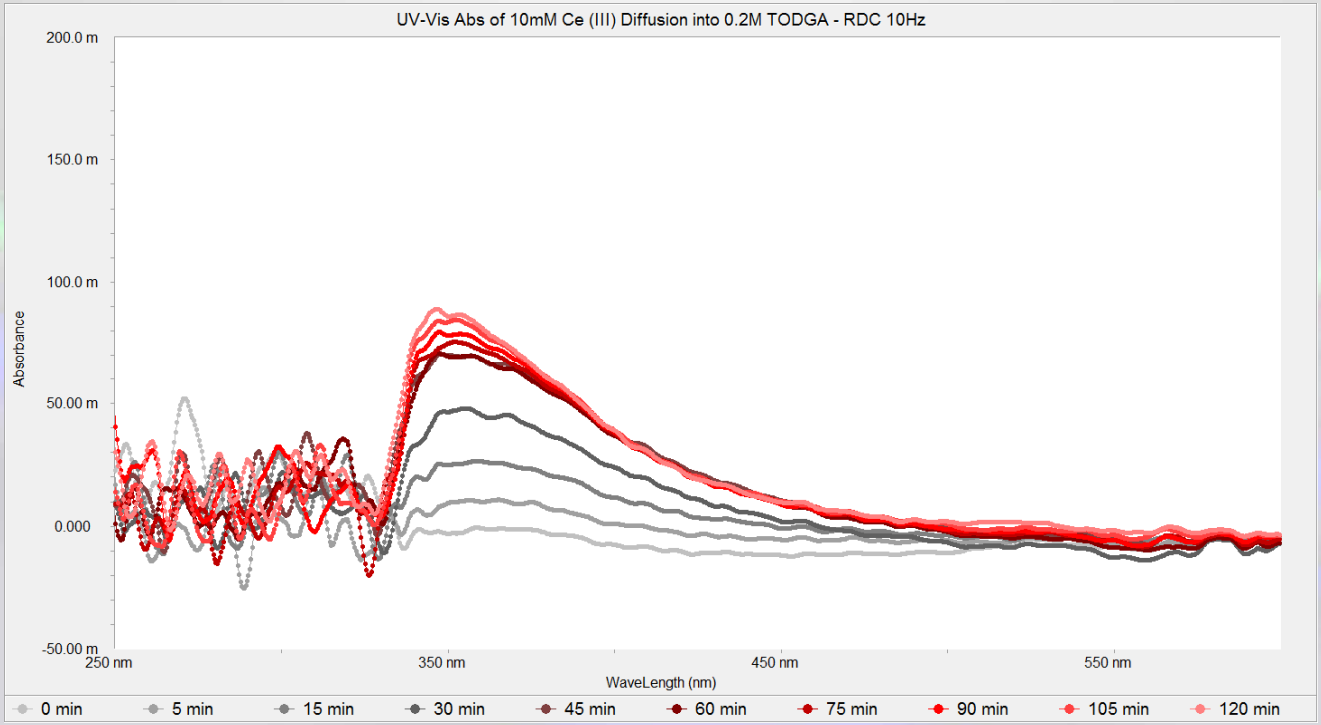
- Varied Rotation Speed



- 7.5 Hz / 450 rpm
- Abs peak @ 343 nm vs 0.2 M TODGA 5O:95K blank
- Peak Abs decreases as rotation speed increases

RDC – Ce(III)/TODGA Extraction

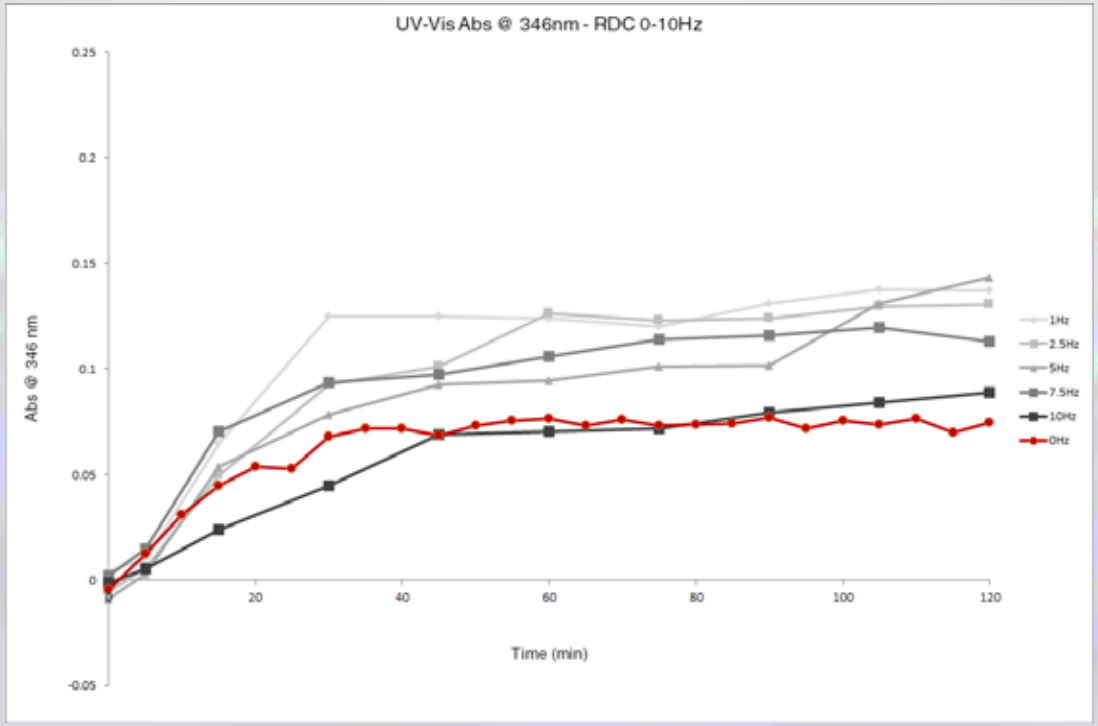
- Varied Rotation Speed



- 10 Hz / 600 rpm
- Abs peak @ 343 nm vs 0.2 M TODGA 5O:95K blank
- Peak Abs decreases as rotation speed increases

RDC – Ce(III)/TODGA Extraction

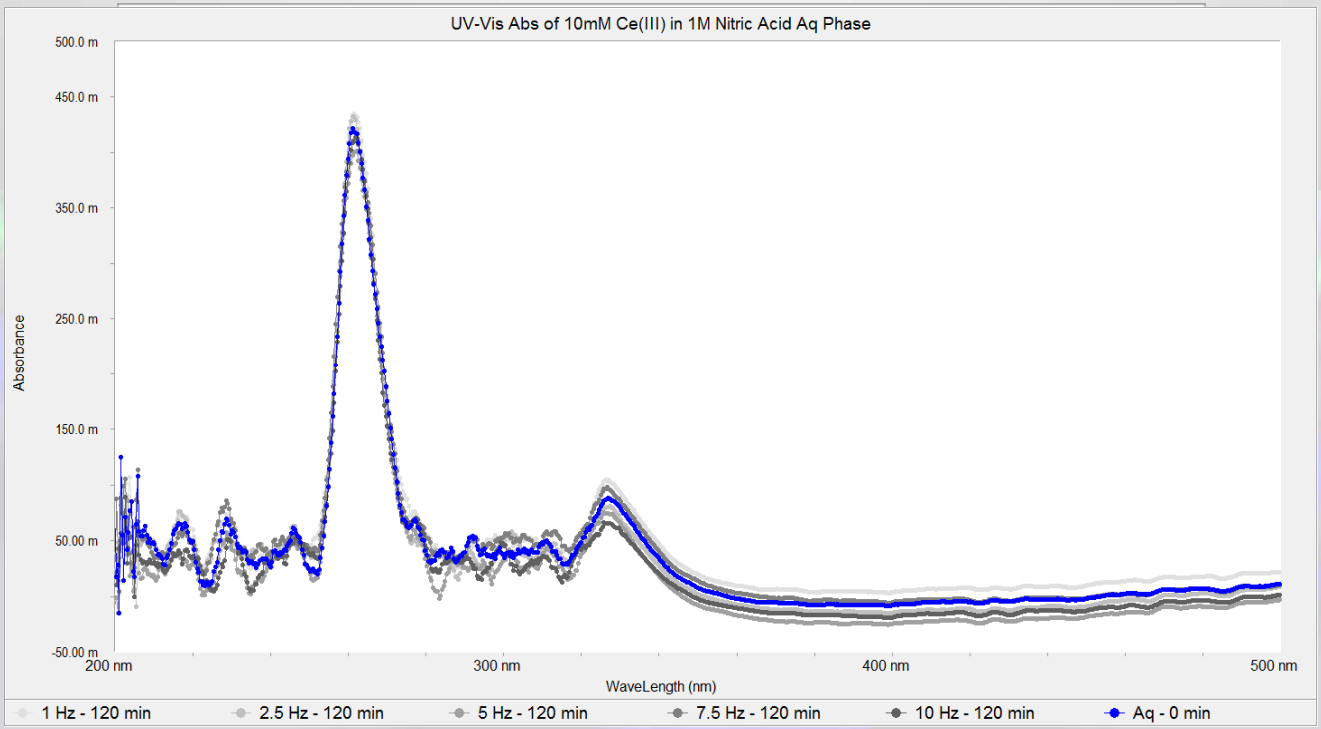
- Varied Rotation Speed



- Same trend as Ce(IV)/TBP system, indicating that TODGA may have to partition into aqueous phase diffusion layer before extraction occurs
- Resulting [TODGA] gradient across diffusion layer
- Larger diffusion layer (slower rotation) allows greater penetration depth and hence more Ce(III) complexation

RDC – Ce(III)/TODGA Extraction

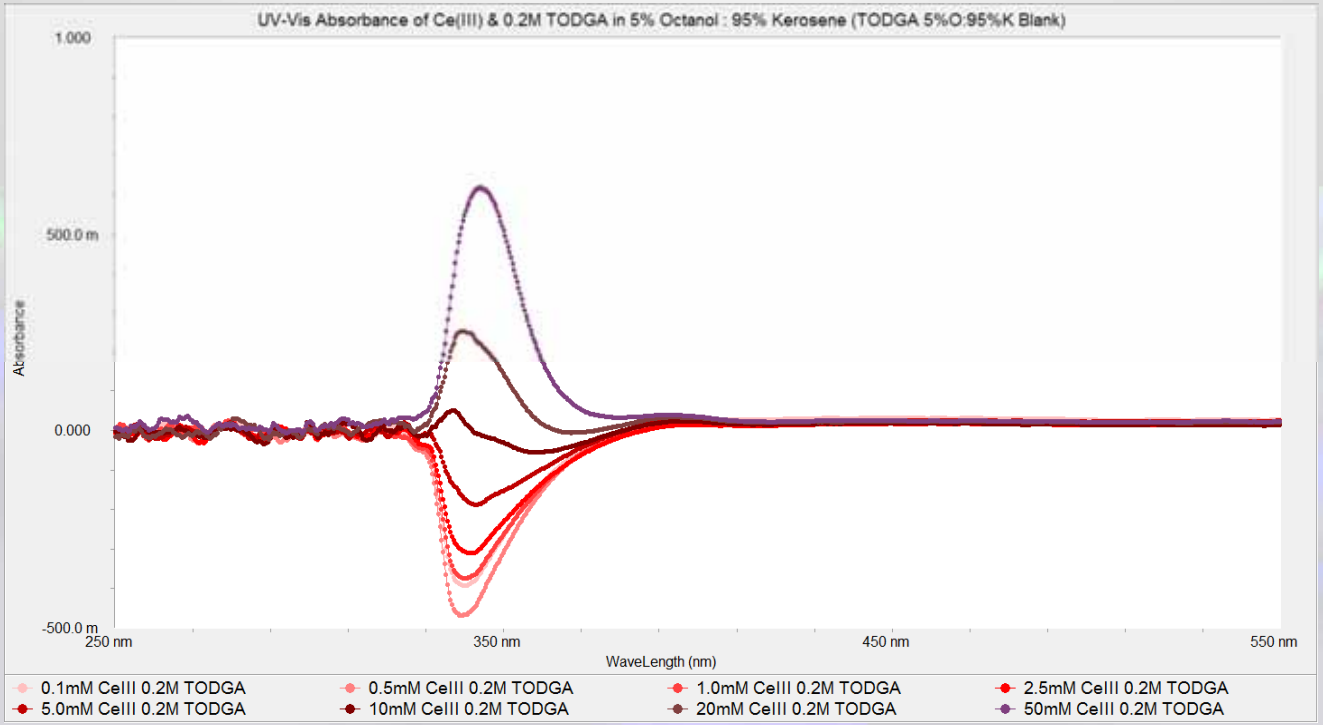
- Varied Rotation Speed



- Extraction appears to saturate after ~40 mins
  - lower D-value than for Ce(IV)/TBP system
  - total extraction of Ce achieved
  - Saturation of diffusion layer?

Mixer-Settler – Ce(III) / TODGA

- Increasing [Ce(III)]

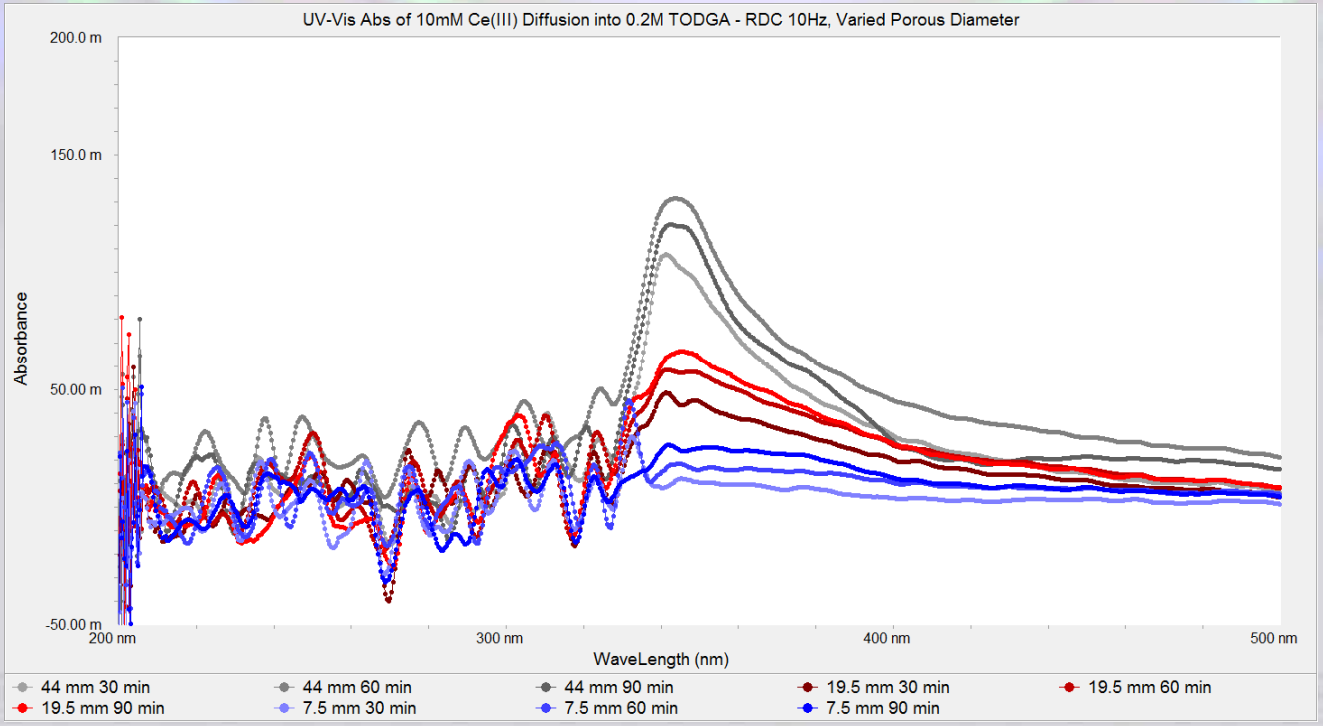


- Abs of organic phase vs 0.2M TODGA 5O:95K blank inverts at low [Ce(III)]
- Ce-TODGA complex increasing absorbance @ 343 nm
- Nitric-TODGA complex reducing absorbance @ 337 nm
- Necessitates HNO_3 contact pre-extraction

RDC – Ce(III)/TODGA Extraction

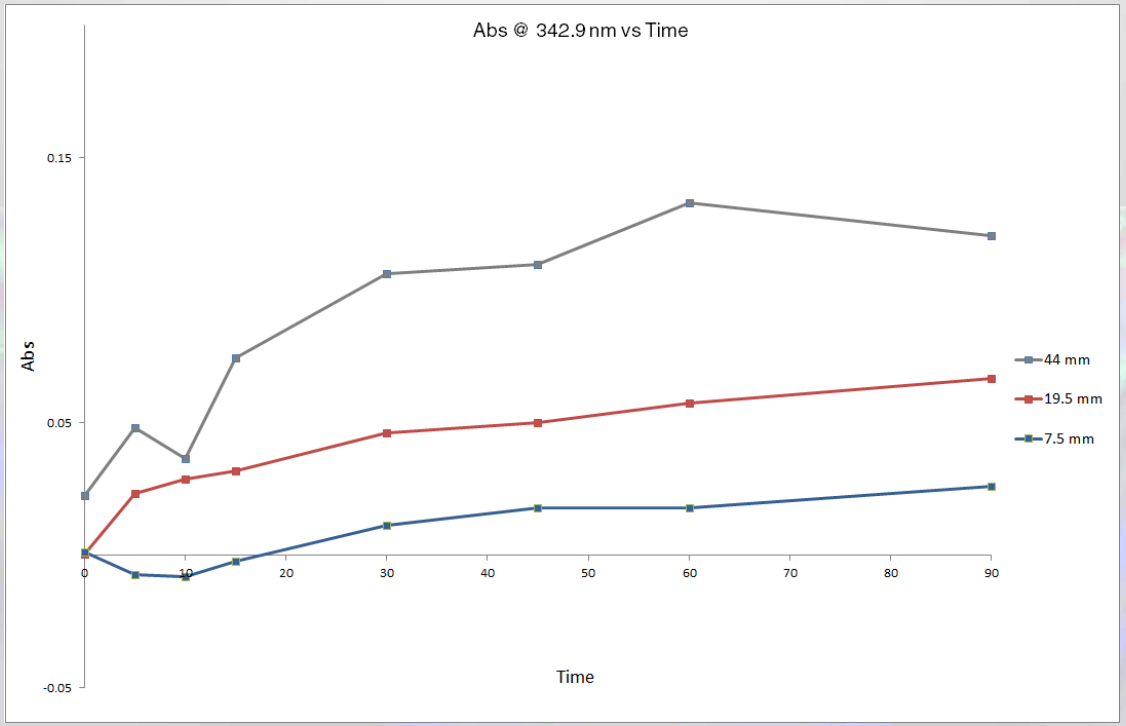
- Varied Interface Diameter

- Conditions
  - 10 mM Ce(III)
  - 0.2M TODGA in 5O:95K
  - Interface diameters: 44 mm, 19.5 mm, 7.5 mm
  - 10 Hz rotation
  - UV-Vis Abs monitoring



RDC – Ce(III)/TODGA Extraction

- Varied Interface Diameter



- Extraction rate decreases with decreasing interface diameter, as expected
- Demonstrates a convenient control parameter
- Useful in assigning rate determining step when building model

Conclusions

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- RDC system commissioned
- Ce(IV)/TBP system results indicate that rate of extraction is dependant on local hydrodynamics – the greater the diffusion layer thickness, the faster the extraction rate
- Extracted entity captured from within diffusion layer…
- …initial diffusion of extractant into aq. phase from organic phase
  - Key interaction between Ce(IV) & TBP occurs on the aq. side of phase boundary
- Similar results seen for Ce(III)/TODGA system … with similar conclusions:
  - Key Ce(III)-TODGA complexation occurs in aq. phase

Future Studies

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- More detailed examination of Ce(III)/TODGA and Ce(IV)/TBP extraction systems using RDC
- Variation of [Ce] RDC experiments
- Variation of [HNO_3] in RDC experiments
- RDC Study of Eu(III)/TODGA extraction
- Build model determination of rate constants of interfacial transfer

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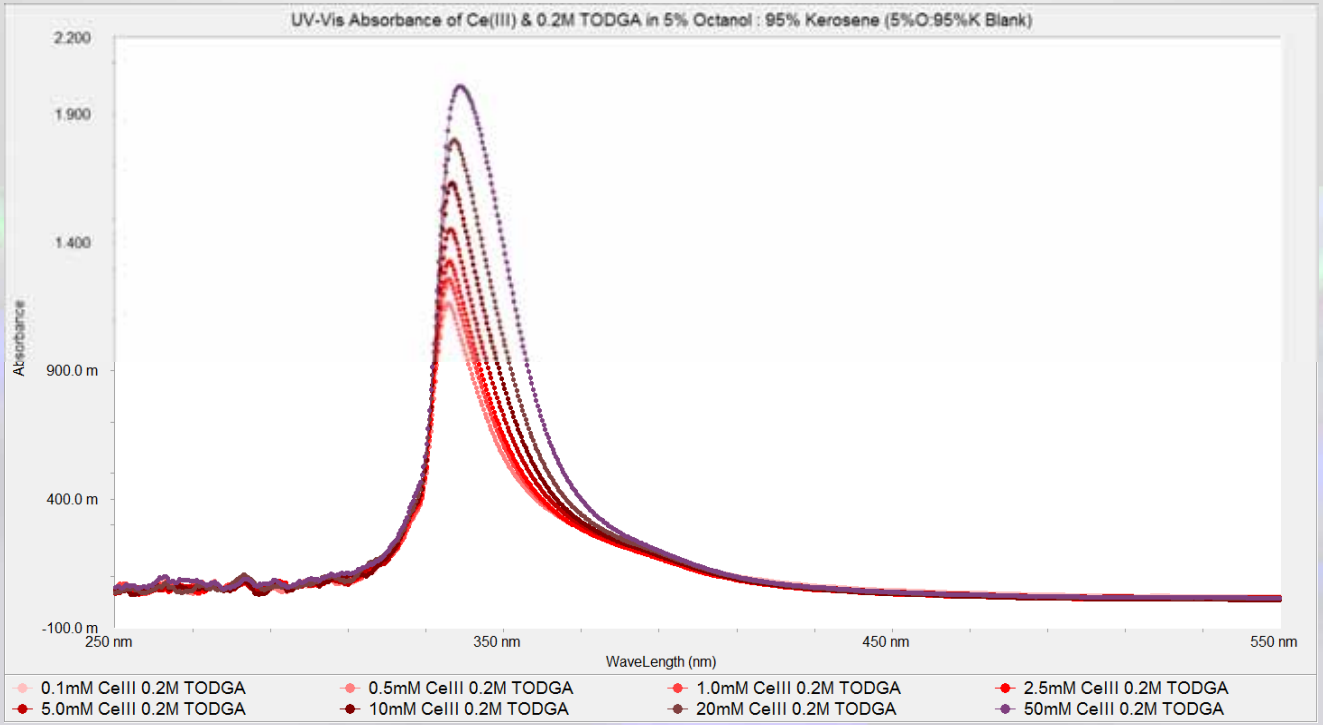
QUESTIONS?

Mixer-Settler – Ce(III) / TODGA

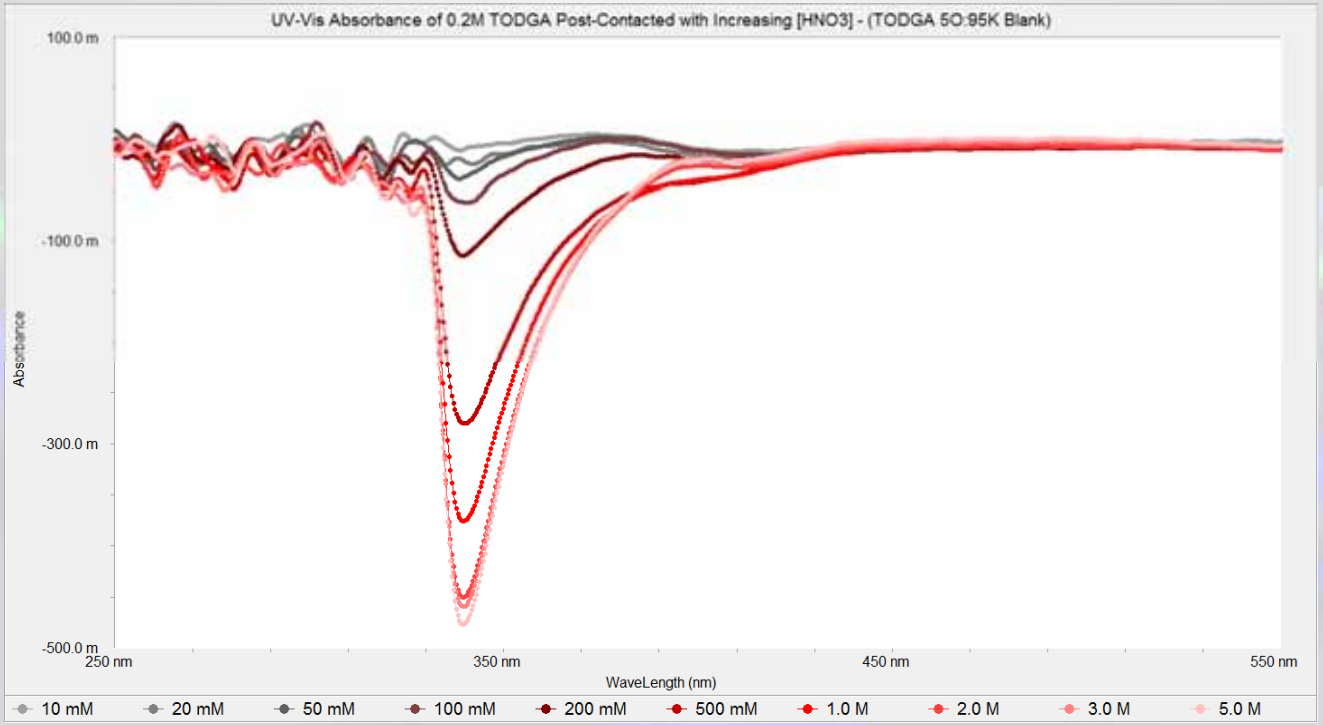
- Increasing [Ce(III)]



- Abs of organic phase vs 5O:95K
- Strong absorbance @ ~340 nm
- Peak height increases with Ce(III) concentration and shifts slightly

Mixer-Settler – HNO_3 / TODGA

- Increasing [HNO_3]



- Abs of organic phase vs 0.2M TODGA 5O:95K blank
- Nitric-TODGA complex reducing absorbance @ 337 nm
- Necessitates HNO_3 contact pre-extraction