Examination of Spectrophotometric Measurement of UCl_3 Concentration up to 9 wt% in LiCl-KCl Melt

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Outline

1. Quantification of ANs and LNs in pyroprocessing

2. Real-time monitoring methods in molten salt

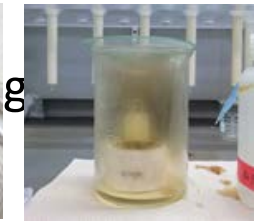
3. Absorption spectroscopic studies of uranium in LiCl-KCl
   - Synthesis of U(III) in LiCl-KCl
   - Spectroscopic characterization of U(III) and U(IV)
   - Concentration dependence of absorbance

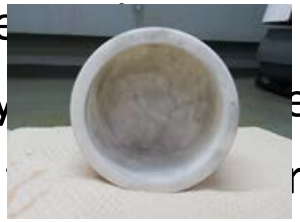
4. Summary and future works

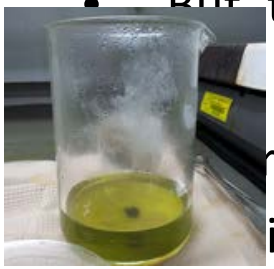
Quantification of ANs and LNs in Pyroprocess

Purpose

- Mass balance



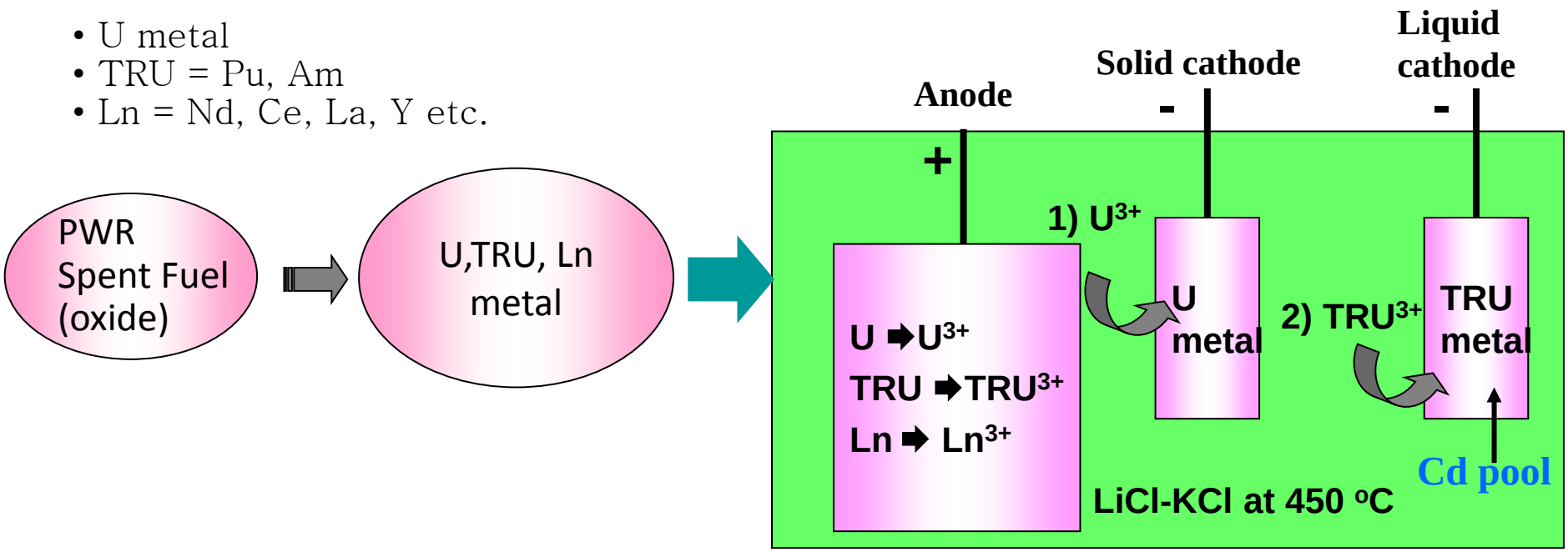




- Information on elements of interest (U, Pu, etc)
- Requires methods for reliable information

Quantification of ANs and LNs in Pyroprocess

- U metal
- TRU = Pu, Am
- Ln = Nd, Ce, La, Y etc.



Salt (DA, NDA)	Trace amount of U, TRU, LN	2-9 wt% U^{3+} <2-4 wt% TRU, LN	<2-4 wt% U, TRU, LN
Product (DA)	Metal phase Oxide Phase	U (decontamination)	U, AN, (LN) (composition)

Real-time measurement of concentration in melt

Requirement

- Reliable, reproducible, and stable methods
- Minimal interference
- Able to quantify a wide range of concentration (up to 9 wt% of U*)*

  $\rightarrow$ *Motivation!*

Potential approaches

- Electrochemical methods

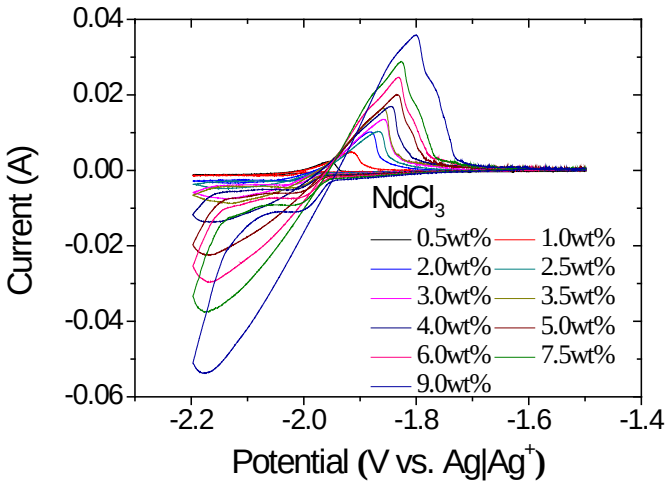
  - CV, RCA, etc.
- Spectroscopic methods

  - Absorption, emission, LIBS, etc.

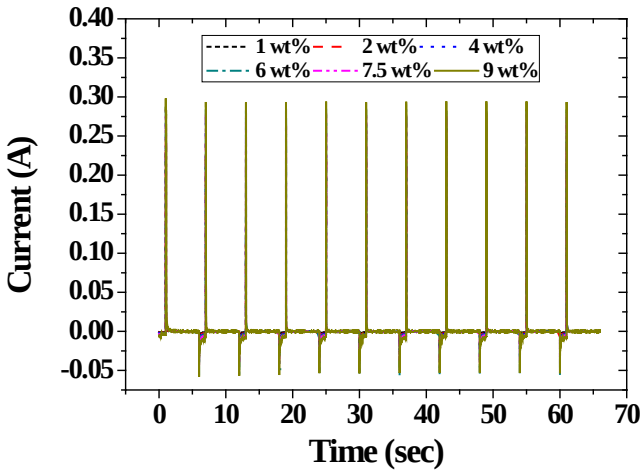
Electrochemical Approaches

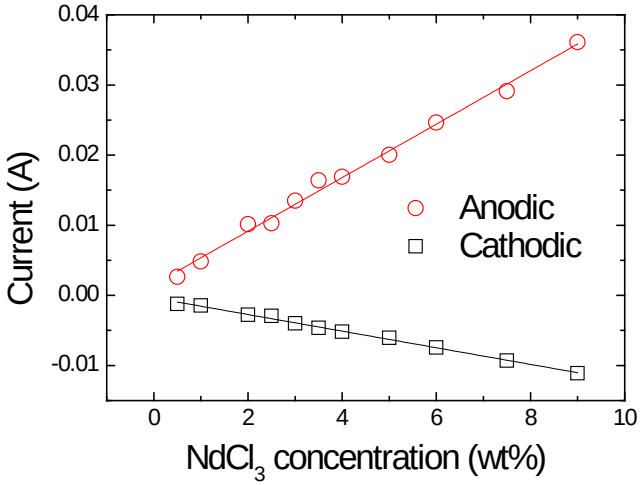
$$Nd^{3+} + 3\,e^- \leftrightarrows Nd^0$$

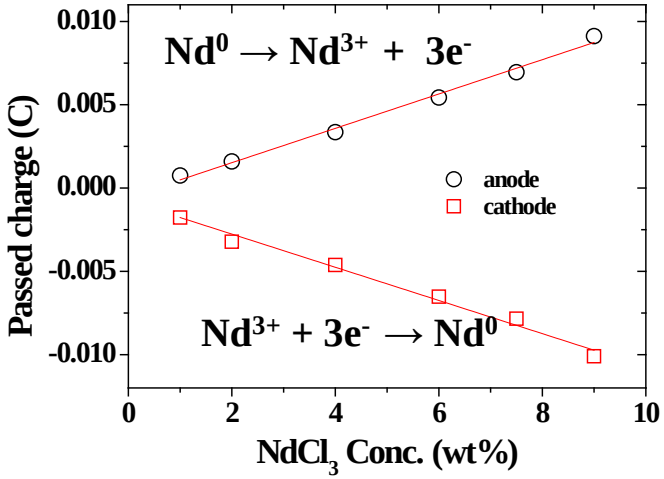
Cyclic Voltammetry (CV)



Repeating Chronamperometry (RCA)

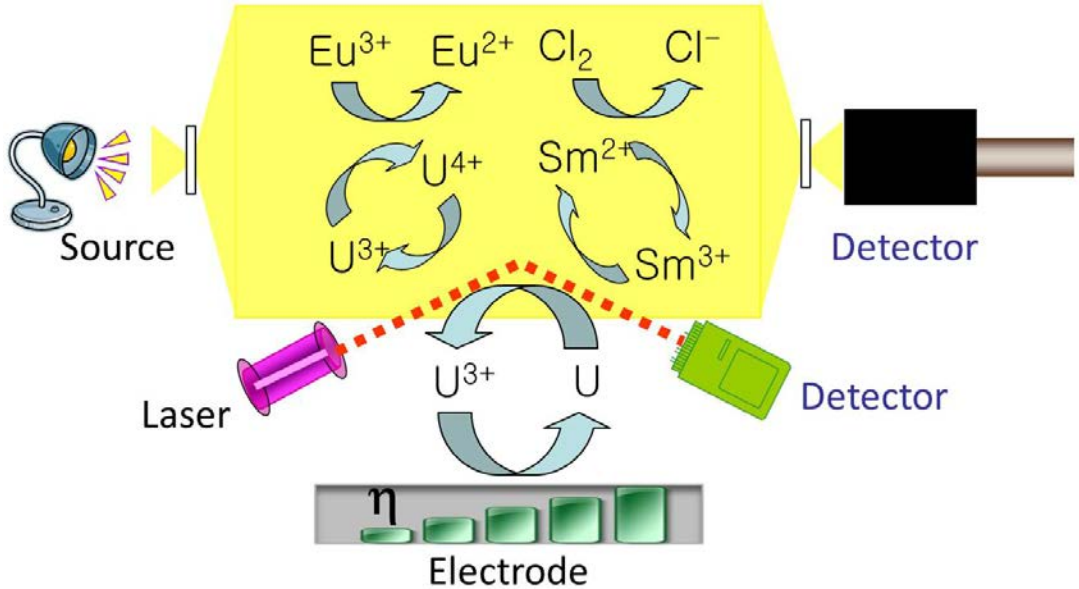






D. H. Kim et al. *Microchem. J.* **114**, 261-265 (2014)

How about Spectrophotometry?



- Absorption, emission
- Speciation
- Real-time monitoring of reactions
- Integration with electro-chemical methods
  - Control of oxidation states

Absorption spectroscopy

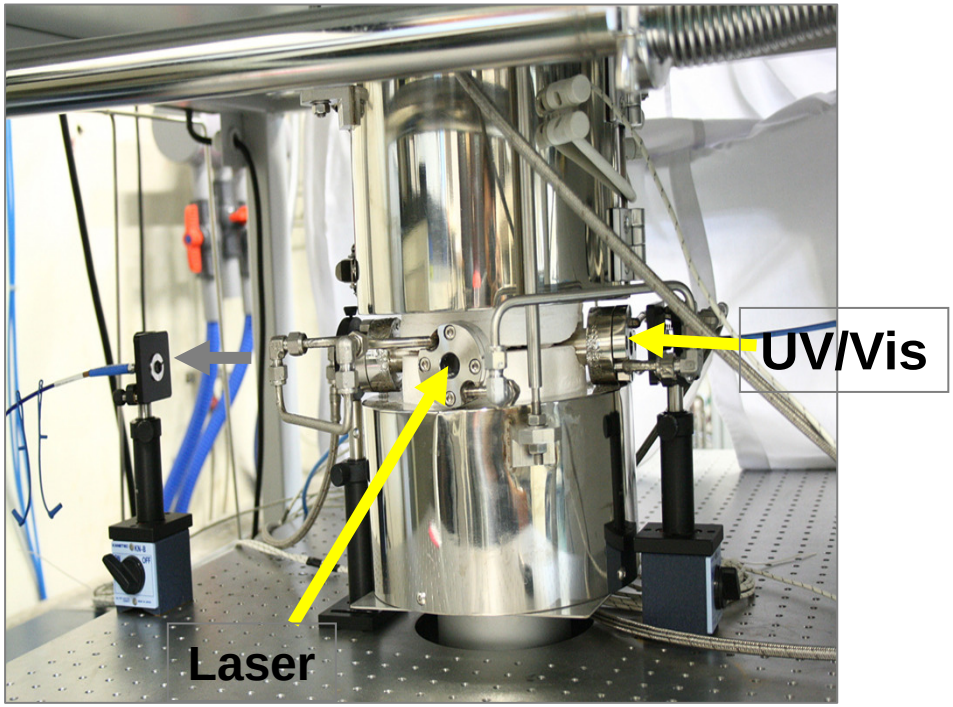
Beer-Lambert law

$$A = \varepsilon bc$$

A: absorbance
ε: molar absortivity ($M^{-1}cm^{-1}$)
b: light path length
c: concentration

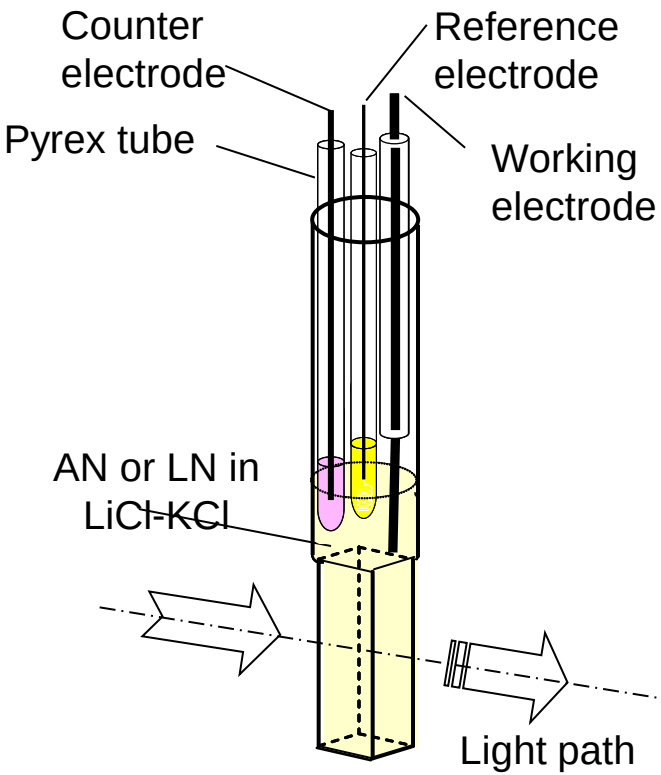
- Quantification of solutes of interest

Experimental setup



- Electrochemical measurement
- Spectroscopic measurement (UV/Vis, fluorescence)

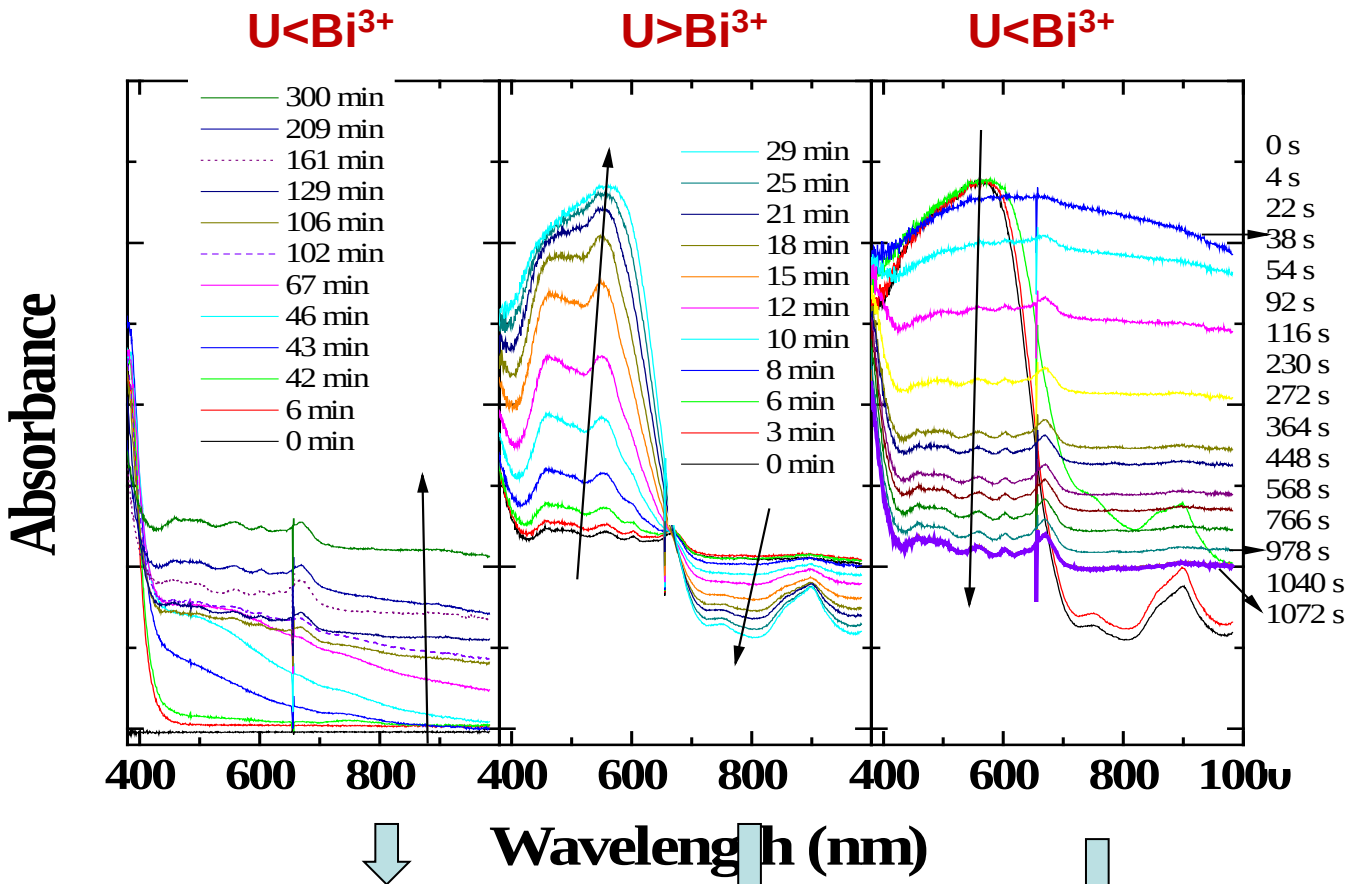
Spectroelectrochemical Cell in Molten Salt



- Integration of electrochemistry and spectrophotometry
- Able to perform real-time measurement of electrochemical reactions

Synthesis of U(III) in LiCl-KCl

- **Synthesis of U(III) & U(IV) in LiCl-KCl by using $BiCl_3$**



$3U^0 + 4Bi^{3+} \rightarrow 3U^{4+} + 4Bi^0$

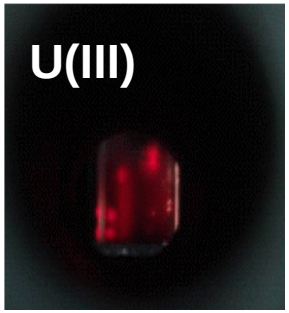
$3U^{4+} + U^0 \rightarrow 4U^{3+}$

$3U^{3+} + Bi^{3+} \rightarrow 3U^{4+} + Bi^0$

S.-E. Bae et al. *Electrochem. Solid-State Lett.*, **13**, F25 (2010).

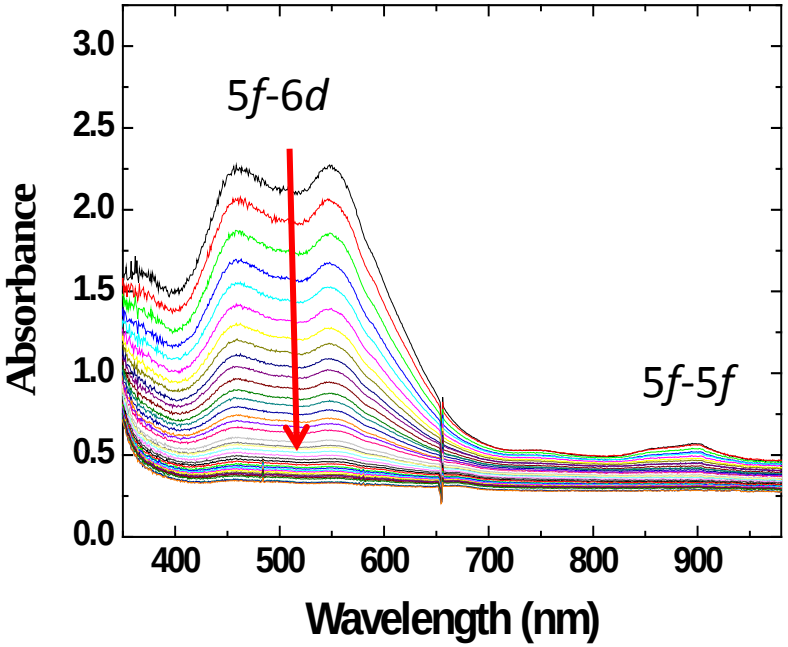
U(III) and U(IV) in molten salts

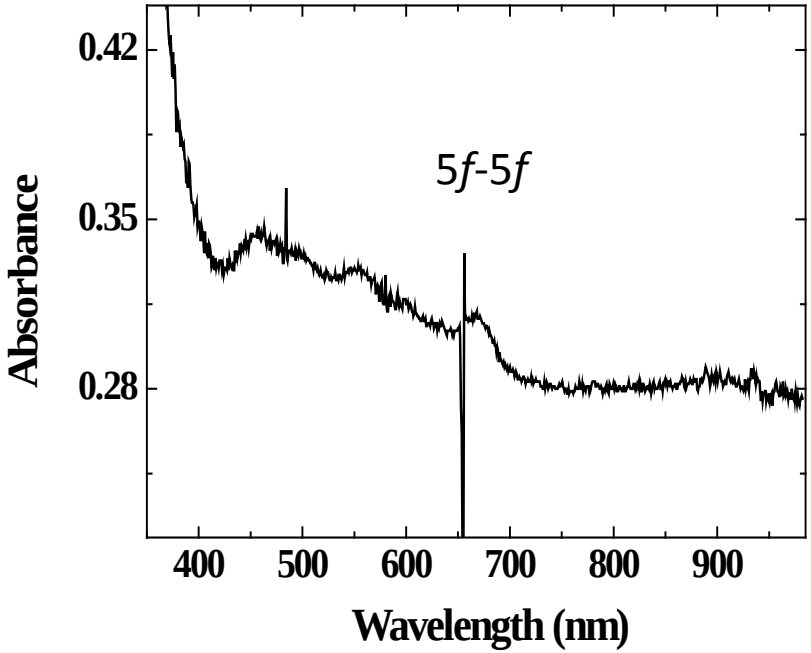
Dark wine



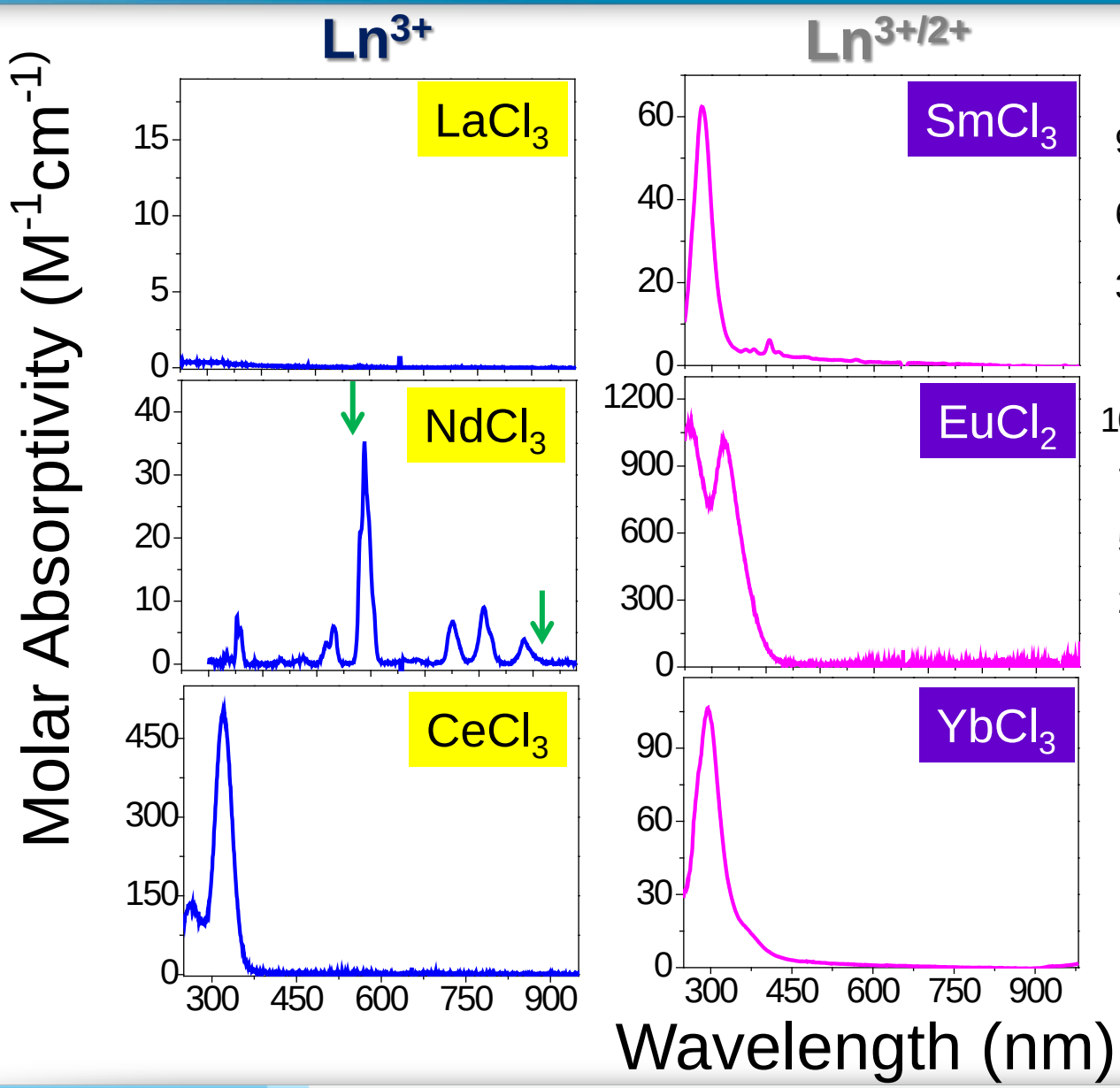
$$U^{3+} \rightarrow U^{4+} + e^{-}$$

pale green





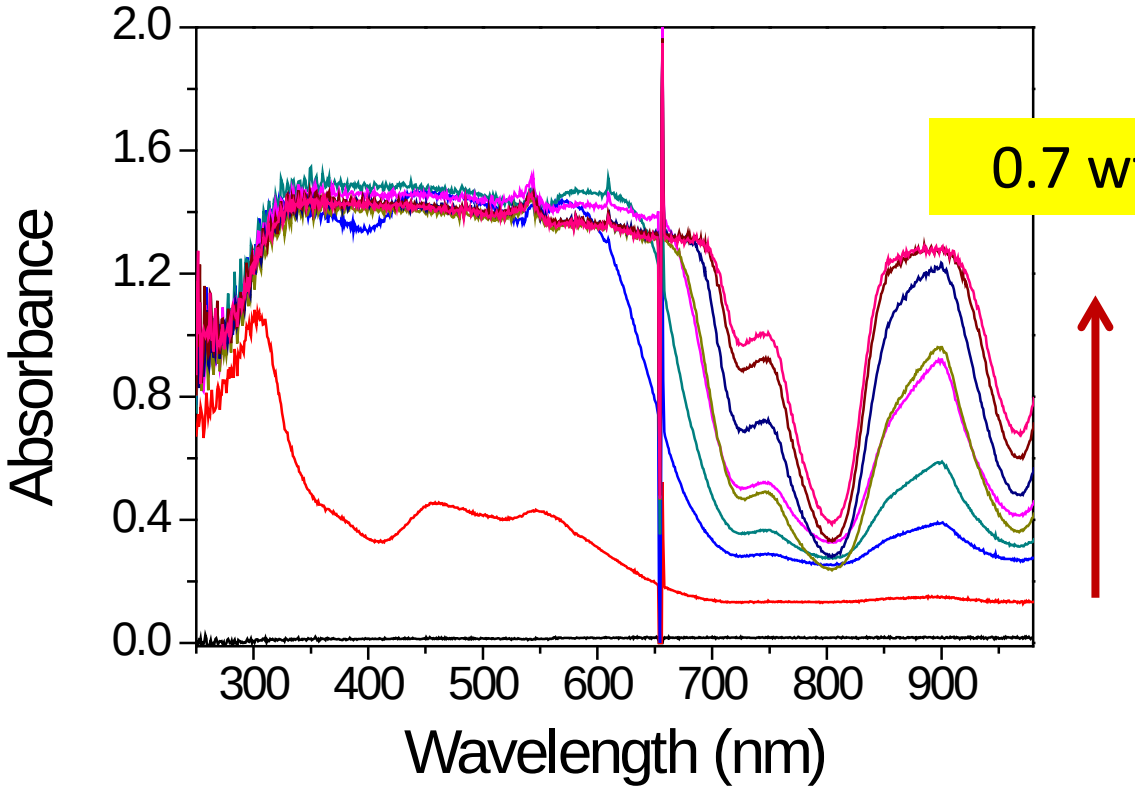
Absorption spectra of LNs and ANs

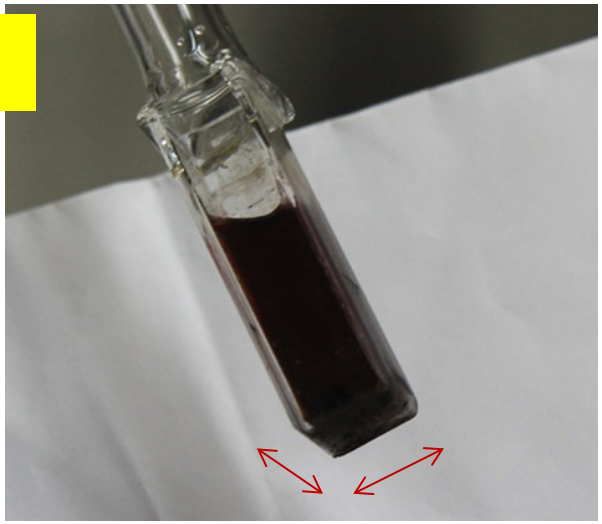


Molar absorptivity ($M^{-1}cm^{-1}$)

- f-f transition < 100
- f-d transition > 500

Absorption spectra of UCl_3

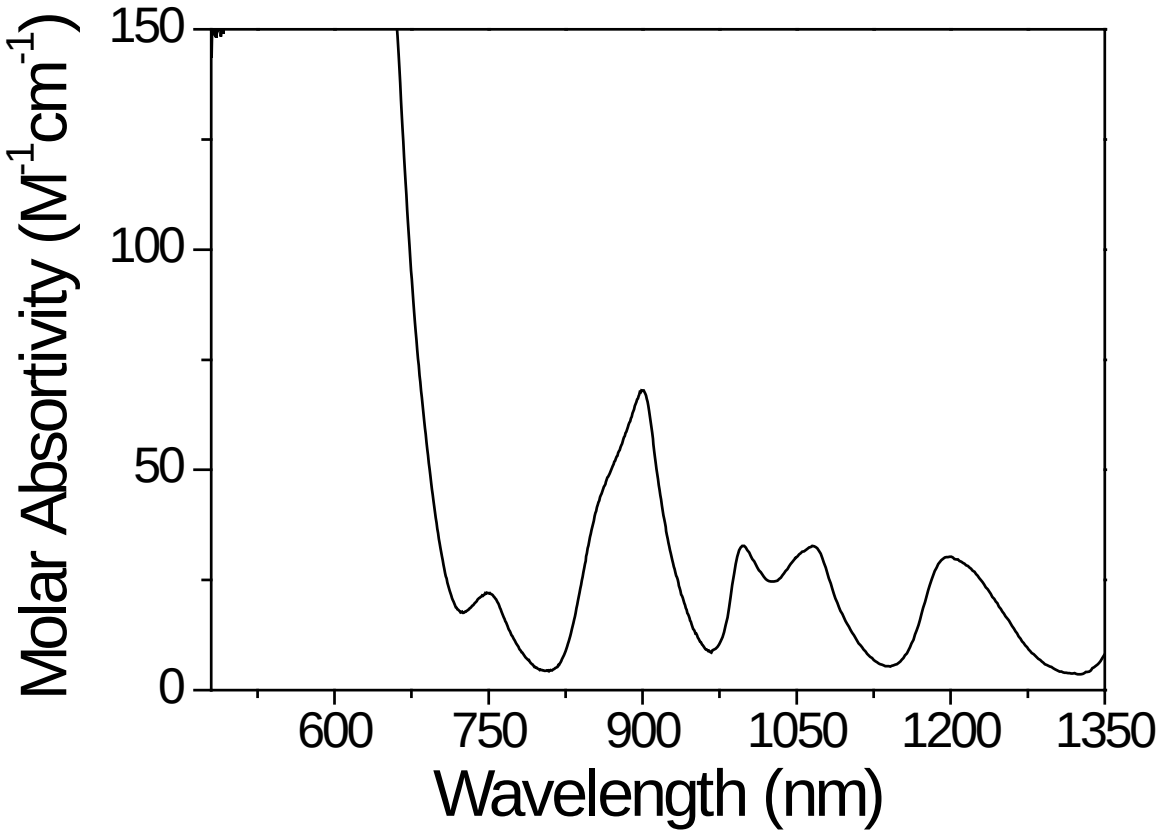




1 cm

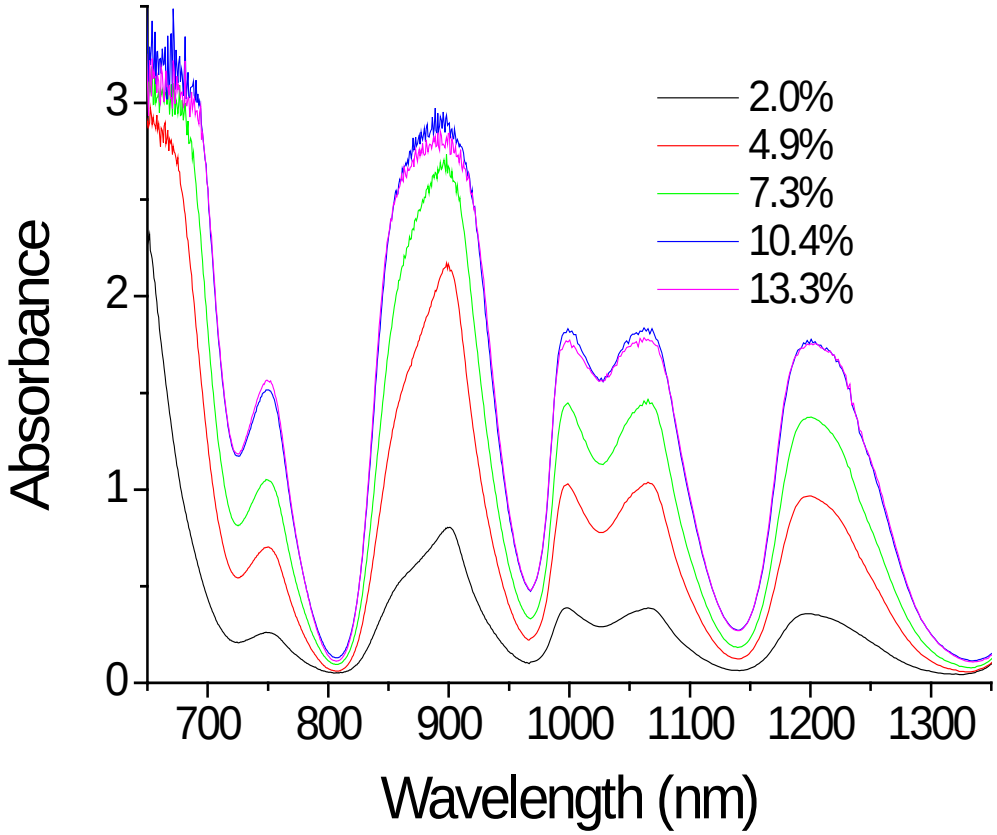
- Used a cell with 1 cm light path length
- Strong UV and visible absorption bands due to *f-d* transitions (color: black)
  - Exceed the upper detection limit at very low concentrations (<0.2 wt%)
- Even weak *f-f* absorption bands in the NIR region are not usable beyond 1 wt%
  → Require a short light path length to reduce absorbance

NIR Absorption spectra of UCl_3



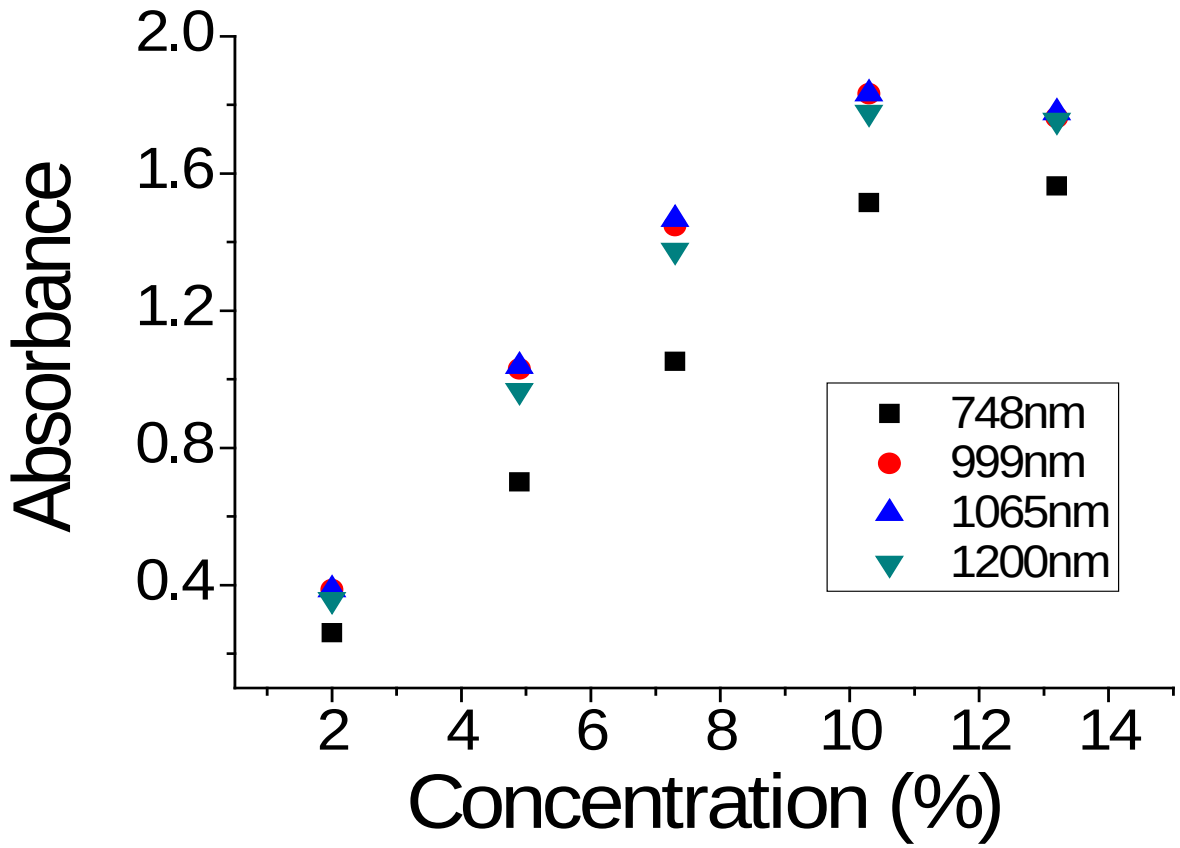
- Quantification of concentrated U is not capable in the UV and visible region
- Extended the spectrum up to 1350 nm
- More f-f transitions (ε = 20-25 $M^{-1}cm^{-1}$)

NIR absorption spectra of concentrated UCl_3



- 1 mm light path length cell
- Concentration was determined by ICP-AES
  - U concentration: 2-13 wt%

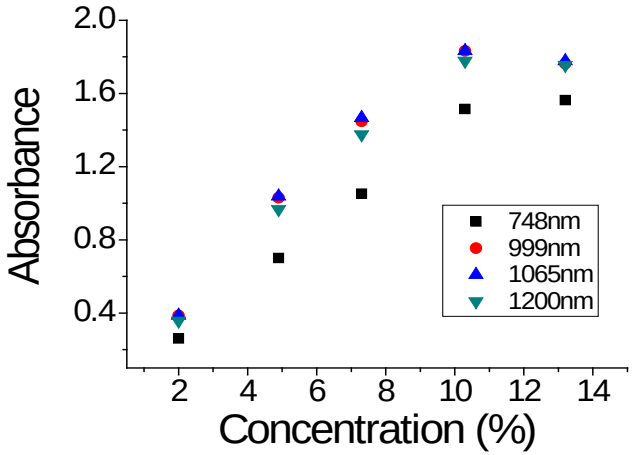
Concentration dependence



- Good linear relationship between absorbance and concentration up to 10 wt%
- Likely applicable to quantification of U up to 9 wt%

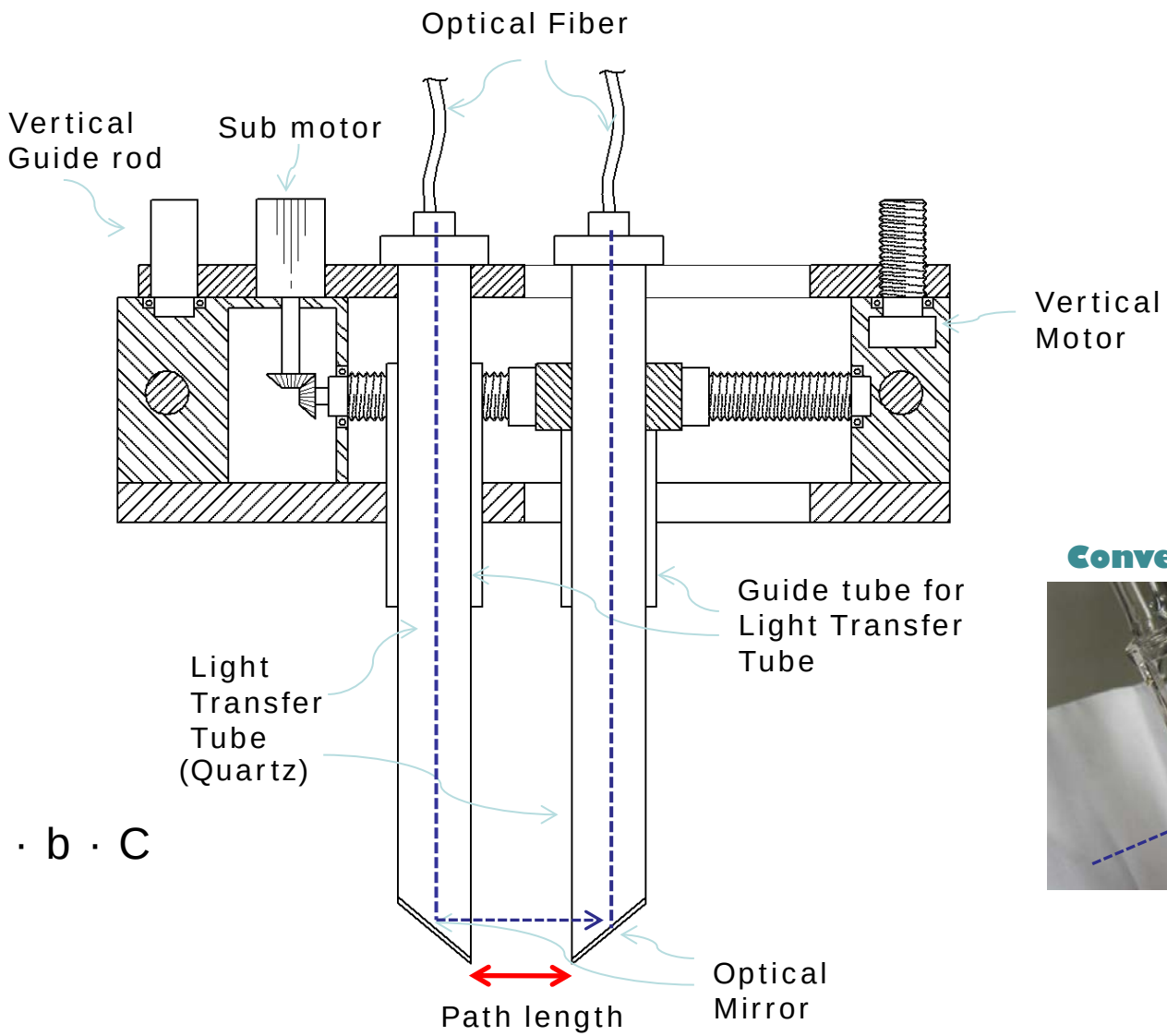
Summary and Future works

- Absorption spectroscopy may quantify the concentration of U up to 9 wt %
  - *f-f* transitions in the NIR region
  - 1 mm light path length cell



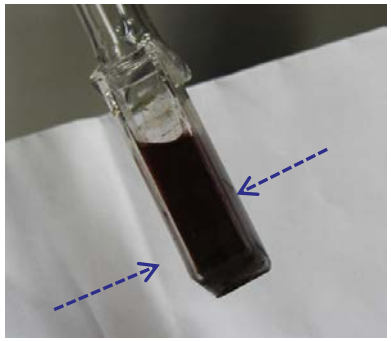
- Precise determination of molar absorptivity in the NIR region
- Measurement of the NIR spectra of LNs and ANs
  - Potential interference
- Electronic interactions between U and other elements in high concentration
- Test with multi-component systems

Design of on-site measurement cell



$$A = \varepsilon \cdot b \cdot C$$

Conventional Cell



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Thank you for your attention!