LA-UR-16-22546
Approved for public release; distribution is unlimited.

Title: Uranium Detection - Technique Validation Report

Author(s): May, Iain
Lujan, Elmer J. W
Reilly, Sean Douglas
Colletti, Lisa Michelle
Mechler-Hickson, Alexandra Marie
Garduno, Katherine

Intended for: Open Source Milestone Report and Presentation for NNSA

Issued: 2016-04-14

Uranium Detection - Technique Validation Report

L.M. Colletti,[1] K. Garduno,[1] E.J.W. Lujan,[1] A.M. Mechler-Hickson,[1,2] I. May,[1] & S.D. Reilly[1]

[1]Chemistry Division, Los Alamos National Laboratory

[2]University of Wisconsin, Madison, Wisconsin

As a LANL activity for DOE/NNSA in support of SHINE Medical Technologies™ 'Accelerator Technology' we have been investigating the application of UV-vis spectroscopy for uranium analysis in solution. While the technique has been developed specifically for sulfate solutions, the proposed SHINE target solutions, it can be adapted to a range of different solution matrixes. The FY15 work scope incorporated technical development that would improve accuracy, specificity, linearity & range, precision & ruggedness, and comparative analysis. Significant progress was achieved throughout FY 15 addressing these technical challenges, as will be summarized in this report. In addition, comparative analysis of unknown samples using the Davies-Gray titration technique highlighted the importance of controlling temperature during analysis (impacting both technique accuracy and linearity/range). To fully understand the impact of temperature additional experimentation and data analyses were performed during FY16. The results from this FY15/FY16 work were presented in a detailed presentation, LA-UR-16-21310, and an update of this presentation is included with this short report summarizing the key findings.

The technique is based on analysis of the most intense U(VI) absorbance band in the visible region of the uranium spectra in 1 M H_2SO_4, at λ_{max} = 419.5 nm. During sample analysis aliquots of uranium solutions of unknown concentration would be diluted into 1 M H_2SO_4 prior to analysis (an accurately known *ca.* 40× dilution), both to allow 'in range' measurement and to maintain specific solution chemistry environment. As the intensity of this transition varies linearly with uranium concentration then the Beer-Lambert law allows concentration to be measured through the following equation: -

$$A = \varepsilon c\, l$$

where *A* = absorbance, ε = molar absorptivity (M^{-1} cm^{-1}), c =concentration (M) & l = cell path length (cm)

In an effort to improve technique accuracy almost all sample concentration analysis was performed through mass measurements (*e.g.* mg/g, wt %), with accurate density measurements used to convert to, and from, molar concentrations at a measured temperature. Thus, "1 M" H_2SO_4 is actually 9.26 wt % H_2SO_4 in H_2O. In addition, a new "reads" data collection method (*vs.* a traditional scan) was developed to reduce uncertainties associated with absorbance values only at wavelengths of most interest; λ_{max} at 419.5 nm, the two adjacent peaks at 409 & 430 nm, baseline wavelengths values at 550 & 600 nm and an additional measurement at 500 nm.

Determination of what we predicted would be more accurate ε values was undertaken by dissolving uranium metal standard material (CRM 112-A) in nitric acid and converting to uranium standard solutions of various concentrations in "1 M" H_2SO_4. In addition, uranium samples were prepared in "0.9

M” (8.348 wt %) and “1.1 M” (10.133 wt %) H_2SO_4, and analyzed by UV-vis to confirm technique range (“1.0 $\pm$ 0.1 M” H_2SO_4). Initially these samples were measured using triplicate 10 mm path length cells from 3 different companies (Starna cells, Hellma Analytics & NSG precision) and triplicate 2 mm & 100 mm path length cells (Starna cells). The 10 mm Starna cells were found to be the most ‘user friendly,’ although all three manufacturers 10 mm path length cells worked well, and provided evidence of the impact of temperature on calculated molar absorptivity (see subsequent discussion). Increased uncertainties associated with the shortened path length precluded further studies with the 2mm path length cells. Technical difficulties, and standard solution concentrations largely incompatible with the path length, prohibited an effective assessment of the value of the longest path length/lowest associated uncertainties 100 mm cell. For all subsequent analysis only the three 10 mm Starna Cells were used.

The next stage of technique development was analysis of 5 actual uranium sulfate samples, 2 of which were very well characterized. Initial comparison of the results obtained from uranium analysis of these samples, both by the UV-vis technique and Davies-Gray titration, indicated that the UV-vis technique systematically underestimated uranium concentration. Temperature fluctuations in the laboratory that correlated with observed ε (increased with temp.) were determined to be a major issue and necessitated additional experimental standard solution measurements to facilitate the determination of ε at lower temps. This allowed for the determination of ε as function of temperature over the range in which assays of the 5 actual samples were measured. Additional discrepancies between analysis techniques could be attributed to assay sample volume and no quantification of sample evaporation over time. Nevertheless, of the one sample that was analyzed by three different operators in triplicate using three different UV-vis cells (27 separate analyses), all apart from one yielded measured uranium concentrations within 0.6 % of the value measured by Davies-Gray. This data indicated that the technique now has high precision and ruggedness, with the comparative analysis revealing that additional temperature control (and quantification of sample evaporation) should lead to greater accuracy.

Any contaminant that absorbs light between 419-600 nm can potentially interfere with the developed UV-vis technique. Previously we have screened a suite of potential corrosion and fission product chemical contaminants and observed that Ru had the most intense transitions in the visible region, and that peak intensities could change as a function of time. Using 129 mg/g uranium sulfate solutions doped with 0, 2.1, 21 & 210 ppm Ru, the impact of the contaminant on the ratios of the 409 nm 430 nm & 500 nm absorbance values vs. the 419.5 nm λ_{max} peak were probed. It was observed that the impact of Ru contamination could be observed through variation in these ratios at lower Ru concentrations than could be observed in measureable change in ‘observed’ uranium concentration. Thus, at the current level of technique accuracy, it should be possible to develop a screening protocol that would reject data in which impactful levels of contaminants were present.

Details of the work are described in the following viewgraphs.

L.M. Colletti, K. Garduno, E.J. Lujan, A. Mechler-Hickson, I. May & S.D. Reilly
(R. Copping & D. Rios)
Chemistry Division

Los Alamos NATIONAL LABORATORY EST. 1943

Uranium Detection

Technique Validation

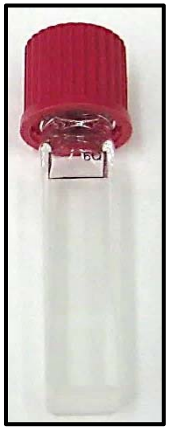
Meeting at SHINE Medical Technologies

3rd March 2016

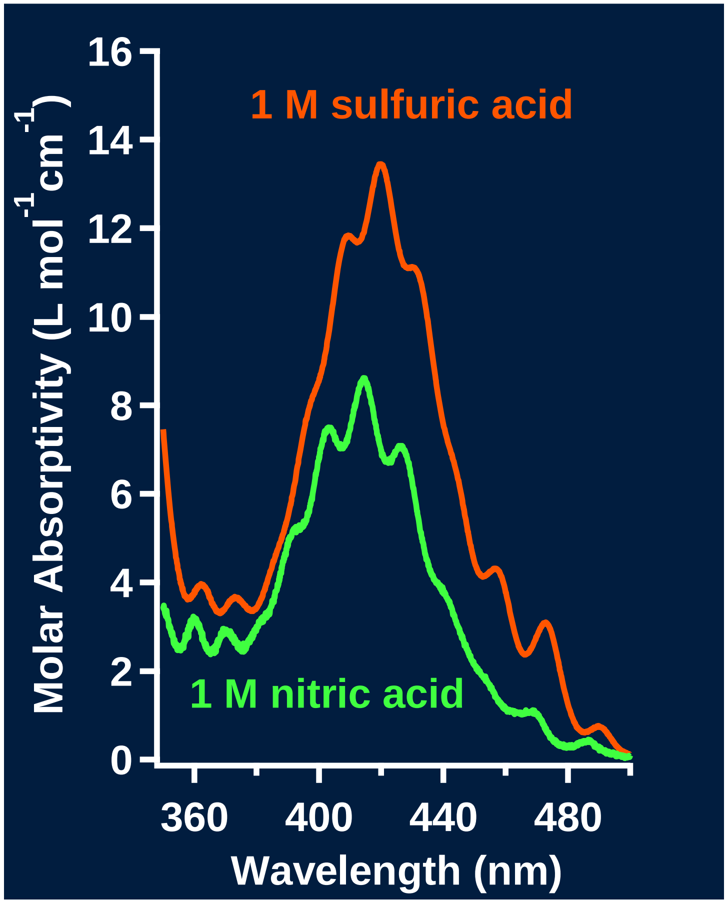
UNCLASSIFIED

Previous Studies
A Visible Spectroscopy Technique for Uranium Analysis

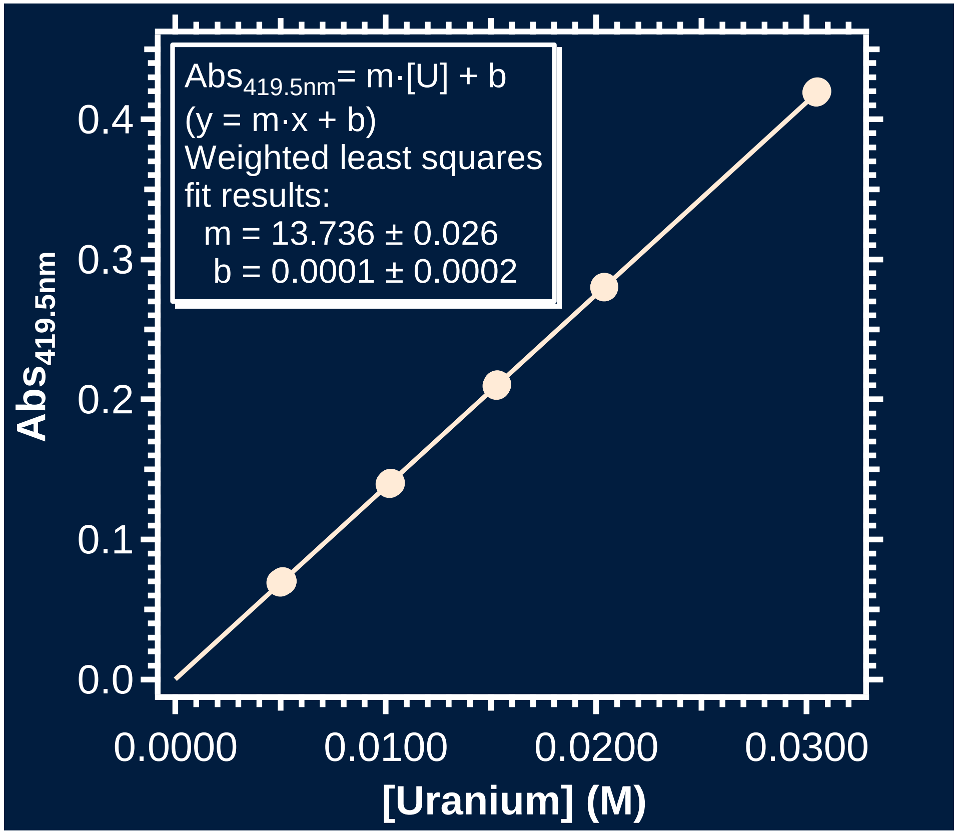
- Uranyl absorption spectroscopy – can be applied to uranium concentration measurement in solution
- $A = \varepsilon c l$
  - A= absorbance
  - ε= molar absorptivity (M^{-1} cm^{-1})
  - c= concentration (M)
  - l= path length, cm



- λ_{max} (peak max, nm) and ε (molar absorptivity) vary with chemical composition
- Previous studies - a small aliquot of sample (*e.g.* 50 μL) diluted into excess of 1 M HNO_3 or H_2SO_4 (2000 μL)



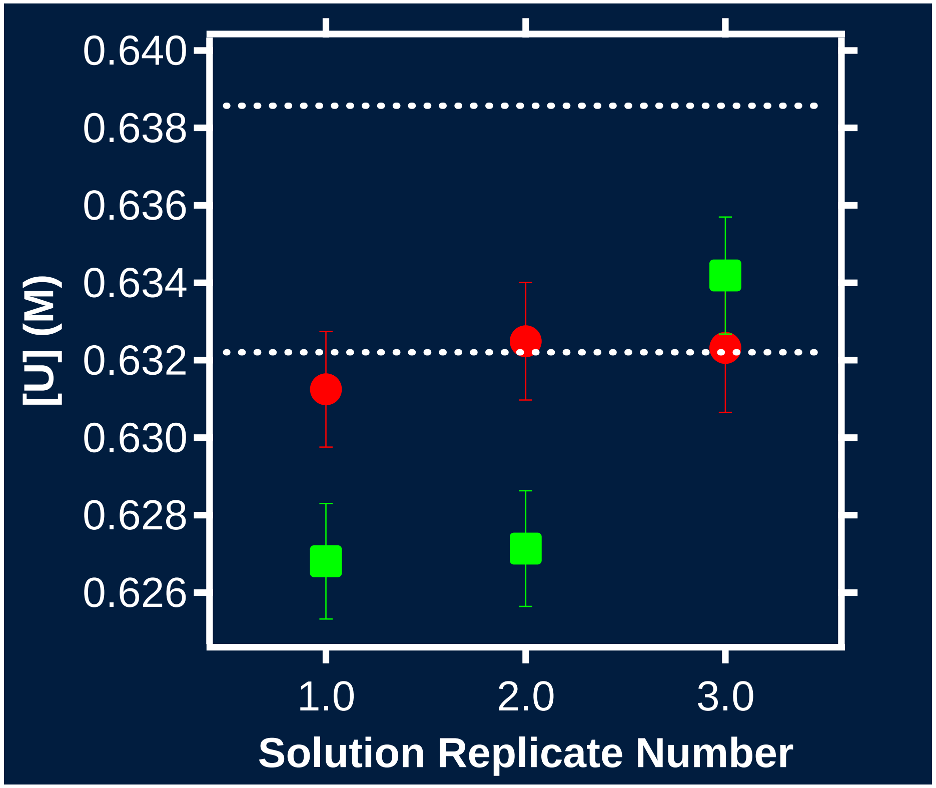
FY14 Work - Molar Absorptivity of Uranium(VI) Determined from Matrix of Standard Uranium Solutions



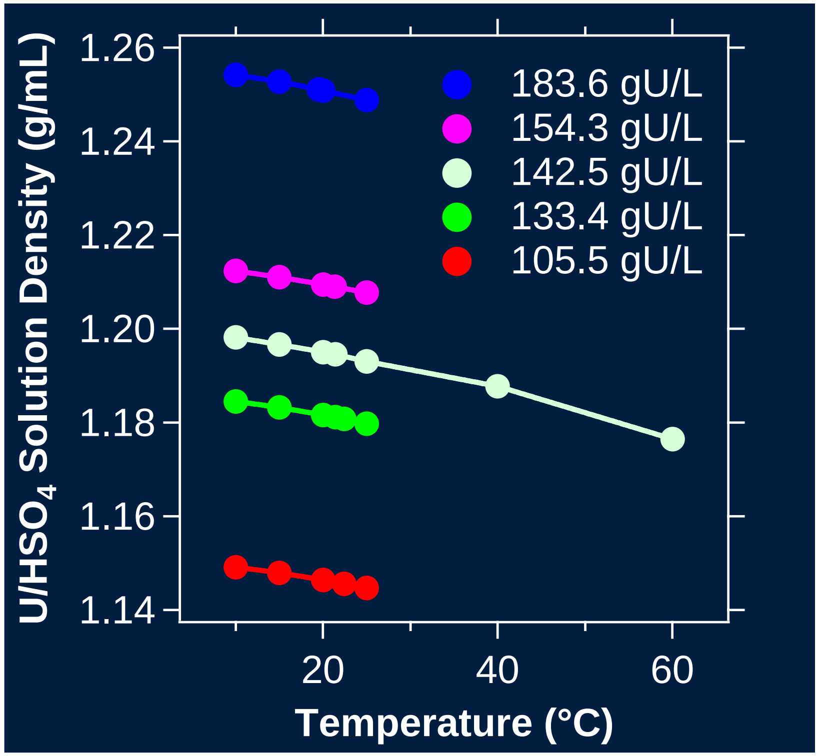
- The molar absorptivity of uranium(VI) in 1.0 ± 0.1 M H_2SO_4 at 19.5 ± 1.7 °C is 13.736 ± 0.026 cm^{-1} M^{-1} at 419.5 nm.

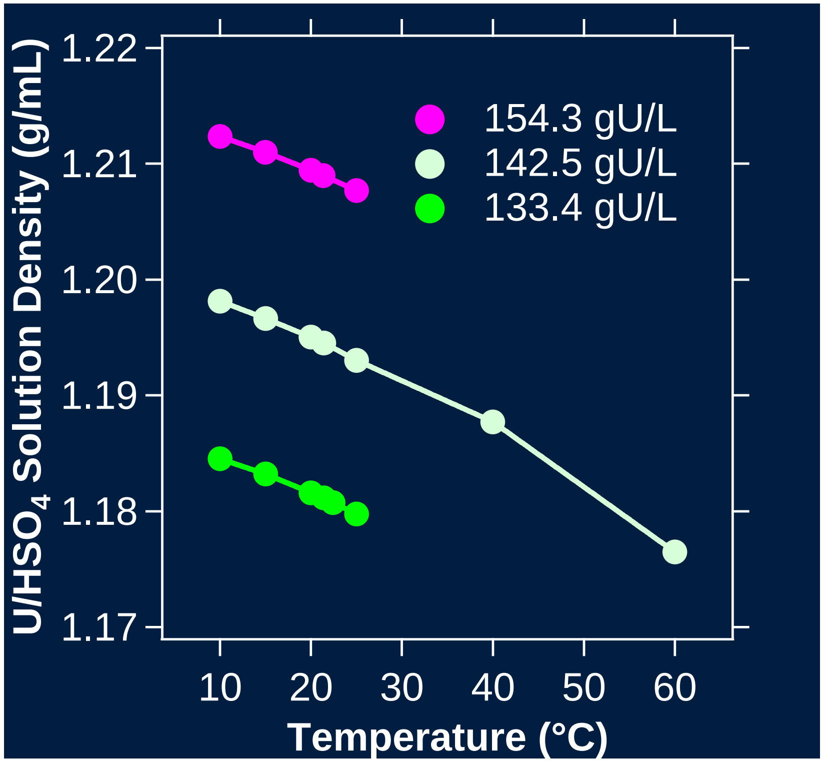
FY14 Work - Assay Method Accuracy Testing (151.2 gU/L, 0.6353 mol/L)

- The white lines represent 1 standard deviation of the known molar uranium concentration based on gravimetric data from solution preparation.
- The square and circle points are the uranium concentrations measured by the spectroscopy assay method using 90 (red) or 50 (green) µL uranium aliquots, respectively.
- The error bars are the standard deviations in these measurements.
- Difference between known and measured values all < 0.7 %. For the 90 µL assays.



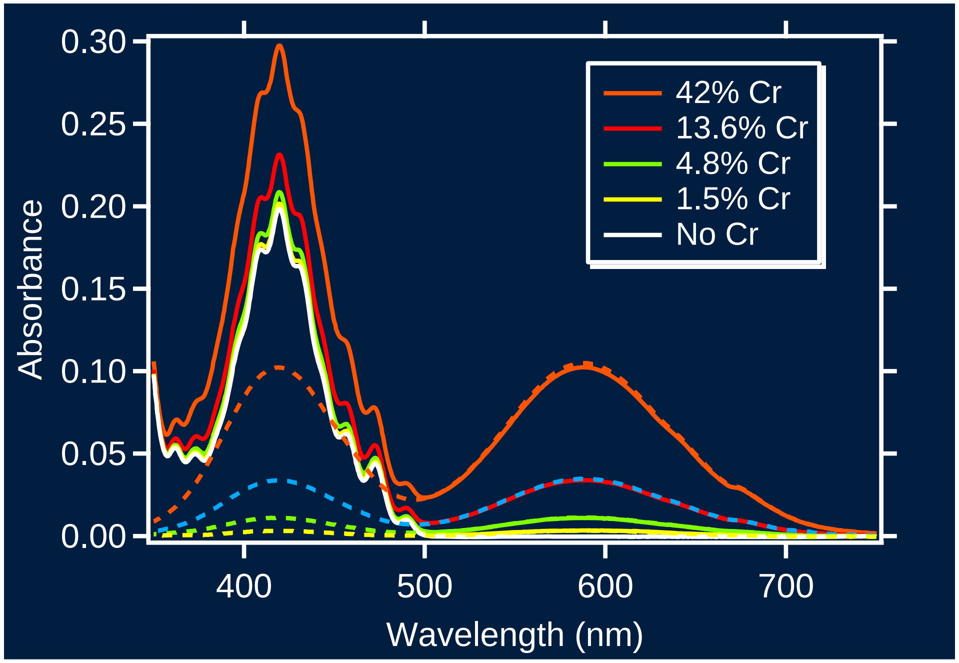
FY 14 Work
Density Measurements on pH1 Uranium Sulfate Solutions

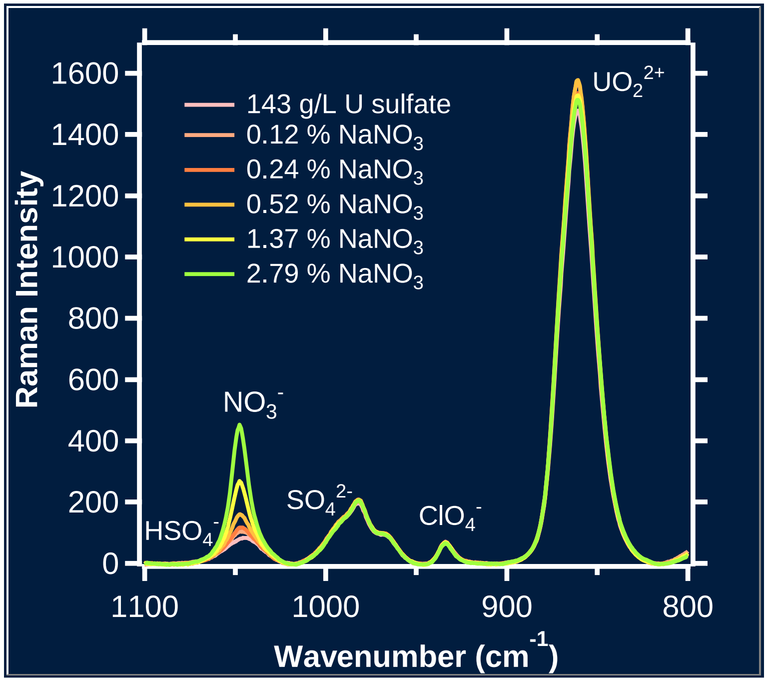




Note: This is one of the last slides where [U] conc. is routinely discussed in terms of volume of solution. From now on all [U] discussed in terms of mass of solution.

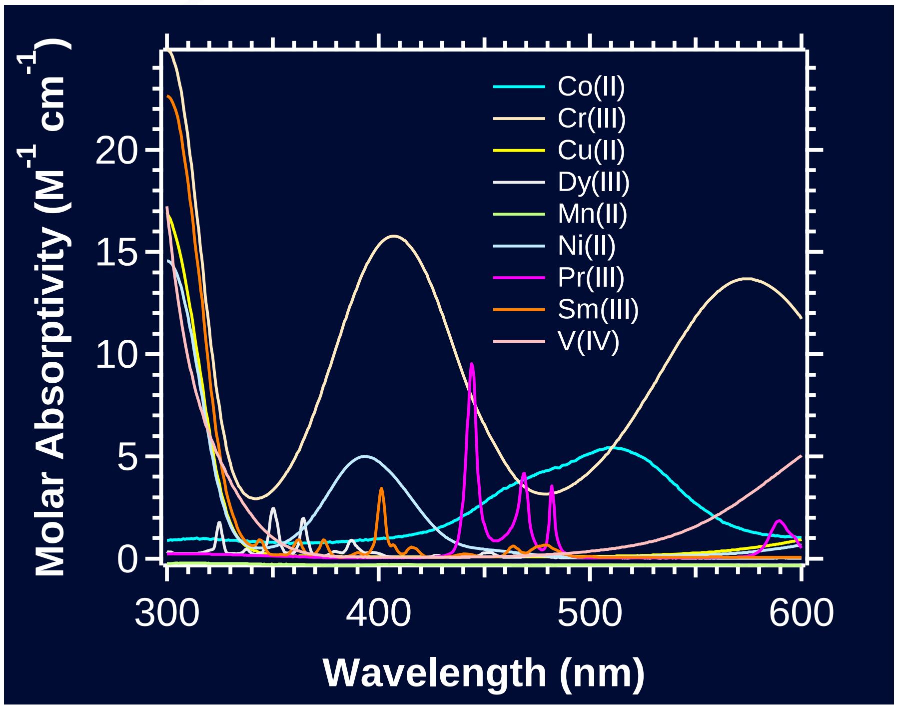
FY14 Work
Analysis of Contaminants and Impurities

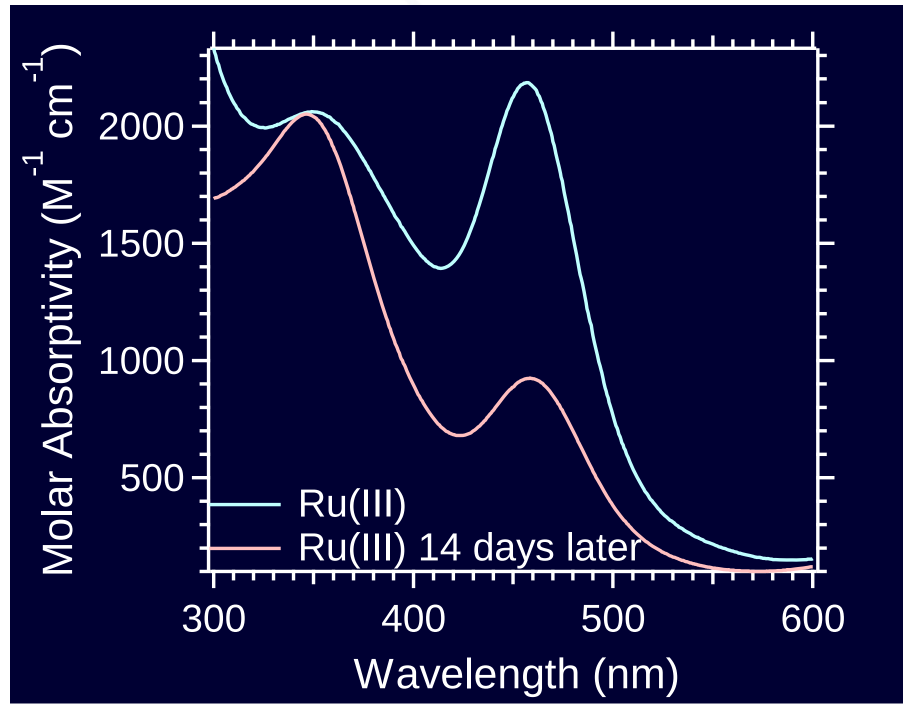




Raman Spectroscopy

FY14 Work
Additional Analysis of Contaminants (1 M H_2SO_4)





FY 14 Work
Guide to Uncertainty Measurements (GUM)

- End of FY14 technique relative uncertainty – “0.5” %
  - 62 % of uncertainty – molar absorptivity value
  - 14 % of uncertainty – cell path length
  - 8 % of uncertainty - spectrometer signal measurement

Technique Development FY15-16
A Summary of Progress

- **Accuracy** - *reducing technique uncertainties*
  - *Improved experimental procedures implemented*
  - *A new issue revealed, temperature, and a mitigation strategy to be implemented*
- **Specificity** - *impact of sample contaminants*
  - *Issue addressed, a mitigation strategy proposed*
- **Linearity & Range** – *concentration and temperature*
  - *Addressed, a temperature effect mitigation strategy to be implemented*
- **Precision & Ruggedness** – *reproducibility*
  - *Addressed*
- **Comparative Analysis** – *Davies-Gray measurements*
  - *Experimental measurements undertaken, and will continue*

Spectrometer Signal
Move from 'Scans' to 'Reads' Method

- Increase signal to noise ratio @ 419.5 nm to increase measurement accuracy
- Cary instrument software allows for rapid scan of full wave length range + enhanced signal to noise averaging @ 419.5 nm
- Example previous test measurement (FY14)
  - Normal collection parameters, baseline corrected absorbance & multiple scans (at least 20 min) – abs. 0.42136 ± 0.00030
  - Modified scan with increased signal to noise averaging @ 419.5 nm (7 min) – abs. 0.41311 ± 0.00015

Accuracy

Reads Method of Data Collection
(for one sample, one measurement, one cell)

Examples Background Data from Spectrophotometer

Background scan, Cell 1 , 23.6 °C
7/9/2015 1:44:46 PM
SAT (s): 5
Total Read time: 98.469 s

Wavelength (nm)	Abs Read 1	Abs Read 2	Abs Read 3
600.000	0.006578	0.006551	0.006557
550.000	-0.004275	-0.004263	-0.004217
500.000	0.007631	0.007665	0.007691
430.000	0.017881	0.017896	0.017893
419.500	0.016612	0.016608	0.016613
409.000	0.013280	0.013300	0.013316

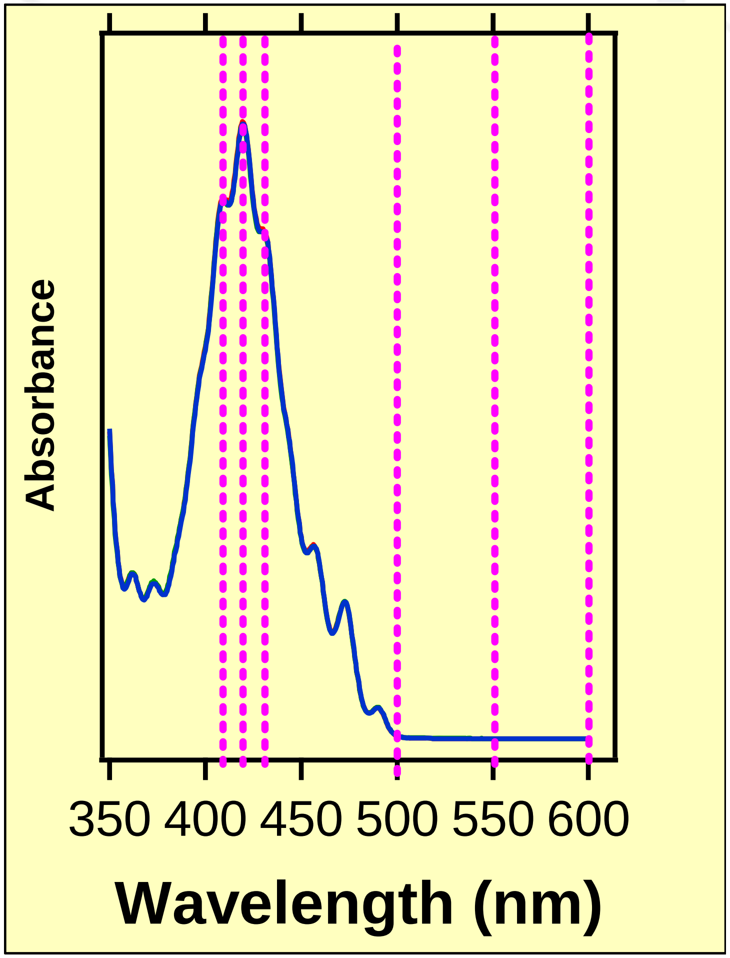
Accuracy

Reads Method of Data Collection

Examples Sample Data from Spectrophotometer

Solution 1100 , Cell 1 , 23.9 °C
7/9/2015 2:42:02 PM
SAT (s): 5
Total Read time: 98.625 s

Wavelength (nm)	Abs Read 1	Abs Read 2	Abs Read 3
600.000	0.012529	0.012534	0.012531
550.000	0.001569	0.001576	0.001564
500.000	0.014262	0.014278	0.014281
430.000	0.208575	0.208577	0.208578
419.500	0.246289	0.246289	0.246282
409.000	0.215309	0.215311	0.215312



Accuracy

Reads Method of Data Collecting
Data Transferred to Spreadsheet

	BACKGROUND READS (H_2SO_4 Bkgd reads)		
Room Temp (°C):	*23.6*	*23.6*	*23.6*
Wavelength	Bkgd_C1_rd1	Bkgd_C1_rd2	Bkgd_C1_rd3
600.0	0.006578	0.006551	0.006557
550.0	-0.004275	-0.004263	-0.004217
500.0	0.007631	0.007665	0.007691
430.0	0.017881	0.017896	0.017893
419.5	0.016612	0.016608	0.016613
409.0	0.013280	0.013300	0.013316
	SAMPLE READS		
Room Temp (°C):	*23.9*	*23.9*	*23.9*
Wavelength	Soln11A_c1_rd1	Soln11A_c1_rd2	Soln11A_c1_rd3
600.0	0.012529	0.012534	0.012531
550.0	0.001569	0.001576	0.001564
500.0	0.014262	0.014278	0.014281
430.0	0.208575	0.208577	0.208578
419.5	0.246289	0.246289	0.246282
409.0	0.215309	0.215311	0.215312

Accuracy

Reads Method of Data Collection

Initial Averaging of Triplicate Measurements

	AVERAGE BACKGROUND READS FOR EACH CELL (H_2SO_4 Bkgd reads)	
Wavelength	Bkgd_C1_rd_Ave	Bkgd_C1_rd_AveSD
600.0	0.006562	0.000014
550.0	-0.004252	0.000031
500.0	0.007662	0.000030
430.0	0.017890	0.000008
419.5	0.016611	0.000003
409.0	0.013299	0.000018
	AVERAGE SAMPLE READS FOR EACH CELL	
Wavelength	Soln11A_c1_Ave	Soln11A_c1_AveSD
600.0	0.012531	0.000003
550.0	0.001570	0.000006
500.0	0.014274	0.000010
430.0	0.208577	0.000002
419.5	0.246287	0.000004
409.0	0.215311	0.000002

Accuracy

Reads Method of Data Collection
Background Corrected Sample Reads

	BACKGROUND-CORRECTED SAMPLE READS FOR EACH CELL (Subtract H_2SO_4 background)		
Wavelength	Soln11A_c1_Ave_BGc	Soln11A_c1_Ave_BGc_Sigma	w_i
600.0	0.005969	0.000014	4.82E+09
550.0	0.005821	0.000031	1.03E+09
500.0	0.006611	0.000032	
430.0	0.190687	0.000008	
419.5	0.229676	0.000005	
409.0	0.202012	0.000018	
	Wt'd Ave	Wt'd SD	
Ave Abs (550–600 nm):	0.0059434	0.0000796	

Accuracy

Reads Method of Data Collection

Final baseline correction generates abs. @ 419.5 nm

	BASELINE-CORRECTED SAMPLE READS FOR EACH CELL (subtract Ave Abs 550–600 nm)	
Wavelength	Soln11A_c1_Ave_ BGcBLc	Soln11A_c1_Ave_ BGcBLc_Sigma
600.0	-0.00005	0.00008
550.0	0.00007	0.00009
500.0	0.00174	0.00009
430.0	0.34962	0.00008
419.5	0.42315	0.00008 (0.02 %)
409.0	0.37116	0.00009

Reads Method of Data Collection
Comments and Evolution of Methodology

- Weighted average of baseline values at 550 and 600 nm introduced
- 'New' Reads method processes each cell separately
  - Initial 'old' reads method averaged the data from each of the three UV-vis cells used
- New baseline reads not always recorded for each cell every day - will implement this procedure for all future measurements

Accuracy

"1.0" M H_2SO_4

Prepared from Fisher cert. 4.00 N (2 M, 17.542 wt. %) H_2SO_4

SOLUTION PREPARATIONS			
H_2SO_4 Bottle No.	17.542 wt % H_2SO_4 Stock Soln. Mass (g)	H_2O Mass (g)	Calc. H_2SO_4 Soln. Conc. (wt % H_2SO_4)
1	251.690	224.997	9.262
2	251.770	225.017	9.263
3	251.820	225.050	9.263
4	258.285	231.003	9.260

- "0.9" M (8.384 wt %) and "1.1" M (10.133 wt %) H_2SO_4 solutions prepared previously (FY 14 work).
- % Difference density ((lit.-meas.)/meas). all < 0.06 %

	DENSITY (g/mL)	
Temp. (°C)	Meas. H_2SO_4	Lit. H_2SO_4
Bottle #1		
20.01	1.06049	1.06093
27.5	1.05734	1.05779
35.0	1.05396	1.05437
Bottle #2		
20.01	1.06036	1.06094
27.5	1.05719	1.0578
35.0	1.05379	1.05438
Bottle #3		
20.01	1.06067	1.06094
27.49	1.05754	1.05781
35.0	1.05409	1.05438
Bottle #4		
20.01	1.06032	1.06092
27.5	1.05715	1.05778
35.0	1.05375	1.05435

Accuracy

Uranium Standard Material
Lower Associated Uncertainty

- CRM (Certified Reference Material) 112-A uranium metal standard
- Material repackaged by NBL – previously known as SRM (Standard Reference Material) 960
- LANL analytical chemistry team dissolved two different pieces of standard metal in nitric acid to produce two solution cuts
- GUM workbench standard uncertainty values provided
  - *ca.* 95 % of the uncertainty associated with the purity of the metal
- Cut A
  - 12.58152 g metal dissolved in nitric acid to yield 125.0549 g soln.
  - 100.58282 ± 0.0062 mgU/gA
- Cut B
  - 12.55217 g metal dissolved in nitric acid to yield 125.0207 g soln.
  - 100.37555 ± 0.0062 mgU/gB

Accuracy

Uranium Standard Material
CRM 112-A Certificate of Analysis

New Brunswick Laboratory
U.S. Department of Energy

Certificate of Analysis
CRM 112-A
Uranium (normal) Metal Assay and Isotopic Standard

Uranium Assay:	0.99975 g U/g metal
Uranium Assay Uncertainty:	0.00006 g U/g metal

	$^{234}U/^{238}U$	$^{235}U/^{238}U$
Atom Ratio:	0.000052841	0.0072543
Atom Ratio Uncertainty:	0.000000082	0.0000040

	^{234}U	^{235}U	^{238}U
Atom Percent:	0.0052458	0.72017	99.27458
Atom Percent Uncertainty:	0.0000081	0.00039	0.00039
Weight Percent:	0.0051579	0.71114	99.28370
Weight Percent Uncertainty:	0.0000080	0.00038	0.00038

Relative Atomic Weight:	238.028918
Relative Atomic Weight Uncertainty:	0.000012

http://science.energy.gov/~/media/nbl/pdf/price-lists/certificates/CRM_112A_Uranium_Metal_Sept_2010.pdf

Preparation of Uranium Sulfate Standard Solutions (1-8)

- Required for re-determination of molar absorptivity values
- Eight known mass aliquots of cut A solution heated to dryness in 100 mL Pyrex volumetric flask.
- Resultant solids suspended with H_2O and again heated to dryness to drive off residual HNO_3/NO_3^-
- Final solids, presumed to be $UO_3{\cdot}xH_2O$, reweighed to estimate x.
- Dissolution in H_2SO_4 ("0.9". "1.0" or "1.1" M), quantitative transfer and final mass measurements (all *ca.* 106 g)
- ***Solution number & sample number - interchangeable***

Picture shows $UO_3{\cdot}xH_2O$ formed during preparation of solns. 11 & 12

Uranium Standard Solutions (1-8)

Soln. No.	Initial Cut A aliquot mass (g)	Solid mass after heat (mg)	H_2SO_4 Conc. (wt %)	Final Solution [U] (Wt %)	x in $UO_3 \cdot xH_2O(s)$
1	1.18753 ± 0.00010	151.2	9.263	0.112672 ± 0.000011	0.84
2	2.37703 ± 0.00008	299.5	9.263	0.225686 ± 0.000016	0.67
3	3.56385 ± 0.00010	449.8	9.263	0.338174 ± 0.000023	0.70
4	4.74965 ± 0.00016	608.1	9.263	0.450727 ± 0.000032	0.94
5	7.12300 ± 0.00007	893.0	8.384	0.676456 ± 0.000042	0.59
6	7.11893 ± 0.00015	884.4	9.263	0.675093 ± 0.000044	0.44
7	7.11870 ± 0.00018	886.8	10.133	0.675200 ± 0.000045	0.49
8	14.24330 ± 0.00012	1775.0	9.263	1.351530 ± 0.000084	0.49

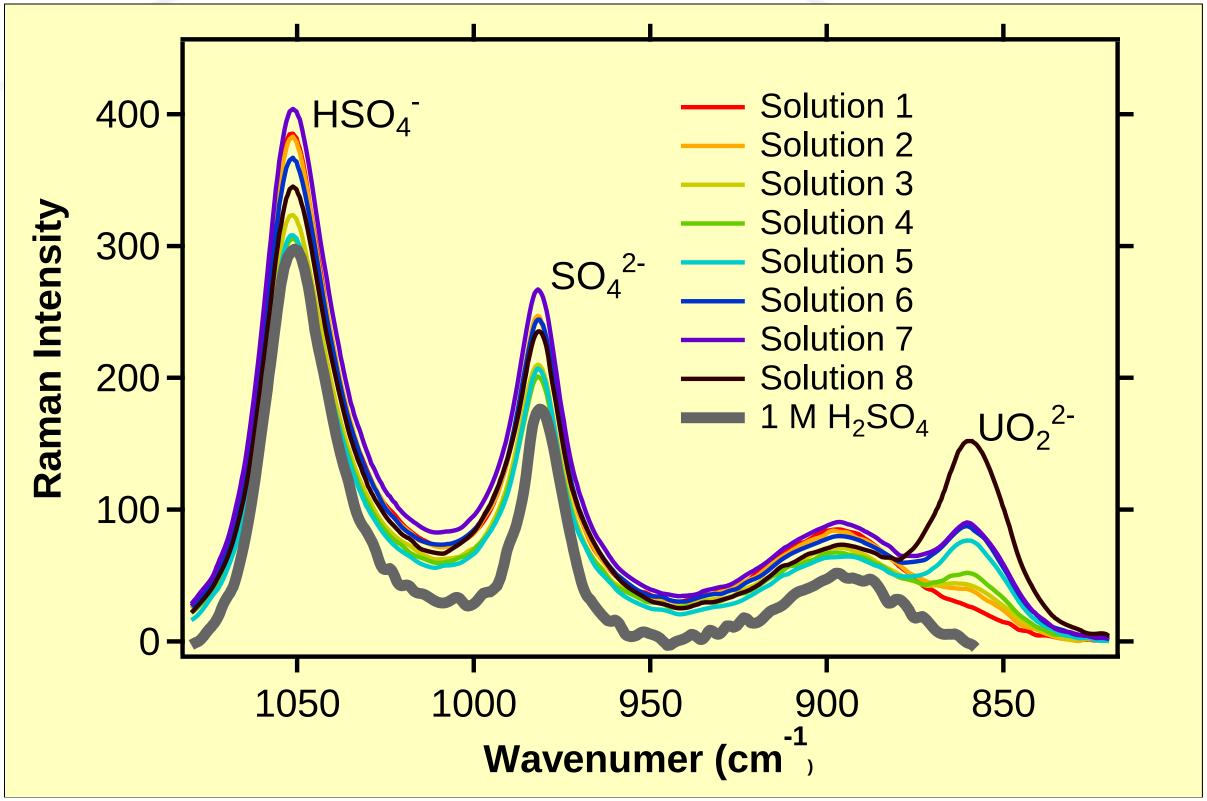
Uranium Standard Solutions (1-8)

Soln. No.	Temp (°C)	[U] @ spec. Temp (mM)	Final Solution H_2SO_4 Conc. Ignoring UO_3 Neutralization (M)[a]	Final Solution H_2SO_4 Conc. Including UO_3 Neutralization (M)[b]
1	29.5	5.0060 ± 0.0007	0.997	0.992
2	29.8	10.0388 ± 0.0012	0.997	0.987
3	29.5	15.0623 ± 0.0018	0.997	0.982
4	28.5	20.1093 ± 0.0024	0.997	0.977
5	29.3	30.0961 ± 0.0034	0.898	0.868
6	28.7	30.1897 ± 0.0035	0.997	0.967
7	29.4	30.3840 ± 0.0035	1.097	1.067
8	27.1	60.9267 ± 0.0068	0.996	0.936

Rare discussion of molarity.

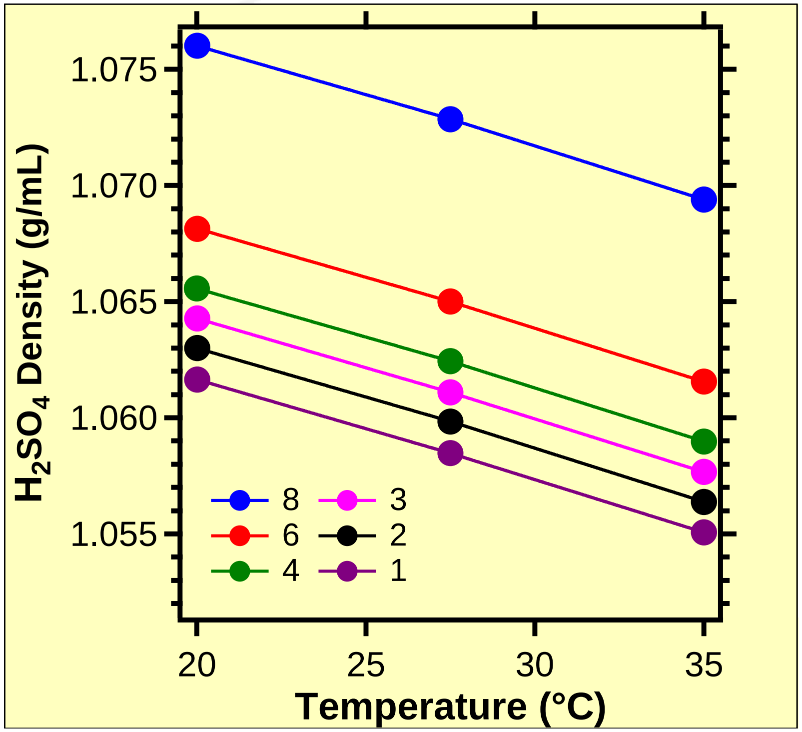
Specificity

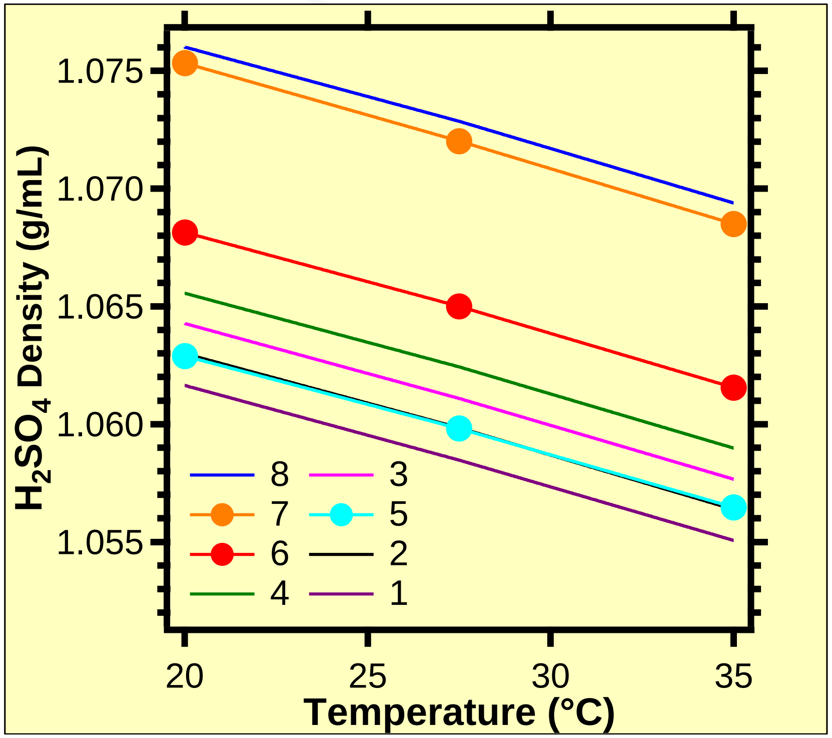
Raman Spectra of Solutions 1-8
confirming nitrate removal



- *Spectra all very similar to that of 1 M H_2SO_4*
- *Less nitrate to remove during preparation of solutions 1-8 vs. solutions 11-12 (see later discussion)*

Density Measurements of Solutions 1-8
Mettler Toledo DM50 (20.0, 27.5 & 35.0 ℃)



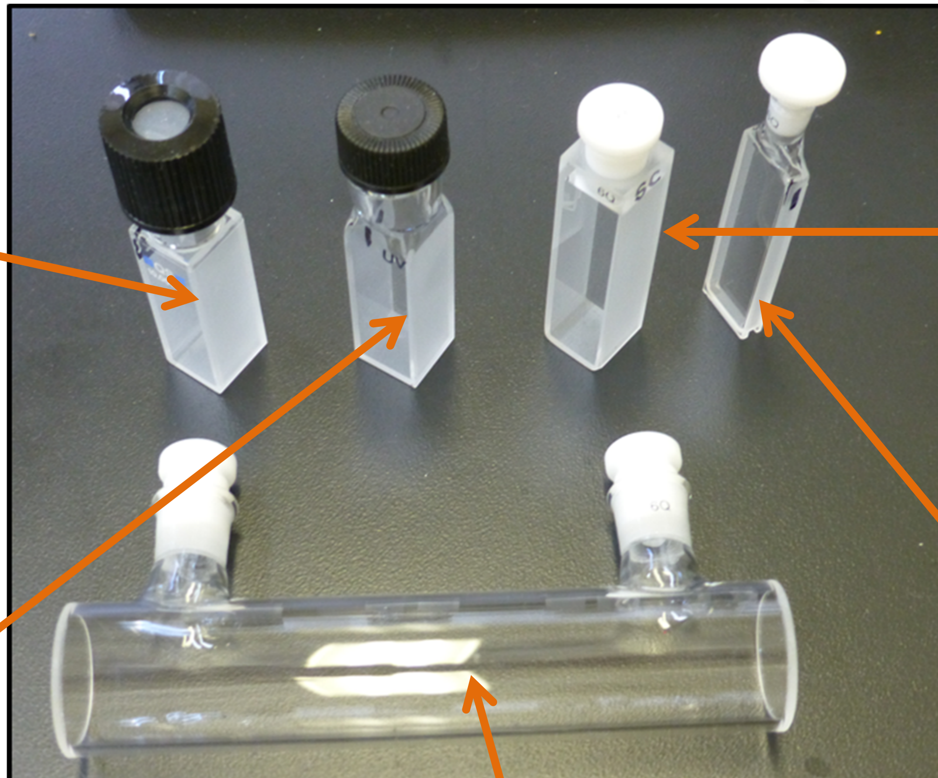


- Samples 1, 2, 3, 4, 6 & 8 all "1" M H_2SO_4
- Samples 5, 6 & 7 all the same [U]
- Sample 5 = "0.9" M H_2SO_4
- Sample 7 = "1.1" M H_2SO_4

Cell Manufacturer and Path Length

Hellma Analytics
(10.00 ± 0.01 mm)

NSG Precision
(10.00 ± 0.02 mm)



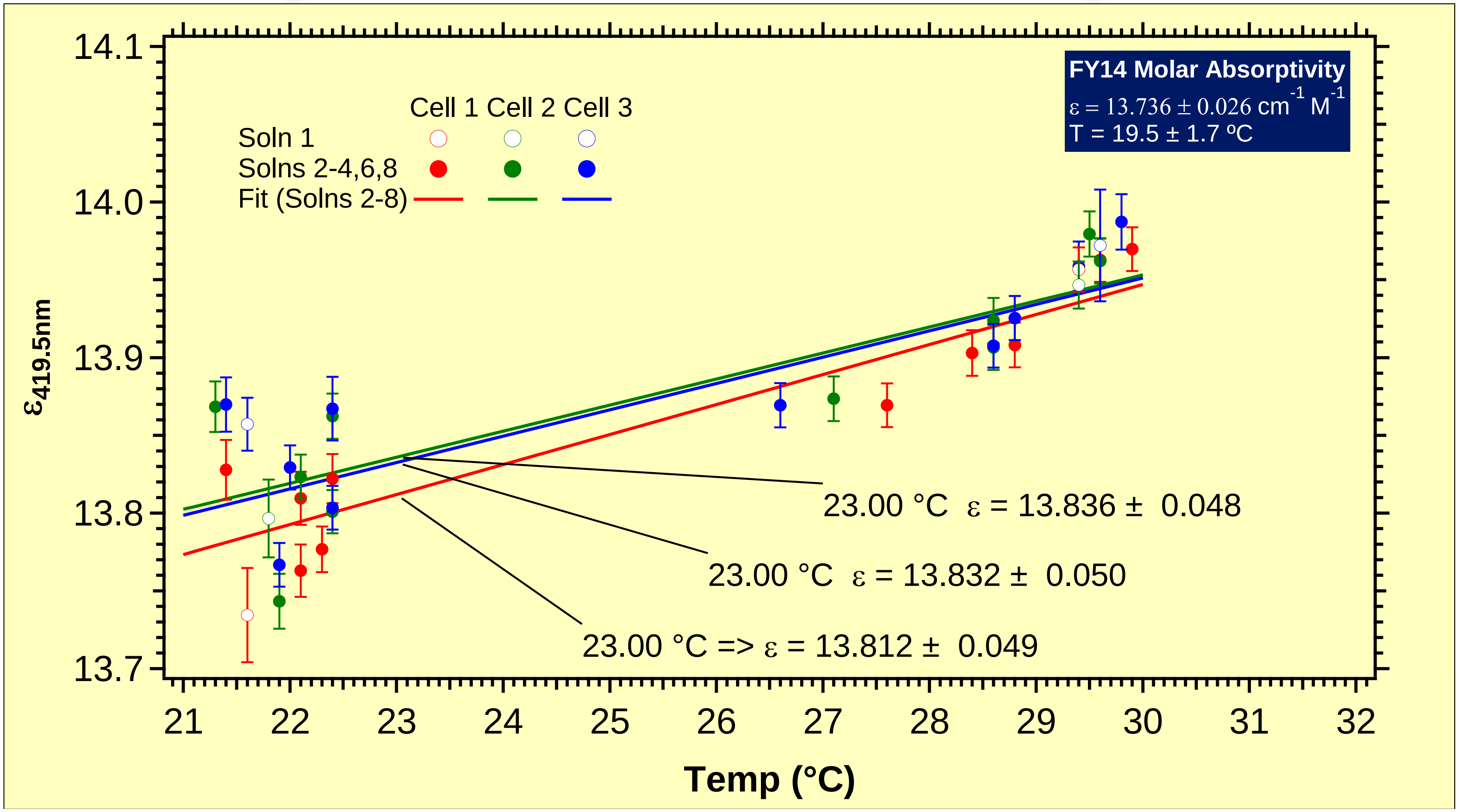
Starna Cells
(10.00 ± 0.01 mm)

Starna Cells
(2.00 ± 0.01 mm)

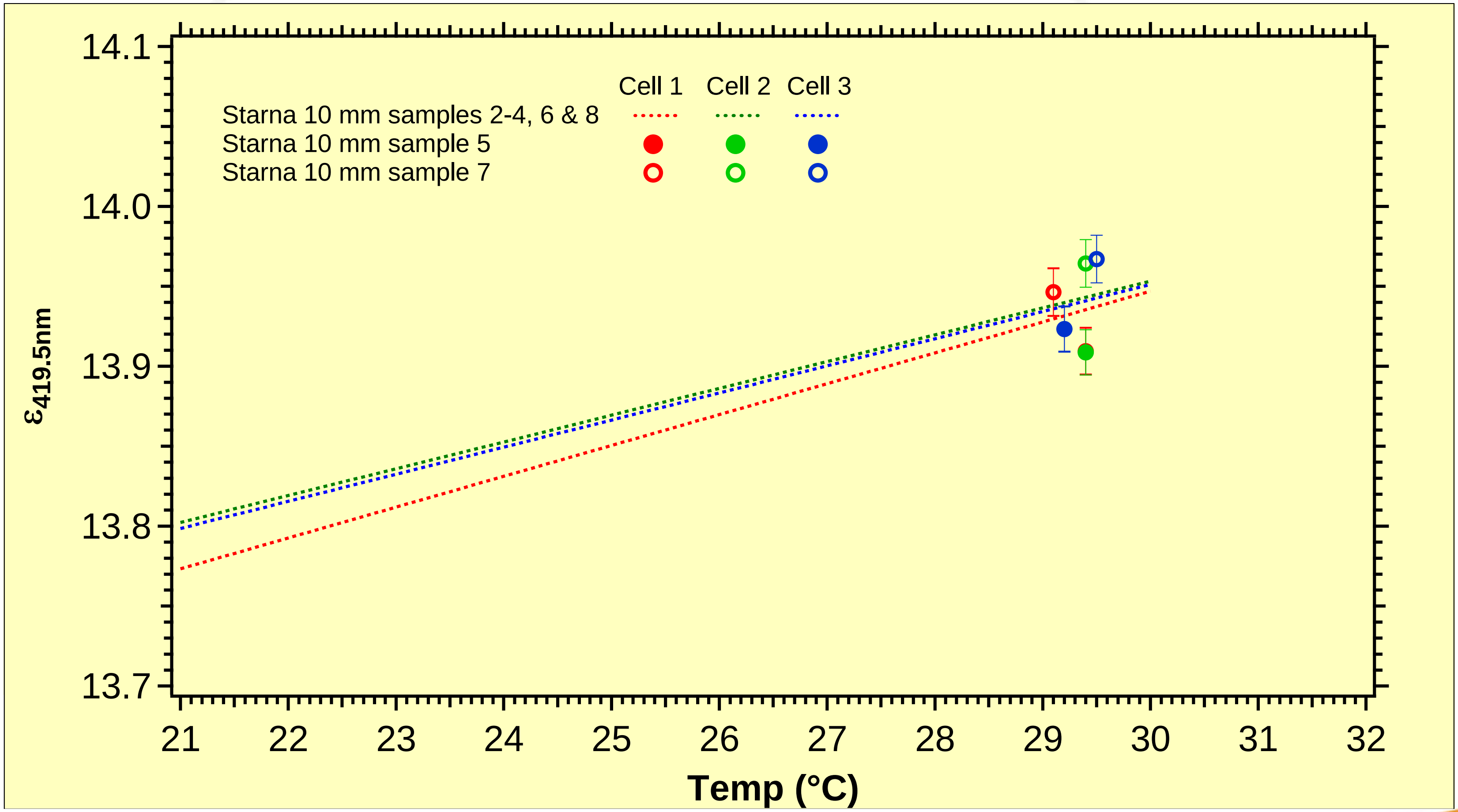
Starna Cells
(100.00 ± 0.02 mm)

Accuracy, Linearity & Range, Precision & Ruggedness

Molar Absorptivity Data
10 mm Starna Cells, *"1 M" H_2SO_4 Solutions Only*



Molar Absorptivity Data - 10 mm Starna Cells
Includes solutions 5 & 7 - "0.9 M" & "1.1 M" H_2SO_4



Molar Absorptivity 10 mm Starna Cell
Analysis and Observations

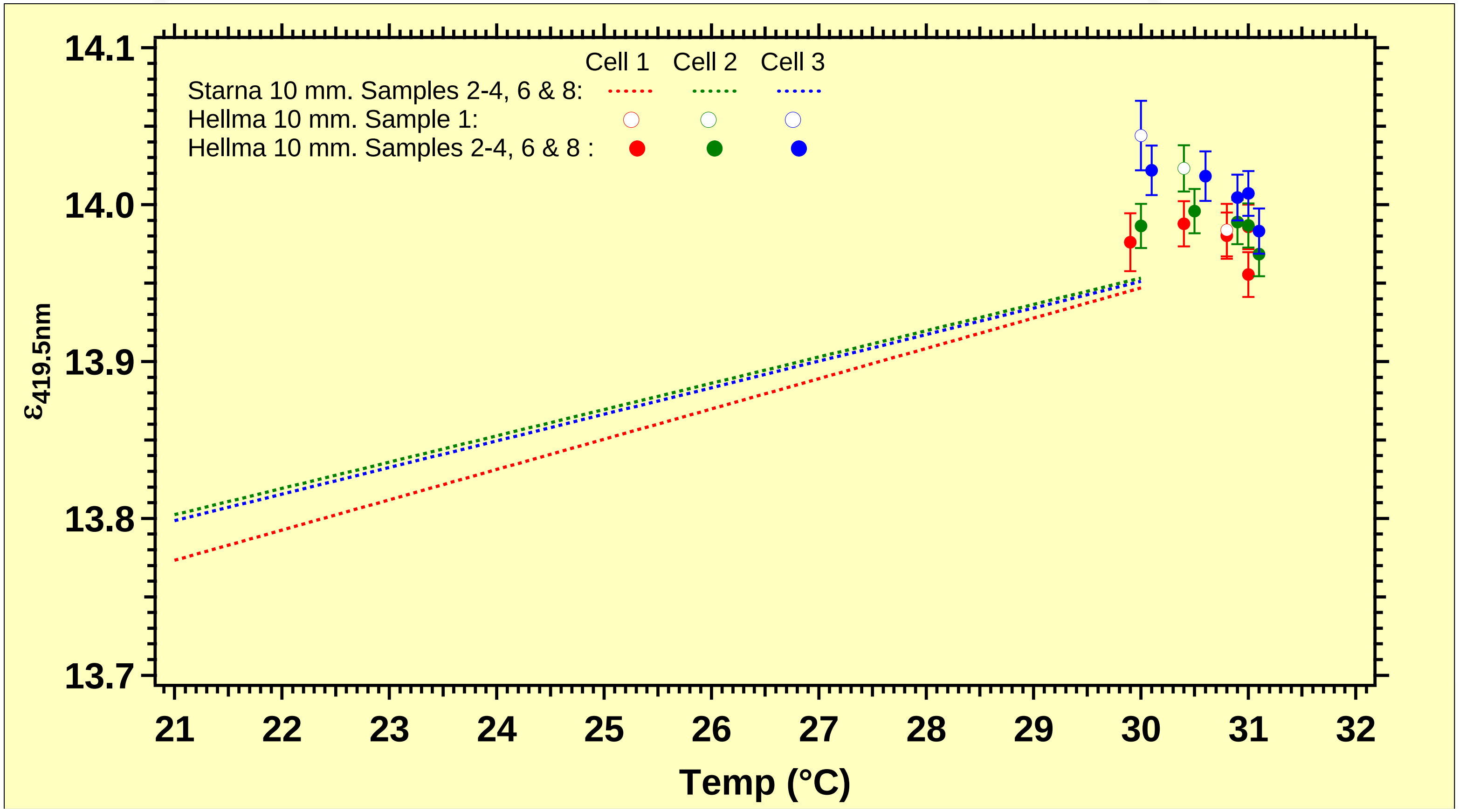
- Temperature dependence on molar absorptivity value could not be ignored
- Discarded data for lowest [U] concentration standard solution, solution 1
- Cells 1-3 – very similar performance
- Technique still valid for "1.0±0.1 M" H_2SO_4
- Lower temp measurements – lower molar absorptivity values
  - Observed in literature for related uranyl systems, see Rao, L. & Tian, G. J. *Chem. Thermodynamics*, **40** (2008) 1001-1006
- Higher temperature measurements recorded in June 2015, with lower temperature measurements recorded in November 2015
- Only room temperature recorded, not solution temperature.
- Likely a small concentration impact on observed molar absorptivity, but the temperature effect more significant.

Molar Absorptivity 10 mm Starna Cell
Analysis and Observations

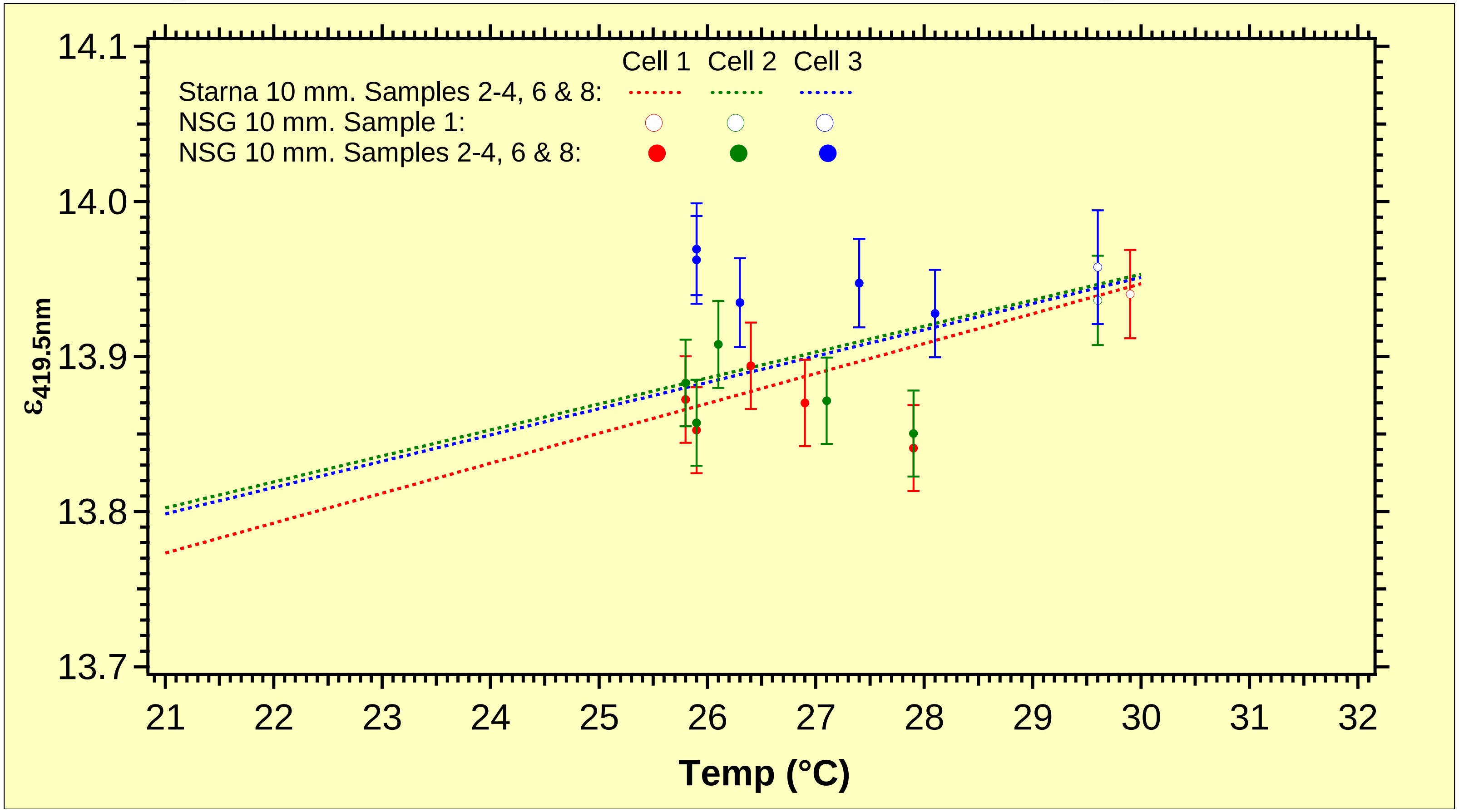
- No measurement of sample evaporation between June and November
  - Davies-Gray results on solution 11 & 12 show significance of evaporation (later discussion)
  - Scatter in lower temperature measurements, increase molar absorptivity uncertainties and may point to different extents of evaporation in different solutions
  - Evaporation would also lead to higher [U], raising absorbance value @ 419.5 nm and thus increasing the 'observed' molar absorptivity values
  - Any increase in observed molar absorptivity will lead to lower observed [U] conc. measurements by developed UV-vis technique

Molar Absorptivity Data

Comparison - 10 mm Starna and 10 mm Hellma Analytics Cells



Molar Absorptivity Data
Comparison - 10 mm Starna and 10 mm NSG Cells



Accuracy, Linearity & Range
Precision & Ruggedness

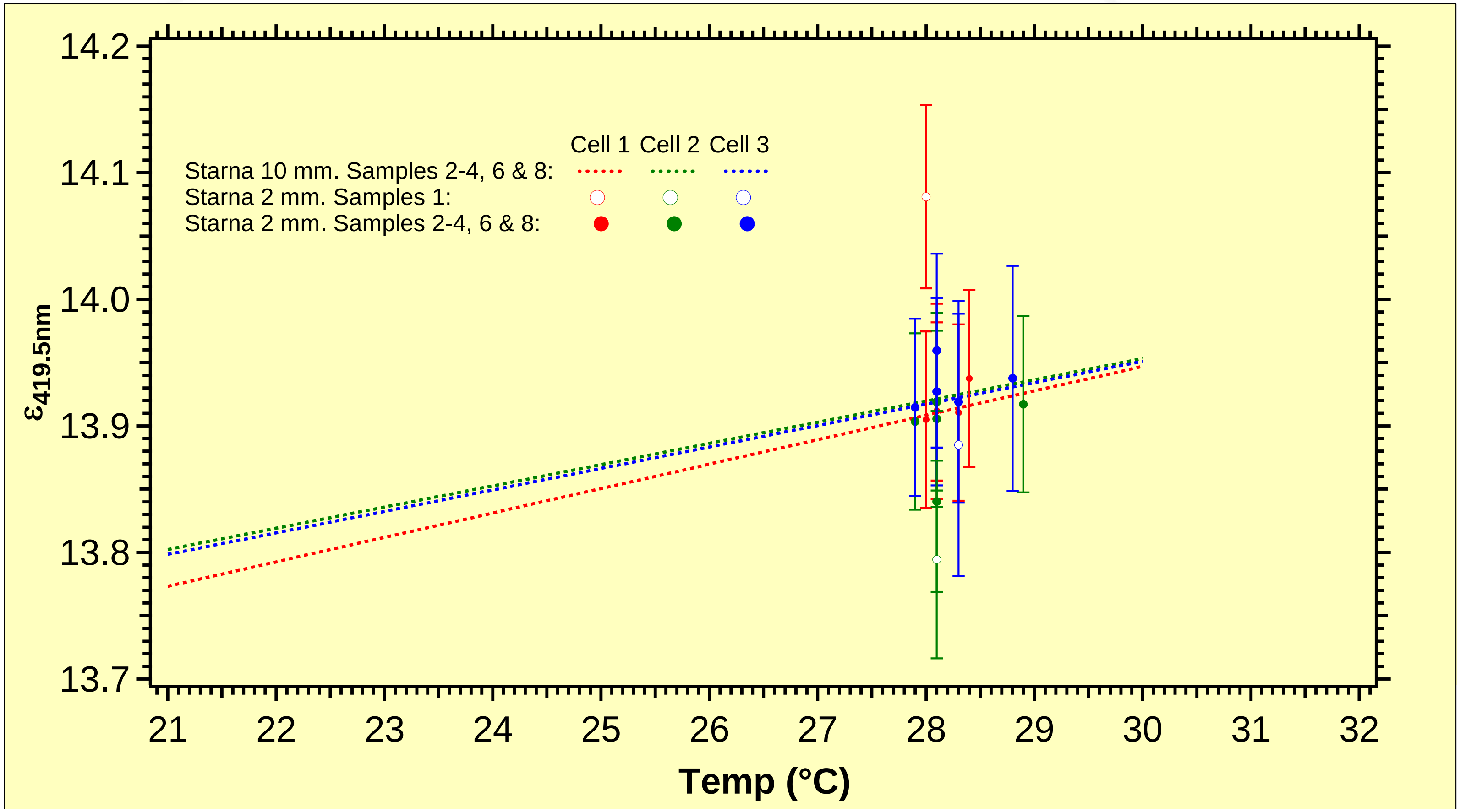
Molar Absorptivity
Comparison of 10 mm Starna, Hellma and NSG Cells

- Starna Cells
  - General consensus among the three operators that these cells were the most “user friendly”
- Hellma cell data recorded at highest temperature range
  - Providing further evidence of significant temperature impact on molar absorptivity
- Lower precision in cell path length for the NSG cells reflected in increased measurement uncertainties
- Appear to be a trend of small decrease in molar absorptivity going through cells 1, 2 & 3 for each of the cell manufacturers
  - No current rationale for this observation

Accuracy, Linearity & Range
Precision & Ruggedness

Molar Absorptivity Data

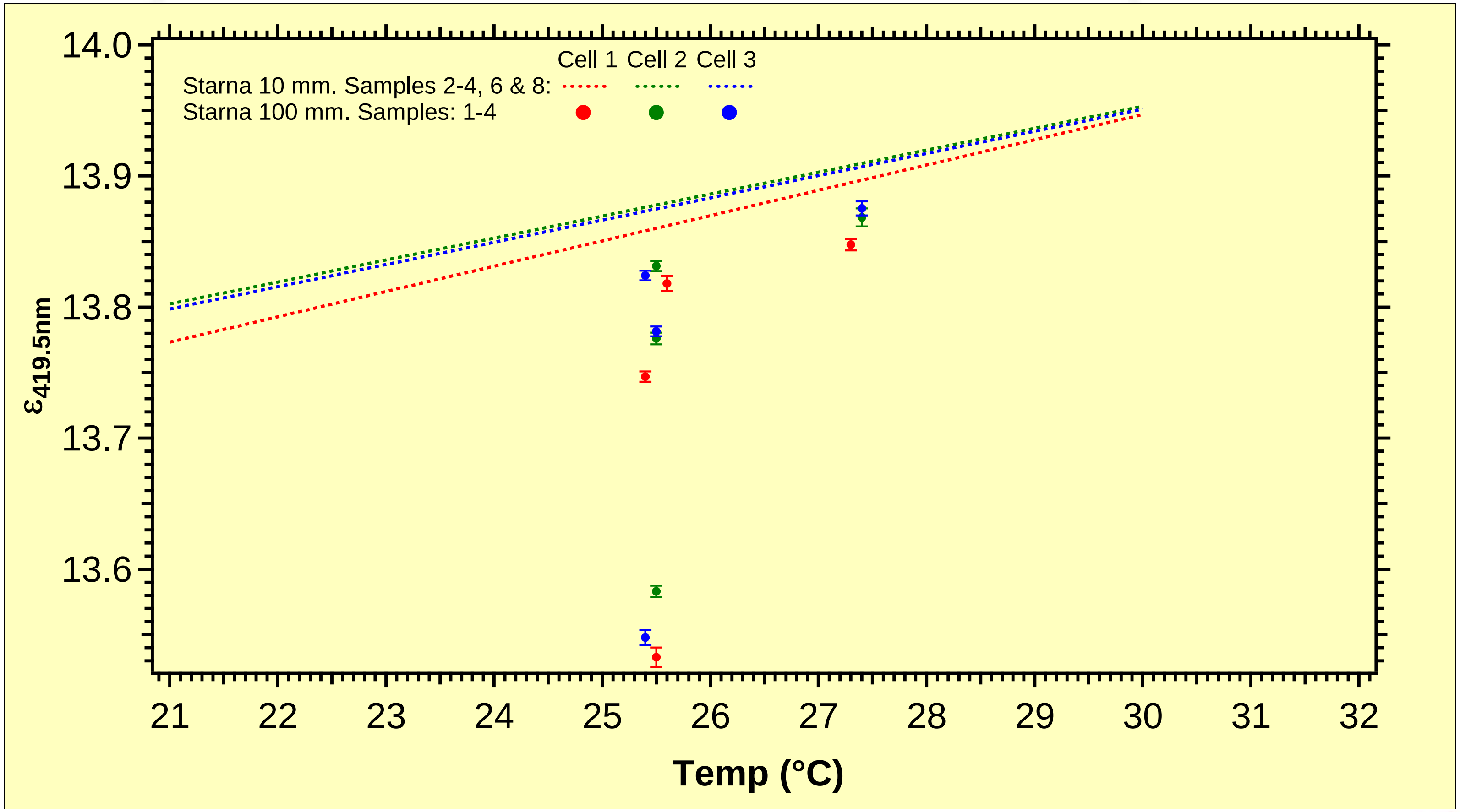
Comparison 2 mm Starna cells vs. 10 mm Starna Cells



Molar Absorptivity Data

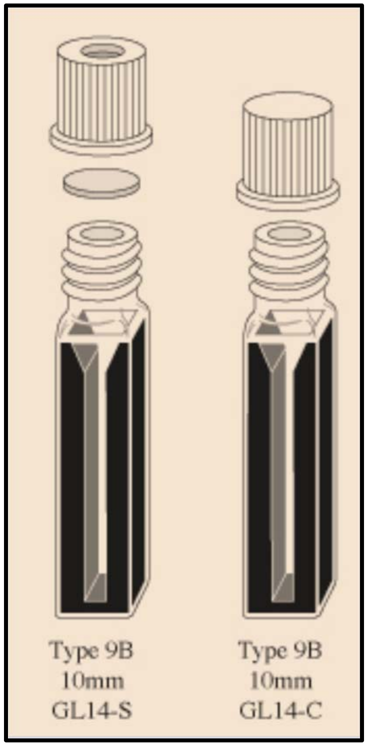
Accuracy, Linearity & Range
Precision & Ruggedness

Comparison 100 mm Starna cells vs. 10 mm Starna Cells



Molar Absorptivity
2 mm & 100 mm Starna Cells Observations

- <u>2 mm cells</u>
  - Significant increase in path length uncertainties
  - Can reduce solution volume without dropping from 10 mm to 2 mm path length cell
- <u>10 mm cells</u>
  - Should provide the lowest path length uncertainties, but difficult to insert into spectrophotometer cell holder (position reproducibility issues)
  - Solution [U] concentrations. too high for detailed study
    - absorbance values @ 419.5 nm for solutions 3 & 4 > 2
  - Could merit further investigation if issues are addressed



www.starnacells.com

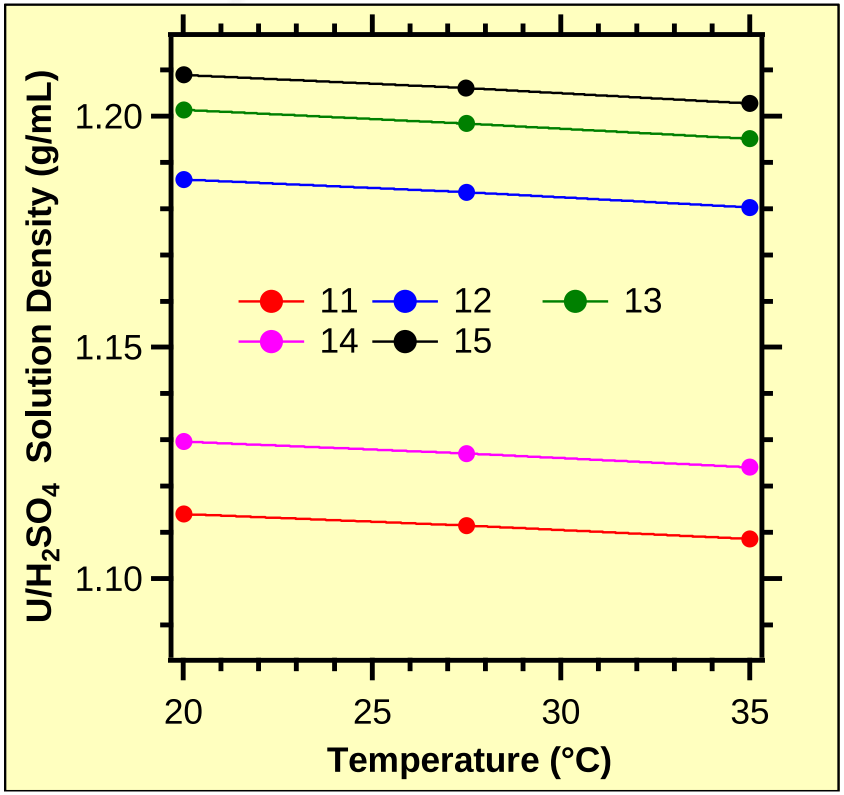
Test Solutions 11-15

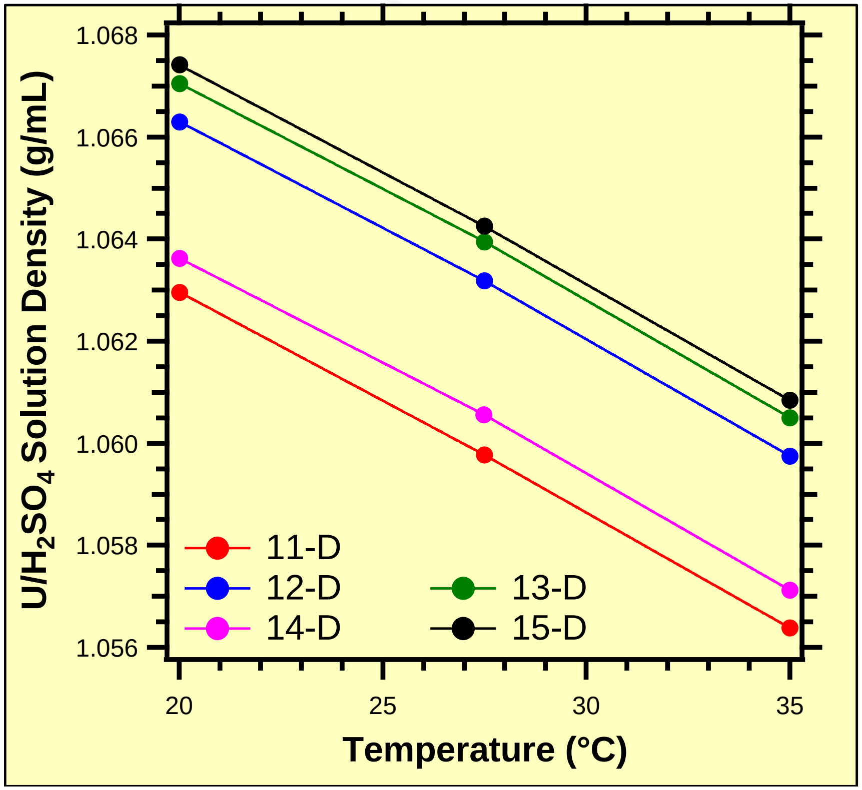
- Solutions 11 & 12
  - Prepared as described for solutions 1-8 using weighed aliquots of 'Cut B' CRM 112-A in nitric acid
  - Differences in sample preparation 11 & 12 vs. 1-8
    - A much greater mass of uranium required (these samples would be assayed)
    - Adjusted to a final H_2SO_4 conc. of '0.1 M' (pH 1) vs. 1.0 M
- Solutions 13 & 15 – repurposed depleted uranium pH 1 stocks already 'in hand'
- Solutions 14
  - Prepared using commercially available uranyl sulfate tri-hydrate ($UO_2SO_4 \cdot 3H_2O$)
  - International Bio-Analytical Industries (IBI)
  - Dissolution in H_2O revealed presence of some insoluble white solids, discarded through centrifugation
  - Adjusted to pH 1 using H_2SO_4

Test Solutions 11-15

Solution Number	U Relative Atomic Weight (g/mol)	[U] (Wt %)	Final Soln Mass (g)	Final Soln pH
11	238.028918 ± 0.000012	7.4144 ± 0.0005	67.4623	1.04
12	238.028918 ± 0.000012	11.5183 ± 0.0007	65.4698	0.90
13	238.04±0.01 ^{dep}U	Unknown	106.6656	0.92
14	238.04±0.01 ^{dep}U	8.3879 ± *0.0004*	64.6229	1.04
15	238.04±0.01 ^{dep}U	Unknown	133.4595	0.94

Density Measurements of Solutions 11-15 and 11-D to 15-D (20.0, 27.5 & 35.0 °C)

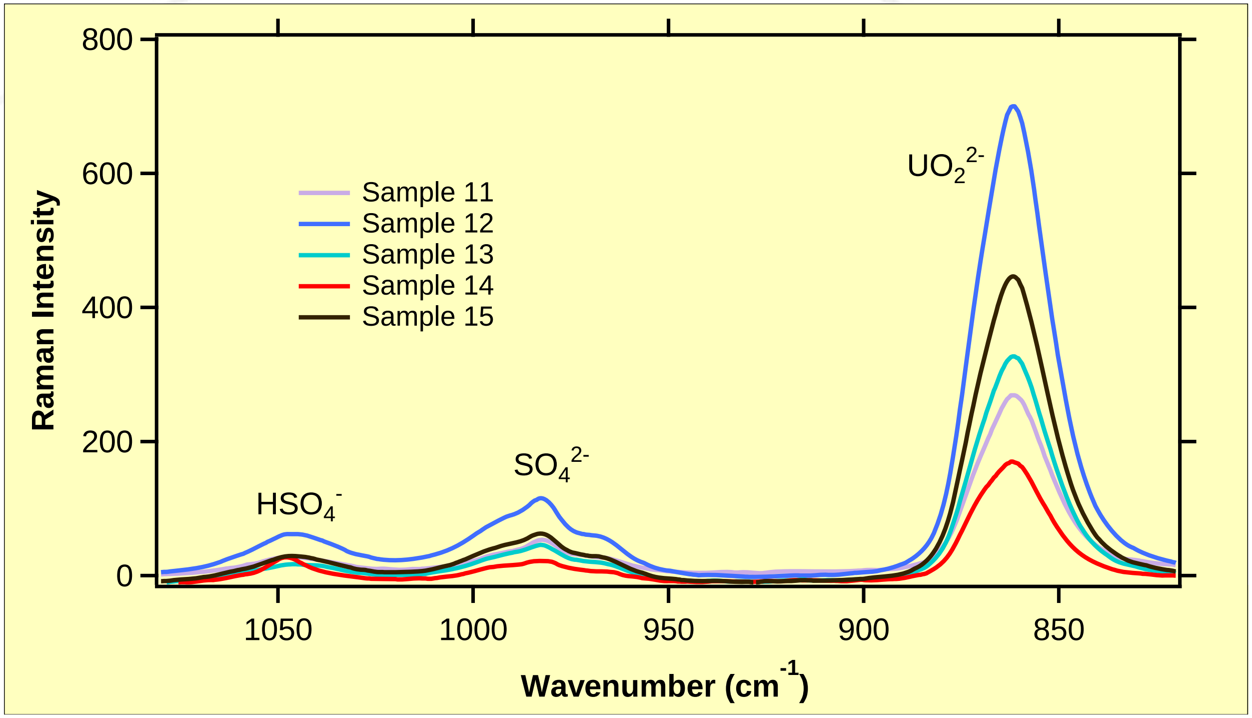




D solutions – assay samples, already diluted in "1 M" H_2SO_4

Specificity

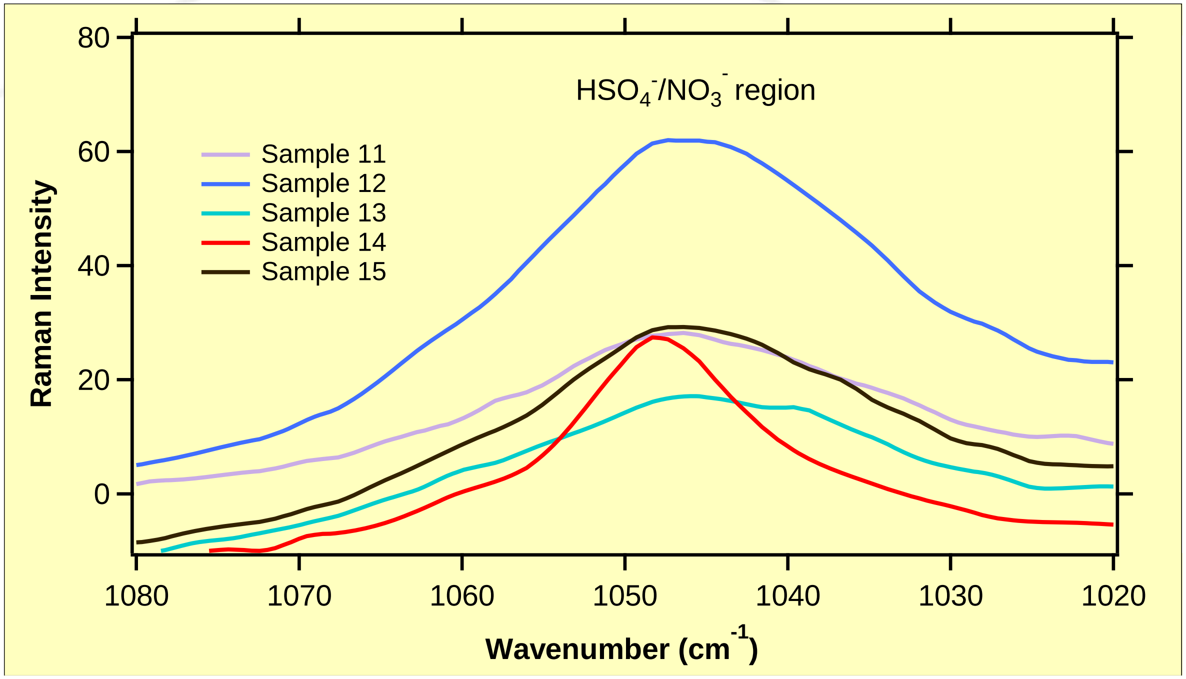
Raman Spectra of Solutions 11-15



- As would be expected, clearly more UO_2^{2+} (uranium) in Solution 11-15 vs. solutions 1-8
- SO_4^{2-} region of spectra more complex vs. solns 1-8, UO_2^{2+} complex bands more dominant
- Solution 14 – peak in HSO_4^- region looks different vs. Solutions 11, 12, 13 & 15

Specificity

Raman Spectra of Solutions 11-15



- *Solutions 11-13 & 15 – no evidence of presence of NO_3^-*
- *Solution 14 – peak in HSO_4^- region appears to be sharper and higher in energy, evidence of NO_3^-?*
- *Solution 14 – prepared from $UO_2SO_4{\cdot}3H_2O$ purchased from IBI*
    - Evidence that this chemical was prepared from a uranium nitrate starting material?

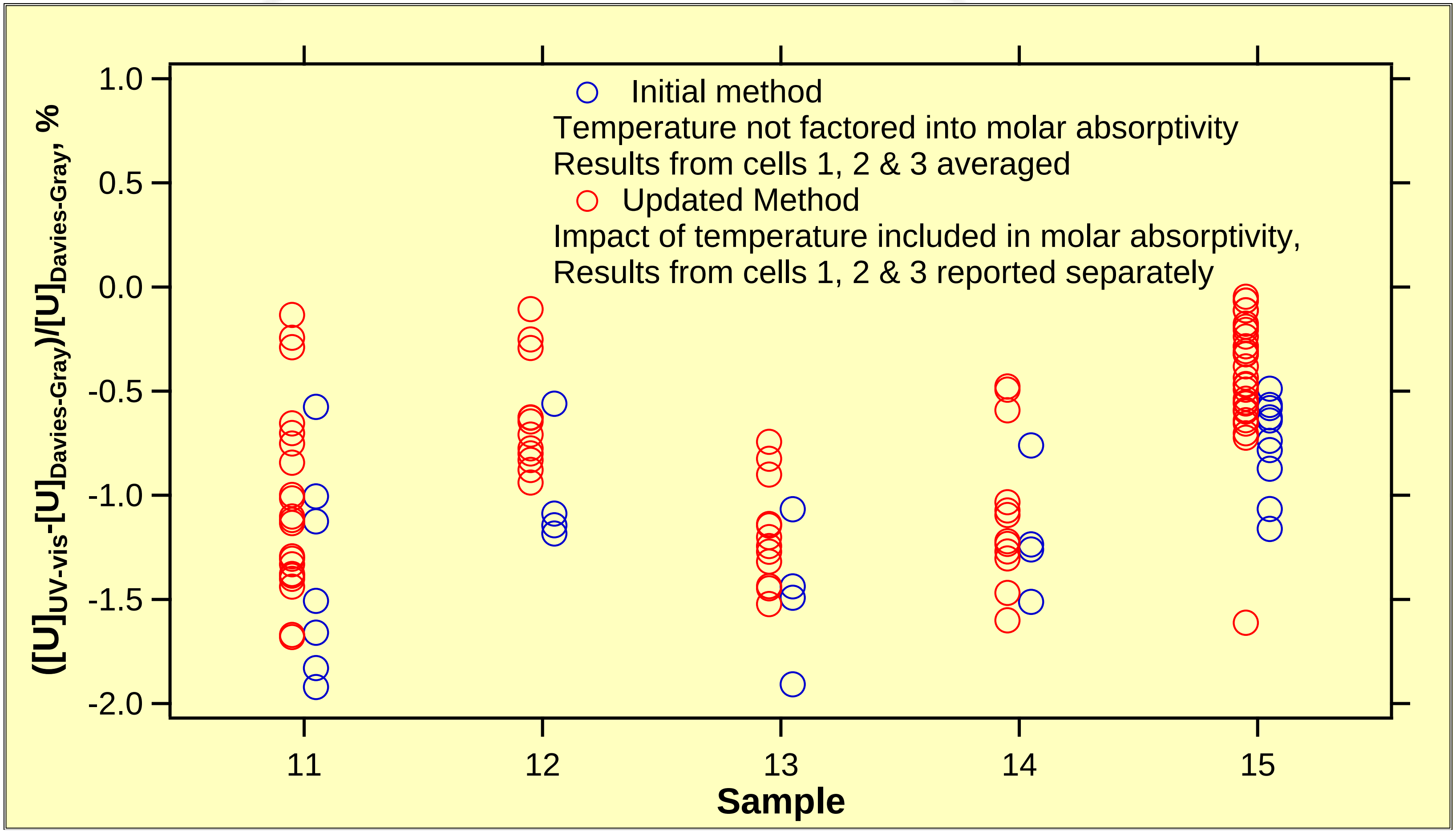
Samples 11-15 UV-vis Analysis

- A, B & C assay analysis
  - 100 μL of sample + 2000 μL of "1 M" H_2SO_4 (mass measurements)
- D assay analysis
  - 1.4 mL of sample + 28 mL of "1 M" H_2SO_4 (mass measurements)
- Each assay sample analyzed in all three 10 mm Starna cells
  - Triplicate "1 M" H_2SO_4 background reads recorded
  - Triplicate sample reads recorded

Samples 11-15 UV-vis Analysis

- Input parameters to spreadsheet used to calc. [U] (g/g)
  - Absorbance value @ 419.5 nm
    - Average triplicate sample reads background corrected, and then baseline corrected
  - The room temperature at the time of the measurement
  - Molar absorptivity at measurement temperature
  - For A, B, C & D samples
    - Density of both 1 M H_2SO_4 and the specific assayed sample at the UV-vis measurement temperature
  - For D' analysis of the D samples
    - Density of the D samples at the UV-vis measurement temperature

Comparison of Methods for Analyzing Solutions 11-15 vs. Davies-Gray Results



All future discussions will relate to the updated method of UV-vis data analysis

Uranium Concentration Analysis - Solutions 11-14 A, B & C assay measurements

Accuracy, Linearity & Range
Precision & Ruggedness
Comparative Analysis

Soln No.	Cell #	Gravimetric Value (mg U/g soln)	Gravimetric σ	Soln A Assay Value (mg U/g soln)	Soln A Assay σ	Soln B Assay Value (mg U/g soln)	Soln B Assay σ	Soln C Assay Value (mg U/g soln)	Soln C Assay σ	Davies-Gray Msmt Value (mg U/g soln)	Davies-Gray Msmt 2σ
11	1	74.144	0.005	73.50	0.29	73.30	0.28	73.35	0.28	74.34	0.07
	2			73.60	0.29	73.27	0.27	73.31	0.28		
	3			73.37	0.30	73.09	0.28	73.10	0.29		
11 repeat	1	74.144	0.005	73.51	0.28	73.85	0.29	73.71	0.30	74.34	0.07
	2			73.31	0.34	73.78	0.29	73.82	0.29		
	3			73.38	0.29	73.52	0.30	73.58	0.30		
12	1	115.183	0.007	114.50	0.44	114.52	0.45	114.52	0.44	115.24	0.08
	2			114.32	0.43	114.35	0.44	114.42	0.43		
	3			114.16	0.44	114.23	0.45	114.28	0.44		
13	1	Unknown		121.74	0.49	122.11	0.48	121.98	0.48	123.59	0.09
	2			121.73	0.48	122.03	0.47	122.10	0.47		
	3			121.63	0.50	121.89	0.49	121.94	0.49		
14	1	83.879	0.004	76.43	0.32	76.40	0.31	76.22	0.31	77.23	0.07
	2			76.27	0.31	76.38	0.31	76.09	0.31		
	3			76.25	0.33	76.28	0.31	75.99	0.31		

Accuracy, Linearity & Range
Precision & Ruggedness
Comparative Analysis

Uranium Concentration Analysis
Solution 15 A, B & C
Assay Measurements

		Gravimetric		Soln A Assay		Soln B Assay		Soln C Assay		Davies-Gray Msmt	
Soln No.	Cell #	Value (mg U/g soln)	σ	Value (mg U/g soln)	σ	Value (mg U/g soln)	σ	Value (mg U/g soln)	σ	Value (mg U/g soln)	2σ
15 (AMH)	1	Unknown		126.98	0.51	126.88	0.50	126.95	0.50	127.58	0.09
	2			126.90	0.49	126.77	0.49	126.83	0.48		
	3			126.82	0.51	126.69	0.50	125.53	0.49		
15 (IM)	1	Unknown		127.19	0.49	127.17	0.49	127.36	0.49	127.58	0.09
	2			127.03	0.48	127.17	0.47	127.10	0.48		
	3			126.99	0.50	127.52	0.50	127.17	0.50		
15 (SR)	1	Unknown		127.50	0.49	127.44	0.49	127.44	0.49	127.58	0.09
	2			127.32	0.47	127.22	0.47	127.22	0.47		
	3			127.50	0.49	127.34	0.49	127.28	0.49		

Chemist

AMH	Alex Meckler-Hickson
IM	Iain May
SR	Sean Reilly

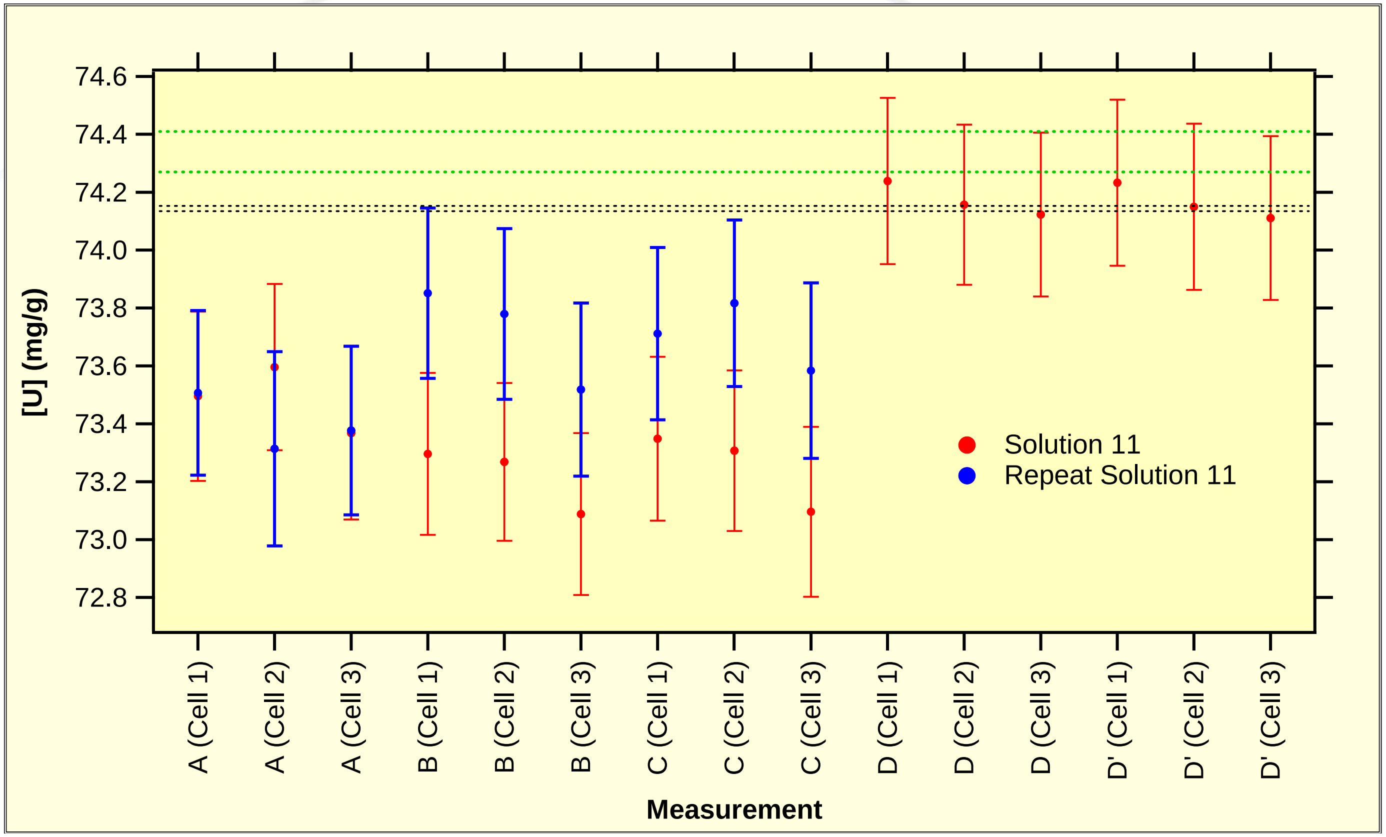
Uranium Concentration Analysis
Solutions 11-15
D assays

Accuracy
Linearity & Range
Precision & Ruggedness
Comparative Analysis

Solution Number	Cell #	Gravimetric Value (mg U/g soln)	Gravimetric σ	Soln D Assay Value (mg U/g soln)	Soln D Assay σ	Soln D' Assay Value (mg U/g soln)	Soln D' Assay σ	Davies-Gray Msmt Value (mg U/g soln)	Davies-Gray Msmt 2σ
11	1	74.144	0.005	74.24	0.29	74.23	0.29	74.34	0.07
	2			74.16	0.28	74.15	0.29		
	3			74.12	0.28	74.11	0.28		
11 repeat	1	74.144	0.005					74.34	0.07
	2								
	3								
12	1	115.183	0.007	115.12	0.44	115.11	0.44	115.24	0.08
	2			114.90	0.43	114.90	0.43		
	3			114.95	0.44	114.95	0.44		
13	1	Unknown		122.67	0.47	122.66	0.47	123.59	0.09
	2			122.47	0.46	122.46	0.46		
	3			122.57	0.47	122.56	0.47		
14	1	83.879	0.004	76.86	0.30	76.81	0.30	77.23	0.07
	2			76.77	0.29	76.70	0.29		
	3			76.85	0.30	76.78	0.30		
15	1	Unknown		126.87	0.48	126.90	0.48	127.58	0.09
	2			126.66	0.47	126.69	0.47		
	3			126.75	0.48	126.78	0.48		

Solution 11

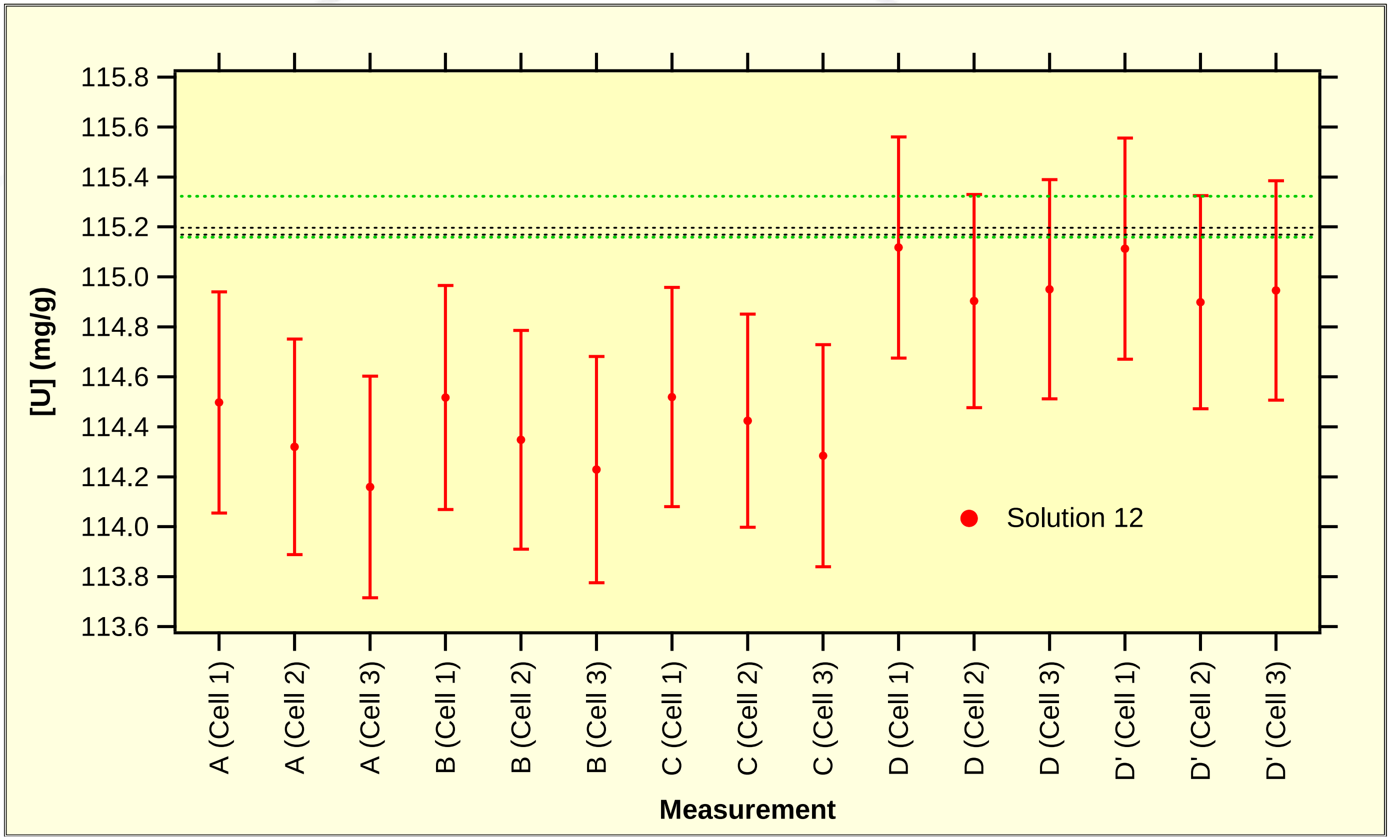
Accuracy, Precision & Ruggedness, Comparative Analysis



- Green dotted lines = ± the expanded uncertainty of the Davies-Gray value for [U] (74.34 mg/g).
- Black dotted lines = ± 2σ of the gravimetrically determined [U] (74.144 mg/g)
- All error bars are ± 1σ of UV-vis determined [U]

Accuracy, Precision & Ruggedness, Comparative Analysis

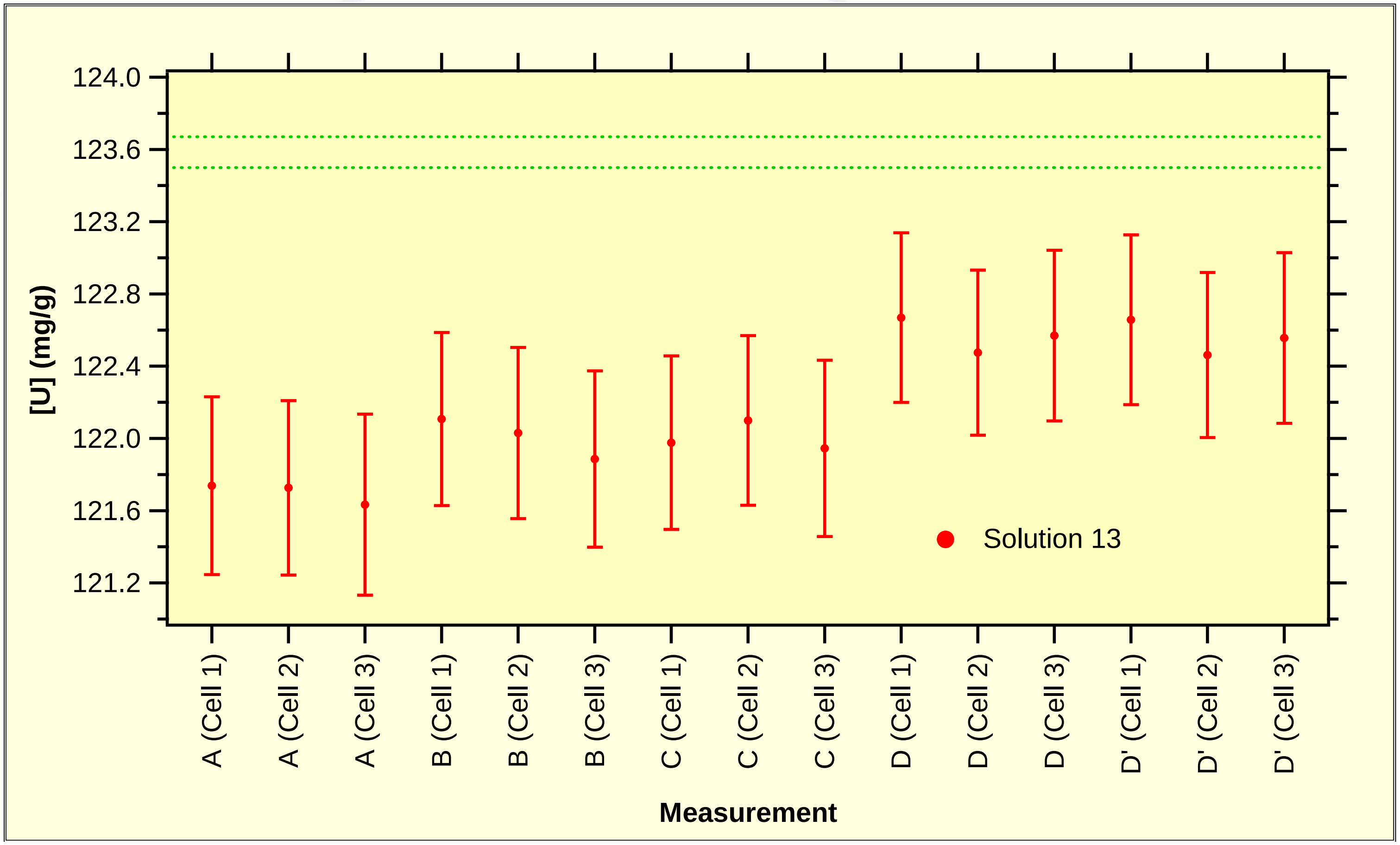
Solution 12



- Green dotted lines = ± the expanded uncertainty of the Davies-Gray value for [U] (115.24 mg/g).
- Black dotted lines = ± 2σ of the gravimetrically determined [U] (115.183 mg/g)
- All error bars are ± 1σ of UV-vis determined [U]

Accuracy, Precision & Ruggedness, Comparative Analysis

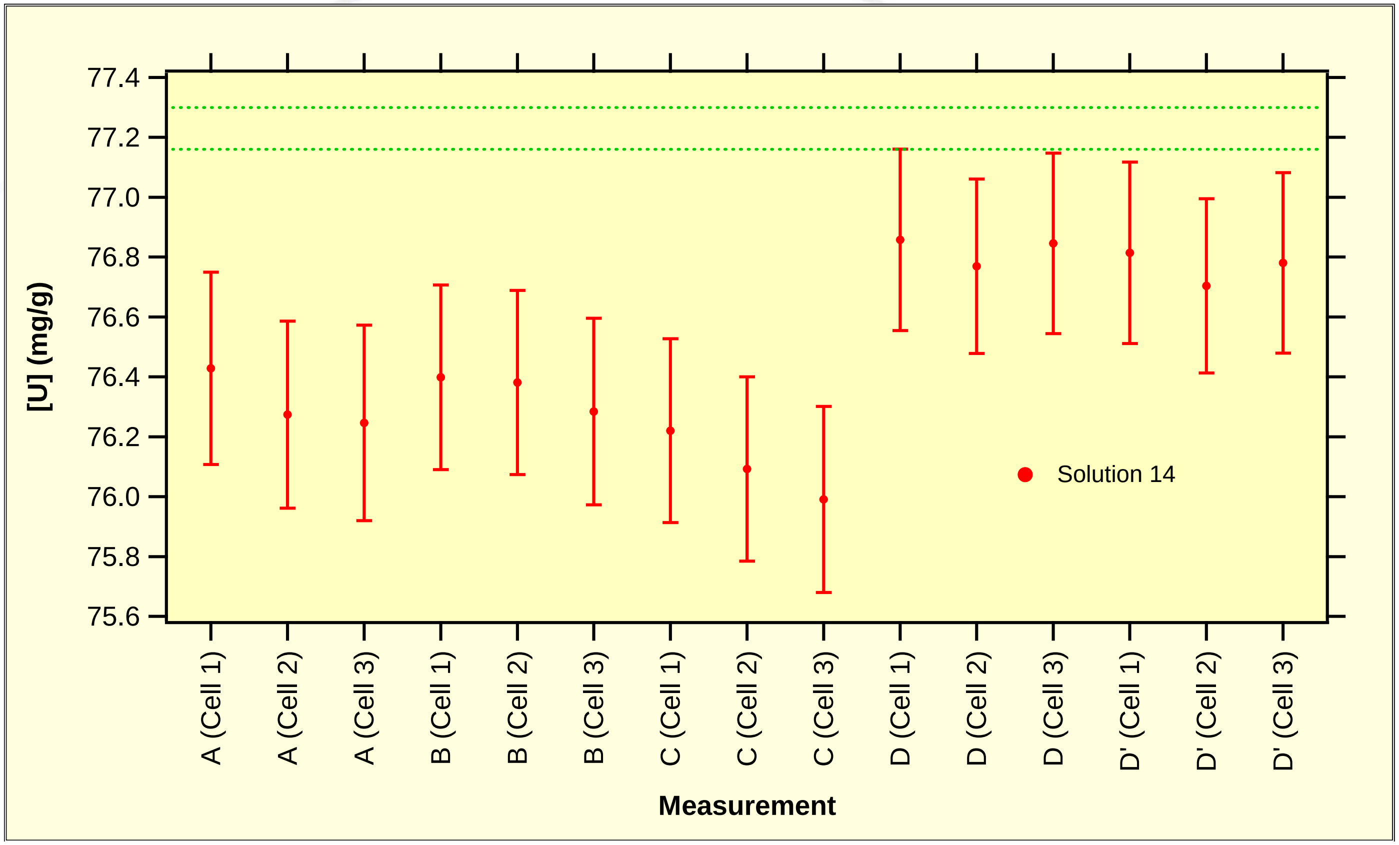
Solution 13



- Green dotted lines = ± the expanded uncertainty of the Davies-Gray value for [U] (123.59 mg/g).
- All error bars are ± 1σ of UV-vis determined [U]

Accuracy, Precision & Ruggedness, Comparative Analysis

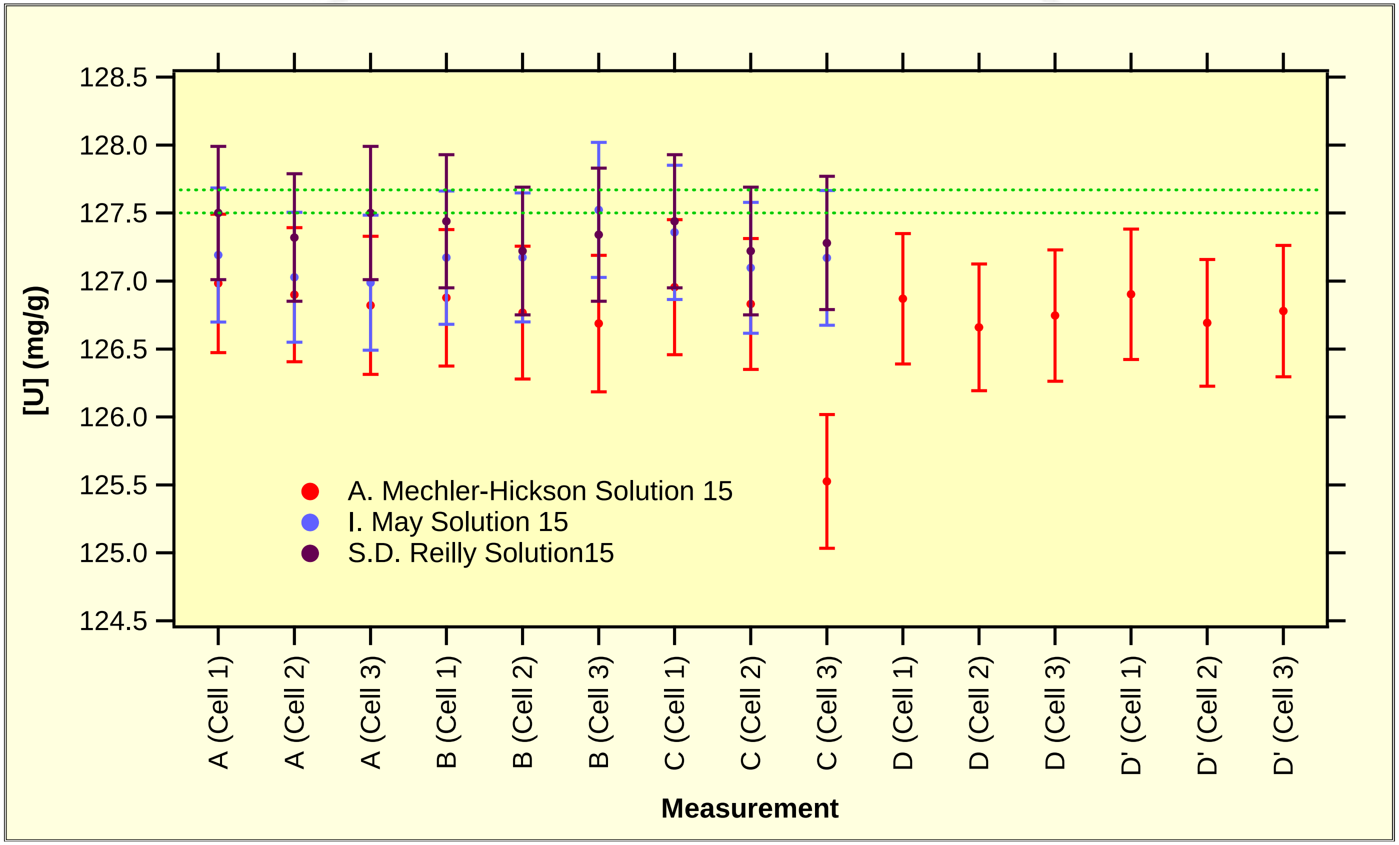
Solution 14



- Green dotted lines = ± the expanded uncertainty of the Davies-Gray value for [U] (77.23 mg/g).
- Gravimetrically determined [U] not shown ("83.879±0.004 mg/g")
- All error bars are ±1σ of UV-vis determined [U]

Solution 15

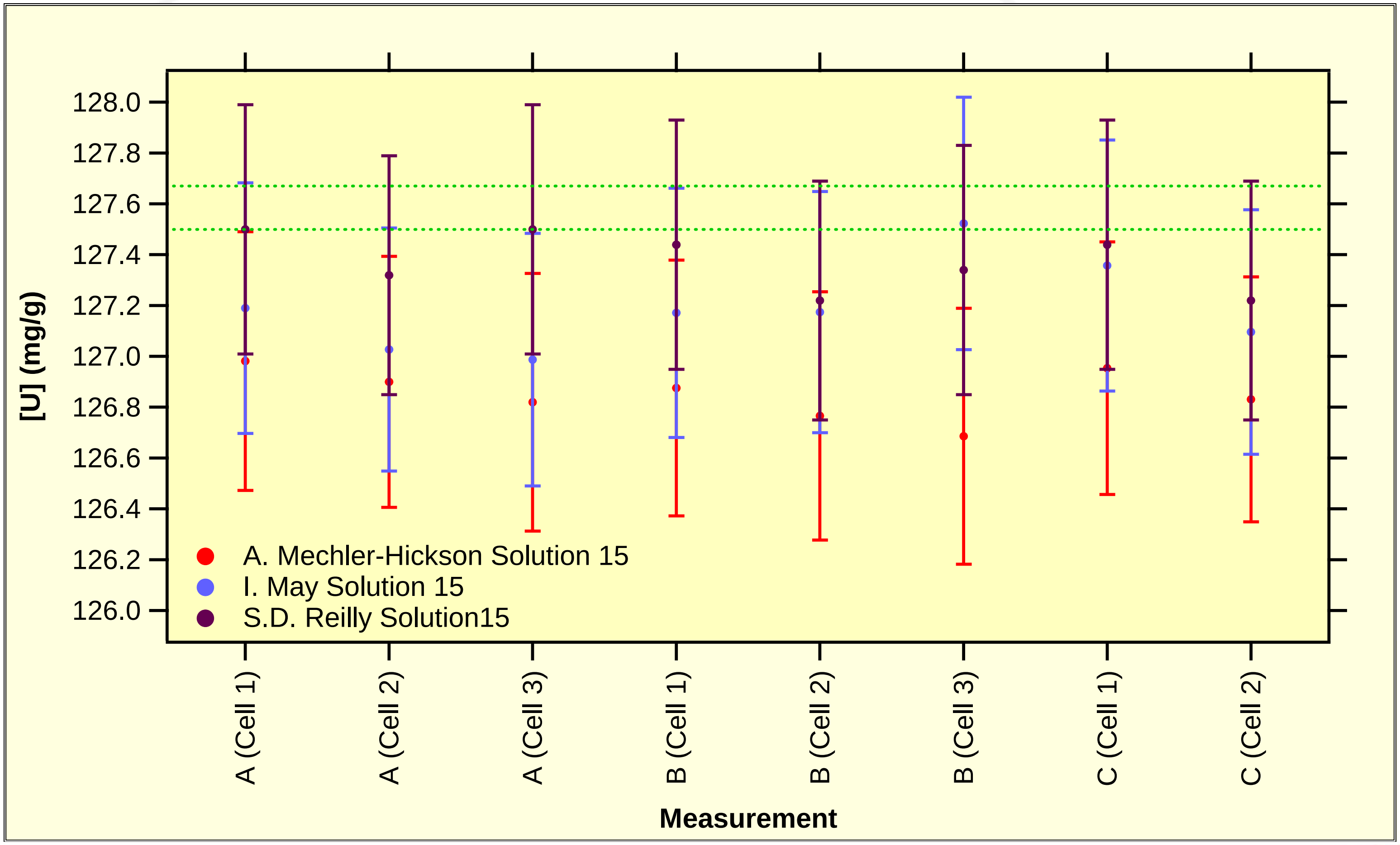
Accuracy, Precision & Ruggedness, Comparative Analysis



- Green dotted lines = ± the expanded uncertainty of the Davies-Gray value for [U] (127.58 mg/g).
- All error bars are ± 1σ of UV-vis determined [U]

Accuracy, Precision & Ruggedness, Comparative Analysis

Solution 15
Different Operators



UV-Vis Analysis of Solutions 11-15 - Observations

- The UV-vis measurements trend to lower measured [U] values than both gravimetric and Davies-Gray data
  - Impact of solution evaporation not taken into consideration
    - Observed for gravimetric vs. Davies-Gray
    - Impact on Molar Absorptivity values previously discussed
  - Measurement of air temperature versus solution temperature
  - For most solutions, better agreement with D and D’ samples vs. A, B & C samples
    - A, B & C sample volumes only just enough for analysis, lower absorbance if light beam not completely passing through sample
- Good agreement in results obtained by different operators (Solution 15)
- Density correction due to assay ‘mixing’ is not significant (D vs. D’ analysis)

Impact of Ruthenium

- Only impacts uranium target (fuel) solution after Mo-99 production
- Even a few ppm Ru in solution can potentially increase the 'observed U' abs. @ 419.5 nm by > 0.1 % .
  - Requires a good understanding of both Ru and U process chemistry concentration levels
- A better understanding of ruthenium spectroscopy in both process type solutions and in 1 M H_2SO_4 assay solution would be useful
  - But likely not a showstopper
- Proposed technical solutions: - either define maximum Ru contaminant tolerance (*e.g.* based on U(VI) peak ratios) and/or subtract out the Ru spectroscopic component during data analysis
  - FY 15 results indicate that both are viable, with a focus on the former

Preparation of Ruthenium Solution Samples

- Prepared using 10,000±100 ppm (μg/mL) ruthenium ICP standard solution
  - NIST traceable, in 20 % HCl
- Dilution of aliquot of this standard solution into Bottle 1 "1.0 M" H_2SO_4 to yield a 100 ppm stock solution
- Subsequent serial dilutions to prepare 10, 1 & 0.1 ppm Ru working solutions in "1.0 M" H_2SO_4

Preparation of Solution Samples 21-24

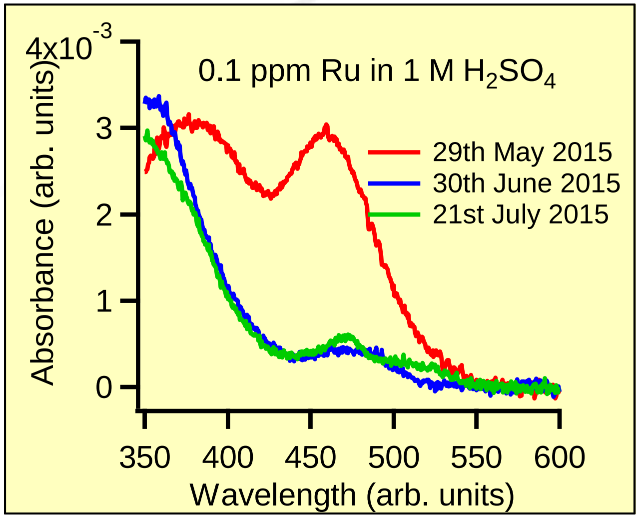
- Measurements made by mass to allow for accurate [U] analysis by UV-vis
- Used *ca.* 150 gU/L pH 1 dU sulfate stock solution
  - Previously used for FY14 Uranium Detection Task
  - FY14 Sample 15, 2/25/14
- Samples 21-24 prepared by adding 0.5 mL of pH 1 dU sulfate solution to 10 mL of Ru spiked "1.0" M H_2SO_4

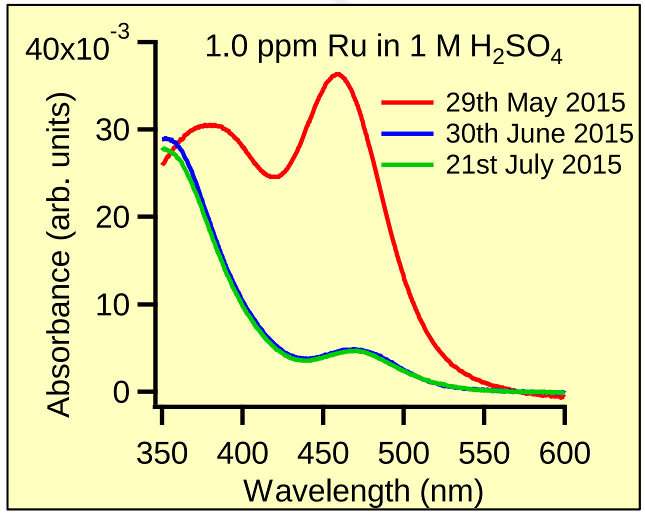
Sample No.	[Ru] (ppm) in "1 M" H_2SO_4	Effective [Ru] (ppm) ***if*** added through original dU sample
21	0	0
22	0.1	2.1
23	1.0	21
24	10.0	210

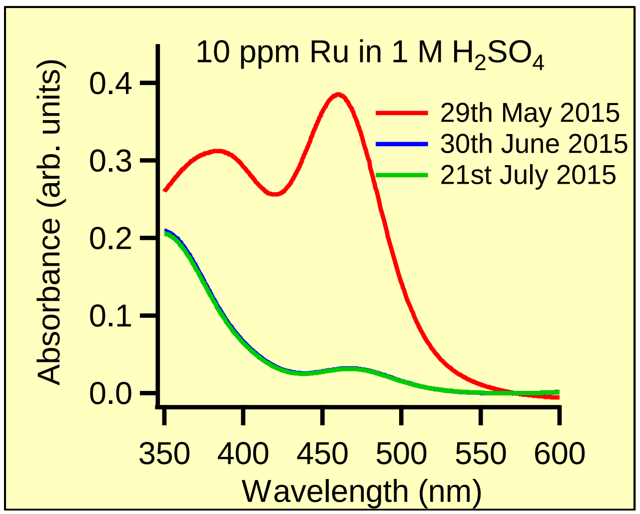
Ruthenium Sample Work 'Caveats'

- Ru standard solution in μg/mL, and pipetting used in dilution (i.e. deviation from accurate mass measurements)
  - However, orders of magnitude difference between Ru concs.
- Ru standard in HCl – trace HCl not removed
  - Impact on speciation cannot be ruled out
- For [U] conc. measurements
  - No individual temperature measurements for 1st June 2015 analysis, thus used end of day value of 26.6 °C
  - For FY14 Sample 15, 2/25/14 uranium
    - Density recorded only to 25.0 °C and extrapolated to 26.6 °C (see previous comment, but no impact observed)
    - Density likely increased with uranium concentration due to sample evaporation (negligible &/or uniform impact)
  - Assume density of Bottle 1 sulfuric acid (ignore 'negligible' impact of up to 210 ppm Ru)

Ruthenium Scans Spectra
average all three 10 mm Starna cells Spectra



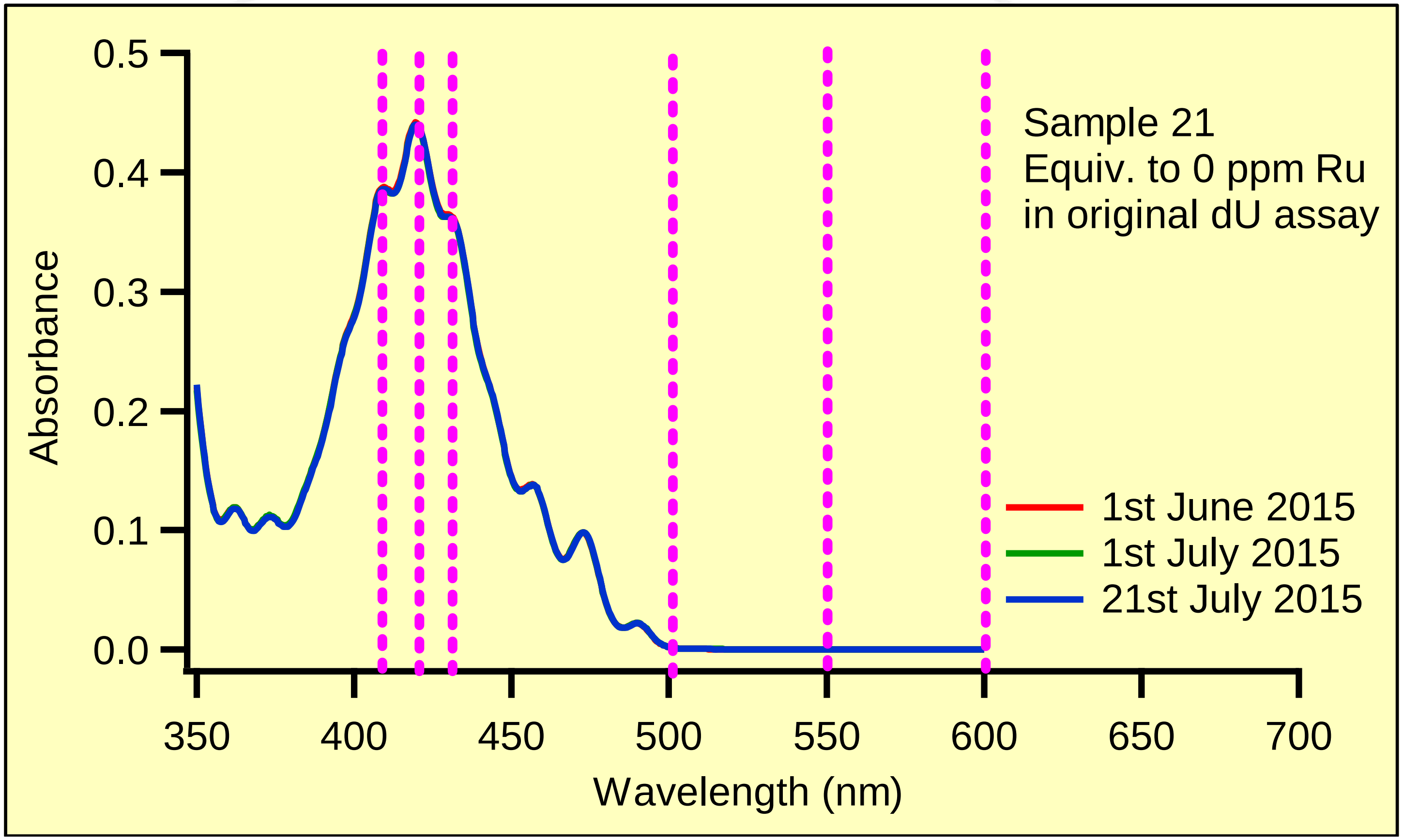




- As previously observed, Ru spectroscopic features change as a function of time
- No observed significant concentration effects at >400 nm

Specificity

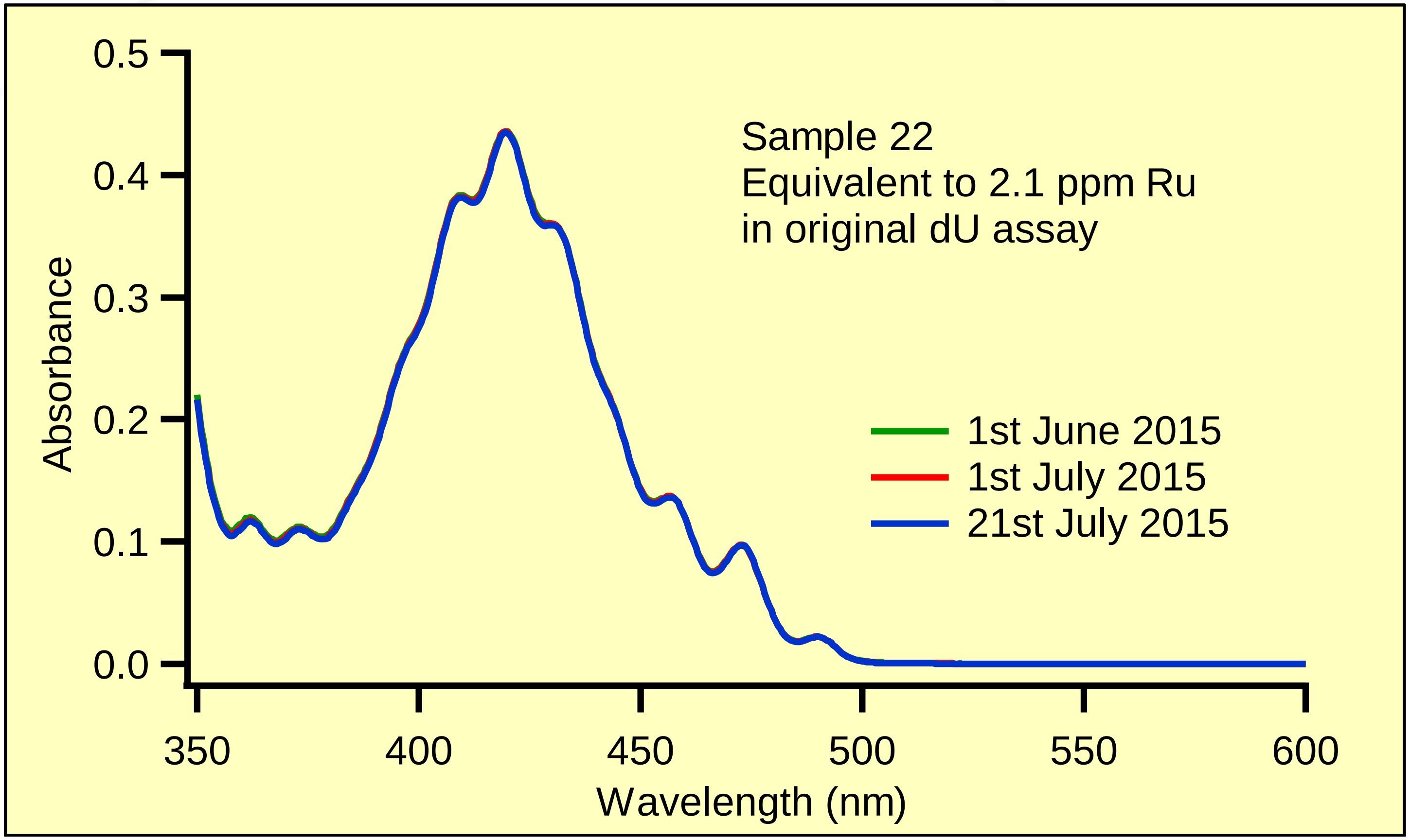
Ruthenium Scans/Reads Spectra
Sample 21



Pink dash lines mark the reads analysis wavelengths @ 600.0, 550.0, 500.0, 430.0, 419.5 & 409.0 nm

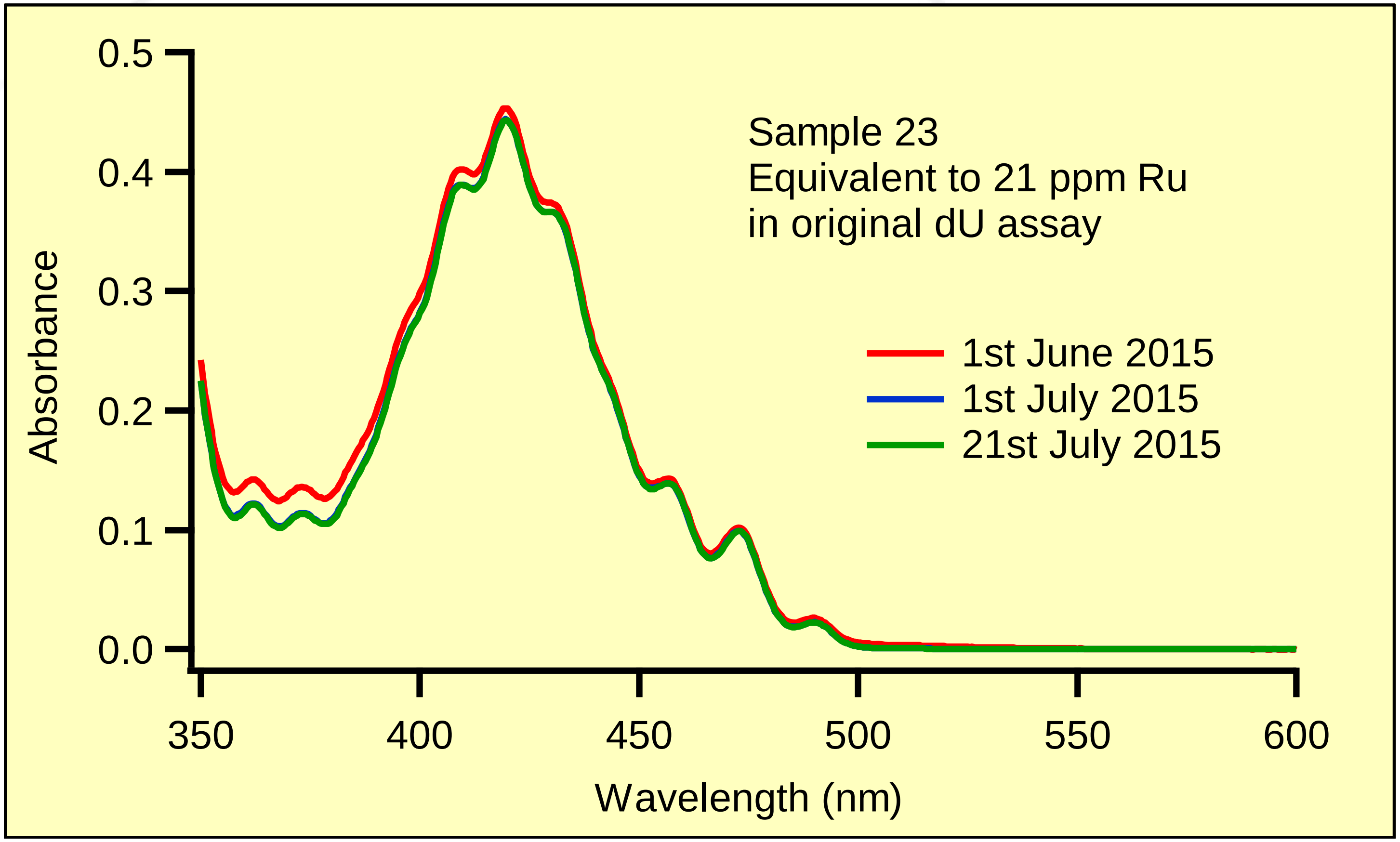
Specificity

Ruthenium Scans Spectra
Sample 22



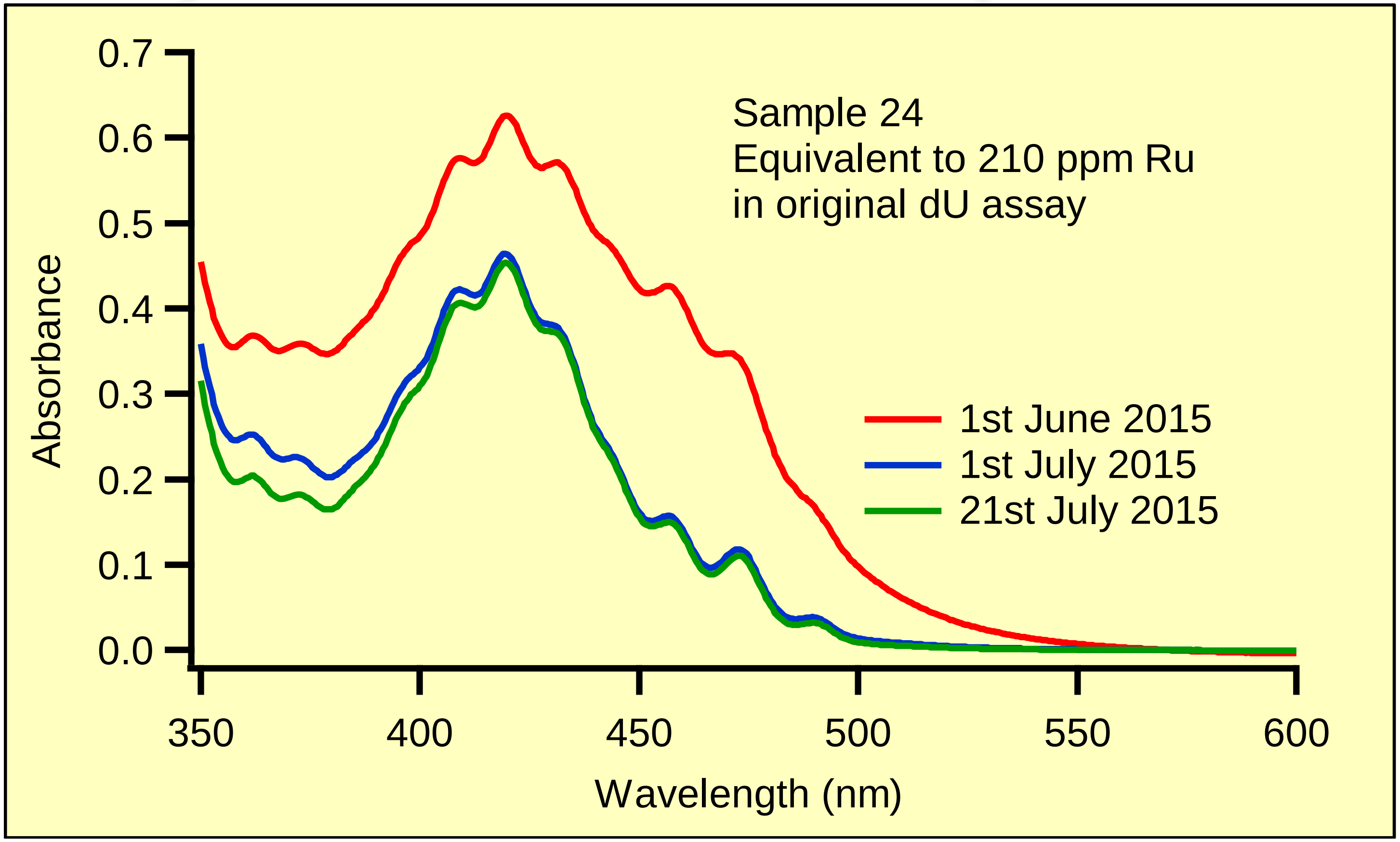
Ruthenium Scans Spectra
Sample 23

Specificity



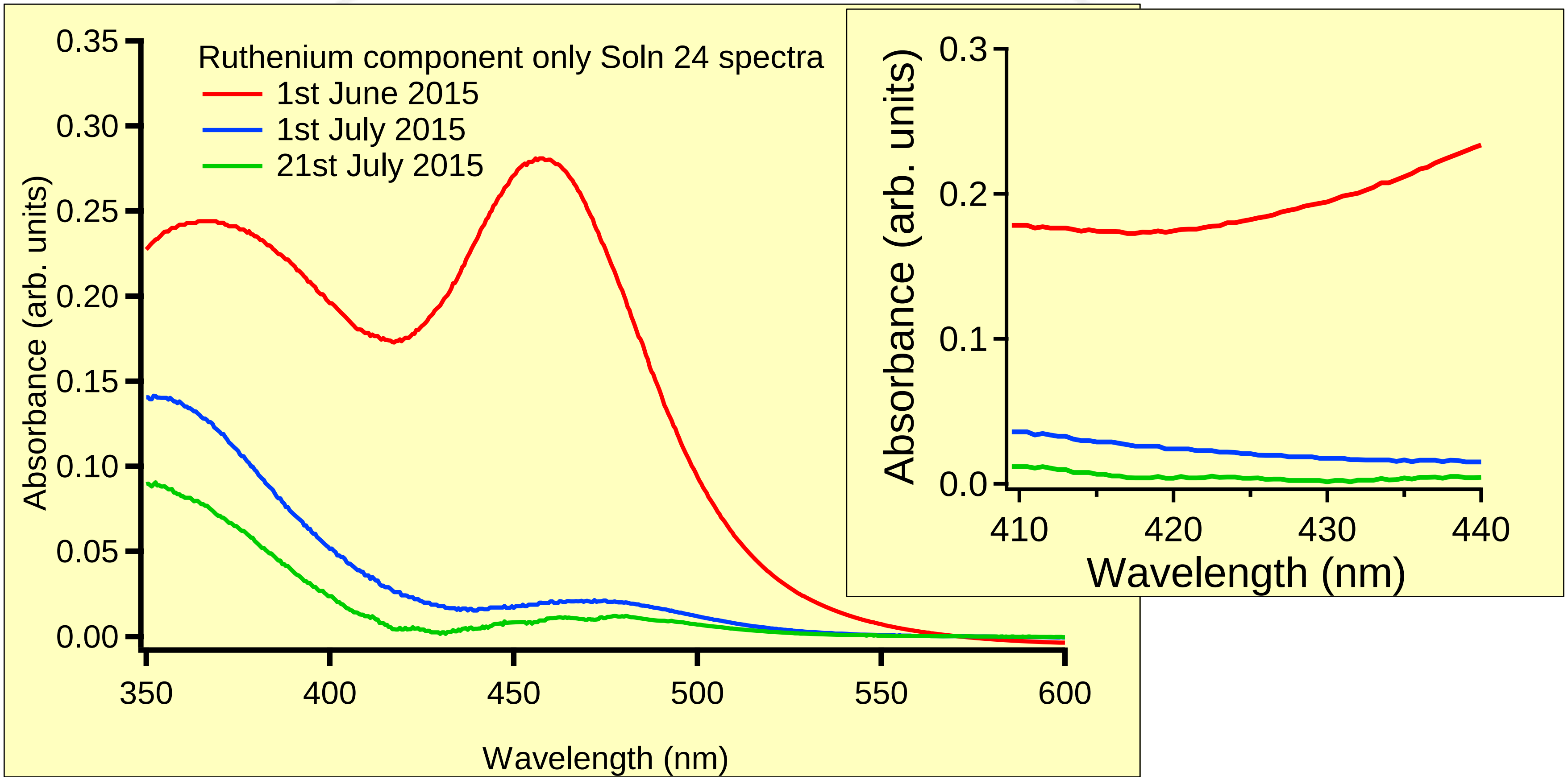
Ruthenium Scans Spectra
Sample 24

Specificity



Specificity

Ruthenium Scans Spectra
Sample 24 – U(VI) Subtracted Out



Impact on 430.0, 419.5 & 409.0 nm peak ratios changes with time

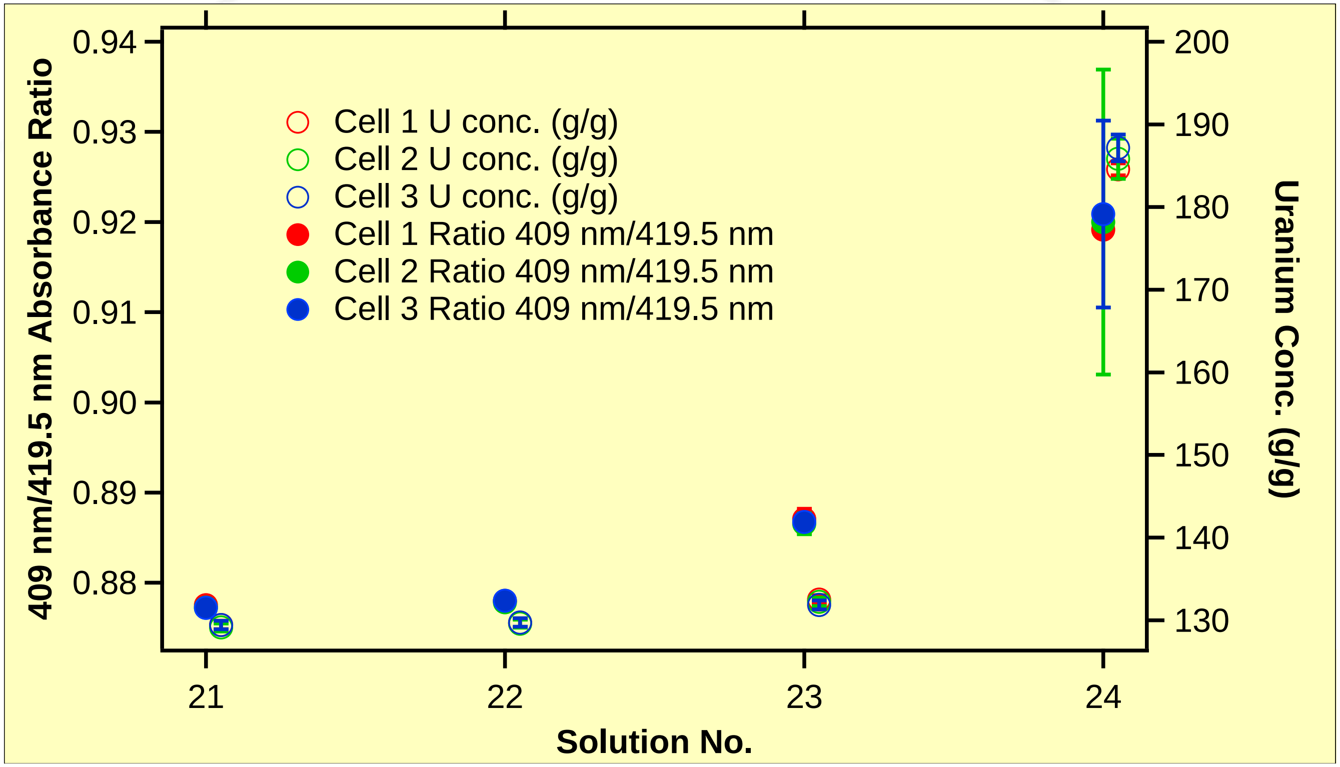
Impact of Ruthenium – "Observed" [U] *reads method analysis*

Cell 1 Data		1st June '15		1st July '15		21st July '15	
Ru (ppm)	Soln. No	[U]	σ	[U]	σ	[U]	σ
0	21	129.43	0.51	129.46	0.49	129.37	0.49
2.1	22	129.67	0.51	129.81	0.50	129.69	0.49
21	23	132.50	0.54	129.46	0.50	129.31	0.51
210	24	184.58	0.73	138.32	0.54	135.39	0.57

Cell 2 Data		1st June '15		1st July '15		21st July '15	
Ru (ppm)	Soln. No	[U]	σ	[U]	σ	[U]	σ
0	21	129.12	0.50	129.03	0.47	129.18	0.47
2.1	22	129.59	0.50	129.62	0.49	129.46	0.48
21	23	132.24	0.52	129.20	0.52	129.22	0.49
210	24	185.83	2.42	138.20	0.59	135.29	0.52

Cell 3 Data		1st June '15		1st July '15		21st July '15	
Ru (ppm)	Soln. No	[U]	σ	[U]	σ	[U]	σ
1	21	129.44	0.51	128.99	0.49	129.22	0.49
2.1	22	129.71	0.52	129.69	0.51	129.60	0.49
21	23	131.85	0.53	129.46	0.51	129.35	0.51
210	24	187.17	1.61	138.51	0.58	135.24	0.55

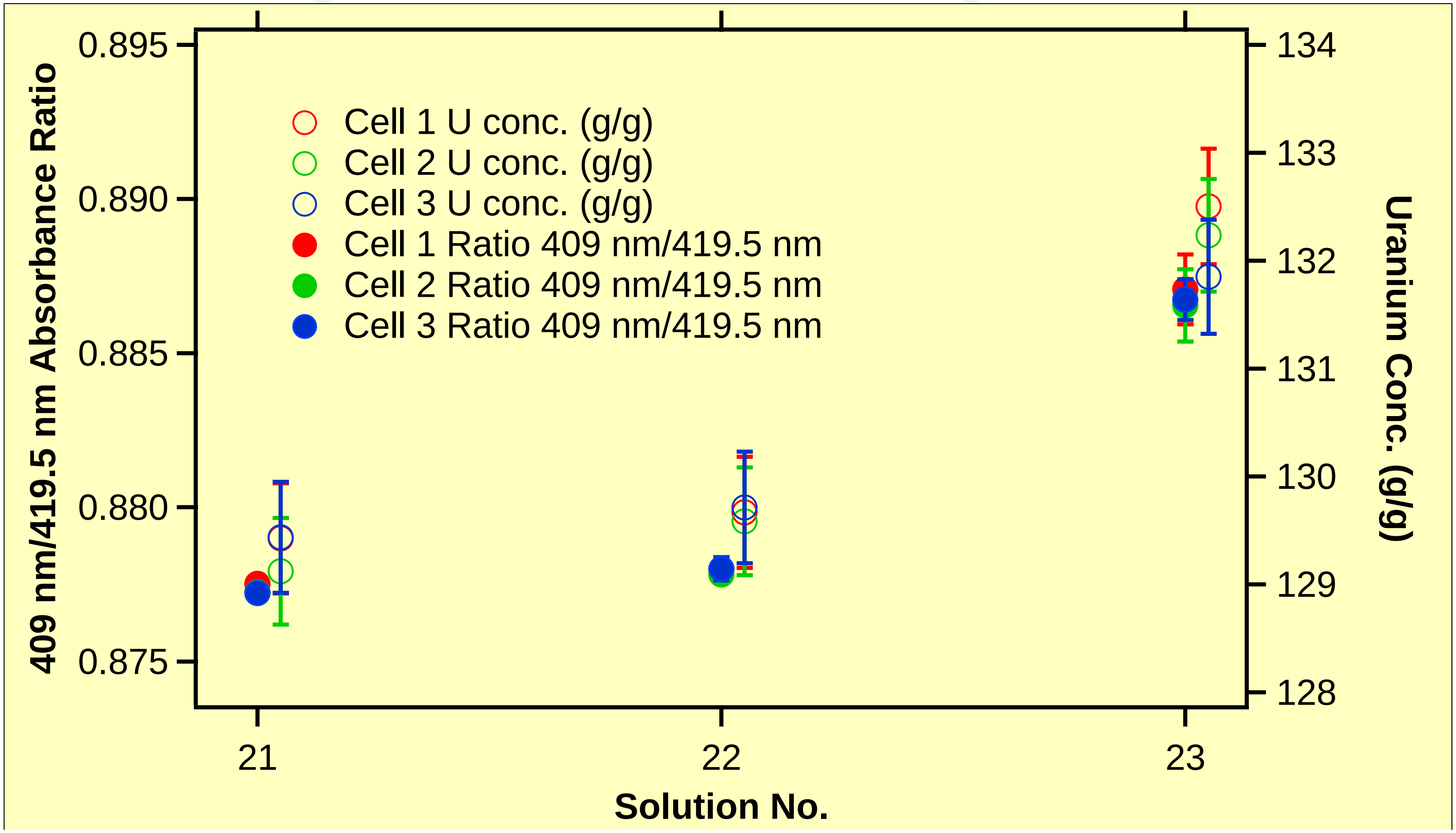
Impact of Ruthenium
Monitoring 409/419.5 nm Abs. Ratios - 1st June 2015 Data



- High uncertainties for Solution 24 absorbance ratios related to the applied reads analysis baseline methodology (a recurring theme)
- Impact of 210 ppm Ru (Solution 24) clearly observed through both peak ratio and '[U]'

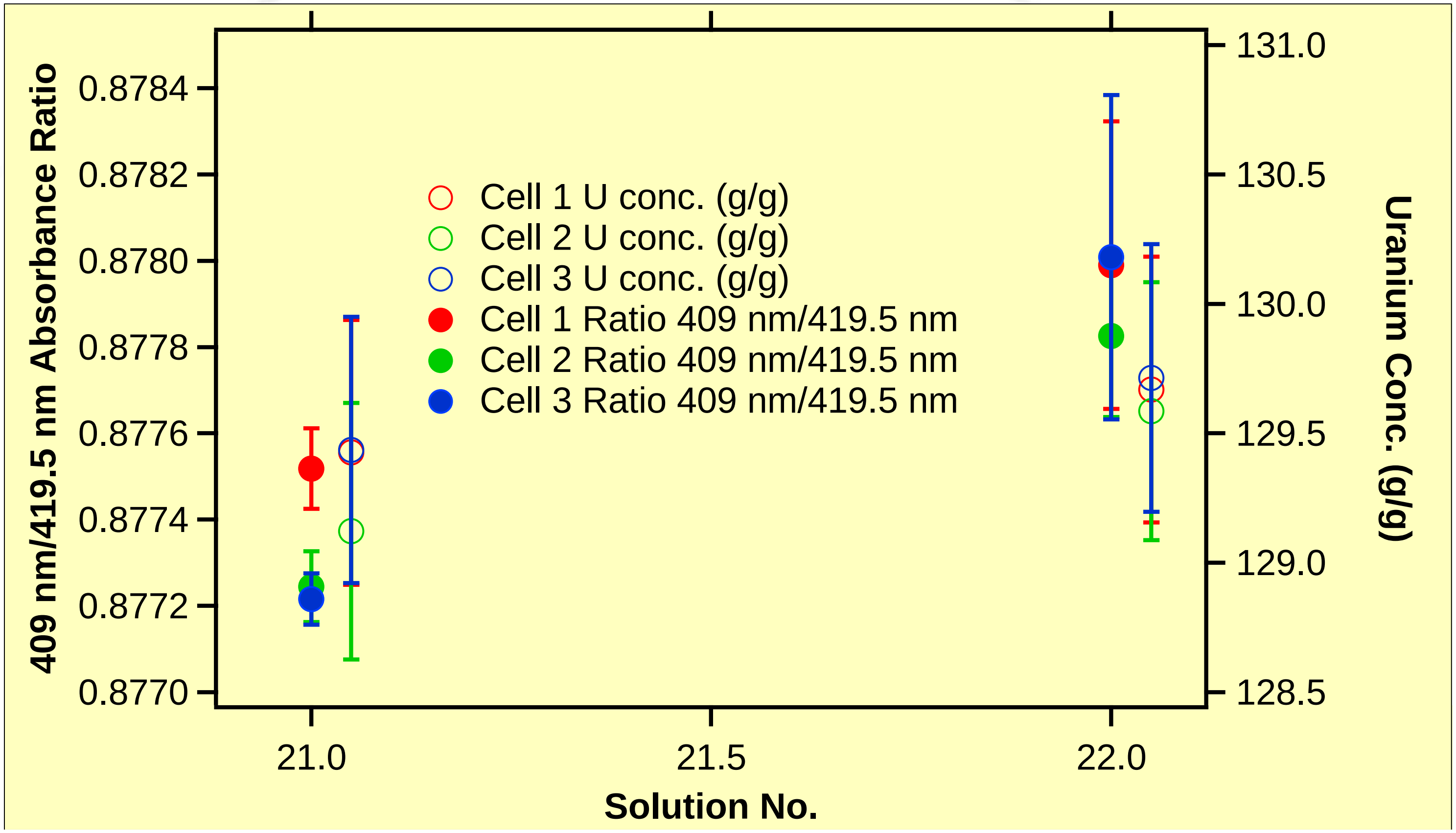
Impact of Ruthenium

Monitoring 409/419.5 nm Abs. Ratios - 1st June 2015 Data



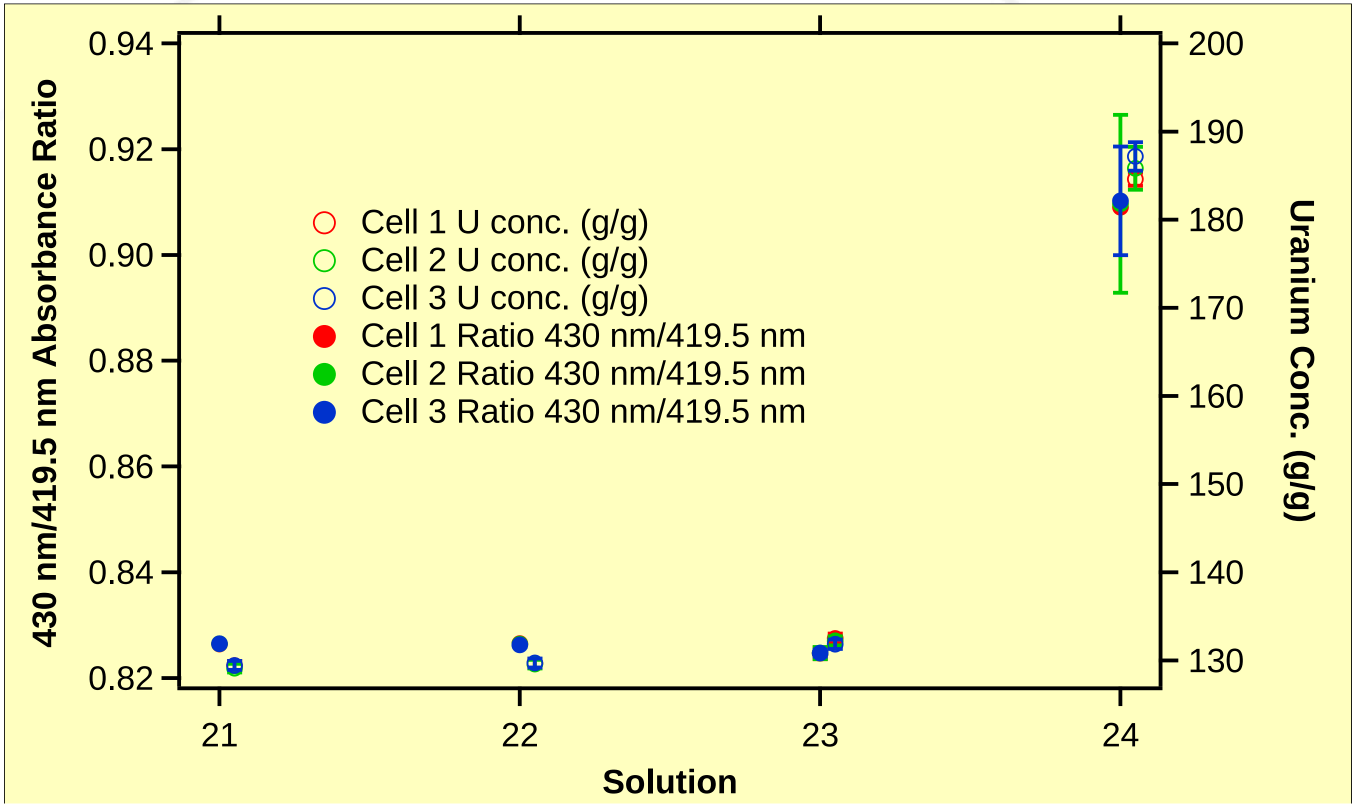
- Impact of 21 ppm Ru (Solution 23) clearly observed through both peak ratio and '[U]'

Impact of Ruthenium
Monitoring 409/419.5 nm Abs. Ratios - 1st June 2015 Data



- Impact of 2.1 ppm Ru (Solution 22) might be observed through peak ratio uncertainties, but not observed in '[U]'.

Impact of Ruthenium
Monitoring 430/419.5 nm Abs. Ratios - 1st June 2015 Data

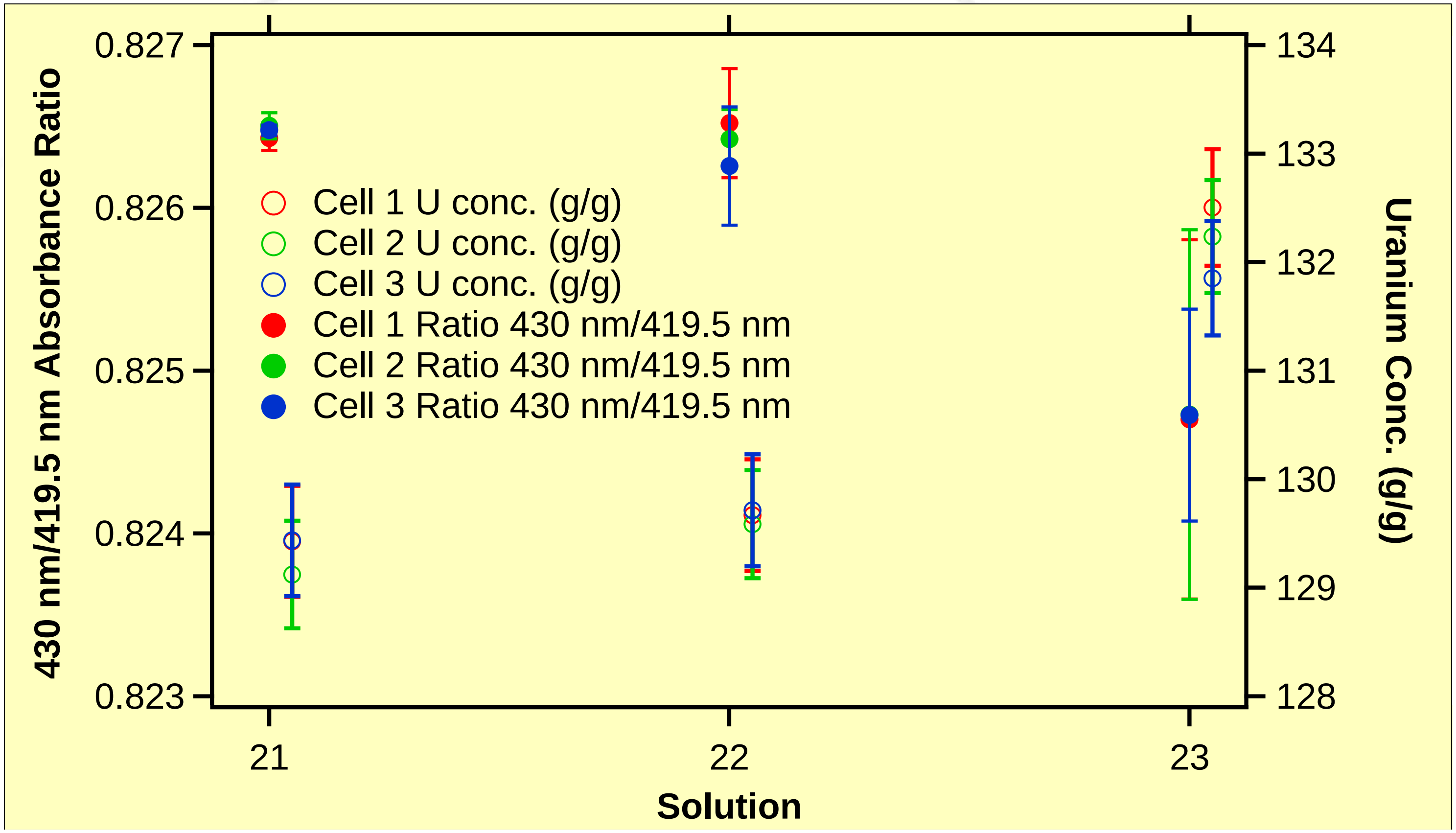


- Impact of 210 ppm Ru (Solution 24) clearly observed through both peak ratio and '[U]'

Accuracy and Specificity

Impact of Ruthenium

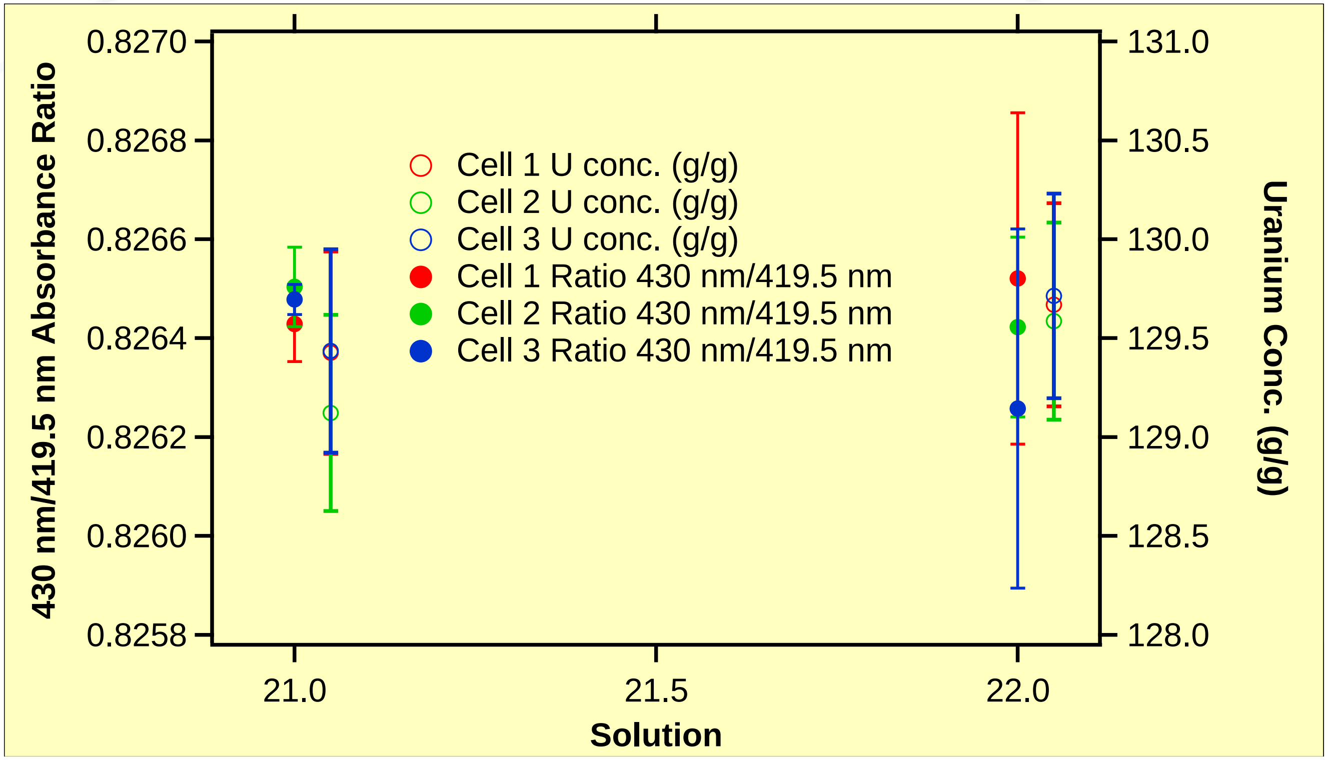
Monitoring 430/419.5 nm Abs. Ratios - 1st June 2015 Data



- Impact of 21 ppm Ru (Soln 23) might be observed through peak ratio/peak ratio uncertainties, and clearly observed in '[U]'.

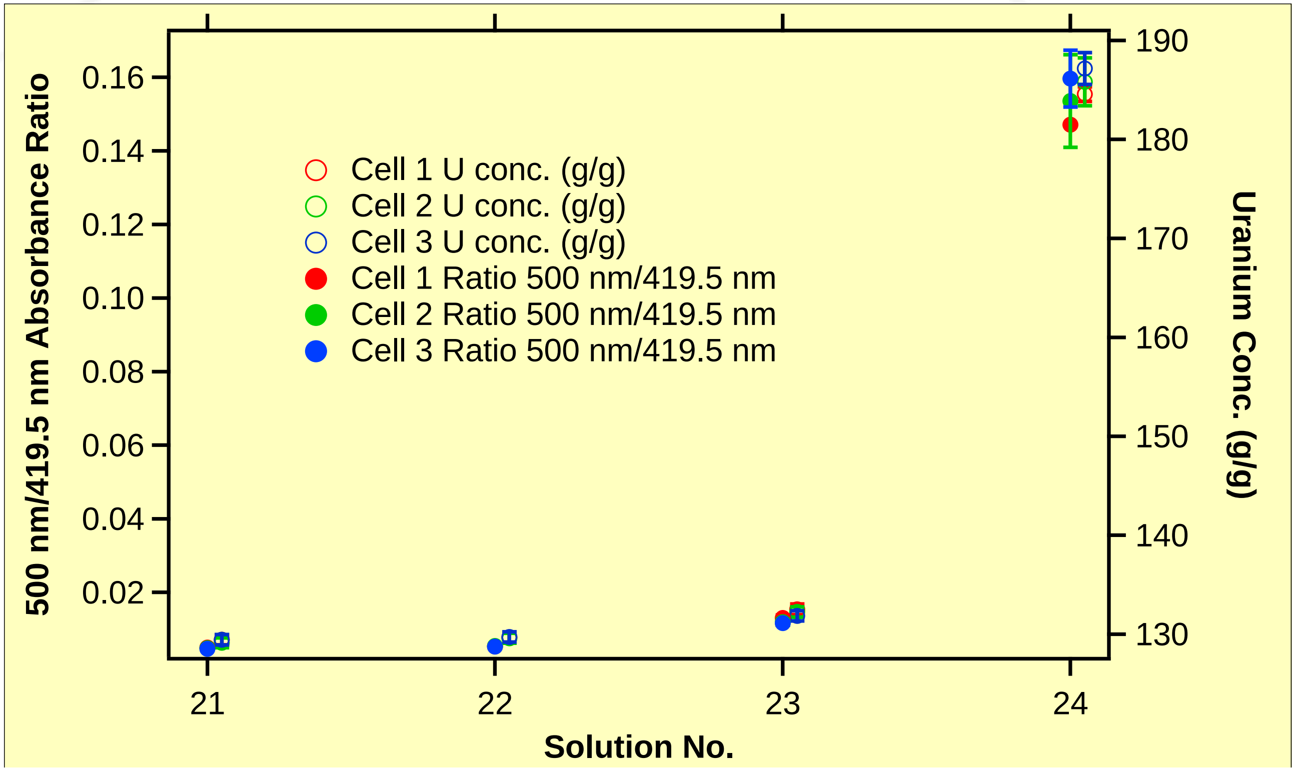
Impact of Ruthenium

Monitoring 430/419.5 nm Abs. Ratios - 1st June 2015 Data



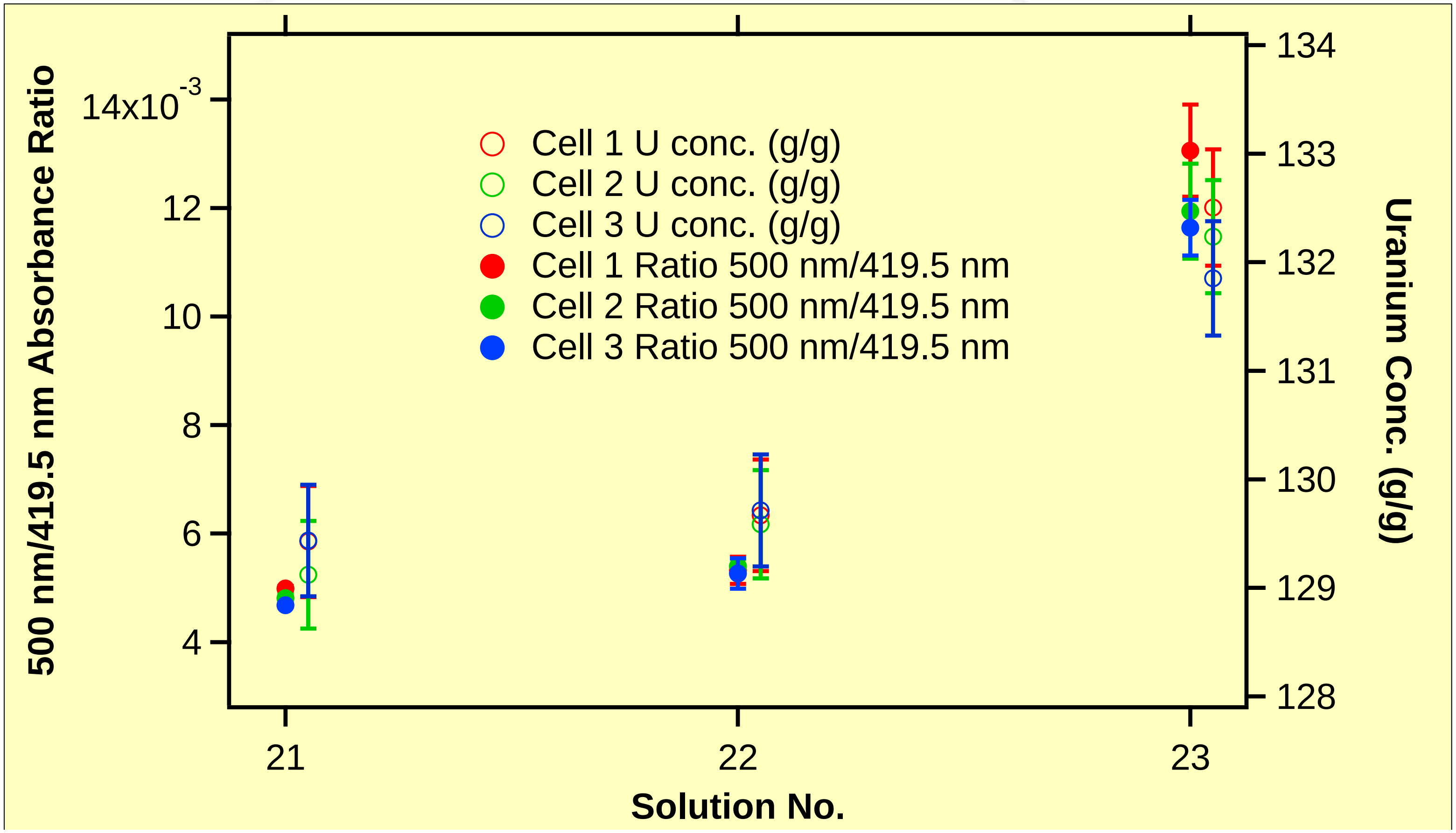
- Impact of 2.1 ppm Ru (Soln 22) might be observed through peak ratio uncertainties, but not observed in '[U]'.

Impact of Ruthenium
Monitoring 500/419.5 nm Abs. Ratios - 1st June 2015 Data



- Impact of 210 ppm Ru (Soln 24) clearly observed through both peak ratio and '[U]'.

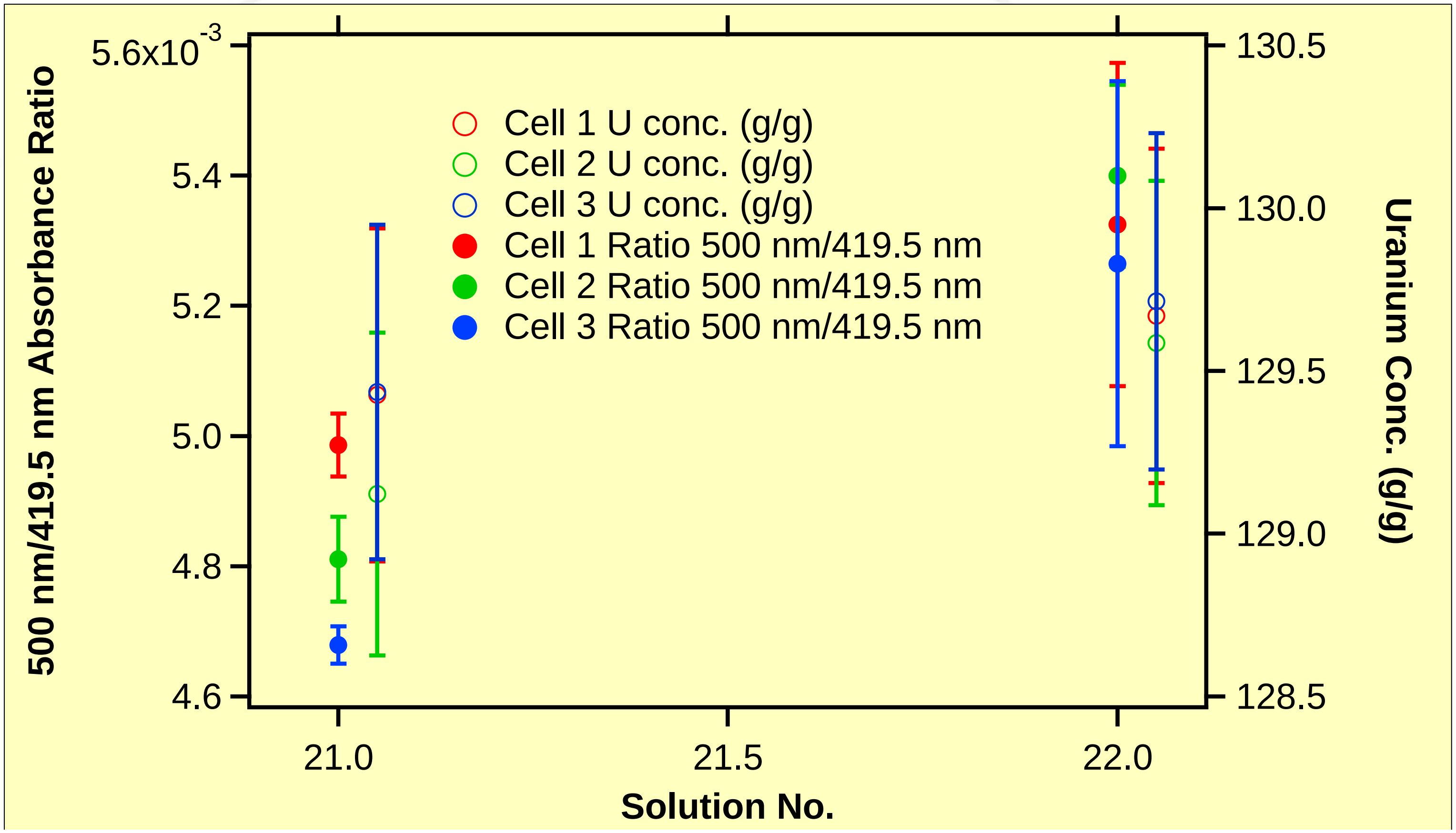
Impact of Ruthenium
Monitoring 500/419.5 nm Abs. Ratios - 1st June 2015 Data



- Impact of 21 ppm Ru (Solution 23) clearly observed through both peak ratio and '[U]'.

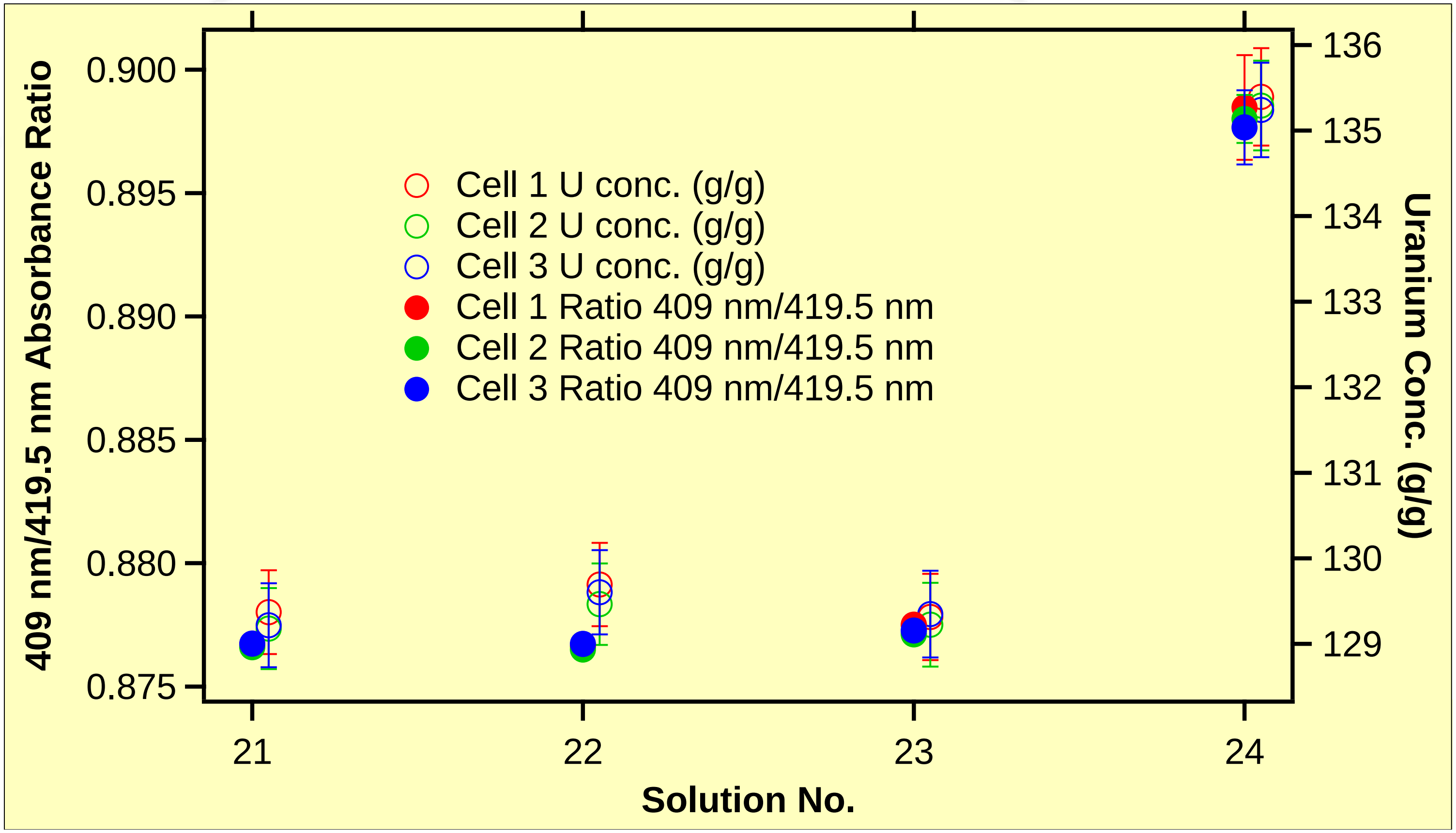
Impact of Ruthenium

Monitoring 500/419.5 nm Abs. Ratios - 1st June 2015 Data



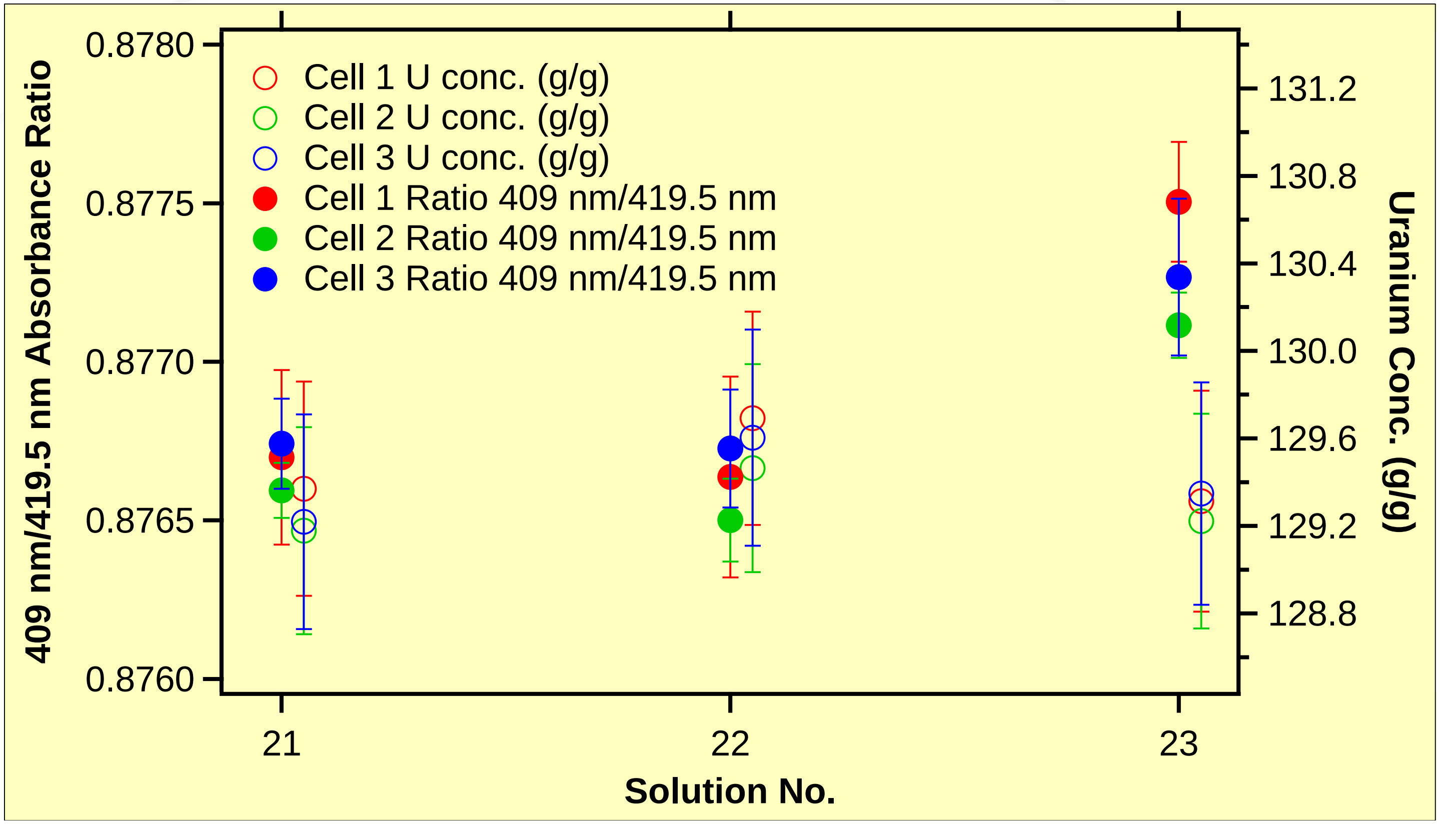
- Impact of 2.1 ppm Ru (Soln 22) might be observed through peak ratio uncertainties, but not by '[U]'.

Impact of Ruthenium
Monitoring 409/419.5 nm Abs. Ratios - 21st July 2015 Data



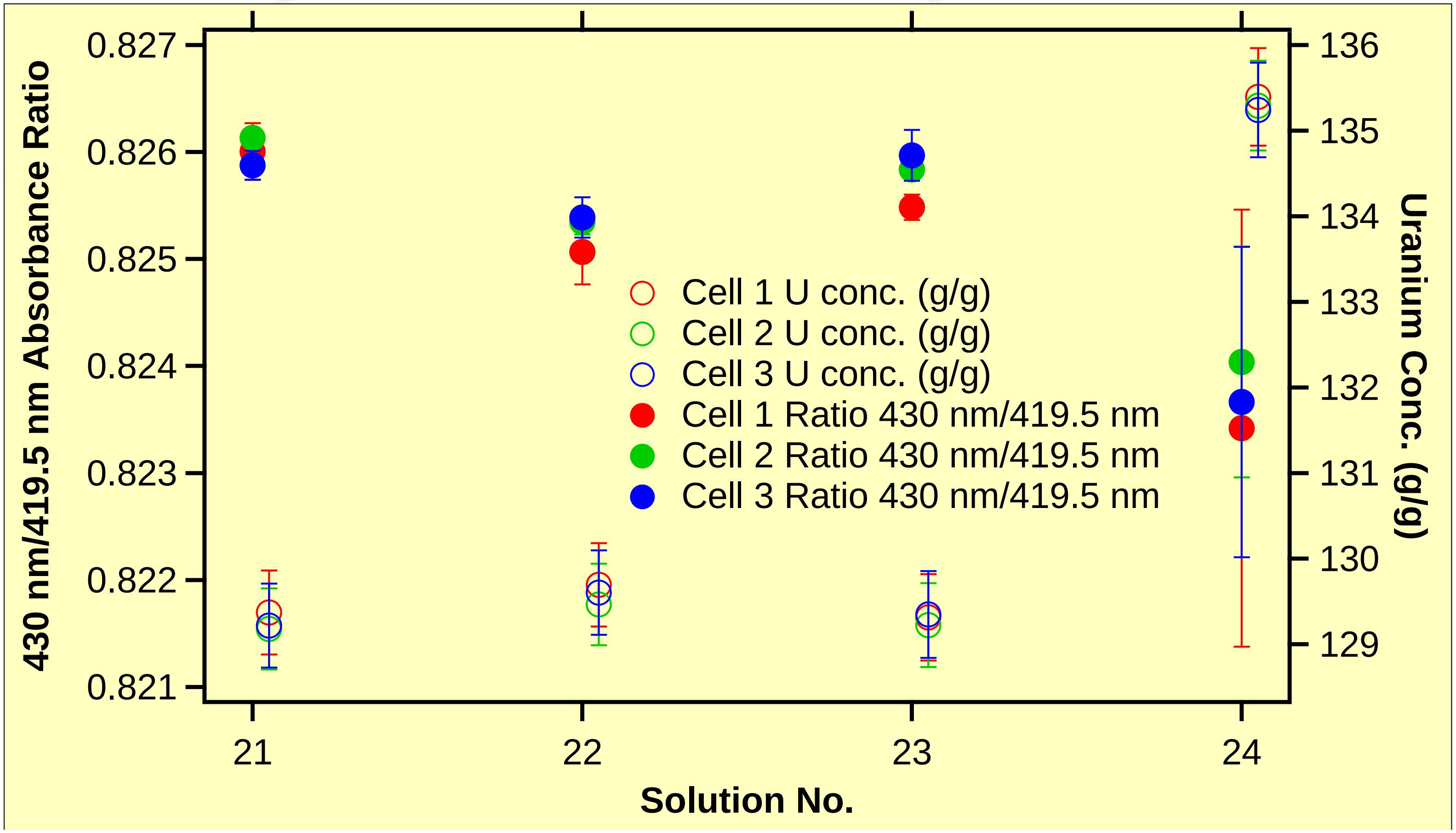
- Impact of 210 ppm Ru (Solution 24) clearly observed through both peak ratio and '[U]'

Impact of Ruthenium
Monitoring 409/419.5 nm Abs. Ratios - 21st July 2015 Data



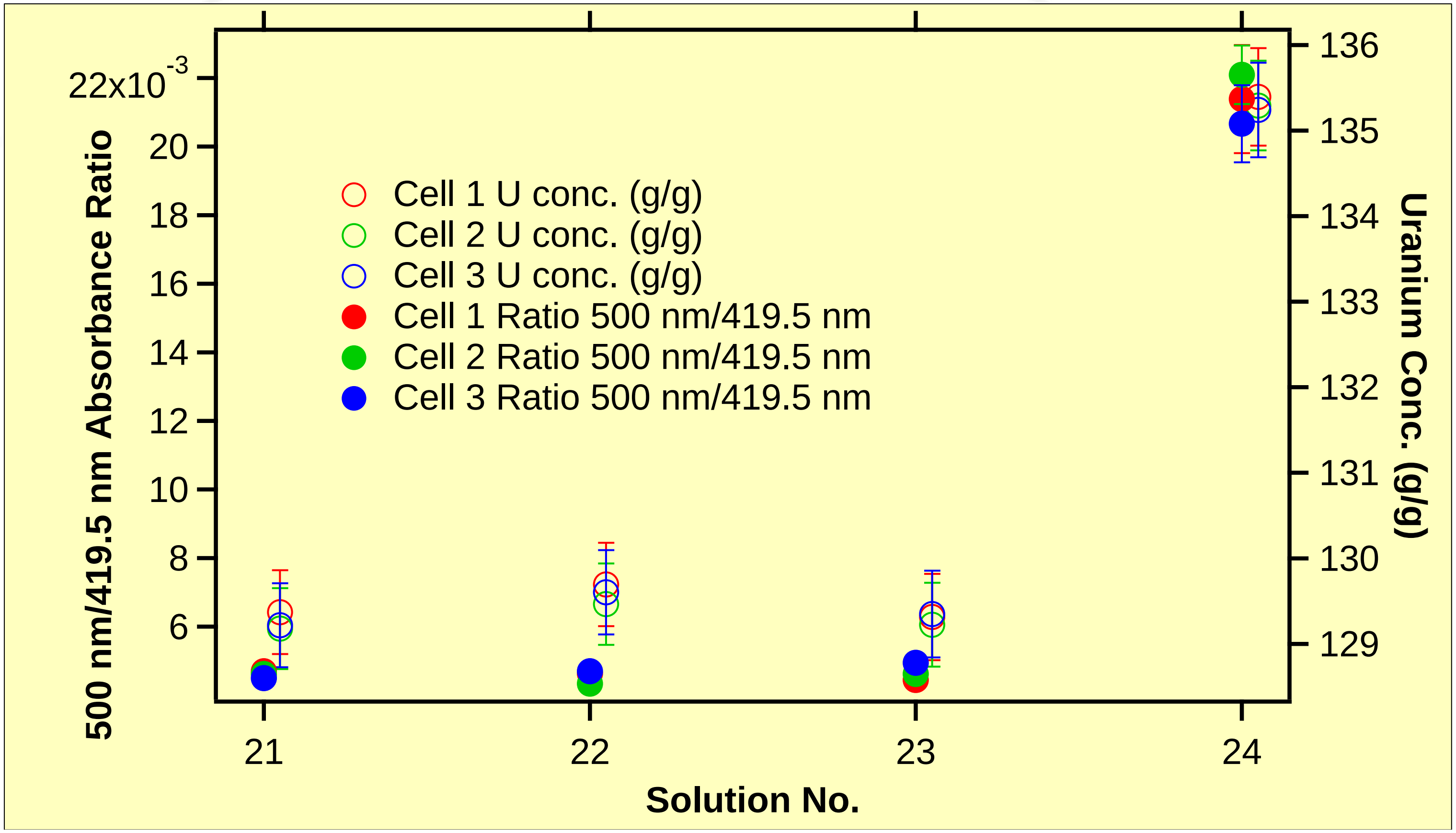
- Impact of 21 ppm Ru (Solution 23) probably observed through peak ratio, but not by '[U]'

Impact of Ruthenium
Monitoring 430/419.5 nm Abs. Ratios - 21st July 2015 Data



- Impact of 210 ppm Ru (Solution 24) could be observed through both peak ratio/peak ratio uncertainties, and definitely by '[U]'

Impact of Ruthenium
Monitoring 500/419.5 nm Abs. Ratios - 21st July 2015 Data



- Impact of 210 ppm Ru (Solution 24) clearly observed through both peak ratio and '[U]'.

Accuracy and Specificity

- Intense absorbance with spectral features that change over time
  – Ideal test for almost any potential interfering contaminant
- Monitoring peaks ratios using reads data can be used to indicate Ru interference
  – ***<u>At least</u>*** to the level of accuracy of our current [U] UV-vis technique
- Experimental protocol can be developed to screen data where peaks ratios/peak ratio uncertainties are outside a certain tolerance ratio

FY 16 Tasks

- Temperature control block
  - All measurements at one temperature
- Simplifies density measurements – now all at one temperature
- Refine our Molar Absorptivity value
  - Use a fresh batch of CRM 112-A
- Repeat measurements of samples 11-15, and additional unknown samples
- Multiple Davies-Gray measurements
  - Correct for any sample evaporation
- Evaluate NIST U standard solution in nitric acid (3164) – 9.994 mg/g ± 0.016 mg/g

Example Temperature Control Unit

Peltier-Controlled Cuvette and Custom Instrumentation
Quantum Northwest
www.qnw.co,/versa20cary60/