

Beryllium Analysis by ICP-OES: A Case Study of Spectral Interferences

2017 BHSC International Symposium on Beryllium
Particles and Detection

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November 14, 2017



LLNL-PRES-741275

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

 **Lawrence Livermore
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THERE ARE KNOWN KNOWNS
THERE ARE THINGS THAT WE KNOW THAT WE KNOW, THERE ARE
KNOWN UNKNOWNNS
THAT IS TO SAY, THERE ARE
THINGS THAT WE NOW KNOW WE DON'T KNOW
BUT THERE ARE ALSO
UNKNOWN UNKNOWNNS
THERE ARE THINGS
WE DO NOT KNOW
WE DON'T KNOW
AND EACH YEAR WE DISCOVER
A FEW MORE OF THOSE
UNKNOWN
UNKNOWNNS

<http://www.amiclarke.com/unknown-unknowns>

Beware of the Unknown Unknowns

LLNL Analytical Laboratory (ALAB)

- AIHA Accredited Laboratory since 1996
- Four staff members
 - Technical Manager, 2 Chemists, 1 Scientific Technologist
- One matrixed (assigned from different organization) Quality Control Chemist
- Primarily analyzes metals by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)
- Sample throughput is about 22,000 samples per year
 - About half are Be swipe samples

ALAB Be Analysis Procedure

- Ammonium Bifluoride digestion
- Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis
 - Looks at two wavelengths
- ICP can suffer from spectral interferences, but corrections for most common expected interferences are incorporated in the method
 - ALAB uses Multicomponent Spectral Fitting (MSF) correction algorithm
- Correction algorithm checked on a daily basis
 - Spectral Interference Check (SIC) standard is a blank containing interferences
 - Criteria is reading for Be must be +/- the Reporting Limit, or +/- 0.0008 mg/L (based on 25 ml of solution), which equates to +/- 0.02 ug of Be in the swipe

What Happened? (sequence of events)

- Powder is procured from Vendor A for additive manufacturing (AM) and machining operations
- Sample of powder is sent to Vendor B for waste characterization
- Waste characterization results are received from Vendor B, indicating the presence of Be at low levels (39 ppm), below CA hazardous waste criterion
- ES&H Team is notified by waste characterization group of unexpected Be results
- Swipe samples are collected from inside of powder containers and from AM equipment
- ALAB reports several Be sample results above the Be release limit
 - The apparent positives were around 0.4 ug/100 cm², which was 2X release limit

Response and Impacts

- Several hundred follow-up swipe samples are collected from potentially contaminated areas and sent to ALAB for rush analysis
- Meetings are held daily for approximately one month to discuss potentially contaminated areas and workers, cleanup plans, additional sampling plans, and communication plans (for LLNL personnel and vendors)
- Occurrence report is issued about unexpected presence of Be in powder
- NNSA Advisory is issued (by DOE HQ) about safety concern related to discovery of Be in powder
- LLNL legal department is contacted to develop correspondence letters for affected vendors

Initial Reporting of Be Swipe Results

- During analysis of Be swipe samples using ICP-OES, primary spectral line had significantly negative reading but secondary line was positive
 - This should've been a flag, but it was assumed that interference on primary line did not impact the secondary line
- Results were reported from secondary line: 0.357 ug, or ~0.4 ug/100 cm²

Sequence No.: 27
 Sample ID: 201707763
 Analyst: ICP4
 Initial Sample Wt:
 Dilution: 25X

Autosampler Location: 25
 Date Collected: 5/9/2017 12:53:51 PM
 Data Type: Original
 Initial Sample Vol:
 Sample Prep Vol:

Nebulizer Parameters: 201707763

Analyte	Back Pressure	Flow
All	198.0 kPa	0.60 L/min

Mean Data: 201707763

Analyte	Mean Corrected Intensity	Conc.	Calib. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD
Sc 361.383	3794048.4	92.375	%	0.0257			0.03%
Be 313.107†	-332615.1	-0.31556	mg/L	0.000112	-7.8890 mg/L	0.00280	0.04%
Be 313.042 Alt†	14905.3	0.01427	mg/L	0.000053	0.35670 mg/L	0.001315	0.37%

Unit is actually ug

Initial Reporting of Be Swipe Results

- Some of the follow-up samples had somewhat negative primary wavelength results, and secondary wavelength results greater than zero, but below the reporting limit
 - Most of the follow-up samples were within +/- of the reporting limit
- There were a few secondary wavelength results that were slightly above the reporting limit



Then the fun began....

- One batch had both wavelengths significantly negative
 - These results were from a different analytical instrument
- A post digestion spike (0.2 ug of Be added to digestate) was done to see what was going on
 - Recoveries were not good: **negative readings at both wavelengths**

Sequence No.: 69
Sample ID: 9067+RL Spk
Analyst: ICP5
Initial Sample Wt:
Dilution: 25X

*10ml sample
55% 4.2e d 2pm std*

Autosampler Location: 61
Date Collected: 5/22/2017 1:12:04 PM
Data Type: Original
Initial Sample Vol:
Sample Prep Vol:

Mean Data: 9067+RL Spk

Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD
Sc 361.383	3074535.4	95.2 %	1.17			1.23%
Be 313.107	-264411.0	-0.13837 mg/L	0.002189	-3.4592 mg/L	0.05472	1.58%
Be 313.042 Alt	-94506.3	-0.05069 mg/L	0.001544	-1.2672 mg/L	0.03859	3.05%

Sequence No.: 70

Autosampler Location: 4

And the fun continued....

- Learned that the samples were taken in areas where a powder containing 90% Ti was used.
- Prepared a standard with 100 ppm Ti, and ran on instrument
 - Negative readings were found at both wavelengths!

```
=====
Sequence No.: 29
Sample ID: Ti 100
Analyst:
Logged In Analyst (Original) : ICP5 New
Initial Sample Wt:
Dilution:
```

```
Autosampler Location: 18
Date Collected: 5/23/2017 11:53:29 AM
Data Type: Reprocessed on 6/28/2017 1:37:44 PM

Initial Sample Vol:
Sample Prep Vol:
```

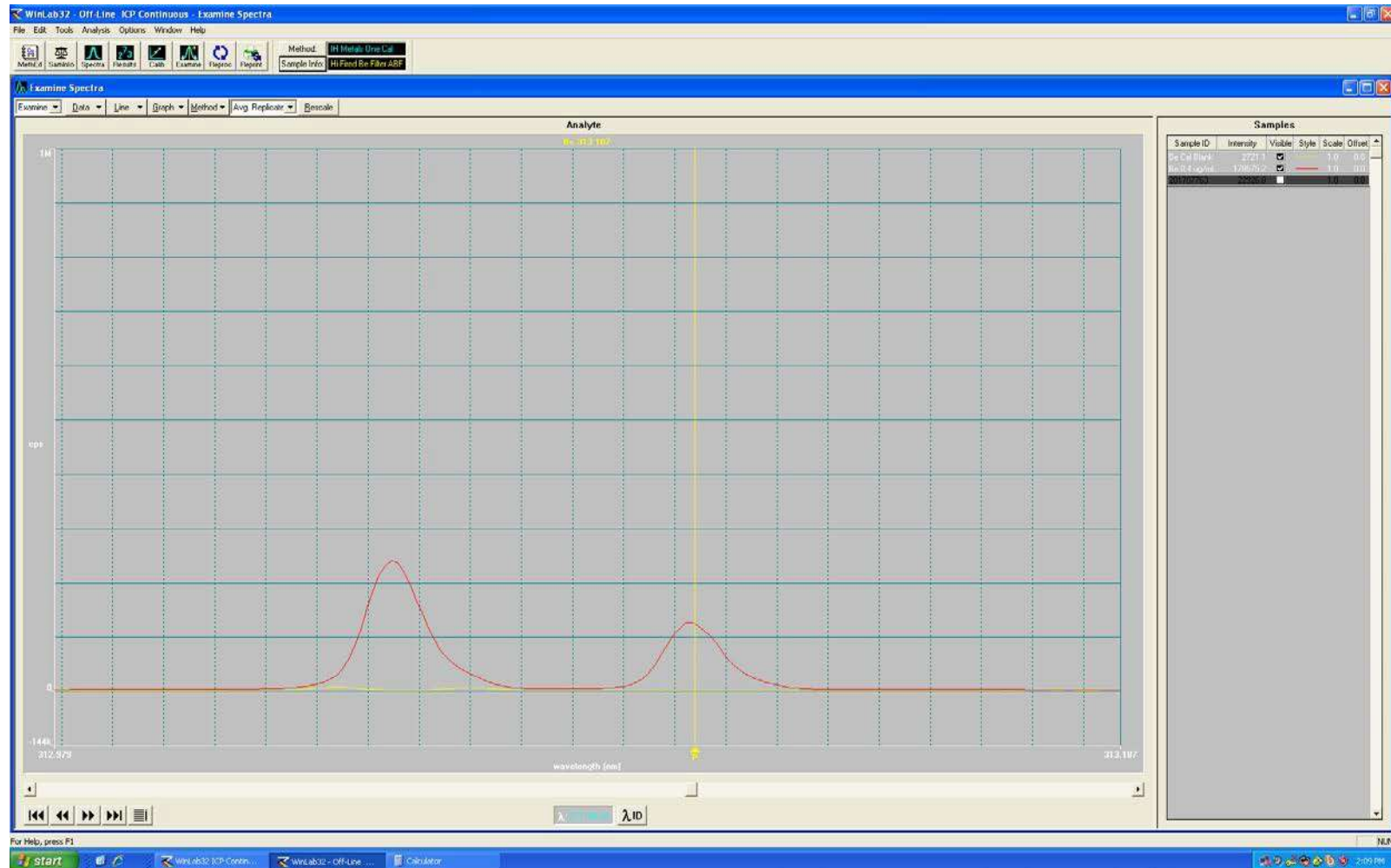
Mean Data: Ti 100

Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD
Be 313.107	-70374.8	-0.03769 mg/L	0.000120	-0.03769 mg/L	0.000120	0.32%
Be 313.042 Alt	-27886.8	-0.01525 mg/L	0.000010	-0.01525 mg/L	0.000010	0.06%
Sc 361.383	-1530.7				107.80	7.04%

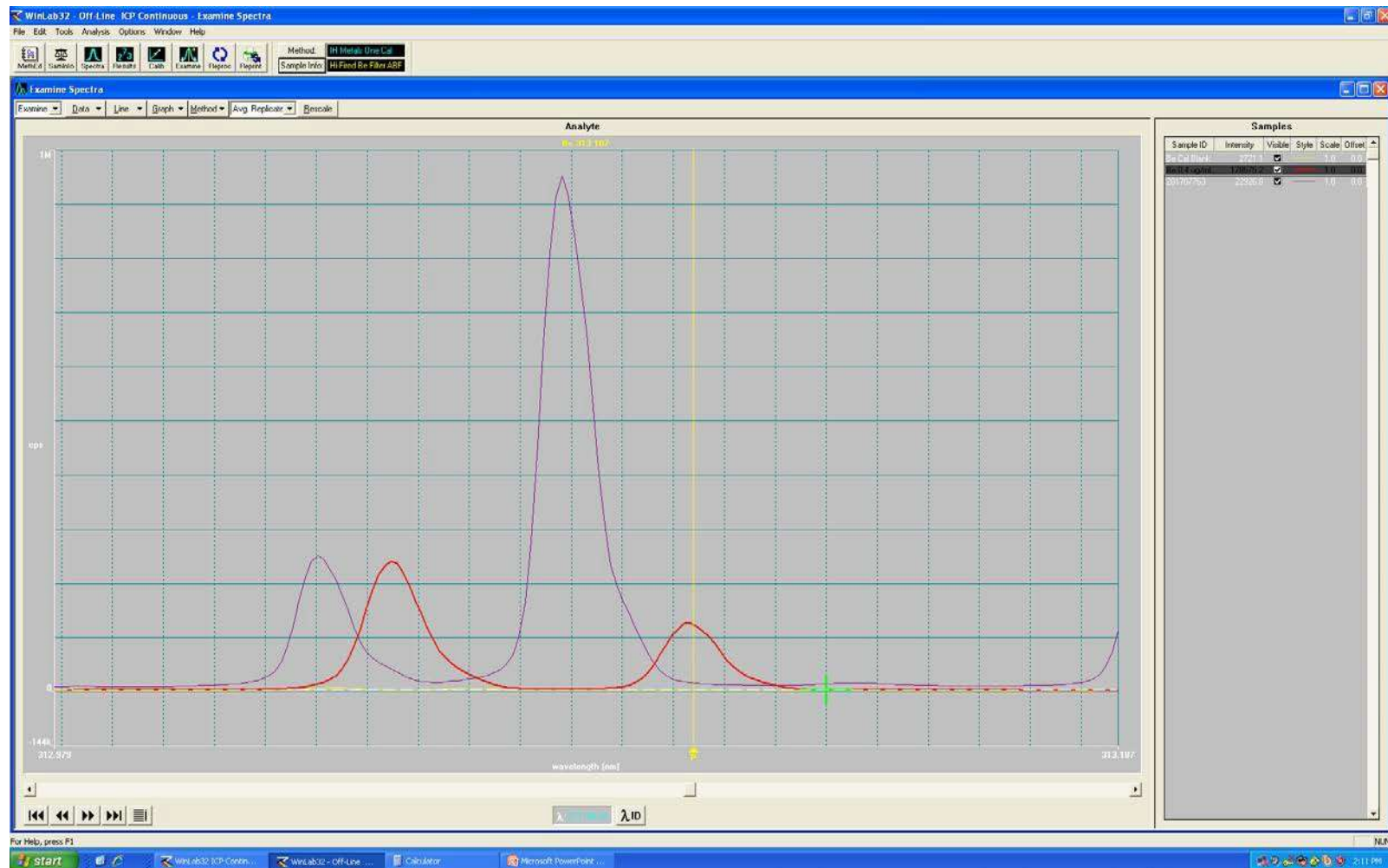
```
=====
Sequence No.: 30
```

```
Autosampler Location: 19
```

Be Std



Be Std + Ti Interferent



So, how do we get those samples analyzed?

- The National Ignition Facility (NIF) at LLNL performs Be analysis using optical fluorometric method



- Asked them to run some spiked samples (0.2 ug of Be added to digestate) to see if their method could handle the Ti
- Their results showed good recoveries of the spikes
 - ALAB acceptance limit of standard at reporting limit is +/-50%
 - Spike recoveries using NIF Method were within those limits

NIF Spike Recoveries on ALAB Digestates

ALAB ID	Unspiked Sample Result	Spiked Sample Result	% Recovery
201709067	<0.02	0.018	90
201709070	<0.02	0.029	145
201708616	<0.02	0.028	140
201708625	<0.02	0.025	125
201808382	<0.02	0.017	85

Response and Impacts - continued

- All samples from the project were re-analyzed at NIF
- Most samples that were originally reported as non-detect remained non-detects
 - A few samples went from detect near the reporting limit to non-detect
- Vendor A, in response to our initial notification, did follow-up testing of their product with 2 different third-party labs, using Direct Current Plasma Emission Spectroscopy and Glow Discharge Mass Spectrometry, respectively, and confirmed that Be was not detectable in their powder (below 5 ppb)
- LLNL cancels the occurrence report and requests cancellation of NNSA Advisory.

https://en.wikipedia.org/wiki/Detection_limit

Can ALAB Analyze Samples with Ti ?

- Not practical to send digestates to NIF on a routine basis
- Added Ti to the MSF model
- It worked!!!



<http://geodavephotography.com/images/happy-picture/36252200-happy-picture.jpg>

Comparison of MSF Model Results Without and With Ti Incorporated

Ti and Ti+Be	No Ti in MSF Model ug/mL		Ti in MSF Model ug/mL	
		%R of Be		%R of Be
0.1 Ti	0.00007		0.00007	
0.1 Ti + 2x RL	0.00155	96.88	0.00156	97.50
0.5 Ti	-0.00017		-0.00005	
0.5 Ti + 2x RL	0.00136	85.00	0.00151	94.38
1.0 Ti	-0.00042		-0.00006	
1.0 Ti + 2x RL	0.0011	68.75	0.00149	93.13
2.0 Ti	-0.00085		0.00000	
2.0 Ti + 2x RL	0.00067	41.88	0.00151	94.38
5.0 Ti	-0.00221		-0.00002	
5.0 Ti + 2x RL	-0.00044	-27.50	0.00169	105.63
10.0 Ti	-0.00412		0.00017	
10.0 Ti + 2x RL	-0.00265	-165.63	0.00172	107.50
20 Ti	-0.00834		0.00021	
20 Ti + 2x RL	-0.00694	-433.75	0.0018	112.50
20 Ti			-0.00004	
20Ti + RL			0.0008	100
30 Ti			-0.00011	
30 Ti + 2x RL			0.00158	98.75
40 Ti			-0.00028	
40 Ti + 2x RL			0.00164	102.5
50 Ti			-0.00023	
50 Ti + 2x RL			0.00155	96.875
100 Ti			-0.00059	
100 Ti + 2x RL			0.00135	84.375

Note: RL =
Reporting Limit, not
Release limit

Single Point Background Correction vs MSF with Ti Data

Ti and Ti+Be	Ti in MSF Model		1 Point Bkg Correction Model	
	ug/mL	%R of Be	ug/ml	%R of Be
0.1 Ti	0.00007		-0.00006	
0.1 Ti + 2xRL	0.00156	97.50	0.00155	96.875
0.5 Ti	-0.00005		-0.00004	
0.5 Ti + 2xRL	0.00151	94.38	0.00145	90.625
1.0 Ti	-0.00006		-0.00008	
1.0 Ti + 2xRL	0.00149	93.13	0.0016	100
2.0 Ti	0.00000		-0.00006	
2.0 Ti + 2xRL	0.00151	94.38	0.00159	99.375
5.0 Ti	-0.00002		0	
5.0 Ti + 2xRL	0.00169	105.63	0.00166	103.75
10.0 Ti	0.00017		0.00017	
10.0 Ti + 2xRL	0.00172	107.50	0.00182	113.75
20 Ti	0.00021		0.0004	
20 Ti + 2xRL	0.0018	112.50	0.00203	126.875
30 Ti	-0.00011		0.00079	
30 Ti + 2xRL	0.00158	98.75	0.00238	148.75
40 Ti	-0.00028		0.00082	
40 Ti + 2xRL	0.00164	102.5	0.00261	163.125
50 Ti	-0.00023		0.00128	
50 Ti + 2xRL	0.00155	96.875	0.00287	179.375
100 Ti	-0.00059		0.00259	
100 Ti + 2xRL	0.00135	84.375	0.00403	251.875

Note: RL =
Reporting Limit, not
Release limit

What Else Can be Done?

- Contacted Eichrom
 - Manufacturer of resins used by radiochemists for sample cleanup
- Referred us to a paper by Sherrod Maxwell (SRS) on exactly this topic
 - Maxwell SL, Bernard MA, Nelson MR, Youmans LD (2008). New method for removal of spectral interferences for beryllium assay using inductively coupled plasma atomic emission spectrometry. Talanta 76:432-440



Maxwell's Method

- $\text{HNO}_3/\text{HCl}/\text{HF}/\text{Peroxide}$ digestion
- Take to dryness
- Convert to 0.2M HF-0.1M HCL
- Cleanup with stacked Diphonex/TEVA columns to remove interferents
- Secondary ion exchange to remove Cr
- Bring to 20 ml prior to analysis by ICP

Interfering Elements for Be

Analyte	Peak(nm)	Intensity
U	312.879	6.0
Zr	312.917	400.0
Nb	312.964	22.0
U	312.973	15.0
Zr	312.976	550.0
Th	312.997	10.0
V	313.027	1020.0
Ce	313.033	50.0
Be ^b	313.042	64000.0
U	313.056	6.0
U	313.073	0.0
Nb	313.079	2200.0
Ti	313.079	150.0
Ce	313.087	65.0
Th	313.107	27.0
Be ^b	313.107	41000.0
Tm	313.126	Not listed
U	313.132	8.0
Hf	313.181	20.0
U	313.199	15.0
Cr	313.206	1000.0
Zr	313.207	7.0
Th	313.226	5.0
Mo	313.259	1800.0
Ce	313.259	30.0

^a As listed in PerkinElmer WinLab32 software v.2.0. ^b Commonly used peaks for determining beryllium by ICP-AES.

From Maxwell et al, 2008

Why these resins?

- Diphonix Resin® has a very high retention for uranium, plutonium, thorium, vanadium, iron, erbium and cerium even in the presence of dilute hydrofluoric acid
- TEVA Resin® retains niobium, titanium, molybdenum, zirconium, and tungsten from dilute hydrofluoric acid–hydrochloric acid solutions.

From Maxwell et al, 2008

Maxwell's Results

Table 3
Average removal results for spectral interferences

Interference (ppm)	Added (ppm)	Measured (%)	Removal
Iron ^a	1000	0.039	99.996
Uranium	300	0.112	99.963
Niobium	100	ND	~100
Molybdenum	100	0.002	99.998
Vanadium	100	0.003	99.997
Zirconium	100	0.082	99.918
Tungsten	100	0.010	99.990
Thorium	50	ND	~100
Plutonium	34.4	0.000048	99.999
Titanium	100	0.736	99.964
Cerium	50	ND	~100
Erbium	100	ND	~100
Chromium	100	50.01	49.99
Chromium ^b	100	8.98	91.02

N = 10. ND = none detected. Added ppm added to have this level interference in 20 ml at ICP-AES.

^a Fe has similar removal at 2500 ppm.

^b Additional anion exchange to remove more Cr.

From Maxwell et al, 2008

Maxwell's Results

Table 4

Be average recovery results (wipes)—interferences added

Emission line (nm)	Be added (ppb)	Be measured after IEX (ppb)	Recovery (%)	Bias (%)	R.S.D. (%)	After anion exchange	Recovery (%)	Bias (%)	R.S.D. (%)
234.861	1.00	1.07	107.29	7.29	7.28	N/A	N/A	N/A	N/A
313.042	1.00	1.60	159.75	59.75	14.79	1.06	105.50	5.50	13.54
313.107	1.00	1.61	161.25	61.25	18.85	1.18	117.61	17.61	10.86

N = 12.

*Be recovery results were improved after anion exchange (removal of Cr reduced its positive interference on Be analysis)

From Maxwell et al, 2008

ALAB Approach

- Do we need to be concerned about all potential interferents?
 - Analyzed original digestate
 - Primary components were Cr, Mo, V, Al and (of course) Ti
 - Ti was present at approximately 1000 mg/L in the digestate
- V is the only element retained on the Diphonex, and it was at about 1 mg/L in the digestate
 - Should not be a problem
- Cr is only present at about 1 mg/L in the digestate
 - Should not be a problem
- Decided to go with just TEVA

ALAB Approach, ctd

- ALAB digestate is 1% ABF
 - 1% ABF is 0.17M HF
 - Very close to the 0.2M used by Maxwell
- Do not want all samples to go through the cleanup
 - Only samples with above 20 mg/L Ti
- Remove a 10 mL portion of the digestate, fortify to 0.1M HCl, pass through TEVA
- Analyze by ICP
 - Preliminary results indicate that there may be about a 10% loss of Scandium internal standard in the cleanup procedure
 - Can reprocess the data without using the internal standard in the calculations

LLNL Validation

- Started with liquid spikes
- Preliminary results showed that Ti started breaking through somewhere above 100 ppm in the digestate
 - Tried two cartridges in series, Be spiked at 2x the reporting limit (0.0016 mg/L)
 - Results shown are for two cartridges in series. Results for the single cartridge are similar.

Liquid Standard - two TEVAs 1000 ppm Ti		
Element	% Recovery	% Removed
Be	100 ± 0	0
Ti	0 ± 0	100
Al	86 ± 2	14
Cr	97 ± 2	3
Fe	105 ± 3	0
Mo	0 ± 0	100
V	69 ± 2	31
n = 2; mean ± one standard deviation		

LLNL Validation, ctd

- Digested powder to achieve about 100 ppm Ti (and other elements) in digestate
- Used one TEVA Cartridge
- Be is at 2x the reporting limit

Powder Samples - one TEVA Ti < 100 ppm		
Element	% Recovery	% Removed
Be	90 ± 4	10
Ti	0 ± 0	100
Al	92 ± 2	8
Cr	100 ± 1	0
Fe	112 ± 15	0
Mo	12 ± 7	88
V	52 ± 8	48
n = 3; mean ± one standard deviation		

LLNL Validation, ctd

- Next, digested increasing masses of powder
 - Be is at 2x the reporting limit
 - Range of Ti is approx. 100 to 1000 ppm in digestate
 - Used two cartridges

Powder Samples - two TEVAs Ti approx 100-1000		
Element	% Recovery	% Removed
Be	77 ± 4	23
Ti	0 ± 0	100
Al	86 ± 2	14
Cr	95 ± 3	5
Fe	101 ± 3	0
Mo	47 ± 13	53
V	71 ± 18	29
n = 9; mean ± one standard deviation		

Conclusions

- Like most analytical methods, ICP-OES is subject to spectral interference
 - Prior to analysis, it is important to know what else may be present in your sample other than the one you are interested in
 - Incorrect results can have major impacts to operations and vendor relationships
- Cleanup looks very promising on a complex metallic powder matrix.
 - Use of correction algorithms and resin columns resulted in good recovery of Be
- Need to continue work to investigate improving Be recovery in powder matrix

Acknowledgments

- ALAB Team
 - Jack Bennett
 - Ruth Harding
 - Cora Madden
 - Christina Navarro-Dizon
 - Debra VanOrder

Any Questions?



